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Orthogonal Functions, Discrete Variable Representation, and Generalized Gauss Quadratures[†]

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The numerical solution of most problems in theoretical chemistry involve either the use of a basis set expansion (spectral method) or a numerical grid. For many basis sets, there is an intimate connection between the spectral form and numerical quadrature. When this connection exists, the distinction between spectral and grid approaches becomes blurred. In fact, the two approaches can be related by a similarity transformation. By the exploitation of this idea, calculations can be considerably simplified by removing the need to compute difficult matrix elements of the Hamiltonian in the original representation. This has been exploited in bound-state, scattering, and time-dependent problems using the so-called, discrete variable representation (DVR). At the core of this approach is the mathematical three-term recursion relationship satisfied by the classical orthogonal functions. This three-term recursion can be used to generate the orthogonal functions as well as to generate the points and weights of Gauss quadratures on the basis of these functions. For the classical orthogonal functions, the terms in the three-term recursion are known analytically. For more general weight functions, this is not the case. However, they may be computed in a stable numerical fashion, via the recursion. In essence, this is an application of the well-known Lanczos recursion approach. Once the recursion coefficients are known, it is possible to compute the points and weights of quadratures on the basis of the generalized weight functions. We review these ideas below and apply then to the generation of the points and weights of the Rys polynomials which have proven useful in the evaluation of multicenter integrals, using Gaussian basis sets in quantum chemistry. In contrast to some approaches, the method advocated is general, numerically stable, and trivial to program.

Mathematical Introduction

All of the classical orthogonal polynomials[1,2] satisfy a three-term recursion relationship on the interval $a \leq x \leq b$ of the form

$$\beta_n \phi_n(x) = (x - \alpha_n)\phi_{n-1}(x) - \beta_{n-1}\phi_{n-2}(x) \qquad (1)$$

$$0 \leq n \leq N - 1$$

with the properties

$$\langle \phi_n | \phi_m \rangle = \int_a^b w(x)\phi_n(x)\phi_m(x)\,dx = \delta_{n,m} \qquad (2)$$

$$w(x) = \text{nonnegative weight function}$$

$$\phi_0(x) = \text{constant}$$

where the coefficients α_n and β_n are known analytically. Associated with these polynomials, $\phi_n(x)$, and weight function, $w(x)$, is a generalized Gauss quadrature with points x_i and weights w_i having the property that any $F(x)$ which is a polynomial of degree $2N - 1$ may be integrated *exactly* using the quadrature rule,

$$I = \int_a^b w(x)F(x)\,dx = \sum_i w_i F(x_i) \qquad (3)$$

From the Hermite interpolation formula, one would expect that N values of the $F(x)$ and N values of $F'(x)$ would be needed to obtain a quadrature rule of this accuracy. By suitably choosing the points to make the weights of the derivative term vanish, one gets $2N - 1$ accuracy with only N values of the function required. The Christoffel−Darboux identity[1] can be used to prove that the points needed are the zeros of the polynomial, $\phi_N(x)$. The required weights, w_i, may also be derived from the Christoffel−Darboux identity.

By rewriting eq 1 as

$$x\phi_n(x) = \alpha_{n+1}\phi_n(x) + \beta_n\phi_{n-1}(x) + \beta_{n+1}\phi_{n+1}(x) \qquad (4)$$

it is simple to see that the condition for the determination of the points and weights of the Gauss quadrature is the same as setting $\phi_N(x)$ to zero in the above equations. When this is done, eq 4 is no more than the tridiagonal representation of the operator x in the orthogonal polynomial basis. The tridiagonal matrix involving the recursion coefficients, α_n and β_n, may be diagonalized to obtain a new representation where the operator

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x is diagonal, with eigenvalues x_i. These eigenvalues are identical to the Gauss points. The Gauss weights are the leading coefficients of the eigenvectors of the tridiagonal matrix. In practice, computation of the points and weights of the Gauss quadrature by diagonalization is much more efficient than the root finding procedure. Golub and Concus[10] have a readily available computer program to carry out the process for all of the common weight functions. The eigenvectors of the tridiagonal matrix, are the so-called coordinate eigenfunctions, $u_i(x)$.

$$u_{\mathrm{i}}(x) = \sum_{n=0}^{N-1} c_n \phi_n(x)$$

$$c_n = \langle \phi_n | u_i \rangle = \int_a^b w(x) \phi_n(x) u_i(x)\, \mathrm{d}x = \sqrt{w_i} \phi_n(x_i)$$

$$u_{\mathrm{i}}(x) = \sum_{n=0}^{N-1} \sqrt{w_i}\, \phi_n(x_{\mathrm{i}}) \phi_n(x)$$

$$\langle u_i | x | u_j \rangle = \delta_{i,j} x_i \tag{5}$$

An alternative representation for $u_{\mathrm{i}}(x)$, which may be derived from the above, is

$$u_i(x) = \frac{1}{\sqrt{w_i}} \prod_{k=1}^{N}{}' \frac{x - x_k}{x_i - x_k} \tag{6}$$

and is the most useful in performing computations. Note that either eq 5 or eq 6 may be used to calculate the value of $u_i(x)$ at any arbitrary point in the interval. While it would be mathematically elegant to have

$$\langle u_i | H(x) | u_j \rangle = \delta_{i,j} H(x_i) \tag{7}$$

for $H(x)$ being any local operator, when the integral is evaluated using the quadrature rule, this only holds if the entire integrand is a polynomial of $2N - 1$ degree or less. However, replacing the matrix element by its quadrature approximation has been demonstrated to be accurate enough in practice to be very useful and is the basis of the DVR. In this new representation, matrix elements of any local function of x are diagonal and equal to the value of the operator at the Gauss quadrature point. Other operators, such as the kinetic energy, which involve differentiation and lower the order of the integrand, may be performed analytically using the product form or using the known derivatives of $\phi_n(x)$. These are most easily computed by differentiating the recursion relation. The product form may also be differentiated, and the results are particularly simple if the derivatives are only required at the quadrature points. This is all that is needed to compute matrix elements of the kinetic energy operator via the quadrature rule. Since typical many-body operators involve sums of operators for each separate particle, and these in turn are sums over separate coordinates, the entire DVR representation of the Hamiltonian is quite sparse. This is of tremendous practical importance in further matrix manipulations such as finding eigenvalues or solving linear equations.[8] We refer the interested reader to the references for further information.

Nonclassical Weights

Calculating the points and weights of a Gauss quadrature when the weight function $w(x)$ is a more general, but still positive definite function, can be approached in a number of ways. For example, by computing the moments,

$$M_j = \int_a^b w(x) x^j\, \mathrm{d}x \tag{8}$$

$$0 \le j \le N - 1$$

and then requiring that the quadrature be exact for all computed moments, one gets a set of $2N$, nonlinear equations which may be solved for the unknown points and weights. The problem is that this approach is numerically unstable. A much better procedure is to use the recursion relationship once values for $\phi_0(x)$ and $\phi_1(x)$ are available. Using the Dirac notation, we have the following step:

(1)

$$|\hat{\phi}_{\mathbf{0}}\rangle = 1$$

$$\beta_0 = \sqrt{\hat{\phi}_{\mathbf{0}} | \hat{\phi}_{\mathbf{0}}}$$

$$|\phi_0\rangle \rightarrow \frac{|\hat{\phi}_{\mathbf{0}}\rangle}{\boldsymbol{\beta}_{\mathbf{0}}} \tag{9}$$

(2)

$$\alpha_1 = \langle \phi_0 | x | \phi_0 \rangle$$

$$|\hat{\phi}_{\mathbf{1}}\rangle = (x - \alpha_1) |\phi_{\mathbf{0}}\rangle$$

$$\beta_1 = \sqrt{\langle \hat{\phi}_{\mathbf{1}} | \hat{\phi}_{\mathbf{1}} \rangle}$$

$$|\phi_1\rangle \rightarrow \frac{|\hat{\phi}_{\mathbf{1}}\rangle}{\beta_1} \tag{10}$$

(3) For $i = 2$ to $i = N - 1$,

$$\alpha_i = \langle \phi_{i-1} | x | \phi_{i-1} \rangle$$

$$|\hat{\phi}_{\boldsymbol{i}}\rangle = (x - \alpha_{\mathrm{i}}) |\phi_{i-1} - \beta_{i-1} |\phi_{i-2}\rangle$$

$$\beta_i = \sqrt{\langle \hat{\phi}_{\boldsymbol{i}} | \hat{\phi}_{\boldsymbol{i}} \rangle}$$

$$|\phi_i\rangle \rightarrow \frac{|\hat{\phi}_{\boldsymbol{i}}\rangle}{\beta_i} \tag{11}$$

The only remaining issue is the computation of the $\alpha_{\boldsymbol{i}}$ and β_i. The approach advocated here is to compute these using some other Gauss quadrature with a related weight function.[13] If no such weight function can be found, it is often effective to use Gauss–Legendre, Gauss–Hermite, Gauss–Laguerre, or even simpler quadrature schemes. So, the required integrals are written

$$I = \int_a^b w_{\mathrm{c}}(x) Q(x)\, \mathrm{d}x = \sum_q w_{\mathrm{q}} Q(x_{\mathrm{q}}) \tag{12}$$

$$Q(x) = \frac{F(x) w(x)}{w_{\mathrm{c}}(x)}$$

TABLE 1: Rys Points for $n = 20$: 150 Point Gauss−Legendre Quadrature

Rys *t*		
0.0	10.0	20.0
0.38772418E−01	0.34516481E−01	0.31101309−E01
0.11608407E+00	0.10345688E+00	0.93278655E−01
0.19269758E+00	0.17211704E+00	0.15537838E+00
0.26815219E+00	0.24030163E+00	0.21734258E+00
0.34199409E+00	0.30780232E+00	0.27910367E+00
0.41377920E+00	0.37439231E+00	0.34057950E+00
0.48307580E+00	0.43982039E+00	0.40166741E+00
0.54946713E+00	0.50380490E+00	0.46223673E+00
0.61255389E+00	0.56602732E+00	0.52211916E+00
0.67195668E+00	0.62612608E+00	0.58109628E+00
0.72731826E+00	0.68369085E+00	0.63888354E+00
0.77830565E+00	0.73825825E+00	0.69510972E+00
0.82461223E+00	0.78931010E+00	0.74929160E+00
0.86595950E+00	0.83627585E+00	0.80080440E+00
0.90209881E+00	0.87854117E+00	0.84885103E+00
0.93281281E+00	0.91546478E+00	0.89243815E+00
0.95791682E+00	0.94640490E+00	0.93037480E+00
0.97725995E+00	0.97075538E+00	0.96131807E+00
0.99072624E+00	0.98798952E+00	0.98389332E+00
0.99823771E+00	0.99770850E+00	0.99690169E+00

Rys *t*	
30.0	40.0
0.28300441E−01	0.25961895E−01
0.84908561E−01	0.77908218E−01
0.14153766E+00	0.12992213E+00
0.19819921E+00	0.18204861E+00
0.25490056E+00	0.23433244E+00
0.31164265E+00	0.28681779E+00
0.36841678E+00	0.33954762E+00
0.42520023E+00	0.39256240E+00
0.48194977E+00	0.44589794E+00
0.53859225E+00	0.49958168E+00
0.59501046E+00	0.55362622E+00
0.65102174E+00	0.60801801E+00
0.70634534E+00	0.66269728E+00
0.76055258E+00	0.71752162E+00
0.81299132E+00	0.77219793E+00
0.86267636E+00	0.82615243E+00
0.90814496E+00	0.87827887E+00
0.94731288E+00	0.92646562E+00
0.97745729E+00	0.96684063E+00
0.99558685E+00	0.99324488E+00
0.97745729E+00	0.96684063E+00
0.99558685E+00	0.99324488E+00

TABLE 2: Rys Weights for $n = 20$: 150 Point Gauss−Legendre Quadrature

Rys *t*		
0.0	10.0	20.0
0.77505948E−01	0.68200188E−01	0.61006721E−01
0.77039818E−01	0.61845284E−01	0.52221480E−01
0.76110362E−01	0.50904229E−01	0.38281515E−01
0.74723169E−01	0.38102267E−01	0.24055398E−01
0.72886582E01	0.26011465E−01	0.12977677E−01
0.70611647E−01	0.16260925E−01	0.60249481E−02
0.67912046E−01	0.93577803E−02	0.24150737E−02
0.64804013E−01	0.49902018E−02	0.83977042E−03
0.61306242E−01	0.24860176E−02	0.25495249E−03
0.57439769E−01	0.11683333E−02	0.68185437E−04
0.53227847E−01	0.52395851E−03	0.16260078E−04
0.48695808E−01	0.22721939E−03	0.35144861E−05
0.43870908E−01	0.96705638E−04	0.70372021E−06
0.38782168E−01	0.41043106E−04	0.13433620E−06
0.33460195E−01	0.17651525E−04	0.25360132E−07
0.27937007E−01	0.78025612E−05	0.49509088E−08
0.22245849E−01	0.35746004E−05	0.10507396E−08
0.16421058E−01	0.16861745E−05	0.25360767E−09
0.10498285E−01	0.77989906E−06	0.70155029E−10
0.45212771E−02	0.27914439E−06	0.18488035E−10

Rys *t*	
30.0	40.0
0.55258305E−01	0.50546241E−01
0.45604926E−01	0.40769296E−01
0.31056038E−01	0.26503018E−01
0.17443123E−01	0.13865046E−01
0.80763299E−02	0.58241064E−02
0.30808558E−02	0.19584424E−02
0.25038722E−03	0.11183616E−03
0.53381348E−04	0.18813052E−04
0.93981326E−05	0.24866554E−05
0.13722805E−05	0.25686316E−06
0.16751152E−06	0.20639501E−07
0.17330106E−07	0.12868808E−08
0.15544888E−08	0.62412844E−10
0.12540417E−09	0.23841810E−11
0.96350274E−11	0.74115120E−13
0.76810552E−12	0.20148347E−14
0.71429832E−13	0.55394092E−16
0.87745585E−14	0.19956309E−17
0.13698412E−14	0.12391027E−18

where $F(x)$ is the original integrand and $w_c(x)$ the comparison weight function.

Numerical Example: The Rys Polynomials

When the molecular orbitals of polyatomic molecules are expanded in a set of nuclear-centered Cartesian Gaussians, matrix elements of the nuclear attraction and electron−electron repulsion operators can be reduced to integrals of the form

$$I_n(t) = \int_0^1 F_n(x^2)\mathrm{e}^{-tx^2}\,\mathrm{d}x \tag{13}$$

where $F_n(x^2)$ is some general polynomial of x^2. In earlier molecular integral codes, the $F_n(x)$ were expressed as known power series expansions and the $I_n(t)$ related to the functions

$$E_n(t) = \int_0^1 x^{2n}\mathrm{e}^{-tx^2}\,\mathrm{d}x \tag{14}$$

TABLE 3: Rys Points for $n = 13$, $t = 10.0$, and Various Size Quadratures

size quadrature		
20	25	50
0.49843241E−01	0.49849793E−01	0.49849793E−01
0.14934657E+00	0.14936576E+00	0.14936576E+00
0.24828110E+00	0.24831137E+00	0.24831137E+00
0.34620056E+00	0.34623895E+00	0.34623895E+00
0.44254918E+00	0.44259134E+00	0.44259134E+00
0.53659977E+00	0.53664070E+00	0.53664070E+00
0.62737436E+00	0.62740966E+00	0.62740966E+00
0.71354463E+00	0.71357169E+00	0.71357169E+00
0.79331740E+00	0.79333577E+00	0.79333577E+00
0.86433101E+00	0.86434192E+00	0.86434192E+00
0.92363168E+00	0.92363715E+00	0.92363715E+00
0.96785751E+00	0.96785958E+00	0.96785958E+00
0.99377527E+00	0.99377564E+00	0.99377564E+00

These were computed using power series expansions for small t, asymptotic expansions for large t, or recursion. Starting values for the recursion were computed from known routines for the incomplete gamma function. Since $I_n(t)$ involves a polynomal integrand, it is clear that the integral can be performed exactly, with the appropriate Gauss quadratures. The underlying orthogonal polynomials are known as the Rys polynomials. In a typical molecular integral code, the highest power of n may be

TABLE 4: Rys Weights for $n = 13$, $t = 10.0$ and Various Size Quadrature

size quadrature		
20	25	50
0.97210964E−01	0.97223040E−01	0.97223040E−01
0.79437340E−01	0.79442440E−01	0.79442440E−01
0.53181455E−01	0.53178778E−01	0.53178778E−01
0.29330260E−01	0.29324318E−01	0.29324318E−01
0.13449451E−01	0.13444613E−01	0.13444613E−01
0.52012983E−02	0.51988088E−02	0.51988088E−02
0.17325540E−02	0.17316444E−02	0.17316444E−02
0.51230682E−03	0.51205493E−03	0.51205494E−03
0.14016577E−03	0.14010963E−03	0.14010963E−03
0.37415707E−04	0.37404942E−04	0.37404942E−04
0.10324469E−04	0.10322561E−04	0.10322561E−04
0.30388289E−05	0.30384953E−05	0.30384953E−05
0.81709400E−06	0.81703814E−06	0.81703815E−06

computed knowing the maximum values of the angular momenta on the molecular centers. Once this is known it becomes a trivial matter to generate the recursion coefficients for any value of t. However, the number of values of t are too numerous to generate the Rys points and weights "on the fly". A practical scheme for the interpolation of the recursion coefficients is needed. We will not consider this further in this paper. Here we content ourselves with showing the accuracy of the recursion technique for a few values of t and n. In Tables 1 and 2, we present the Rys points and weights for a variety of Rys parameters for $n = 20$ using 150 point Gauss−Legendre quadrature. The results are accurate to all figures presented and are unchanged for Gauss-Legendre quadratures above 40. The next Tables 3 and 4 show the Rys points and weights for $n = 13$ using 20/25/50 point Gauss−Legendre quadrature. The points and weights are converged to sufficiently high precision at 25 point quadrature. In contrast, the moment procedure[12] is only accurate to about 4 decimal places.

Conclusion

We have discussed the relationship between orthogonal polynomials and generalized Gauss quadratures and briefly mentioned how they may be used to simplify the construction of matrix representations of the Hamiltonian for typical many-body problems. A numerical example, derived from quantum chemistry, has been given showing how the recursion may be used to numerically construct the points and weights of the Rys polynomials. Calculations are in progress which use these polynomial discretizations in the time domain to find accurate solutions of the time-dependent Schroedinger equation for general potentials.

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