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A Gaussian Quadrature Procedure for Use in the Solution of the Boltzmann Equation and Related Problems

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A new Gaussian quadrature procedure is developed for integrals of the form $\int_0^\infty e^{-y^2} y^p F(y)\, dy$ for $p = 0$, 1 and 2. Recursion relations are derived for the coefficients in the general three term recurrence relation for the polynomials whose roots are the quadrature abscissae. A comparison with the Gauss–Laguerre quadrature procedure is presented. Solutions of the chemical kinetic Boltzmann equation are obtained with a discrete ordinate method based on this Gaussian quadrature procedure. The results are compared with previous solutions obtained with a polynomial expansion method.

1. INTRODUCTION

Kinetic theory problems invariably involve the evaluation of averages over a Maxwellian distribution function, p^M. Specifically, if $F(c)$ is some function of speed c, the equilibrium average of F is

$$\begin{aligned} \bar{F} &= \int p^M(c)\, F(c)\, d\mathbf{c} \\ &= \frac{4}{\sqrt{\pi}} \int_0^\infty e^{-y^2} y^2 F(y)\, dy, \end{aligned} \tag{1}$$

where $p^M(c) = (m/2\pi kT)^{3/2} \exp(-mc^2/2kT)$, m is the mass, and $y = (m/2kT)^{1/2} c$ is the dimensionless speed. The present paper is concerned with the development of a Gaussian quadrature procedure for integrals of the type in Eq. (1), and their application to a solution of the Boltzmann equation (BE).

For integration over the half-infinite range, primitive integration algorithms such as the trapezoidal rule, or Simpson's rule are not very efficient since in order to attain convergence the integrations typically must be carried out to large y. A Gauss–Laguerre quadrature procedure could be employed if a change of variable to reduced energy $x = y^2$ is made. The integration in Eq. (1) is then

$$\bar{F} = \frac{2}{\sqrt{\pi}} \int_0^\infty e^{-x} \sqrt{x}\, F(\sqrt{x})\, dx. \tag{2}$$

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This quadrature is based on abscissae which correspond to the roots of Laguerre polynomials, orthogonal on the interval $[0, \infty]$ with weight function e^{-x}. However, the natural weight function to use for integrals of the type in Eqs. (1) and (2) is $e^{-y^2}y^2$ (or $e^{-x}\sqrt{x}$). Moreover, the integrands, F, that arise in kinetic theory are typically functions of the reduced speed y rather than the reduced energy, x, as discussed later in this paper.

Consequently, it would appear that a quadrature procedure based on abscissae which correspond to the roots of polynomials orthogonal on the interval $[0, \infty]$ with weight function $e^{-y^2}y^2$ would be better suited to kinetic theory problems. Such polynomials have been introduced in a previous paper [1] in connection with the calculation of eigenvalues of the Lorentz–Fokker–Planck equation. These polynomials were also considered by Copic and Petrisic [2] who suggested they be called Maxwell polynomials.

In the present paper, the calculation of abscissae and weights for integrals over the interval $[0, \infty]$ with the generalized weight function $e^{-y^2}y^p$, $p = 0$, 1 and 2, is considered. The case $p = 2$ is of particular interest in kinetic theory and has been reported earlier in an unpublished report [2]. Several other researchers [3–6], have performed calculations for the case $p = 0$. Some aspects of the procedures for generating abscissae and weights employed in this paper are new. For the cases $p = 0$ and 2, comparisons are made with the limited results reported earlier. General schemes for calculating Gaussian quadrature abscissae and weights have been discussed by other workers [7, 8].

The present paper also considers the application of this quadrature procedure to a solution of the BE for the velocity distribution function (VDF). The method most often employed in the solution of the BE is a moment method which involves the expansion of the VDF in terms of a set of polynomials which are generally either Laguerre (Sonine) or Hermite polynomials. A second method involves the replacement of the integration in the integral equation with an approximate numerical algorithm. In this method, referred to as the discrete ordinate method, the VDF is evaluated at a set of discrete points. Both methods of solution reduce the BE to a set of linear algebraic equations for the expansion coefficients in the polynomial method and for the VDF at a set of points in the discrete ordinate method.

The discrete ordinate method, has been employed in the study of Couette flow [9, 10], in hot atom systems [11, 12], in the dynamics of stellar evolution [13] and in several applications to atmospheric problems [14–16]. One advantage of this method of solution is that matrix elements of the kernel are not required. Rather, the kernel in the integral equation must be calculated which can be done even for realistic collision models. A change in the set of points is a trivial matter whereas a change in the polynomial basis functions is a major modification in the moment method since matrix elements must be reevaluated. For certain types of polynomials, such as those introduced in this paper, this calculation can be a formidable problem since the polynomials are not classical and the mathematical machinery, such as a generating function, which might facilitate the calculation of matrix elements [17], does not exist.

The present paper considers a discrete ordinate method of solution of the BE in connection with a nonequilibrium model reactive system introduced in an earlier paper [18]. The earlier paper employed an expansion of the VDF in Laguerre polynomials and for some situations many terms in this expansion are required. Consequently, matrix elements of the Boltzmann collision operator of rather high order need to be calculated. Although general methods for the evaluation of these matrix elements have been developed [17], the numerical calculation of the higher order matrix elements is subject to round-off errors. Consequently the polynomial method can become inefficient for such problems and the discrete ordinate method might be preferred. The present paper considers a detailed comparison of these two methods of solution of the CE. In subsequent papers, application of the discrete ordinate method to particular hot atom problems [19, 20] will be considered.

Section 2 presents a discussion of the calculation of the coefficients in the general three term recurrence formula for the polynomials. The method of the evaluation of the weights and points is described in Section 3. Section 4 involves a comparison of the derived quadrature formulae with the Gauss–Laguerre quadrature formula. The application to a solution of the BE is given in Section 5.

2. Polynomial Recurrence Relation

The set of polynomials $Q_n^{(p)}$ orthogonal on the interval $[0, \infty]$ with weight function $w(y) = e^{-y^2} y^p$ is considered. These polynomials satisfy a general three term recurrence formula of the type [21, 22],

$$Q_{n+1}^{(p)} = (y - \alpha_n^{(p)})\, Q_n^{(p)} - \beta_n^{(p)}\, Q_{n-1}^{(p)} \tag{3a}$$

with $Q_0^{(p)} = 1$ and $Q_1^{(p)} = y - \Gamma[\frac{1}{2}(p+2)]/\{2\Gamma[\frac{1}{2}(p+1)]\}^{1/2}$ for the particular set considered here. The calculation of the quadrature abscissae and weights is based on the coefficients $\alpha_n^{(p)}$ and $\beta_n^{(p)}$ in Eq. (3a) and it is their calculation which presents the principal difficulty.

The polynomials generated by Eq. (3a) are not normalized. The corresponding normalized polynomials $B_n^{(p)} = Q_n^{(p)}/\sqrt{\gamma_n^{(p)}}$ satisfy the recurrence relation

$$yB_n = \sqrt{\beta_{n+1}}\, B_{n+1} + \alpha_n B_n + \sqrt{\beta_n}\, B_{n-1}, \tag{3b}$$

where the normalization factors are given by

$$\begin{aligned} \gamma_n^{(p)} &= \int_0^\infty e^{-y^2} y^p (Q_n^{(p)})^2\, dy \\ &= \langle Q_n^{(p)2} \rangle, \end{aligned} \tag{4}$$

where the symbol $\langle\ \rangle$ denotes the integration over y with weight function $w(y)$ and will be referred to as the average over y. The coefficients $\beta_n^{(p)}$ in Eq. (3) are related to $\gamma_n^{(p)}$ as given by [21]:

$$\beta_n^{(p)} = \gamma_n^{(p)}/\gamma_{n-1}^{(p)}, \qquad n = 1, 2 \cdots. \tag{5}$$

The $\alpha_n^{(p)}$ quantities are the moments with the normalized polynomials, given by

$$\alpha_n^{(p)} = \langle y B_n^{(p)2} \rangle. \tag{6}$$

If the polynomials are generated with a Schmidt orthogonalization procedure [23], the normalization factors $\gamma_n^{(p)}$ are found to become increasingly small as n increases. The calculation very rapidly fails due to the accumulation of round-off errors. An alternate procedure based on recurrence relations was developed by Steen *et al.* [3] and was valid only for $p = 0$.

In the present paper, three separate recurrence relations are derived for $\alpha_n^{(p)}$ and $\beta_n^{(p)}$. The derivations are based on the Christoffel–Darboux identity [21, 22] given by

$$\sum_{k=0}^{n} B_k^{(p)2} = \sqrt{\beta_{n+1}^{(p)}}\,[B_{n+1}^{(p)\prime} B_n^{(p)} - B_{n+1}^{(p)} B_n^{(p)\prime}]. \tag{7}$$

If Eq. (7) is multiplied by $yw(y)$ and integrated, one finds that

$$\begin{aligned} \sum_{k=0}^{n} \alpha_k^{(p)} &= \sqrt{\beta_{n+1}^{(p)}}\,\langle y B_{n+1}^{(p)\prime} B_n^{(p)} \rangle \\ &= 2\sqrt{\beta_{n+1}^{(p)}}\,\langle y^2 B_{n+1}^{(p)} B_n^{(p)} \rangle, \end{aligned} \tag{8}$$

where an integration by parts has been performed on the integral $\langle y B_{n+1}^{(p)\prime} B_n^{(p)} \rangle$. It is useful to point out that the integral $\langle y B_{n+1}^{(p)} B_n^{(p)\prime} \rangle = 0$ since $y B_n^{(p)\prime}$, a polynomial of degree n, is orthogonal to $B_{n+1}^{(p)}$. With repeated use of Eq. (3) and the orthogonality condition

$$\int_0^\infty w(y)\, B_n^{(p)} B_m^{(p)}\, dy = \delta_{nm}$$

one finds that,

$$\sum_{k=0}^{n} \alpha_k^{(p)} = 2\beta_{n+1}^{(p)}(\alpha_n^{(p)} + \alpha_{n+1}^{(p)}). \tag{9}$$

Equation (9) gives $\beta_{n+1}^{(p)}$ in terms of the lower order $\alpha_k^{(p)}$ coefficients and is not subject to round-off errors. However, Eq. (9) must be supplemented with a second relation which gives $\alpha_k^{(p)}$ up to $k = n + 1$.

If Eq. (3) is squared and averaged, one gets that,

$$\langle y^2 B_n^{(p)2} \rangle = \beta_{n+1}^{(p)} + \alpha_n^{(p)2} + \beta_n^{(p)}. \tag{10}$$

The left hand side of Eq. (10) can be evaluated as follows. The average of Eq. (7) gives,

$$\begin{aligned}(n+1) &= \sqrt{\beta_{n+1}^{(p)}}\langle B_{n+1}^{(p)\prime} B_n^{(p)}\rangle \\ &= \langle y B_{n+1}^{(p)} B_{n+1}^{(p)\prime}\rangle, \end{aligned} \tag{11}$$

where the second equality results from the average of Eq. (3) with n replaced by $n+1$ after multiplication by $B_{n+1}^{(p)\prime}$. An integration by parts yields,

$$\langle y B_n^{(p)} B_n^{(p)\prime}\rangle = -(p+1)/2 + \langle y^2 B_n^{(p)2}\rangle \tag{12}$$

so that with Eq. (11), one finds that

$$\langle y^2 B_n^{(p)2}\rangle = n + (p+1)/2. \tag{13}$$

With Eq. (13) in Eq. (10), one finds that

$$\beta_{n+1}^{(p)} + \alpha_n^{(p)2} + \beta_n^{(p)} = n + (p+1)/2. \tag{14}$$

Equation (14) can be combined with Eq. (9) to give a recurrence relation for $\alpha_k^{(p)}$ given by,

$$\alpha_{n+1}^{(p)} = \sum_{k=0}^{n} \alpha_k^{(p)}/[2n + (p+1) - 2\alpha_n^{(p)2} - 2\beta_n^{(p)}] - \alpha_n^{(p)}. \tag{15}$$

With Eq. (9) the term $\beta_n^{(p)}$ that appears in Eq. (15) can be written in terms of $\alpha_k^{(p)}$ up to order n so that Eq. (15) is essentially a recurrence relation for $\alpha_n^{(p)}$ alone.

A third recurrence relation can be derived by multiplying Eq. (7) by y^2 and averaging. With Eq. (13), one gets the result,

$$\tfrac{1}{2}(n+1)(n+p+1) = \sqrt{\beta_{n+1}^{(p)}}[\langle y^2 B_{n+1}^{(p)\prime} B_n^{(p)}\rangle - \langle y^2 B_{n+1}^{(p)} B_n^{(p)\prime}\rangle]. \tag{16}$$

With an integration by parts for $\langle y^2 B_{n+1}^{(p)\prime} B_n^{(p)}\rangle$, one has that,

$$\begin{aligned}(n+1)(n+p+1) = 4\sqrt{\beta_{n+1}^{(p)}}\,[&\langle y^3 B_{n+1}^{(p)} B_n^{(p)}\rangle - \tfrac{1}{2}(p+2)\langle y B_{n+1}^{(p)} B_n^{(p)}\rangle \\ &- \langle y^2 B_{n+1}^{(p)} B_n^{(p)\prime}\rangle]. \end{aligned} \tag{17}$$

Use of Eqs. (3) and (11) yields,

$$\begin{aligned}\langle y^2 B_{n+1}^{(p)} B_n^{(p)\prime}\rangle &= \sqrt{\beta_{n+1}^{(p)}\beta_n^{(p)}}\langle B_n^{(p)\prime} B_{n-1}^{(p)}\rangle \\ &= n\sqrt{\beta_{n+1}^{(p)}}. \end{aligned}$$

The two remaining integrals in Eq. (17) are evaluated with repeated use of Eq. (3). The final result is,

$$(n+1)(n+p+1) = 4\beta_{n+1}^{(p)}[\alpha_n^{(p)}(\alpha_n^{(p)} + \alpha_{n+1}^{(p)}) + \beta_n^{(p)} + \tfrac{1}{2}]. \tag{18}$$

TABLE I

Starting Values of $\alpha_n^{(p)}$

P	$\alpha_0^{(p)}$	$\alpha_1^{(p)}$
0	$\frac{1}{\sqrt{\pi}}$	$\frac{2}{(\pi-2)\sqrt{\pi}}$
1	$\frac{\sqrt{\pi}}{2}$	$\frac{\sqrt{\pi}(\pi-2)}{2(4-\pi)}$
2	$\frac{2}{\sqrt{\pi}}$	$\frac{4(4-\pi)}{\sqrt{\pi}(3\pi-8)}$

Equations (9), (14) and (18) are the desired results. Various combinations of these three recurrence relations gave algorithms for which round-off errors accumulated rapidly. However, since these recurrence relations are algebraically very simple, a computer program was written which employed multiple precision arithmetic subroutines for which arithmetic operations could be performed to any preassigned number of significant figures. Equations (9) and (15) were used in these calculations which require the first two values of $\alpha_k^{(p)}$ listed in Table I. The quantities $\alpha_n^{(p)}$ and $\beta_n^{(p)}$ for $p = 0, 1$ and 2 could be calculated to almost any order n. Essentially one significant figure is lost with each iteration. For $p = 0$ and 1, calculations were carried out to order $n = 20$. In this calculation 43 significant figures were retained. For the case $p = 2$, required for application to a solution of the BE, these coefficients were evaluated up to $n = 100$. In this calculation, 133 significant figures were retained. This calculation of $\alpha_n^{(p)}$ and $\beta_n^{(p)}$ for $p = 2$ and n up to 100 required only several seconds of computer time. For $p = 0$, the values of these coefficients were in agreement (to 15 significant figures) with those listed by Galant [4], which do not go beyond $n = 20$.

The procedures developed in this paper for the calculation of the coefficients in the general three term recurrence relation, Eq. (3), work extremely well. The methods employed in the derivation of the recurrence relations, Eqs. (9), (14) and (18), are applicable to non-integer values of p, and other intervals and weight functions, provided that the various integrals exist and the integration by parts can be carried out.

3. Calculation of Abscissae and Weights

The Nth order Gaussian quadrature formula is of the form

$$\int_0^\infty e^{-y^2} y^p f(y)\, dy \simeq \sum_{i=1}^{N} w_i^{(p)} f(y_i^{(p)}), \tag{19}$$

TABLE IIa

Quadrature Abscissae and Weights; $w(y) = e^{-y^2}$

	y_i	w_i
$N = 2$	0.3001939310608394(0)	0.6405291796843786(0)
	0.1252421045333717(+1)	0.2456977457683793(0)
$N = 4$	0.1337764469960676(0)	0.3253029997569190(0)
	0.6243246901871900(0)	0.4211071018520622(0)
	0.1342537825644992(+1)	0.1334425003575195(0)
	0.2262664477010362(+1)	0.6374323486257276(−2)
$N = 8$	0.5297864393185113(−1)	0.1341091884533595(0)
	0.2673983721677653(0)	0.2683307544726388(0)
	0.6163028841823999(0)	0.2759533979884218(0)
	0.1064246312116224(+1)	0.1574482826187903(0)
	0.1588855862270055(+1)	0.4481410991746290(−1)
	0.2183921153095858(+1)	0.5367935756025333(−2)
	0.2863133883708075(+1)	0.2020636491324107(−3)
	0.3686007162724397(+1)	0.1192596926595344(−5)
$N = 16$	0.1975365846007727(−1)	0.5052463202137790(−1)
	0.1028022452379175(0)	0.1136085568941510(0)
	0.2473976694524551(0)	0.1629212923145450(0)
	0.4466962259616832(0)	0.1835628011162462(0)
	0.6930737203019995(0)	0.1654386377556098(0)
	0.9794041703307299(0)	0.1165724905535033(0)
	0.1299789321277036(+1)	0.6199969609915657(−1)
	0.1649854240397434(+1)	0.2391970961868355(−1)
	0.2026808152168867(+1)	0.6409914424050132(−2)
	0.2429450491602143(+1)	0.1135695310688778(−2)
	0.2858266528543266(+1)	0.1252862213295624(−3)
	0.3315769275038698(+1)	0.7950495719622457(−5)
	0.3807377116755898(+1)	0.2590007619415064(−6)
	0.4343606345470172(+1)	0.3611549139742782(−8)
	0.4946377204048386(+1)	0.1537677916189839(−10)
	0.5675017934041922(+1)	0.8674204452494624(−14)

where $y_i^{(p)}$ are the N roots of the polynomial $B_N^{(p)}(y)$ and $w_i^{(p)}$ are the corresponding weights. The abscissae $y_i^{(p)}$ were calculated by diagonalizing the tri-diagonal matrix

$$J = \begin{pmatrix} \alpha_1^{(p)} & \sqrt{\beta_1^{(p)}} & 0 & \cdots & 0 \\ \sqrt{\beta_1^{(p)}} & \alpha_2^{(p)} & \sqrt{\beta_2^{(p)}} & \cdots & 0 \\ 0 & \sqrt{\beta_2^{(p)}} & \alpha_3^{(p)} & \cdots & 0 \\ \vdots & \vdots & \vdots & & \\ 0 & 0 & 0 & \cdots & \alpha_N^{(p)} \end{pmatrix}$$

TABLE IIb

Quadrature Abscissae and Weights; $w(y) = e^{-y^2}y$

	y_i	w_i
$N = 2$	0.5466400565221693(0)	0.3252320794479061(0)
	0.1518176674506265(+1)	0.1747679205520937(0)
$N = 4$	0.2800995401403832(0)	0.1139990543365298(0)
	0.8320770658174104(0)	0.2692323797134971(0)
	0.1556389870300421(+1)	0.1107889566826584(0)
	0.2463284959722103(+1)	0.5979609267314704(−2)
$N = 8$	0.1218127678061463(0)	0.2397877317765308(−1)
	0.3882449491473571(0)	0.1092506819189940(0)
	0.7651497067658092(0)	0.1797622678433810(0)
	0.1224690624761160(+1)	0.1351751653621029(0)
	0.1751398297664409(+1)	0.4552181928573556(−1)
	0.2343383197810315(+1)	0.6064921853788935(−2)
	0.3016608849956826(+1)	0.2448536436477049(−3)
	0.3831371300820741(+1)	0.1516914696753451(−5)
$N = 16$	0.4775799543737674(−1)	0.3795307814831678(−2)
	0.1575643611266753(0)	0.2136808301992049(−1)
	0.3236556568455920(0)	0.5595857089379011(−1)
	0.5391473546675038(0)	0.9587168277747507(−1)
	0.7970053979972014(0)	0.1169082070371872(0)
	0.1090958307363892(+1)	0.1029363012162623(0)
	0.1415975970714936(+1)	0.6468246716393942(−1)
	0.1768437030466615(+1)	0.2831911613754905(−1)
	0.2146149962010079(+1)	0.8362647991652432(−2)
	0.2548365652625752(+1)	0.1597736202726321(−2)
	0.2975896592510777(+1)	0.1870134647150351(−3)
	0.3431483868308089(+1)	0.1243935496206526(−4)
	0.3920694119664905(+1)	0.4208466925294357(−6)
	0.4454120573510955(+1)	0.6051847030054333(−8)
	0.5053674269642785(+1)	0.2643406562982473(−10)
	0.5778478847939104(+1)	0.1524594098604790(−13)

as described elsewhere [22]. The corresponding weights are given in terms of the first component, q_{0i} of the ith normalized eigenvector of J, that is,

$$w_i^{(p)} = m^{(p)} q_{0i}^2,$$

where $m^{(p)} = \int_0^\infty e^{-y^2} y^p \, dy$. The results of these calculations are shown in Table II for $p = 0, 1$ and 2, and orders $N = 2, 4, 8$ and 16. For each set of the points, the monomial integrals

$$\int_0^\infty e^{-y^2} y^p y^n \, dy = \frac{1}{2} \Gamma\left(\frac{n + p + 1}{2}\right)$$

TABLE IIc

Quadrature Abscissae and Weights; $w(y) = e^{-y^2}y^2$

	y_i	w_i
$N = 2$	0.7539869079898871(0)	0.2738413467266824(0)
	0.1734055298879163(+1)	0.1692721159996965(0)
$N = 4$	0.4238628193900528(0)	0.7649092266787873(−1)
	0.1014332104566760(+1)	0.2435439494642453(0)
	0.1742437375162050(+1)	0.1162953035510695(0)
	0.2639813333635586(+1)	0.6783287043185401(−2)
$N = 8$	0.1990000637984294(0)	0.9599144336400067(−2)
	0.5059526450205794(0)	0.7072944976303661(−1)
	0.9041682182040568(0)	0.1573668870039431(0)
	0.1372615723971598(+1)	0.1429322724003870(0)
	0.1900969572329702(+1)	0.5431444004253597(−1)
	0.2490479841967435(+1)	0.7835224153141577(−2)
	0.3158780677105240(+1)	0.3338952597020048(−3)
	0.3966720403265353(+1)	0.2149767232664775(−5)
$N = 16$	0.8174913389984520(−1)	0.7050727473210895(−3)
	0.2154761962759740(0)	0.7107111654073120(−2)
	0.4003530517087630(0)	0.2844188515941899(−1)
	0.6298538771405607(0)	0.6660235171398239(−1)
	0.8976124329697087(0)	0.1025785712747278(0)
	0.1198149260240153(+1)	0.1077502032531791(0)
	0.1527188184719962(+1)	0.7747156370638879(−1)
	0.1881745606015598(+1)	0.3763106373385135(−1)
	0.2260132964654088(+1)	0.1204873635560290(−1)
	0.2661980315279350(+1)	0.2453208613776865(−2)
	0.3088376381635592(+1)	0.3020309847850189(−3)
	0.3542256017930265(+1)	0.2092121075871870(−4)
	0.4029312272760483(+1)	0.7314637349679360(−6)
	0.4560203031431090(+1)	0.1080646863902574(−7)
	0.5156826768007481(+1)	0.4828081616137754(−10)
	0.5878114488915572(+1)	0.2840126937112534(−13)

were calculated for $n = 0$ to $n = 2N$, and were in agreement with the above result to the accuracy of the abscissae and weights in Table II. For the case $p = 2$, the results for $N = 2, 4$ and 8 agree with those in [2] to their stated accuracy of 7–8 significant figures. Whereas these earlier calculations fail beyond $N = 13$, in the present work abscissae and weights up to $N = 100$ were evaluated for use in subsequent applications; (see Section 5). For case $p = 0$, the present results shown in Table IIa agree with the results obtained by other workers [3, 4, 6]. The results of Huang and Giddens are correct to only 3–4 significant figures.

4. Comparison of Quadrature Formulae

It is of considerable interest to compare the newly derived quadrature procedure with the Gauss–Laguerre formula, of the form

$$\int_0^\infty e^{-x} f(x)\, dx \simeq \sum_{i=1}^{N} v_i f(x_i),$$

where x_i and v_i are the abscissae and weights, respectively, and are tabulated. Many different types of integrals which could be calculated analytically were integrated with the formula above and also with Eq. (19). The results for two integrals are discussed here which demonstrate the usefulness of the new quadrature formulae. The first integral is

$$I_1(\gamma) = \int_0^\infty x^2 e^{-\gamma x^2 - x}\, dx$$
$$= [\sqrt{\gamma\pi}(1 + 1/2\gamma)\exp(1/4\gamma)\operatorname{erfc}(1/2\sqrt{\gamma}) - 1]/4\gamma^2$$

TABLE III

Comparison of Quadrature Formulae: $I_1(\gamma)$

N	Laguerre	$p=0$	$p=1$	$p=2$
$\gamma = 0.02$, exact value = 1.62632				
2	1.64296	1.44464	1.72768	1.74032
4	1.62592	1.61808	1.62408	1.62712
8	1.62632	1.62632	1.62632	1.62632
$\gamma = 0.10$, exact value = 0.96178				
2	0.81513	1.15062	1.14917	0.94200
4	0.96744	0.97484	0.98157	0.96031
8	0.96182	0.96202	0.96196	0.96168
16	0.96178	0.96178	0.96178	0.96178
$\gamma = 1.0$ exact value = 0.15923				
2	0.17326	0.15290	0.16105	0.15763
4	0.16502	0.15922	0.15923	0.15923
8	0.16140	0.15923		
16	0.16002			
32	0.15923			
$\gamma = 10$ exact value = 0.99164(−2)				
2	1.04941(−2)	0.98616(−2)	0.99210(−2)	0.99160(−2)
4	1.01200(−2)	0.99164(−2)	0.99164(−2)	0.99164(−2)
8	0.99883(−2)			
16	0.99418(−2)			
32	0.99287(−2)			

TABLE IV

A comparison of Quadrature Formulae: $I_2(\gamma)$

N	Laguerre	$p=2$	Laguerre	$p=2$
	$\gamma = 1/512$		$\gamma = 1/64$	
2	23.6105	22.6495	8.40107	8.06226
4	22.9827		8.17994	
8	22.7664		8.10358	
16	22.6907		8.07682	
Exact values	22.6495		8.06226	
	$\gamma = 1$		$\gamma = 8$	
2	1.44641	1.41334	1.06248	1.05758
4	1.41421	1.41421	1.06066	1.06062
8	1.41919		1.06179	1.06066
16	1.41600		1.06120	
Exact value	1.41421		1.06066	
	$\gamma = 128$		$\gamma = 512$	
2	1.00390	1.00360	1.00098	1.00090
4	1.00390	1.00383	1.00098	1.00096
8		1.00389		1.00097
16		1.00390		1.00098
Exact value	1.00390		1.00098	

and the second integral is the average of the speed dependent collision frequency $Z(x)$ that occurs in kinetic theory given by

$$Z(x) = [e^{-\gamma x} + (\sqrt{\pi}/2)(2\sqrt{\gamma x} + 1/\sqrt{\gamma x})\,\mathrm{erf}(\sqrt{\gamma x})]1/\sqrt{\pi},$$

where γ is the mass ratio of the colliding species.

The integral considered is,

$$I_2(\gamma) = \frac{1}{\sqrt{\pi}} \int_0^\infty e^{-x} \sqrt{x}\, Z(x)\, dx$$
$$= (1 + 1/\gamma)^{1/2}.$$

The rate of convergence of the different numerical quadrature procedures is shown in Tables III and IV. In each of the cases considered, the integrals were transformed to a form compatible with the quadrature formula used. For $I_1(\gamma)$ shown in Table III, Gauss–Laguerre quadrature formulae converge rapidly for $\gamma \to 0$ as would be expected and rather slowly for large γ. The slow convergence is due to the occurrence of $\sqrt{x}$ in the integrand when the transformation to speed variable $y = \sqrt{x}$ is made.

The new quadrature formula based on $w(\gamma) = e^{-\gamma^2}\gamma^p$ gives rapidly convergent results over the whole range of values of γ. For γ large, the rapid convergence is to be expected, but for small γ the convergence is still extremely good.

The results for $I_2(\gamma)$ are quite similar. For large mass ratios ($\gamma \to \infty$), $Z(x) \sim \sqrt{x}$ and the Laguerre formula is exact for $N = 2$. However, the new quadrature procedure, considered in this case with $p = 2$, converges very rapidly in this limit. For small mass ratios ($\gamma \to 0$), $Z(x)$ is independent of x and the integrand in $I_2(\gamma)$ depends on $\sqrt{x}$. The convergence with the Laguerre quadrature formula is very slow whereas the result is exact for $N = 2$ with the newly derived quadrature.

5. Solution of the Boltzmann Equation

In this section, the departure from equilibrium for a model reactive system of the type A + B → products is considered. A discussion of the details of the model was given in an earlier paper [18]. In the present paper, species B is assumed to be present in large excess and at equilibrium, similar to the procedure adopted in a previous time dependent study [24]. The primary objective is to compare the previous results obtained with the polynomial method with a new discrete ordinate method.

The energy distribution function of species A, $P(x)$, is given by

$$P(x) = P^M(x)[1 - \phi(x)],$$

where $x = mc^2/2kT$ is the reduced translational energy, $P^M(x) = 2(x/\pi)^{1/2}e^{-x}$ is the equilibrium Maxwellian energy distribution. The quantity $\phi(x)$ is the perturbation of the distribution function due to the reactive process and is given by a linear integral equation [18] of the form,

$$\int_0^\infty K(x', x)\, P^M(x')\, \phi(x')\, dx' - Z(x)\, P^M(x)\phi(x) = -P^M(x)\left[R(x) - \int_0^\infty P^M(x')\, R(x')\, dx'\right], \tag{20}$$

where $K(x', x)$ is the Wigner–Wilkins kernel [25] given by

$$K(x', x) = \tfrac{1}{2}aQ^2(\pi/x')^{1/2}\{\operatorname{erf}(Q\sqrt{x} + R\sqrt{x'}) + e^{x'-x}\operatorname{erf}(R\sqrt{x} + Q\sqrt{x'}) \pm [\operatorname{erf}(Q\sqrt{x} - R\sqrt{x'}) + e^{x'-x}\operatorname{erf}(R\sqrt{x} - Q\sqrt{x'})]\}, \tag{21}$$

where the + (−) sign refers to $x' > x$ ($x' < x$). In Eq. (21) $Q = \frac{1}{2}(\gamma^{-1/2} + \gamma^{1/2})$, $R = \frac{1}{2}(\gamma^{-1/2} - \gamma^{1/2})$, $\gamma = m_B/m_A$, $a = \pi d^2(2kT/\pi m_A)^{1/2}$ and πd^2 is the total cross section for elastic A–B collisions. Although the notation is different, (20) is essentially Eq. (11) of Ref. [18]. The form of the kernel $K(x', x)$ versus x and x' depends on γ and is characterized by a maximum at $x = x'$ and has a discontinuous first

derivative there. The quantity $Z(x)$ in (20) is the energy dependent collision frequency defined by

$$Z(x) = \int_0^\infty K(x, x')\, dx' \tag{22}$$

and given by [25],

$$Z(x) = a\gamma^{-1/2}[e^{-\gamma x} + (\sqrt{\pi}/2)\{2(\gamma x)^{1/2} + (\gamma x)^{-1/2}\}\, \mathrm{erf}(\gamma x)^{1/2}]. \tag{23}$$

The quantity $R(x)$ is the energy dependent reactive collision frequency defined by [26],

$$R(x) = (2kT/\pi\mu)^{1/2}(M_A M_B x)^{-1/2}[G(-\sqrt{x}) - G(\sqrt{x})], \tag{24}$$

where

$$G(\sqrt{x}) = \int_0^\infty \exp[-(x' + \sqrt{M_B x})^2/M_A]\, \sigma^*(E) x'^2\, dx' \tag{25}$$

with $M_A = m_A/(m_A + m_B)$, $M_B = 1 - M_A$ and $\mu = m_A m_B/(m_A + m_B)$. In (25) $\sigma^*(E)$ is the total reactive cross section as a function of the relative translational energy E, taken to be the line-of-centers form, that is,

$$\begin{aligned} \sigma^*(E) &= 0, && E < E^*, \\ &= \pi d_R^2(1 - E^*/E), && E \geqslant E^*, \end{aligned}$$

where E^* is the threshold energy and d_R is a reactive hard sphere diameter. The form of $R(x)$ is determined by the mass ratio γ and the reduced threshold energy $\varepsilon^* = E^*/kT$ as discussed in detail elsewhere [26]. Of particular interest, is that for large γ, $P^M(x)\, R(x)$ is essentially zero until near $x = \varepsilon^*$ and then rises rapidly to a maximum followed by a near exponential decay over a short range in x.

Solutions to Eq. (20) are sought and the departure from equilibrium is expressed in terms of the fractional decrease in the rate of reaction from the equilibrium value [18], that is, in terms of

$$\eta = \int_0^\infty P^M(x)\, \phi(x)\, R(x)\, dx \Big/ \int_0^\infty P^M(x)\, R(x)\, dx. \tag{26}$$

Equations (20) and (26) together with the associated definitions are the basic equations.

There are two important features of Eq. (20) which must be carefully noted before solutions are sought. The first is that with the detailed balance condition

$$K(x', x)\, P^M(x') = K(x, x')\, P^M(x) \tag{27}$$

and with (22) one finds that (20) can be rewritten in the form,

$$\int_0^\infty K(x', x)\, P^M(x')[\phi(x') - \phi(x)]\, dx' = -P^M(x) \left[R(x) - \int_0^\infty P^M(x')\, R(x')\, dx' \right]. \quad (28)$$

In view of (28), the discontinuity in the first derivative, or cusp, of $K(x', x)$ at $x' = x$ does not play an important role. This feature of the integral equation was not appreciated in a recent application [14]. Some of the numerical methods described in the Appendix of this previous work were motivated by the existence of the discontinuity in the derivative of K and, are largely unnecessary as discussed later in this paper.

A second important feature of (20) is that particle number is conserved, that is, integration of (20) over x gives zero on both sides of the equation. Consequently, (20) determines $\phi(x)$ only to within an additive constant. A unique solution is determined by requiring the normalization [18],

$$\int_0^\infty P^M(x)\, \phi(x)\, dx = 0, \quad (29)$$

usually referred to as the auxiliary condition.

The discrete ordinate method of solution of Eq. (20) involves the numerical integration over x' in (20) with some suitable quadrature formula. Due to the occurrence of the Maxwellian weight function in (20) and the semi-infinite integration range a possible choice is the Gauss–Laguerre quadrature formula, that is,

$$\int_0^\infty e^{-x} f(x)\, dx \simeq \sum_{i=1}^N v_i f(x_i), \quad (30)$$

where x_i are the roots of the Laguerre polynomial of degree N and v_i are the corresponding weights. Application of this quadrature rule to (20) at each of the points $x = x_i$, yields the set of linear equations

$$\sum_{j=1}^N V_j K(x_j, x_i)\, \phi(x_j)\, P^M(x_j) - \phi(x_i)\, P^M(x_i) \sum_{j=1}^N V_j K(x_j, x_i)$$
$$= -P^M(x_i) \left[R(x_i) - \sum_{j=1}^N V_j P^M(x_j)\, R(x_j) \right], \quad (31)$$

where $V_j = v_j e^{x_j}$. It is important to notice that although the exact analytic form of $Z(x)$ is known, (Eq. (23)), it is evaluated numerically with (22). The purpose of this procedure is to ensure that particle conservation is conserved exactly despite the approximation inherent in the quadratures. If (31) is multiplied by V_i and summed over i and the detailed balance result

$$P^M(x)\, Z(x) = \int_0^\infty P^M(x')\, K(x, x')\, dx' \quad (32)$$

is used, then both sides of (31) vanish identically. It is important to mention that this is essentially equivalent to the methods described in the Appendix of a recent paper [14]. The somewhat involved manipulations described there simply ensure detailed balance and particle conservation.

With particle conservation imposed exactly, the set of equations (31) is not linearly independent and an additional equation must be specified. This additional equation is the auxiliary condition, Eq. (29), which when written in quadrature form is,

$$\sum_{j=1}^{N} V_j P^M(x_j)\,\phi(x_j) = 0. \tag{33}$$

Equation (33), together with the first $N-1$ equations in (31) specifies $\phi(x_j)$. The quantity η is then given by

$$\eta = \sum_{j=1}^{N} V_j P^M(x_j)\,\phi(x_j)\,R(x_j) \Big/ \sum_{j=1}^{N} V_j P^M(x_j)\,R(x_j). \tag{34}$$

The quadrature procedure introduced in Section 2 was also employed in much the same manner.

With the change of variable $x = y^2$, one finds, in place of Eqs. (31), (33) and (34), that,

$$2\sum_{j=1}^{N} W_j K(y_j^2, y_i^2)\,P^M(y_j^2)\,\phi(y_j^2)\,y_j - 2P^M(y_i^2)\,\phi(y_i^2)\sum_{j=1}^{N} W_j K(y_j^2, y_i^2)\,y_j$$

$$= -P^M(y_i^2)\left[R(y_i^2) - 2\sum_{j=1}^{N} W_j P^M(y_j^2)\,R(y_j^2)\,y_j\right], \tag{35}$$

$$\sum_{j=1}^{N} W_j P^M(y_j^2)\,\phi(y_j^2)\,y_j = 0 \tag{36}$$

and

$$\eta = \sum_{j=1}^{N} W_j P^M(y_j^2)\,\phi(y_j^2)\,R(y_j^2)\,y_j \Big/ \sum_{j=1}^{N} W_j P^M(y_j^2)\,R(y_j^2)\,y_j. \tag{37}$$

In Eqs. (35)–(37), $W_j = w_j e^{y_j^2}/y_j^2$.

Tables V and VI show the rate of convergence of η as calculated with the discrete ordinate method. It is important to note that Eqs. (31) and (35) were solved for $P^M\phi$ rather than for ϕ itself. The Gauss–Laguerre and the new quadrature procedures were employed in these calculations. The new quadrature procedure appears to be preferable and gives moderately rapid convergence to three significant figures. It is important to point out that for most practical applications, rapid convergence to 2–3 significant figures would be sufficient. For the larger values of γ and ε^* in Table VI the rate of convergence has slowed considerably. This slow convergence is easily understood when one considers the details of the calculation of η. In Fig. 1a, the

TABLE V

Convergence of η; Comparison of Discrete Ordinate Methods[a]

N	$\varepsilon^* = 2$		$\varepsilon^* = 5$		$\varepsilon^* = 8$	
	New quadrature	Laguerre	New quadrature	Laguerre	New quadrature	Laguerre
5	0.2169[b]	0.2346	0.06513	0.07020	0.01474	0.01571
10	0.2131	0.2221	0.06300	0.06791	0.01404	0.01683
15	0.2126	0.2195	0.06268	0.06737	0.01392	0.01715
25	0.2123	0.2167	0.06255	0.06601	0.01387	0.01656
40	0.2122	0.2181	0.06251	0.06812	0.01385	0.01889
Polynomial method[c]	0.2122		0.06249		0.01385	

[a] $\gamma = 1$, $d = d_R$.
[b] Results with the new quadrature procedure, $p = 2$.
[c] From 5–10 terms in the polynomial expansion were used.

TABLE VI

Convergence of η; Comparison of discrete ordinate methods[a]

N	$\varepsilon^* = 5$		$\varepsilon^* = 10$		$\varepsilon^* = 15$	
	New quadrature	Laguerre	New quadrature	Laguerre	New quadrature	Laguerre
5	1.5964	1.6262	0.04927	0.7299	—	—
10	0.8892	0.8836	0.2585	0.3179	0.1053	0.08442
15	0.8330	0.8417	0.2049	0.2110	0.07703	0.09823
25	0.8167	0.8245	0.2079	0.2103	0.08471	0.08584
40	0.8111	0.8170	0.2052	0.2081	0.08291	0.08501
60	0.8096	0.8129	0.2045	0.2062	0.08248	0.08348
Polynomial method[b]	0.8087		0.2041		0.08224	

[a] $\gamma = 10$, $d = d_R$.
[b] From 8–12 terms in the polynomial expansion were used.

graph of $P^M \phi R$ (see (26)) is shown versus y. The contribution to η for γ and ε^* large [26], comes from large values of y (the maximum in P^M occurs at $y = 1$) and over a small range of reduced speeds. With a total of 60 quadrature points, only 10 points, shown explicitly in Fig. 1a, are used directly in the calculation of η. An increase in the total number of quadrature points does not substantially alter the actual number that fall within this important interval.

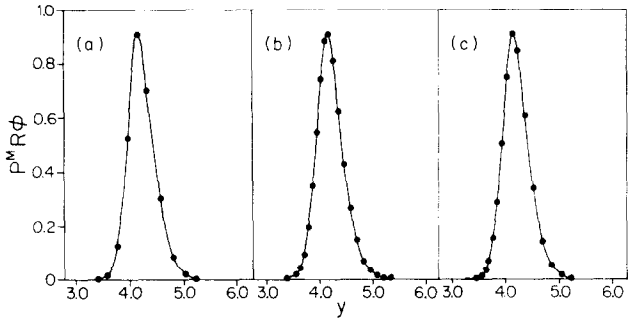

FIG. 1. Variation of $P^M R\phi$ versus y. (a) New weights and points, $N = 60$, $s = 1.0$; (b) $N = 100$, $s = 0.35$; (c) two interval method, $N_1 = 10$, $N_2 = 30$, $y_{max} = 5.5$ (see text). $P^M R\phi$ in arbitrary units; $\gamma = 10$, $\varepsilon^* = 15$.

An improvement in these results can be obtained by suitably scaling the points in the quadrature, that is, by a change of variable $z = y/s$ such that

$$\int_0^\infty f(y)\,dy = s\int_0^\infty f(sz)\,dz = s\sum_{j=1}^{N} W_j f(sz_j). \tag{38}$$

With $s < 1$, the quadrature points are scaled to smaller values. The variation of η with the scale factor s for $\gamma = 10$ and $\varepsilon^* = 15$, and several different orders N, is shown in Table VII. Although no detailed error analysis has been carried out, it appears that the best choice for s is the value for which the variation of η with s is a minimum. For $N = 80$ and 100 and $s \approx 1$, the large values of y_i lead to an overflow in

TABLE VII

Variation with the Scale Factor[a]

s/N	40	60	80	100
1.00	0.082908	0.082482	—	—
0.90	0.082767	0.082427	0.082331	—
0.80	0.082650	0.082381	0.082309	0.082280
0.70	0.082563	0.082345	0.082291	0.082270
0.60	0.082512	0.082318	0.082277	0.082262
0.50	0.082436	0.082303	0.082267	0.082256
0.40	0.020198	0.082036	0.082263	0.082253
0.38	0.00428	0.080435	0.082261	0.082253
0.36	0.00046	0.072560	0.082215	0.082253
0.34	0.00003	0.048254	0.081730	0.082250
0.32		0.015739	0.078077	0.082191
0.30		0.001854	0.060416	0.081430

[a] $\gamma = 10$, $\varepsilon^* = 15$, $d = d_R$; polynomial result 0.082244.

the calculation of the kernel so that values of η are not shown. The result with $N = 100$ and $s \simeq 0.38$ agrees remarkably well with the result with the expansion method. The small discrepancy is most probably due to numerical round-off errors in the polynomial method. In any event, three figure accuracy is all that is required in practical applications. The graph of $P^M R\phi$ versus y for $N = 100$ and $s = 0.35$ is shown in Fig. 1b and illustrates the improvement in the final result with the introduction of 20 quadrature points in the important reduced speed interval.

In view of the bebaviour shown in Figs. 1a and b, it is clear that accurate solutions can be calculated if the quadrature points are concentrated in the region of speed space which contributes most to η. Although the solution ϕ is required for all y, perhaps fewer points are required in the interval below some value $y = y_0$, where $P^M\phi \approx 0$. With this in mind, additional calculations were carried out with the division of the semi-infinite interval into two intervals $[0, y_0]$ and $[y_0, \infty]$, where y_0 was

TABLE VIII

Convergence of η; Two Interval Method

N_1	N_2[a]	$\gamma = 10, \varepsilon^* = 15$	$\gamma = 20, \varepsilon^* = 20$	$\gamma = 40, \varepsilon^* = 25$
5	5	0.023190	0.02590	—
	10	0.081831	0.14325	—
	15	0.080677	0.13818	—
	20	0.080482	0.13696	—
	30	0.080413	0.13624	—
	40	0.080405	0.13602	—
10	5	0.020469	0.09509	—
	10	0.083829	0.10784	0.15539
	15	0.082585	0.10578	0.15221
	20	0.082361	0.10546	0.15146
	30	0.082272	0.10533	0.15115
	40	0.082256	0.10531	0.15109
15	5	0.020470	0.09505	—
	10	0.083827	0.10785	0.15335
	15	0.082583	0.10579	0.15060
	20	0.082359	0.10546	0.14995
	30	0.082269	0.10533	0.14970
	40	0.082254	0.10531	0.14965
20	5	0.020470	0.09506	—
	10	0.083826	0.10785	0.15339
	15	0.082582	0.10578	0.15062
	20	0.082358	0.10546	0.14997
	30	0.082269	0.10533	0.14971
	40	0.082253	0.10531	0.14966
	Polynomial result	0.082244	0.10527	0.14926

[a] N_1 and N_2 are the number of quadrature points in the first and second interval, respectively; see text.

defined (rather arbitrarily) such that $P^M R$ is 1/20th of the maximum value. The new quadrature procedure was employed in the second interval with a change of variable as given by,

$$\int_{y_0}^{\infty} f(y)\,dy = \int_0^{\infty} f(\sqrt{y^2 + y_0^2})\, y/\sqrt{y^2 + y_0^2}\,dy.$$

A scale change was also employed (see (38)) so that there were no quadrature points beyond some large value, $y_{\max}$. A Gauss–Legendre quadrature was employed for the first interval with an appropriate variable change, that is,

$$\int_0^{y_0} f(y)\,dy = \frac{y_0}{2}\int_{-1}^{1} f[\,y_0(y+1)/2\,]\,dy.$$

The convergence of η versus the number of quadrature points in the two intervals is shown in Table VIII. It is clear that 10 points in the first interval and 20–30 points in the second is all that is required to give convergence to three significant figures. The entries that are not shown had too few points and meaningful results were not obtained. Results of calculations with additional points in both intervals and not shown in Table VIII agreed with the values shown for $N_1 = 20$ and $N_2 = 40$, so that these have converged. What is of interest is that reasonable results can be obtained with a small number (20–40) of quadrature points. Moreover, a large fraction of these points do fall within the important speed interval, as shown in Fig. 1c.

6. Summary

The present work has demonstrated the usefulness of a discrete ordinate method based on a new quadrature formula in the solution of the chemical kinetic Boltzmann equation. It is anticipated that this method of solution will prove more efficient than traditional polynomial expansion methods, particularly in applications to realistic systems for which input data such as cross sections are available only in numerical form. Applications to the chemical kinetics of hot atom systems have been described elsewhere [27].

It is important to note that the discontinuity in the derivative of the kernel does not play an important role. In particular, although (22) can serve as a useful check of the quadrature procedure employed, quite accurate results are obtained even though the numerical integration over K (see (22)) is accurate to only a few percent. This is so provided detailed balance and particle conservation is ensured, as in (35). Consistent with particle conservation is the normalization condition which is satisfied exactly as in (33) and (36).

Although the final results of earlier papers [14–16] are correct, some of the numerical methods introduced there are not necessary. In particular, the interpolation

described in the Appendix of [14] motivated by the presence of the cusp in the kernel is not required. Also the discussion in [16] with regard to the difficulty of satisfying the normalization condition is somewhat misleading. The normalization condition can always be imposed exactly as an additional constraint. The important point is the realization that particle conservation must be ensured, and this requirement is easily met as in the present paper.

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