Evaluation of high-order JWKB phase integrals

Margaret G. Barwell[a] and Robert J. Le Roy

Guelph-Waterloo Centre for Graduate Work in Chemistry, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1

Petri Pajunen[b] and Mark S. Child

Theoretical Chemistry Department, Oxford University, 1 South Parks Rd., Oxford OX1 3TG, England
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Two simple and reliable quadrature procedures for evaluating JWKB phase integrals of the form $\oint dr\, f(r)/[E - U(r)]^{k+1/2}$ for integer $k > 0$ and any smooth potential $U(r)$ are derived, tested, and compared. Their development allows calculations based on the higher-order JWKB quantization conditions to be done with virtually the same ease now associated with use of the first-order approximation. Applications to date include calculation of two-term and three-term (i.e., third- and fifth-order) JWKB eigenvalues and the direct calculation of diatomic molecule centrifugal distortion constants for both analytic and numerical potential energy functions.

I. INTRODUCTION

The Jeffries,[1] Wentzel,[2] Kramers,[3] Brillouin[4] (JWKB) "asymptotic" approximation is a widely used approximate method for solving the one-dimensional or radial Schrödinger equation. However, with few exceptions,[5-9] it is the single-term or first-order version of this approximation which has been used in practical applications. The importance of the higher-order versions of the JWKB approximation has been examined in a variety of contexts.[9-15] However, previous methods for evaluating the higher-order phase integrals either restricted consideration to special types of potential functions such as[10,12] the family $V(x) = x^{2m}$, or were difficult to apply accurately to a general potential function.[11] The present paper removes these constraints by presenting two simple and reliable quadrature procedures for evaluating these integrals, which may readily be applied to any type of potential energy function.[16,17]

The JWKB phase integrals considered in the present work may be written in the general form

$$I_k(E) = \oint_\Gamma dr\, f(r)/[E - U(r)]^{k+(1/2)} , \tag{1}$$

where k is an integer, E a constant, $f(r)$ a linear combination of powers of r times powers of $U(r)$ and its derivatives, and Γ is any contour in the complex plane (see Fig. 1) which encircles the range of values of r for which $E > U(r)$. For $k \leq 0$, this expression is equivalent to a sum of integrals along the segments of the real line [$r = Rl(y)$ in Fig. 1] on which $E > U(r)$:

$$I_k(E) = \sum_i L_k^i(E) = \sum_i 2 \int_{r_1(i)}^{r_2(i)} dr\, f(r)/[E - U(r)]^{k+(1/2)} , \tag{2}$$

where the turning points r_1 and r_2 are defined by

$$U(r_1) = E = U(r_2) . \tag{3}$$

The $L_k^i(E)$ integrals of Eq. (2) may be rewritten as

$$L_k^i(E) = 2 \int_{r_1}^{r_2} dr\, F(r)/[(r_2 - r)(r - r_1)]^{k+(1/2)} , \tag{4}$$

where the function

$$F(r) = f(r)\{(r_2 - r)(r - r_1)/[E - U(r)]\}^{k+(1/2)} \tag{5}$$

is well behaved on the whole interval $[r_1, r_2]$. For these $k \leq 0$ cases, a variety of standard numerical techniques may then be used to generate reliable values of the integrals in Eq. (4); one of the best of these would be the Gauss–Mehler quadrature procedure.[16,19]

For the $k > 0$ integrals arising both in the higher-order JWKB approximation and in certain applications of the first-order method (e.g., to the calculation of diatomic molecule centrifugal distortion constants[16]), the integrals of Eq. (2) have nonintegrable singularities at the turning points r_1 and r_2. Two quadrature procedures suitable for these cases are described below. To simplify their presentation, throughout Secs. II and III the function $U(r)$ is assumed to have the form shown in Fig.

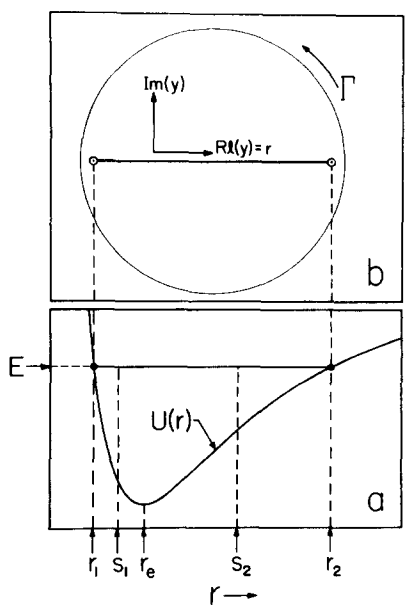

FIG. 1. Schematic drawing of quantities associated with the integrals of Eq. (1); $r = Rl(y)$.

[a] Present address: Box 215, Deep River, Ontario, Canada K0J 1P0.

[b] Present address: Department of Physical Chemistry, University of Helsinki, Meritullinkatu 1 C, SF-00170 Helsinki 17, Finland.

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1, so that there are exactly two finite-valued turning points for any choice of E, and $U(r)$ has a simple minimum somewhere between them. Generalizations of these techniques to problems involving more than two turning points are presented elsewhere.[17]

II. METHOD 1: INTEGRATION BY PARTS ON THE REAL LINE

A. Description of the method

The first step in this approach is to rewrite the general integral in Eq. (1) as

$$I_k(E) = A_k \frac{\partial^k}{\partial E^k} \oint_\Gamma dr\, f(r)/[E - U(r)]^{1/2} = 2A_k \frac{\partial^k}{\partial E^k} \int_{r_1}^{r_2} dr\, f(r)/[E - U(r)]^{1/2} , \quad (6)$$

where

$$A_k = (-1)^k \frac{2}{1}\frac{2}{3}\frac{2}{5} \cdots \frac{2}{2k-1} = (-1)^k 2^{2k} k!/(2k)! . \quad (7)$$

Taking the second version of Eq. (6) and integrating by parts once prior to each stage of differentiation would yield an expression of the form

$$I_k(E) = 2A_k \int_{r_1}^{r_2} dr\, h(r)/[E - U(r)]^{1/2} , \quad (8)$$

where $h(r)$ is well behaved at the turning points r_1 and r_2. However, the integration by parts step virtually always [depending on the nature of $f(r)$] introduces a factor of $[U'(r)]^{-2}$ into the function $h(r)$, where the prime denotes differentiation with respect to r. This would give the integrand of Eq. (8) a nonintegrable singularity at the point $r = r_e$ where $U(r)$ has its minimum (see Fig. 1). This difficulty is removed if one interrupts the range of integration at two fixed points s_1 and s_2, chosen such that (see Fig. 1)

$$r_1 < s_1 < r_e < s_2 < r_2 . \quad (9)$$

Defining the integration intervals t and c as

$$t = [r_1, s_1] + [s_2, r_2] , \qquad c = [s_1, s_2] , \quad (10)$$

respectively, Eq. (6) may be rewritten as

$$I_k(E) = 2 \int_c dr\, f(r)/[E - U(r)]^{k+(1/2)} + 2A_k \frac{\partial^k}{\partial E^k} \int_t dr\, f(r)/[E - U(r)]^{1/2} . \quad (11)$$

This expression summarizes the essence of Method 1.

Since the interval c includes no zeros of $[E - U(r)]$, the integrand $f(r)/[E - U(r)]^{k+(1/2)}$ is well behaved there and the first integral in Eq. (11) may be accurately evaluated using virtually any standard quadrature formula. At the same time, the second term in Eq. (11) may be reduced to a similarly tractable integral by iteratively integrating by parts and differentiating with respect to E, k times. In particular, applying one cycle of this procedure to the last term in Eq. (11) yields

$$2A_k \frac{\partial^{k-1}}{\partial E^{k-1}} \left\{ \int_t dr [f'(r)U'(r) - f(r)U''(r)][U'(r)]^{-2} / [E - U(r)]^{1/2} + f(s_2)/U'(s_2)[E - U(s_2)]^{1/2} - f(s_1)/U'(s_1)[E - U(s_1)]^{1/2} \right\} . \quad (12)$$

The function multiplying $[E - U(r)]^{-1/2}$ in the integral in this expression is the analog of $h(r)$ in Eq. (8); it is well behaved across the whole of the interval t, so this integral is finite and may be evaluated using standard quadrature techniques.[18] As indicated by Eq. (12), each of the k cycles of this procedure will also yield two additional terms associated with the values of the integrand at s_1 and s_2. However, both they and their derivatives with respect to E (the latter being required if $k > 1$) are quite straightforward to evaluate.

B. Numerical techniques

In present applications of the above procedure, all of the integrals were evaluated using the appropriate Gaussian quadrature formulae.[18] In particular, the integrals over the central region c used the ordinary Gauss–Legendre formula [Eq. (25.4.30) in Ref. 18], while those over the two terminal regions t [e.g., see Eq. (12)] were computed using the Gauss–Mehler formula [Eq. (25.4.36) of Ref. 18]. These procedures are sufficiently precise that 16-point quadratures are often sufficient to yield integrals converged to machine accuracy (in IBM double precision, 15 digits). If the t integrals are to be calculated accurately, it is essential that the two turning points r_1 and r_2 be determined as precisely as possible, because of the (integrable) singularities in the integrands at these points. However, the choice of the intermediate points s_1 and s_2 has virtually no effect on the results unless they are set extremely close to the turning points or to r_e. In most calculations performed using this method, these intermediate points were defined as $s_1 = (r_1 + r_e)/2$ and $s_2 = (r_e + r_2)/2$.

C. Applications

The method described above has been programmed and used to calculate both the phase integrals occurring in the first-order JWKB expressions for diatomic molecule centrifugal distortion constants,[16] and those arising in the two- and three-term JWKB quantization condition.[20,21] In both applications, the integrals which arise may be expressed in the general form

$$I_{k,l}^{m,n} = \oint_\Gamma dr\, [\partial^m U(r)/\partial r^m]^n / r^l [E - U(r)]^{k+(1/2)} . \quad (13)$$

The centrifugal distortion constant calculations involve $m = n = 0$ integrals with $k = 1$–3 and $l = 0$–8, while the quantization conditions involve the integrals $I_{1,0}^{2,1}$, $I_{2,0}^{4,1}$, and $I_{3,0}^{2,2}$. In both cases, most calculations have been performed using an analytic potential energy function $U(r)$. Use of numerical potentials makes the computations more complicated because derivatives of $U(r)$ must be generated at the quadrature mesh points using interpolation procedures. However, when the given potential points are sufficiently precise and smooth, this presents no serious difficulty.

The above method required only a few seconds of execution time on an IBM 360-75 to yield one-term, two-term, and three-term JWKB eigenvalues accurate to 12 digits for all 24 levels of the $B_z = 10^4$ LJ(12, 6) model potential considered in Ref. 20. Since finding each eigenvalue in each approximation required calculations at several trial energies, it is clear that this technique is very efficient. Moreover, within this procedure, performing calculations at energies E near a potential asymptote is essentially no more difficult than performing calculations at energies near the potential minimum. Diatomic molecule centrifugal distortion constants for LJ(12, 6) potentials have also been calculated in this way[16] and compared with first-order JWKB values obtained by Kirschner[22] using the method of Kirschner and Watson[23]; to the number of digits quoted by Kirschner (up to seven), the agreement was exact.

An independent check on the validity of the above procedure is provided by the internal consistency checks carried out for the centrifugal distortion constant calculations.[16] These checks are based on the fact that, in this application, the function $U(r)$ appearing in Eq. (13) is the centrifugally distorted effective interaction potential

$$U(r) \equiv U_j(r) = U_0(r) + j(j+1)\hbar^2/2\mu r^2 \ , \tag{14}$$

where j is the rotational quantum number of the diatom and μ its reduced mass. The fact that

$$\frac{\partial}{\partial[j(j+1)]}\left(I^{0,0}_{k,l}(E,j)\right) = -\frac{\hbar^2}{2\mu}\frac{\partial}{\partial E}\left[I^{0,0}_{k,l+2}(E,j)\right] = (k+\tfrac{1}{2})(\hbar^2/2\mu)\, I^{0,0}_{k+1,l+2}(E,j) \tag{15}$$

allows estimates of the higher-order (i.e., higher k) integrals to be obtained from differences between directly calculated (by the present method) values of the lower-order integrals. The excellent agreement[16] between these first-difference estimates and the directly calculated values of the higher-order integrals provided an unambiguous internal verification of the validity of the present technique for treating these higher-order phase integrals.

III. METHOD 2: DIRECT INTEGRATION ON THE REAL LINE

A. Description of the method

In the second approach, it is first convenient to make the change of variables

$$r = \tfrac{1}{2}(r_2 + r_1) + \tfrac{1}{2}(r_2 - r_1)z \ , \tag{16}$$

which maps the range between the turning points $[r_1, r_2]$ onto the interval $[-1, +1]$, and maps the contour Γ of Fig. 1 onto the similar contour Γ' around the cut from -1 to $+1$ in the z plane. Equation (1) may then be written as

$$I_k(E) = \tfrac{1}{2}(r_2 - r_1)\oint_{\Gamma'} dz\, F(z)/(1-z^2)^{k+(1/2)} \ , \tag{17}$$

where

$$F(z) = f(r)\{(1-z^2)/[E - U(r)]\}^{k+(1/2)} \ . \tag{18}$$

Since $F(z)$ is well behaved on the interval $[-1, +1]$, it may be accurately represented by the polynomial expansion

$$F(z) = \sum_{n=0}^{N-1} a_n z^n \ , \tag{19}$$

so that Eq. (17) becomes

$$I_k(E) = \tfrac{1}{2}(r_2 - r_1)\sum_{n=0}^{N-1} a_n J(k,n) \tag{20}$$

and its evaluation requires only a knowledge of the expansion coefficients $\{a_n\}$ and evaluation of the integrals

$$J(k,n) \equiv \oint_{\Gamma'} dz\, z^n/(1-z^2)^{k+(1/2)} \ . \tag{21}$$

Using standard techniques for integration in the complex plane, it is readily shown that (see Appendix)

$$J(k,n) = 2\pi(-1)^{n/2}\binom{-k-\frac{1}{2}}{-k+n/2} \ , \quad \text{for } n \text{ even and } n \geq 2k \ ; \qquad = 0 \ , \quad \text{otherwise} \ , \tag{22}$$

where the factor $\binom{a}{b}$ is the usual binomial expansion coefficient.[24]

The only problem remaining is the determination of the coefficients $\{a_n\}$ of the polynomial approximation (19) to $F(z)$. To do this, $F(z)$ is first evaluated at N points $z_1, z_2, \ldots, z_N$ on the real line in the range $[-1, 1]$, so that

$$\begin{aligned} F(z_1) &= \sum_{n=0}^{N-1} a_n (z_1)^n \\ F(z_2) &= \sum_{n=0}^{N-1} a_n (z_2)^n \\ &\vdots \\ F(z_N) &= \sum_{n=0}^{N-1} a_n (z_N)^n \ , \end{aligned} \tag{23}$$

or in matrix form

$$\mathbf{F} = \mathbf{Z}\,\mathbf{A} \ . \tag{24}$$

Inverting the matrix of coefficients $(\mathbf{Z})_{\alpha\beta} = (z_\alpha)^{\beta-1}$ yields

$$\mathbf{A} = \mathbf{Z}^{-1}\,\mathbf{F} \tag{25}$$

or

$$a_n = \sum_{m=1}^{N} (\mathbf{Z}^{-1})_{n+1,m} F(z_m) \ . \tag{26}$$

Substituting Eq. (26) into (20) now yields the simple Gaussian-like integration formula associated with Method 2:

$$I_k(E) = \tfrac{1}{2}(r_2 - r_1)\sum_{m=1}^{N} w_m^k F(z_m) \ , \tag{27}$$

where the weights w_m^k are simply

$$w_m^k = \sum_{n=2k}^{N-1} (\mathbf{Z}^{-1})_{n+1,m} J(k,n) \ . \tag{28}$$

The points $\{z_m\}$ may be chosen in any convenient manner, but use of the Chebyshev points

$$z_m = \cos[m\pi/(N+1)] \tag{29}$$

is expected to give particularly good results.[25]

TABLE I. Chebyshev points from Eq. (29) and the associated weights calculated from Eq. (28) for various N and k values.

z_m	$w_m^{k=1}$	$w_m^{k=3}$
	$N=11$	
0.9659258262890683	22.06633397656787	228.3214545745810
0.8660254037844386	−37.69911184307752	−720.4719152232592
0.7071067811865475	35.60471674068432	1139.3509357018984
0.5000000000000000	−37.69911184307752	−1357.1680263507907
0.2588190451025208	36.57672889044161	1447.1946273399755
0.0000000000000000	−37.69911184307752	−1474.4541520848097
−0.2588190451025208	36.57672889044161	1447.1946273399755
−0.5000000000000000	−37.69911184307752	−1357.1680263507907
−0.7071067811865475	35.60471674068432	1139.3509357018984
−0.8660254037844386	−37.69911184307752	−720.4719152232592
−0.9659258262890683	22.06633397656787	228.3214545745810
	$N=15$	
0.9807852804032304	29.62981929591175	1164.639428963841
0.9238795325112868	−50.26548245743668	−3580.432803129281
0.8314696123025452	47.72092686124880	5525.620597073791
0.7071067811865475	−50.26548245743664	−6534.512719466765
0.5555702330196022	49.12943331558201	7020.542275282852
0.3826834323650898	−50.26548245743658	−7276.911407677031
0.1950903220161283	49.44900912828539	7400.700330802901
0.0000000000000000	−50.26548245743656	−7439.291403700618
−0.1950903220161283	49.44900912828539	7400.700330802901
−0.3826834323650898	−50.26548245743658	−7276.911407677031
−0.5555702330196022	49.12943331558201	7020.542275282852
−0.7071067811865475	−50.26548245743664	−6534.512719466765
−0.8314696123025452	47.72092686124880	5525.620597073791
−0.9238795325112868	−50.26548245743668	−3580.432803129281
−0.9807852804032304	29.62981929591175	1164.639428963841
	$N=21$	
0.9898214418809327	40.91258980361040	6364.91821744174
0.9594929736144974	−69.11503837897816	−19267.83229098791
0.9096319953545184	65.80507790523560	29317.26172550868
0.8412535328311812	−69.11503837898373	−34478.42376106038
0.7557495743542583	67.78308420797106	37049.70046340271
0.6548607339452851	−69.11503837899778	−38499.30026119479
0.5406408174555976	68.30792716563759	39357.74970048209
0.4154150130018864	−69.11503837900795	−39887.54536375314
0.2817325568414297	68.49459295516724	40205.64256060925
0.1423148382732851	−69.11503837901213	−40378.03411697539
0.0000000000000000	68.54383971474920	40431.72625305376
−0.1423148382732851	−69.11503837901213	−40378.03411697539
−0.2817325568414297	68.49459295516724	40205.64256060925
−0.4154150130018864	−69.11503837900795	−39887.54536375314
−0.5406408174555976	68.30792716563759	39357.74970048209
−0.6548607339452851	−69.11503837899778	−38499.30026119479
−0.7557495743542583	67.78308420797106	37049.70046340271
−0.8412535328311812	−69.11503837898373	−34478.42376106038
−0.9096319953545184	65.80507790523560	29317.26172550868
−0.9594929736144974	−69.11503837897816	−19267.83229098791
−0.9898214418809327	40.91258980361040	6364.91821744174

The precision of the approximation (19) clearly improves with increasing N, but at the same time, the inversion of $\mathbf{Z}$ becomes computationally increasingly difficult as the addition of more points makes this matrix increasingly singular. However, once the inversion is achieved, the corresponding weights $\{w_m^k\}$ may be readily computed and stored, so that evaluation of $I_k(E)$ using Eq. (27) requires simply the N function evaluations for $F(z_m)$.

B. Numerical techniques

Consideration of Eqs. (22) and (28) shows that, for a even number of integration mesh points $N=2l$, there are the same number of nonzero contributions to each of the weights w_m^k as if $N=2l-1$. Thus, the improvement in accuracy achieved on going from $N=2l-1$ to $N=2l$ is expected to be substantially less than that achieved on increasing the number of mesh points from $N=2l$ to $N=2l+1$. This was verified by a number of numerical examples. It is therefore recommended that applications of Eq. (27) should normally use odd values of N. In the same vein, the fact that $J(k,n)=0$ for $n<2k$ implies that a restriction on the number of mesh points required for any given case is $N\geq 2k+1$.

In present applications of Method 2, the points $\{z_m\}$ were chosen as the Chebyshev points of Eq. (29). The inversion of $\mathbf{Z}$ was performed in double precision arithmetic on a UNIVAC-1108 computer (i.e., using 18 significant digits). Sample sets of points and weights $\{z_m, w_m^k\}$ for $k=1$ and 3 for each of $N=11$, 15, and 21 are listed in Table I. Generation of the weights appropriate to any other choice of mesh points would of course be quite straightforward.

C. Applications

This method has been tested by using it to calculate the one-term, two-term, and three-term JWKB eigenvalues of the model LJ(12, 6) potential considered in Ref. 20. For $v\leq 10$, exact agreement with the 12-digit eigenvalues shown there[20] was achieved with values of N ranging from 11 to 15, but for $v>10$ (level $v=10$ being bound by only ~18% of the well depth ϵ), the value of N required to give 12-digit convergence increased steadily to $N=29$ for $v=20$ (bound by 0.3% of ϵ) and $N=33$ for the highest bound level $v=23$ (bound by 0.0003% of ϵ). This growth in the number of required mesh points is due to the extreme anharmonicity of realistic potential functions at energies near the dissociation limit. However, the stability of the method under even these extreme conditions attests to its reliability.

While the test of this approach described above was for the case of an analytic potential, its use with numerical potentials should be quite straightforward. Indeed, for the latter case, it has distinct advantages over Method 1, since only interpolated values of the potential and of those derivatives appearing in the function $f(r)$ are required. In contrast, the integration by parts of Method 1 introduces additional higher order derivatives with each increase in k. Thus, Method 2 is expected to have somewhat better numerical stability for problems involving numerical potentials.

IV. DISCUSSION AND CONCLUSIONS

Two equivalent methods for evaluating integrals of the form of Eq. (1) have now been derived and tested. Both are very efficient and reliable, even for the difficult case of energies lying very near a potential asymptote. However, while the derivation of Method 1 is somewhat more transparent, it is distinctly more complicated to program and changes in the composition of $f(r)$, even for cases which correspond to the same value of k, may require substantial reprogramming.[16] In contrast, Method 2 is very simple to program, and the changes associated with use of different $f(r)$ functions and different values of k are simply the recoding of the $f(r)$ for-

mula and the selection of a different set of weights, respectively. Moreover, it should also be computationally somewhat faster, although the total amount of computer time required for these integrations is sufficiently small that this will not usually be an important advantage.

On the other hand, Method 1 is usually slightly more stable than is Method 2, a fact that may be of importance when extremely high accuracy is desired. The reason for this is of course the fact that the former breaks the range of integration up into three segments, which allows it to treat the behavior of the integrand in different regions independently. This flexibility is particularly important at energies very near a potential asymptote where the potential is very anharmonic. It also makes Method 1 the more appropriate technique for cases in which the potential or its derivatives are discontinuous at points on the interval $[r_1, r_2]$. An additional advantage of this formulation is the fact that it facilitates the derivation of simple analytic expressions for the characteristic near-dissociation behavior of integrals of the form of Eq. (1), and hence of various physical quantities which depend on them.[16,20]

In conclusion, it appears that Method 2 will usually be the best way to evaluate integrals of the form of Eq. (1), although Method 1 may occasionally be required for difficult cases. Generalization of Method 2 to the case of multiple turning point problems is described elsewhere.[17]

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APPENDIX: EVALUATION OF THE INTEGRALS $J(k,n)$

To evaluate the integrals $J(k,n)$, we choose the contour of integration Γ' to be a circle centered at $z=0$ with radius R, where $R>1$, so that

$$z = R e^{i\theta} , \tag{A1}$$

$$dz = i R e^{i\theta} d\theta . \tag{A2}$$

Equation (21) may then be rewritten as

$$J(k,n) = (-1)^{-k-(1/2)} \oint_{\Gamma'} dz\, z^{n-2k-1} (1-z^{-2})^{-k-(1/2)} . \tag{A3}$$

Since $|z|>1$ on the chosen contour, the binomial expansion

$$(1-z^{-2})^{-k-(1/2)} = \sum_{p=0}^{\infty} \binom{-k-\frac{1}{2}}{p} (-1)^p z^{-2p} \tag{A4}$$

is valid. Substituting it into Eq. (A3) and using the definitions of Eqs. (A1) and (A2) yields

$$J(k,n) = \sum_{p=0}^{\infty} (-1)^{p-k} \binom{-k-\frac{1}{2}}{p} R^{n-2k-2p} \int_0^{2\pi} d\theta\, e^{i(n-2k-2p)\theta} . \tag{A5}$$

The integral remaining in Eq. (A5) is clearly equal to $2\pi\delta_{p,(1/2)n-k}$, so that this sum collapses to

$$J(k,n) = 2\pi(-1)^{n/2} \binom{-k-\frac{1}{2}}{-k+n/2} , \quad \text{for } n \text{ even and } n \geq 2k , \tag{A6}$$

$$= 0 , \quad \text{otherwise} ,$$

where the conditions on n arise from the requirements that p be a nonnegative integer, and[24]

$$\binom{-k-\frac{1}{2}}{-k+n/2} = \frac{\Gamma(\frac{1}{2}-k)}{\Gamma\left(\frac{n}{2}+1-k\right)\Gamma\left(\frac{1-n}{2}\right)} = \left\{\left(\frac{n}{2}-k\right) B\left(\frac{n}{2}-k, \frac{1}{2}-\frac{n}{2}\right)\right\}^{-1} . \tag{A7}$$

From the definition of the gamma function (see Sec. 6 of Ref. 18), it is clear that

$$J(k,2k) = 2\pi(-1)^k \tag{A8}$$

and that all of the other nonzero values of $J(k,n)$ may be generated from the recursion relation

$$J(k,n+2) = J(k,n)\left[(n/2+1)/(n/2+1-k)\right] . \tag{A9}$$

These last two equations provide a particularly simple way of evaluating these integrals, and hence of evaluating the weights of Eq. (28).

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