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Representation of generally mixed multivariate aerosols by the quadrature method of moments: I. Statistical foundation

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Abstract

The quadrature method of moments (QMOM), a promising new tool for aerosol dynamics simulation is extended to generally mixed multicomponent particle populations. This paper develops the mathematical and statistical foundation for a fully multivariate extension of the QMOM using principal components analysis (PCA). In essence, the full particle distribution function is systematically replaced by a set of lower-order mixed moments and corresponding multivariate quadrature points optimally assigned through PCA and back projection. The resulting PCA–QMOM is illustrated for a multivariate normal particle population in order to compare quadrature point assignments with analytic results, but the method is applicable to arbitrary distributions. Physical and optical properties can be reliably estimated by summation over the PCA-assigned quadrature points. Application of the PCA–QMOM to the dynamics of generally mixed particle populations evolving under condensation, coagulation, and sintering is described in the following paper (Part II).
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1. Introduction

The method of moments (MOM) has been developed in recent years into a powerful and efficient simulation tool that is now a viable alternative to sectional and modal methods for representing aerosol microphysical processes in atmospheric models (Wright, McGraw, Benkovitz, & Schwartz

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2000; Yu, Kasibhatla, Wright, Schwartz, McGraw, & Deng, 2003). Operationally, the MOM is a method for direct tracking of the lower-order moments of a particle distribution function (pdf) rather than the distribution itself. This reduction in number of variables contributes much to the computational efficiency of the method while offering unique advantages for engineering applications requiring simulation of particle populations under conditions that can include new particle formation, evaporation, growth by condensation and coagulation, and complex mixing flows (Hulburt & Katz, 1964; McGraw & Saunders, 1984; Pratsinis, 1988; Jurcik & Brock, 1993; La Violette, Berry, & McGraw, 1996; Yu et al., 2003). Closure of the moment evolution equations, which has always been a key issue with the MOM, has been achieved for general particle growth laws by combining the MOM with quadrature methods resulting in the quadrature method of moments (QMOM) (McGraw, 1997; Barrett & Webb, 1998). In addition to achieving closure, the QMOM, by exploiting a fundamental mathematical connection between moments and quadrature abscissas and weights (Press & Teukolsky, 1990), yields a systematic and accurate prescription for reliable estimation of the physical and optical properties of a particle population directly from its lower-order moments (McGraw, Huang, & Schwartz, 1995; Wright, 2000; Rosner, McGraw, & Tandon, 2003). Recently the QMOM has been extended to model the chemically resolved dynamics of multicomponent internally mixed aerosols (McGraw & Wright, 2003) (the assumption of internal mixing reduces the problem to a univariate one for which the composition of a particle is determined from its mass).

With a few mostly bivariate exceptions (e.g., Strom, Okada, & Heintzenberg, 1992; Xiong & Pratsinis, 1993; Wright, McGraw, & Rosner, 2001), pdfs have generally been approximated using only a single (univariate) particle coordinate, such as radius or mass. On the other hand, there is a growing need for reliable multivariate pdf models in such diverse fields as combustion, nano-particle synthesis, and assessment of radiative and health effects of atmospheric aerosols and their impact on climate. This is driven, in part, by new advances in the technology for particle measurement. For example, field-deployable, single-particle mass spectroscopic techniques now furnish the composition of multicomponent aerosols in real time and on a particle-by-particle basis (Murphy & Thomson, 1995; Suess & Prather, 1999). Multicomponent thermodynamic models (Clegg, Brimblecombe, & Wexler, 1998), capable of estimating the phase stability and evaporation rates of mixed particles, provide yet another driver for development of a multivariate aerosol model as such detailed information is underutilized in a univariate description. The analysis of single-particle measurements has spurred the development of sophisticated software tools for multivariate data visualization, analysis, and compression (Imre, 2003). The need for efficient microphysical-based simulations that can be run in real time and compared with these new kinds of measurements has, in turn, motivated our development of the present multivariate, statistically based aerosol model. Interestingly, some of the methods developed below for simulation (Section 2.2) are better known historically for their applications to data analysis and compression.

The great efficiency of moment methods makes them ideal candidates for multivariate applications. The following sections develop the mathematical foundation for a fully multivariate extension of the QMOM using principal components analysis (PCA). The resulting PCA–QMOM is illustrated in Section 3 for a multivariate normal particle population in order to compare various quadrature point assignments with analytic results, but the method is by no means limited to this case. In Section 4 we describe how to estimate physical and optical properties of a particle population, and obtain closure of the moment evolution equations, directly from the mixed moments tracked in a simulation. This paper (Part I) describes application of PCA to the QMOM with an arbitrary number of quadrature points per variable. The following paper (Part II) gives several illustrations of the method including its application to the simulation of generally mixed aerosols evolving under condensation and coagulation. The illustrations of Part II will use the simplest implementation of the method described here with two quadrature points per variable (e.g., 2^h quadrature points for an aerosol having h components).

2. Mathematical approach

In this paper we treat generally mixed, multivariate pdfs for which internally mixed and externally mixed particle populations are special limiting cases. For definiteness, examples of the pdfs will be drawn mostly from the composition space of a multicomponent, but otherwise uniform-particle aerosol (i.e. an aerosol consisting of a distribution of spherical particles with homogeneous mixing within each particle). The description of particles of mixed size and shape is presented in Part II.

2.1. Multivariate distribution functions, moments, and quadrature approximations for generally mixed particle populations

Consider the multivariate pdf for particle number, $f(m_1, m_2, \ldots, m_h)$ where h is the number of components. This distribution function gives the number of particles per unit volume having component masses m_1 between m_1 and $m_1 + \mathrm{d}m_1$, etc. Note that $f(m_1, m_2, \ldots, m_h)$ is still not the most general description possible because it assumes that each particle is homogeneously mixed. (For example, a homogeneously mixed particle and a "core–mantle" particle each having the same overall composition would not be distinguished in this representation; although they could be distinguished by the methods to be described if additional variables were introduced.) For ease of presentation, we will limit discussion to distributions of the type $f(m_1, m_2, \ldots, m_h)$ whose treatment, while not the most general case possible, requires a considerable advance in the representation of multivariate particle populations.

The total mass distribution, giving the total mass of particles per unit volume having m_1 between m_1 and $m_1 + \mathrm{d}m_1$, etc. is

$$q(m_1, m_2, \ldots, m_h) = (m_1 + m_2 + \cdots + m_h) f(m_1, m_2, \ldots, m_h). \tag{2.1}$$

For internal mixtures these multivariate distributions reduce to univariate forms $f(m)$ and $q(m)$ dependent only on the total particle mass, $m = m_1 + m_2 + \cdots + m_h$ (McGraw & Wright, 2003). Other distribution functions are also obtainable from the full distribution, e.g., the marginal distributions of the multivariate number distribution are defined as

$$f_1(m_1) = \int f(m_1, m_2, \ldots, m_h)\, \mathrm{d}m_2\, \mathrm{d}m_3 \ldots \mathrm{d}m_h, \tag{2.2}$$

etc.

Multivariate mixed moments of the number distribution are defined as

$$\mu_{kl\ldots w} \equiv \langle m_1^k m_2^l \ldots m_h^w \rangle_f = \int m_1^k m_2^l \ldots m_h^w f(m_1, m_2, \ldots, m_h)\, \mathrm{d}m_1\, \mathrm{d}m_2 \ldots \mathrm{d}m_h, \tag{2.3}$$

where we will used the simplified notation, with moments $\mu_{kl\ldots w}$, in cases where no ambiguity can arise, and the more complete angular bracket notation otherwise. Thus, the total mass of all the particles per unit volume is

$$M = \sum_i \langle m_i \rangle_f \tag{2.4}$$

which is also equal to the zeroth moment of the internal mixture mass distribution, $q(m)$, and to the first mass moment of the internal mixture number distribution, $f(m)$.

Moments suitable for comparison with the mass (m) moments of an internal mixture can be calculated as combinations of the general mixed moments of multivariate distributions. Thus the kth mass moment of $f(m)$ is

$$\langle (m_1 + m_2 + \cdots + m_h)^k \rangle_f = \int m^k f(m)\,\mathrm{d}m, \tag{2.5}$$

where the left-hand side is a linear combination of multivariate mixed moments whose coefficients are defined by the expansion. Similarly, we can define the m-moments of the individual species distributions of an internal mixture $q_i(m) = m_i f(m)$:

$$\int m^k q_i(m)\,\mathrm{d}m = \langle (m_1 + m_2 + \cdots + m_h)^k m_i \rangle_f, \tag{2.6}$$

where the right-hand side is a linear combination of mixed moments of the type defined by Eq. (2.3). Thus, any of the moments arising in the treatment of internal mixtures can be obtained in terms of the more general mixed moments. In an external mixture, $f(m_1, m_2, \ldots, m_h)$ simply decomposes into a sum of noninteracting particle populations. These can be multivariate themselves, but are usually taken to be univariate for ease of simulation. Accordingly, here there is no need to further examine the external mixing case. Indeed, the more interesting case that the pdf decomposes into a set of multivariate populations that *do* interact is handled using the PCA–QMOM in Part II.

Consider N-point quadrature approximations to some of the multidimensional integrals given above—other cases follow in similar fashion. The quadrature points (to illustrate for the bivariate case) are of the form $\{m_{1j}, m_{2j}, w_j\}$ for $j = 1, \ldots, N$. We will use a subscript i to label species and subscripts j, and sometimes k, to label quadrature points. The weight of the jth quadrature point is w_j. The quadrature approximation to Eq. (2.3) is

$$\mu_{kl\ldots w} \approx \sum_{j=1}^{N} m_{1j}^k m_{2j}^l \ldots m_{hj}^w w_j. \tag{2.7}$$

In similar fashion, the quadrature approximation to Eq. (2.6) is

$$\langle m^k \rangle_{q_i} \approx \sum_{j=1}^{N} m_{ij} m_j^k w_j, \tag{2.8}$$

where $m_j = m_{1j} + m_{2j} + \cdots + m_{hj}$ is total mass for quadrature point j. We are especially interested in assignments of the quadrature points for which, for certain moments, the approximate equalities of Eqs. (2.7) and (2.8) become exact.

The key to the QMOM is the mathematical method that allows optimal assignment of the quadrature points when only the moments of the pdf are known. Mathematical techniques for assigning quadrature points in higher dimension, although the subject of a number of articles and monographs (see, e.g., Engels, 1980), are not as developed as in the univariate case; especially in cases where only the lower-order moments of the weight functions (i.e. the pdfs) are known. Quadrature points were assigned in a bivariate extension of the QMOM by inverting different sets of nine mixed-moments, to obtain corresponding sets of three quadrature points in the plane and, alternatively, by inverting 36 mixed-moments, using a nonlinear search algorithm, to obtain 12 points (Wright et al., 2001). A variant of the three-point quadrature assignment was recently applied to the simulation of coagulating and sintering nanoparticles in flames (Rosner & Pyykonen, 2002). These assignments, although accurate and resulting in simulation times that are orders of magnitude faster than a full 2D sectional approach, can still be computationally intensive when a nonlinear search is required and are not readily extendable to higher dimensions. The remaining parts of this section introduce a systematic and highly efficient approach to the assignment of quadrature points in higher dimension.

2.2. Principal components analysis

PCA is a statistical method in which the lower-order mixed moments forming the elements of the covariance matrix are utilized for the characterization and analysis of multivariate data (Johnson & Wichern, 1992; Diamantaras & Kung, 1996). The covariance matrix is constructed as follows: suppose a multivariate particle population characterized by the *normalized* pdf, or probability density function, $\tilde{f}(x_1,x_2,\ldots,x_h)$, where x_i can refer to the mass of species i, as above, or to some other variable. The covariance matrix Σ is the symmetric $h \times h$ matrix having elements:

$$\Sigma_{ij} = \mathrm{cov}(x_i,x_j) \equiv \langle x_i x_j \rangle_{\tilde{f}} - \langle x_i \rangle_{\tilde{f}} \langle x_j \rangle_{\tilde{f}}, \tag{2.9}$$

where the quantities on the right-hand side are lower-order mixed-moments in the notation of Eq. (2.3). PCA approaches the interpretation of the variance–covariance structure of $\tilde{f}(x_1,x_2,\ldots,x_h)$ by forming linear combinations of the original variables, x_i. The principal components are those linear combinations having coefficients given by the elements of the eigenvectors, $\mathbf{g}_j$, of Σ. The eigenvectors form the columns of an orthogonal matrix, $\mathbf{G}$, which transforms Σ to diagonal form (Johnson & Wichern, 1992):

$$\mathbf{G}^{\mathrm{T}} \Sigma \mathbf{G} = \mathbf{D}. \tag{2.10}$$

$\mathbf{G}^{\mathrm{T}}$ is the transpose of $\mathbf{G}$. $\mathbf{D}$ is a diagonal matrix containing as its elements the nonnegative eigenvalues of Σ ordered according to decreasing size $\lambda_1 \geqslant \lambda_2 \geqslant \cdots \geqslant \lambda_h \geqslant 0$. Following this ordering, the jth column of $\mathbf{G}$, which we denote by the vector $\mathbf{g}_j$, is the normalized eigenvector of Σ corresponding to the eigenvalue λ_j ($\Sigma \mathbf{g}_j = \lambda_j \mathbf{g}_j$). Thus, the jth principal component is the projection:

$$y_j = \mathbf{G}_{1j} x_1 + \mathbf{G}_{2j} x_2 + \cdots + \mathbf{G}_{hj} x_h$$

with variance $\langle y_j^2 \rangle - \langle y_j \rangle^2 = \lambda_j$. $\mathbf{G}_{ij}$ is the element located in the ith row and jth column of $\mathbf{G}$. The principal coordinates are uncorrelated as $\mathrm{cov}(y_i, y_j) = \mathbf{D}_{ij} = 0$ for $i \neq j$.

Figs. 1 and 2 show a collection of 1000 points (small points in the figure) sampled from a bivariate distribution $\tilde{f}(x_1,x_2)$ in the original coordinates (x_{1i},x_{2i}) and in the principal coordinates

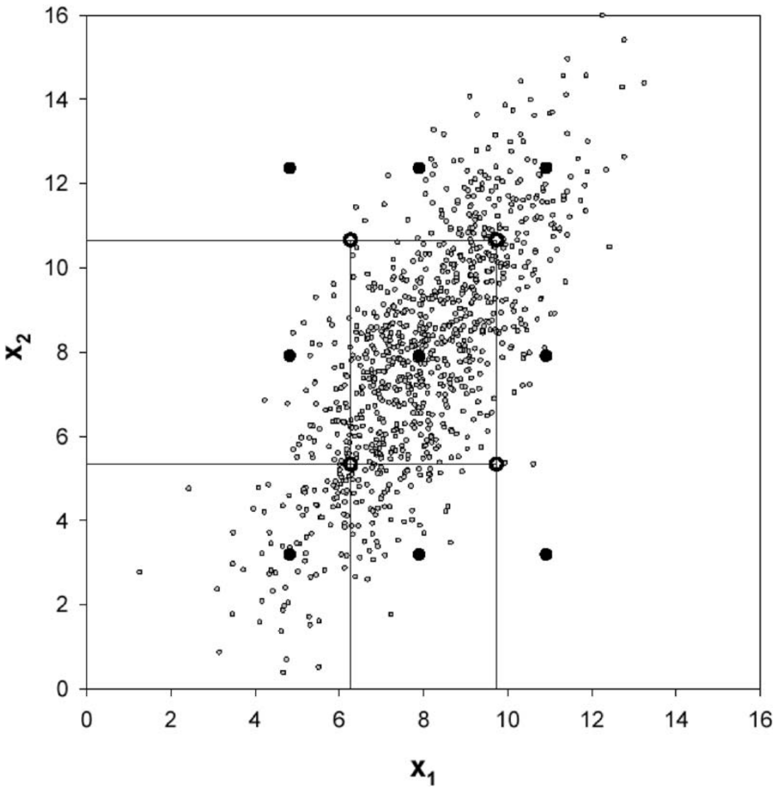

Fig. 1. Assignment of quadrature points in the original coordinates frame: Figure shows 1000 points sampled from a bivariate pdf in the original state variables, x_1 and x_2. Open circles: Quadrature points derived from moments $\{0, 1, 2\}$ along each coordinate (these have equal weights). Closed circles: Quadrature points derived from moments $\{0, 1, 2, 3, 4, 5\}$ along each coordinate (these have differing weights).

(y_{1i}, y_{2i}): $y_{1i} = \mathbf{G}_{11}(x_{1i} - \langle x_1 \rangle) + \mathbf{G}_{21}(x_{2i} - \langle x_2 \rangle)$, $y_{2i} = \mathbf{G}_{12}(x_{1i} - \langle x_1 \rangle) + \mathbf{G}_{22}(x_{2i} - \langle x_2 \rangle)$ centered on the mean. In centered coordinates where each point is represented by a vector from the origin, and $\vec{\mu}$ locates the mean, these equations may be written more compactly as $\vec{y}_i = \mathbf{G}^{\mathbf{T}}(\vec{x}_i - \vec{\mu})$. (Assignment of the quadrature points is discussed in the following subsection.) As expected from the eigenvalue ordering described above, the largest variance occurs for the first principal component, y_1.

From the lower-order mixed-moments, alone, PCA provides a technique for extracting those uncorrelated linear combinations of the original coordinates that best characterize the variability of the pdf. Furthermore, significant data compression can often result upon replacing the original, h-dimensional, representation with a reduced, k-dimensional one, using just the first k principal components. The latter property of PCA can be especially useful when the original dimensionality is large ($h \gg 1$) and has been widely utilized in signal and image data compression (Diamantaras & Kung, 1996). For the present study, PCA finds its most valuable application in the assignment of quadrature points. This is described in the following subsection. The compression features of PCA are further illustrated in Part II.

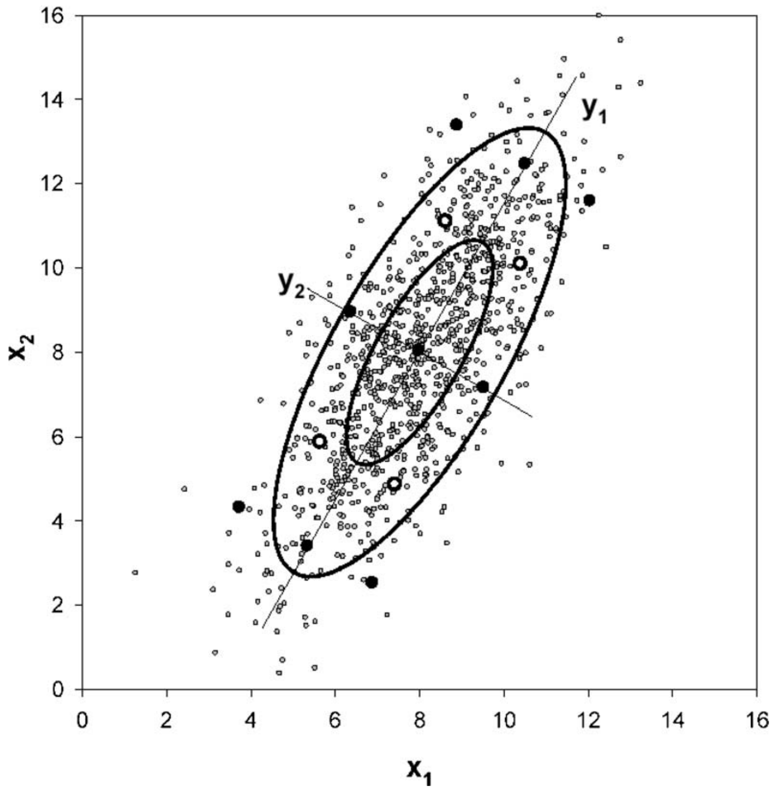

Fig. 2. Assignment of quadrature points in the principal coordinates $\{y_1, y_2\}$ frame: Sampled points are the same as in Fig. 1. Open circles: Quadrature points derived from moments $\{0, 1, 2\}$ along each principal coordinate (these have equal weights). Closed circles: Quadrature points derived from moments $\{0, 1, 2, 3, 4, 5\}$ along each principal coordinate (these have differing weights). Ellipsoids for σ (one standard deviation) and 2σ (two standard deviations) obtained from the covariance matrix, as described in Section 3, are also shown.

2.3. Application of PCA to the assignment of quadrature points in the multivariate QMOM

We begin with a brief summary of the correspondence between moments and quadrature abscissas and weights in the univariate case of one-coordinate dimension (McGraw, 1997; Wright et al., 2000). Such univariate distributions arise naturally in the multivariate problem as projections of the multivariate distribution onto the axis of a single coordinate (cf. Eq. (2.2)). The univariate quadrature points along each coordinate are subsequently used to assign quadrature points in h dimensions from h univariate moment sequences; each sequence consisting of moments of the pdf projected onto one of the h principal axes. Although the pdf itself is unknown, the moments from pdf projection onto an arbitrary axis are obtained as linear combinations of the mixed-moments whose evolution is tracked in the original coordinate frame. The mixed-moments are shown to transform as tensor elements under a rotation of the coordinate frame.

A special form of two-point quadrature (with equal weights) suffices to recover the first three integral moments $\{\mu_0, \mu_1, \mu_2\}$ where a single index is used here for the univariate case. These have coordinates

$$\{\{x_1, w_1\}, \{x_2, w_2\}\}$$
$$=\{\{\mu_1/\mu_0 - \sqrt{\mu_2/\mu_0 - (\mu_1/\mu_0)^2}, 0.5\mu_0\}, \{\mu_1/\mu_0 + \sqrt{\mu_2/\mu_0 - (\mu_1/\mu_0)^2}, 0.5\mu_0\}\} \tag{2.11}$$

with the property that $\mu_k = x_1^k w_1 + x_2^k w_2$ for $k = 0, 1, 2$. Removal of the restriction of equal weights results in general two-point and three-point quadratures with recovery of the first four integral moments $\{\mu_0, \mu_1, \mu_2, \mu_3\}$ and first six integral moments $\{\mu_0, \mu_1, \mu_2, \mu_3, \mu_4, \mu_5\}$, respectively. Algorithms for obtaining general n-point quadratures from moment sequences have been developed (McGraw, 1997). An especially efficient approach utilizes the subroutine ORTHOG from *Numerical Recipes*, and can be applied to ordinary moment sequences, provided n is not too large, as well as to "modified moments", which are linear combinations of the ordinary moments (Press, Teukolsky, Vetterling, & Flannery, 1992). For example, ORTHOG has proven to be a highly efficient and robust algorithm for obtaining general three-point quadratures from six-moment sequences in simulations of atmospheric aerosols by the QMOM (Wright et al., 2000; Yu et al., 2003).

Without loss of generality, it is often more convenient to obtain quadrature point representations for normalized pdfs centered on the origin. Quadrature points for unnormalized–uncentered pdfs are trivially recovered by multiplying the normalize weights by particle number density and translating the centered abscissas to the true coordinate means. In terms of the normalized and centered moments, $\tilde{\mu}_k$:

$$\tilde{\mu}_k = \int (x - \langle x \rangle)^k \tilde{f}(x)\,\mathrm{d}x,$$

where $\tilde{\mu}_0=1$ and $\tilde{\mu}_1=0$, Eq. (2.11) simplifies to $\{\{\tilde{x}_1, \tilde{w}_1\}, \{\tilde{x}_2, \tilde{w}_2\}\}=\{\{-\sqrt{\tilde{\mu}_2}, 0.5\}, \{\sqrt{\tilde{\mu}_2}, 0.5\}\}$. The centered moments are computed in terms of same-order and lower-order moments of the uncentered pdf. Thus: $\tilde{\mu}_2 = \mu_2 - \mu_1^2$, $\tilde{\mu}_3 = \mu_3 - 3\mu_2\mu_1 + 2\mu_1^3$, etc., where $\mu_0 = 1$. Similar expansions are readily carried out for multivariate mixed-moments. Thus, e.g., $\tilde{\mu}_{20} = \mu_{20} - (\mu_{10})^2$, $\tilde{\mu}_{11} = \mu_{11} - \mu_{10}\mu_{01}$, etc., with $\mu_{00} = 1$, showing that the covariance matrix elements (Eq. (2.9)) are centered mixed-moments.

2.3.1. Back projection

Our assignment of quadrature points in higher dimension makes use of the method of back projection and is similar to image construction from back projected densities in tomography. The approach is illustrated in Figs. 1 and 2 for the assignment of quadrature points in the bivariate plane. In Fig. 1 the PCA method is not used; instead the test pdf, $f(x_1,x_2)$, is simply projected onto the original coordinate axes to obtain the corresponding marginal distributions $f_1(x_1)$ and $f_2(x_2)$. In fact, it is the moments of these marginal distributions, and not the distributions themselves, that we require. These are for $f_1(x_1)$, $\{\mu_{00}, \mu_{10}, \mu_{20}, \mu_{30}, \mu_{40}, \mu_{50}, \ldots\}$ and for $f_2(x_2)$, $\{\mu_{00}, \mu_{01}, \mu_{02}, \mu_{03}, \mu_{04}, \mu_{05}, \ldots\}$. Thus for projections along the original coordinate axes, the projected moments are simply subsets of the bivariate mixed moments of $f(x_1,x_2)$. Inversion of the x_1 moments gives quadrature points along the x_1 axes, $\{x_{1k}, w_{1k}\}$ for $k = 1, \ldots, n$ and similarly for inversion of the x_2 moments to obtain $\{x_{2l}, w_{2l}\}$ for $l = 1, \ldots, m$. The positions of these points for the three-moment inversions, $\{\mu_{00}, \mu_{10}, \mu_{20}\}$ and $\{\mu_{00}, \mu_{01}, \mu_{02}\}$, from Eq. (2.11), are indicated in Fig. 1 by the intersection points of the horizontal and vertical hairlines with the coordinate axes. Back projection refers simply to running these projected-distribution quadrature points, which lie on the axes, orthogonally back through the coordinate space to obtain a set of quadrature points in the bivariate plane with abscissas located at the intersections of the back projection lines. These are the $N = nm$ quadrature points $\{x_{1k}, x_{2l}, w_{1k}w_{2l}\}$ for $k = 1, \ldots, n$ and $l = 1, \ldots, m$, with obvious extensions to three and higher dimensions. Note that assigning the bivariate quadrature weights as products of the univariate weights correctly preserves normalization. In the simple case that the projected distributions are represented using normalized two-point quadratures ($n = m = 2$), with $w_{11} = w_{12} = w_{21} = w_{22} = 0.5$, the four points resulting from back projection (open circles) have equal weights of 0.25. The filled circles result on back projection following the calculation of general three-point quadratures along each coordinate axes using the projected distribution moments $\{\mu_{00}, \mu_{10}, \mu_{20}, \mu_{30}, \mu_{40}, \mu_{50}\}$ and $\{\mu_{00}, \mu_{01}, \mu_{02}, \mu_{03}, \mu_{04}, \mu_{05}\}$ in the construction. The resulting nine quadrature points will in general have nonequal weights.

Although Fig. 1 illustrates the method of back projection for assigning quadrature points in higher dimensions, it is clear, even from visual inspection, that this particular assignment, projecting onto the original coordinate axes, is far from optimal. Significant weights appear in regions where the pdf density is low, and the distribution of quadrature points is not at all matched in shape to the pdf. Indeed the only positive feature of this assignment is that the resulting quadrature points correctly reproduce the moments used in the back projection construction itself. In general, *only* these moments will be correctly reproduced. The optimal assignment results on back projection from the principal axes (y_1, y_2), Fig. 2, as we now show. For this construction we first require the centered moments from pdf projections along each of the *principal* axes. Once these have been obtained, location of the quadrature points along each axes, required for the back projection, follows as in any univariate moment inversion (see above). Thus, we focus here on obtaining the projected pdf moments in the principal coordinate frame.

2.3.2. Rotation of multivariate mixed moments to the principal coordinate frame

Inspection of Eq. (2.3) shows the multivariate mixed-moments to involve centered coordinate products in a way that suggests their transformation as tensor elements under axes rotation. This is indeed the case and it is readily shown that centered moments of order s, where $s = k + l + \cdots + w$ is the sum of the indices appearing in Eq. (2.3), transform into each other as the h^s elements of a symmetric tensor, $\mathbf{T}$, of rank s. For second-order moments, these are the elements of the covariance matrix, $T_{ij} = \Sigma_{ij} = \tilde{\mu}_{ij}$.

Transformation to the principal frame is described by the matrix $\mathbf{G}$ of Eq. (2.10):

$$T'_{mn} = \sum_i \sum_j \mathbf{G}_{im}\,\mathbf{G}_{jn} T_{ij}, \tag{2.12a}$$

and T'_{mn} has the same elements as the diagonal matrix $\mathbf{D}$. Similarly, the third-order moments transform as the elements of the third-rank tensor:

$$T'_{mno} = \sum_i \sum_j \sum_k \mathbf{G}_{im}\,\mathbf{G}_{jn}\,\mathbf{G}_{ko} T_{ijk}, \tag{2.12b}$$

and so on for higher-order moments and higher-rank tensors. For a bivariate problem, Eq. (2.12b) describes the transformation of $2^3 = 8$ tensor elements. These elements are symmetric to permutations of their indices and are identified with the moments by a pattern: $T_{111} = \tilde{\mu}_{30}$, $T_{112} = T_{121} = T_{211} = \tilde{\mu}_{21}$, $T_{122} = T_{212} = T_{221} = \tilde{\mu}_{12}$, and $T_{222} = \tilde{\mu}_{03}$ that is readily extended to the h-variate case. (The number of tensor indices, or tensor rank, equals the sum of the exponents, $k + l + \cdots + w$ appearing in Eq. (2.3). Index values, which vary from 1 to h, label the coordinates, and the number of times a given value appears equals the exponent of that coordinate appearing in Eq. (2.3).) The transformed moments are

$$\tilde{\mu}'_{kl} = \int y_1^k y_2^l \tilde{f}_{\mathrm{PCA}}(y_1, y_2)\,\mathrm{d}y_1\,\mathrm{d}y_2 \tag{2.13}$$

where $\tilde{f}_{\mathrm{PCA}}$ is the transformed version of $\tilde{f}$. Specifically, Eq. (2.12b) is a recipe for calculating the third-order moments of pdf projections onto the principal axes. Two of these, $\tilde{\mu}'_{30} = T'_{111}$ and $\tilde{\mu}'_{03} = T'_{222}$, are required when general two-point and higher-order quadratures are used.

2.3.3. Assignment of quadrature points through back projection in the principal frame

Fig. 2 shows the distribution of quadrature points in the principal frame. The open circles are the four points obtained from three-moment inversions with the primed moment sets, $\{\tilde{\mu}'_{00}, \tilde{\mu}'_{10}, \tilde{\mu}'_{20}\}$ and $\{\tilde{\mu}'_{00}, \tilde{\mu}'_{01}, \tilde{\mu}'_{02}\}$. Because $\tilde{\mu}'_{00} = 1$, and $\tilde{\mu}'_{10} = \tilde{\mu}'_{01} = 0$, Eq. (2.11) simplifies to give the quadrature points $y_1 = \pm\sqrt{\lambda_1}$; $y_2 = \pm\sqrt{\lambda_2}$, located along the principal axes, with weights of 1/2 where the λ_i are eigenvalues of the covariance matrix. After back projection we obtain the four points shown in the figure with coordinates $\{\pm\sqrt{\lambda_1}, \pm\sqrt{\lambda_2}\}$ in the principal frame and identical weights of 1/4. If we limit the calculations to inversion of the first three integral moments along each axes, this pattern persists to higher dimensions: for h dimensions the coordinates of the 2^h quadrature points in the principal frame are

$$\{\pm\sqrt{\lambda_1}, \pm\sqrt{\lambda_2}, \ldots, \pm\sqrt{\lambda_h}\} \tag{2.14}$$

with identical weights of 2^{-h}. The filled circles of Fig. 2 show the location of nine quadrature points obtained from general three-point quadratures along each principal axes by applying ORTHO to the projected primed moment sequences $\{\tilde{\mu}'_{00}, \tilde{\mu}'_{10}, \tilde{\mu}'_{20}, \tilde{\mu}'_{30}, \tilde{\mu}'_{40}, \tilde{\mu}'_{50}\}$ and $\{\tilde{\mu}'_{00}, \tilde{\mu}'_{01}, \tilde{\mu}'_{02}, \tilde{\mu}'_{03}, \tilde{\mu}'_{04}, \tilde{\mu}'_{05}\}$. These sequences are obtained from Eq. (2.12) and its extension to fourth- and fifth-rank tensor transformations for the corresponding order moments. The nine quadrature points (filled circles) with unequal weights result after back projection.

To investigate which moments are correctly reproduced from these points, we need one additional property inherent to the assignment of quadrature points through back projection. This is moment factorization. To illustrate for the bivariate case:

$$\mu_{kl} = \sum_{ij} y_{1i}^k y_{2j}^l w_{1i} w_{2j} = \left(\sum_i y_{1i}^k w_{1i}\right)\left(\sum_j y_{2j}^l w_{2j}\right) = \mu_{k0}\mu_{0l}, \tag{2.15}$$

where the prime superscripts have been omitted because the factorization of Eq. (2.15) applies to whichever frame is used for back projection and does not depend on being in the principal frame. The first equality follows from the use of back projected abscissas and weights. Such factorization of the moments indeed occurs when the pdf itself factors, e.g., again for the bivariate case, $f(y_1, y_2) = f_1(y_1)f_2(y_2)$. If such factorization of the pdf occurs, as it does for a multivariate normal distribution (Section 3), it will occur in the principal frame, and all combinations of lower-order mixed-moments will be given correctly by Eq. (2.15). For example, for the nine-point quadrature of Fig. 2 all 36 bivariate moments of the form μ_{kl} for $k, l = 0, \ldots, 5$ will be exactly reproduced. Note from the tensor transformation equations (Eq. (2.12)) that if a full set of moments of order s is determined in one frame, the set is determined in all rotated frames. Thus, the 21 bivariate moments of orders $0, \ldots, 5$ are exactly determined by the nine-point quadrature of Fig. 2, in *every* rotated frame, if the pdf is factorable in the principal frame. Finally, whether the pdf is factorable of not, the full set of second-order moments, which comprise the elements of the covariance matrix, are correctly described by either the four-point or the nine-point quadratures of Fig. 2. We have already seen that the diagonal elements are given correctly. For the off-diagonal elements in the principal frame $\tilde{\mu}'_{11} = \tilde{\mu}'_{10}\tilde{\mu}'_{01} = 0$, as the first equality is assured by Eq. (2.15). Thus, whether the pdf factors or not, the PCA quadrature construction exactly reproduces the full set of second-order moments (diagonal and off-diagonal) in the principal frame and, therefore, in all rotated frames (of course this exactness is preserved on translation and normalization of the quadrature points as well as on rotation). The trend continues with increasing number of components and the 2^h quadrature points from even the simplest, three moments per coordinate, construction (Eq. (2.14)) recover all elements entering the $h \times h$ covariance matrix of an h-variate problem, as well as the first- and zeroth-order moments representing pdf location and normalization. For example, the four quadrature points of Fig. 2 (open circles) give correctly the two variances and covariance of the bivariate pdf when projected onto the axes of any rotated frame. These efficacious properties demonstrate that the combination of PCA and back projection results in an optimized assignment of quadrature points for use in the multivariate QMOM.

In this section, we have shown how to assign quadrature points using the PCA transformation to obtain a set of abscissas, illustrating for the bivariate case, $\{y_{1k}, y_{2l}\}$ and weights $w_{1k}w_{2l}$ for $k = 1, \ldots, n$ and $l = 1, \ldots, m$. It is sometimes convenient to relabel these points using a single index in a one-to-one but otherwise arbitrary mapping ($\{k, l\} \leftrightarrow \{j\}$). For example, with $j = m(k-1) + l$, all points will be represented as j takes on integral values from 1 to nm. Thus, the quadrature points in the principal frame may be represented by the vectors $\vec{y}_j$ having components $\{y_{1j}, y_{2j}\}$ and weights $w_j = w_{1k}w_{2l}$, where j corresponds to the $\{k, l\}$ pair in the mapping. In Section 2.2 we obtained the relation $\vec{y}_i = \mathbf{G}^{\mathrm{T}}(\vec{x}_i - \vec{\mu})$ for transforming points to the PCA coordinates. The inverse of this linear relation transfers the quadrature points generated in the principal frame back to the original frame where they will be used:

$$\vec{x}_j = \mathbf{G}\vec{y}_j + \vec{\mu}, \tag{2.16}$$

where the components of $\vec{\mu}$ are given in terms of the normalized first-order moments, for example, $\{\mu_{10}, \mu_{01}\}$ in the bivariate case. The weights are, of course, unchanged during this transformation.

The present assignment yields quadrature points that are in one-to-one correspondence with a set of moments, but unlike previous applications of the QMOM in one and two dimensions, the present assignment is not free of additional constraints on the points. For example, with the otherwise unconstrained bivariate assignment of Wright et al. (2001), three quadrature points are in correspondence with nine moments, 12 points with 36 moments, etc. Thus the number of quadrature points is minimized, but the inversion of the moment set to get these points can be ill-determined, or at best difficult to carry out. With the PCA assignment, on the other hand, four quadrature points, constrained to have equal weights and lie on the corners of a rectangle, are in one-to-one correspondence with only six moments (one for normalization, two for location of the mean, and three for the elements of the covariance matrix). This flexibility to include additional constraints and still have a well-defined mapping is a very useful feature of the QMOM. The fewer number of moments reproduced in the PCA–QMOM is more than compensated by the computational ease with which the quadrature abscissas and weights can be assigned. In Part II we show how to update the moments in an aerosol dynamics simulation using quadrature points in the original coordinate frame.

3. Illustrative calculations for a multivariate normal population

Implementation of the PCA–QMOM is especially transparent when the pdf is a multivariate normal (Gaussian) distribution. Real aerosol populations often approximate normal distributions after an appropriate coordinate transformation, the best known example being the log-normal distribution, which is normal in $z = \log(m)$. Such coordinate transformations are examined in Part II. Here we analyze the case that the distribution is already normal for the insight that such an analysis provides into the workings of the PCA–QMOM.

The multivariate normal distribution has the form (Feller, 1971):

$$f(x_1, x_2, \ldots, x_h) = \gamma^{-1} \exp[-q(\vec{x})], \tag{3.1a}$$

where γ^{-1} normalizes the distribution, $\vec{x} = (x_1, x_2, \ldots, x_h)$ is now a row vector, and

$$q(\vec{x}) = \sum_{i,j=1}^{h} q_{ij} x_i x_j = \vec{x}\mathbf{Q}\vec{x}^{\mathrm{T}}. \tag{3.1b}$$

The normal density centered at $\vec{\mu} = (\mu_1, \mu_2, \ldots, \mu_h)$ is given by $f(\vec{x} - \vec{\mu})$. The coefficient matrix $\mathbf{Q}$ is the inverse of the covariance matrix Σ introduced in Section 2, $\mathbf{Q} = \Sigma^{-1}$, and the normalization constant is determined by the equation: $\gamma^2 = (2\pi)^h |\Sigma|$, where $|\Sigma| = |\mathbf{Q}|^{-1}$ is the determinant of Σ (Feller, 1971). The transformation to principal coordinates also transforms Eq. (3.1b) to a sum of square terms and factors Eq. (3.1a): $\mathbf{D}^{-1} = \mathbf{G}^{\mathrm{T}}\mathbf{Q}\mathbf{G}$, where $\mathbf{G}$ is as in Eq. (2.10) and $\mathbf{D}^{-1}$ is the inverse of $\mathbf{D}$. Thus the left-hand side of Eq. (3.1a) factors in the principal frame into a product of 1D normal distributions:

$$f_{\mathrm{PCA}}(y_1, y_2, \ldots, y_h) = f_1(y_1) f_2(y_2) \ldots f_h(y_h), \tag{3.2a}$$

where

$$f_i(y_i) = \frac{1}{\sqrt{2\pi\lambda_i}} \exp\left[-\frac{y_i^2}{2\lambda_i}\right], \tag{3.2b}$$

consistent with the normalization of Eq. (3.1).

Assignment of quadrature points by back projection is the required choice for a factorable pdf, even when the factors are non-Gaussian distributions. Consider, e.g., the quadrature approximation to bivariate integrals over a known kernel function $\phi(y_1, y_2)$:

$$\begin{aligned}
\int\!\!\int \phi(y_1, y_2) f_{\mathrm{PCA}}(y_1, y_2)\, \mathrm{d}y_1\, \mathrm{d}y_2 &= \int\!\!\int \phi(y_1, y_2) f_1(y_1) f_2(y_2)\, \mathrm{d}y_1\, \mathrm{d}y_2 \\
&= \int f_1(y_1) \left(\int \phi(y_1, y_2) f_2(y_2)\, \mathrm{d}y_2 \right) \mathrm{d}y_1 \approx \int f_1(y_1) \left(\sum_l \phi(y_1, y_{2l}) w_{2l} \right) \mathrm{d}y_1 \\
&\approx \sum_{k,} \sum_{l} \phi(y_{1k}, y_{2l}) w_{1k} w_{2l} \equiv \sum_j \phi(y_{1j}, y_{2j}) w_j.
\end{aligned} \tag{3.3}$$

Here the assignment of quadrature abscissas and weights is identical to that of the back projection method of Section 2, but emerges naturally as the direct product of 1D quadratures due to the factorization of $f_{\mathrm{PCA}}(y_1, y_2)$. The first equality results from factorization of the pdf. The third and fourth approximate equalities apply 1D quadrature to the principal coordinates y_2 and y_1, respectively. The last equality simply relabels the quadrature points using a single index ($\{k, l\} \to \{j\}$) as in Section 2. The weight of the jth quadrature point is, as in back projection, given by $w_j = w_{1k}w_{2l}$, where j corresponds to the $\{k, l\}$ pair in the mapping and varies from 1 to the total number of quadrature points N. Higher-order quadrature abscissas and weights for the standard weigh function of Eq. (3.2b) are available in tabulated form (Abramowitz & Stegun, 1972), ORTHOG is not required. For two-point quadrature, $w_{i1} = w_{i2} = 1/2$ and $y_{i1} = -\sqrt{\lambda_i}$, $y_{i2} = +\sqrt{\lambda_i}$ just as with the equal-weight two-point quadratures of Section 2. In general there will be $N = \prod_{i=1}^{h} N_i$ quadrature points in h dimensions with N_i-point quadrature along principal coordinate i.

PCA is based on the covariance matrix and does not require that the pdf be factorable or have multivariate normal form. On the other hand, the application of PCA to multivariate normal distributions reproduces a greater number of moments because of the factorization, as described in Section 2, and yields contours of constant pdf density directly from the moments. The contours of constant density for an h-dimensional multivariate normal distribution are the ellipsoids defined by the quadratic form:

$$(\mathbf{x} - \mu)\Sigma^{-1}(\mathbf{x} - \mu)^{\mathrm{T}} = c^2. \tag{3.5}$$

These ellipsoids are centered at $\mu=(\mu_1, \mu_2, \ldots, \mu_h)$ and have axes $\pm c\lambda_i^{1/2}\mathbf{g}_i$ in the notation of Section 2. Fig. 2 shows the disposition of ellipsoids for σ (one standard deviation) and 2σ (two standard deviations) obtained from Eq. (3.5) for $h = 2$ and $c = 1$ and $c = 2$, respectively. The 1σ ellipsoid is inscribed in the rectangle having as its corners the abscissas from the four-point quadrature scheme. The trend continues to higher dimension. For example, in three dimensions there are eight quadrature points having identical weights ($w_j = 1/8$) and coordinates $\{\pm\sqrt{\lambda_1}, \pm\sqrt{\lambda_2}, \pm\sqrt{\lambda_3}\}$ located at the corners of a rectangular parallelepiped into which is inscribed the σ ellipsoidal surface from Eq. (3.5) for $h = 3$ and $c = 1$.

It is important to emphasize that all of the quantities introduced in this section, apart from the full pdf itself, were obtainable using only lower-order moments upto and including the second-order moments of the covariance matrix. These include the principal coordinates, principal values, which are the variances in the principal frame, quadrature points for 2^h-point quadrature, and ellipsoidal probability surfaces for estimating the shape and breadth of the distribution. Together these moment-derived quantities furnish considerable information about the pdf, and a direct route to the estimation of its physical and optical properties represented as integrals over a known kernel function as in Eq. (3.3).

4. Physical and optical properties and closure of the moment evolution equations

Thus far we have focused on the assignment of quadrature points and not on their use in the QMOM—estimation of aerosol properties and moment evolution. Both applications require the estimation of integrals of the type:

$$I = \int \phi(\vec{x}) f(\vec{x}) d\vec{x} \approx \sum_{j=1}^{N} \phi(x_{1j}, x_{2j}, \ldots, x_{hj}) w_j, \tag{4.1}$$

where the kernel $\phi(\vec{x})$ is known. This may represent an optical kernel, such as an extinction coefficient, or a dynamical kernel for a microphysical process (e.g., sedimentation, condensation growth, cloud activation, etc.) governing aerosol evolution. In the latter case the quadrature approximation becomes the right-hand side of a linear differential equation describing moment evolution. The fact that the evolved moments can then be inverted to give updated quadrature points, by the methods described in Section 2, completes the closure cycle for moment evolution (McGraw, 1997). Closure methods are illustrated for multivariate condensation and coagulation kernels in Part II.

Quadrature approximations work best where the kernel is smooth and well approximated by polynomial forms. In the univariate case it is known that the quadrature approximation of Eq. (4.1) is exact for N-point quadrature for kernels of polynomial degree less than or equal to $2N-1$: $\phi(x)=a+bx+cx^2+\cdots+ex^{2N-1}$ with arbitrary coefficients. Physically realistic kernels can usually fit well by fifth-order polynomials, and the corresponding three-point quadratures have proven highly accurate (McGraw et al., 1995; McGraw & Wright, 2003). (However, see Wright et al. (2002) for some exceptionally nonsmooth kernels requiring special treatment.) For the multivariate case, the number of mixed moments that are exactly reproduced increases rapidly with number of quadrature points and with dimension. Consider, e.g., the 2^h-point quadrature of Eq. (2.14). This will be exact for general $f(\vec{x})$ when the kernel is of the form:

$$\phi(\vec{x})=a+\sum_{i=1}^{h}b_i x_i+\sum_{i=1}^{h}\sum_{j=1}^{h}c_{ij}x_i x_j. \tag{4.2}$$

This expression contains $1+h+h(h+1)/2=(h^2+3h+2)/2$ distinct terms corresponding to the number of distinct mixed-integral moments that will be exactly reproduced by the 2^h quadrature points of Eq. (2.14) (these include all of the moments entering into the covariance matrix). In the special case that the pdf factors:

$f(\vec{x})=f_1(x_1)f_2(x_2)\times\cdots\times f_h(x_h)$, the number of moments exactly reproduced increases to 3^h (these are the factorable moments $\mu_{ijk\ldots}=\mu_{i00\ldots}\times\mu_{0j0\ldots}\times\mu_{00k\ldots}\times\cdots$ for $i,j,k,\ldots=$ 0–2). If, in addition to factorization, the factors are symmetric about their mean values, as is the case with the multivariate normal distribution, for example, the number of moments exactly reproduced increases to 4^h ($\mu_{ijk\ldots}=\mu_{i00\ldots}\times\mu_{0j0\ldots}\times\mu_{00k\ldots}\times\cdots$ for $i,j,k,\ldots=$ 0–3). This last result derives form the fact that the (centered) third moments along each coordinate vanish for a symmetric distribution, and thus are also reproduced exactly by the equal-weight two-point quadratures along each coordinate (i.e. equal-weight two-point quadrature is equivalent to general two-point quadrature for the symmetric distribution case).

5. Summary

A new method has been developed for extending the moment-based representation of aerosols to multivariate particle populations. In essence, the full pdf has been replaced by a set of lower-order mixed-moments and corresponding quadrature points assigned through PCA and back projection. The assignment of quadrature points is central to the QMOM, which has been extended here using PCA to the multivariate domain. For calculations, the quadrature abscissas can be viewed as surrogate particle compositions, with weights given by the quadrature weights, optimally assigned through PCA. Aerosol physical and optical properties, usually calculated by numerical integration over a known kernel function, provided the full pdf is known, or by summation over a large number of measured single-particle compositions, can now be estimated reliably and accurately as a summation over a small number of PCA-assigned quadrature points derived from moments. For example, multivariate kernels of the kind given in Eq. (4.1), arise naturally in multicomponent thermodynamic models of vapor–particle exchange (Clegg et al., 1998; Capaldo, Pilinis, & Pandis, 2000), and their evaluation is often the time-limiting step in aerosol models. With the PCA–QMOM the number of calls to the thermodynamic module is minimized as the rates of vapor–particle exchange are required only at those few particle compositions specified by the quadrature points.

The steps for locating multivariate quadrature points from moments using PCA can be summarized as follows: (1) Set up the covariance matrix, Σ, consisting of the centered moments of second order in the original coordinates, and solve the eigenvalue problem associated with this matrix to obtain the ordered principal values $\{\lambda_i\}$ and the matrix $\mathbf{G}$. (2) Obtain the quadrature points first along each principal axes. Note that inspection of the principal values will help decide how many points to take. For example, one might use three-point quadrature along y_1 and two-point or even one-point quadratures along those remaining axes for which the variances are small. For higher-order quadratures, one will need to carry more moments for computing the higher-order projected moments using the tensor transformations of Eq. (2.12), and invert the resulting projected moment sequences using ORTHOG. (3) Back project to obtain the abscissa locations in higher dimension and form the product weights (cf. Eq. (2.15) for the bivariate case). For equal-weight two-point quadratures along each axes, the location of the points is given immediately by Eq. (2.14) and one can bypass steps 2–3. (4) Convert quadrature points to original coordinates using Eq. (2.16).

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