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Numerical Integration for Polyatomic Systems

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A numerical integration package is presented for three-dimensional integrals occurring in electronic structure calculations, applicable to all polyatomic systems with periodicity in 0 (molecules), 1 (chains), 2 (slabs), or 3 dimensions (crystals). The scheme is cellular in nature, based on Gaussian product formulas and it makes use of the geometrical symmetry. Convergence of accuracy with the number of points is rapid and use of the program has been made easy.

1. INTRODUCTION

In many problems in physics and engineering three-dimensional integrals appear that cannot be solved analytically. This may be due to particular features, such as singularities of the integrand, or to an awkward region. Numerical integration is called for in these cases, but is not so straightforward in three dimensions as it is in one dimension. In this paper we discuss numerical integration in the calculation of the electronic structure of molecules and crystals. The integrands in this case have singularities at certain points in 3D space, i.e., at the sites of the nuclei. Many of the techniques to handle such integrands, including coordinate transformations and division of the integration region into subregions, are individually well known. However, they have not been merged before into one consistent scheme to treat automatically, with guaranteed convergence, the pertinent 3D electronic structure integrals, for both finite systems (molecules) and infinite systems (chains, slabs, crystals). The presented scheme originates from a method developed for crystals [1], which has been modified and improved in many details to enhance efficiency and accuracy and which has been generalized to include *all* polyatomic systems.

It is not our purpose here to present new developments in the *theory* of numerical integration. Rather we describe and justify the particular choice of integration variables, subregions, and integration formulae, which together constitute the solution to the problem at hand. Although we deal exclusively with integrals for polynuclear electronic systems, some of the results are conceivably applicable in very different areas of physics. The method is exhibited in some detail, including technicalities that turned out to be crucial for the performance.

Numerical integration has a number of advantages in electronic structure calculations, apart from that it provides a means of evaluating otherwise intractable integrals:

(a) It is easy to apply to (in principle) all integrals, such as the matrix elements of the operators in the one-electron Schrödinger equation and various properties expressible as integrals involving the charge density. The awkward truncated expansions, different for each type of integral, that occur in many analytic evaluation schemes, can thus be avoided. Moreover, numerical integration lends itself naturally to efficient execution as the vectorization and parallellization capabilities of a computer can be exploited to their full potential.

(b) As the requirement of analytic integrability is removed one is free in the choice of basis functions (Slater-type orbitals, Gaussians, plane waves, numerical atomic functions, ...) and, related to this, numerical integration enables one unified method for electronic structure calculations on all material systems, ranging from finite molecules to systems that are infinite periodic in one, two, or three dimensions.

The difficulty to attain high accuracies has been a drawback of 3D integration methods. It will be demonstrated that with our scheme it is possible to achieve arbitrarily high accuracy. It is fair to say, however, that *very* high precision requires many integration points. Computational efficiency of an analytical method (if available) may therefore be greater when higher accuracies (more than eight digits, say) are required. For hamiltonian matrix elements a relative accuracy of ca. 10^{-3} is usually adequate.

An integration formula, or approximation A is defined by N points $\mathbf{x}_i$ and weights w_i, so that

$$\int f(\mathbf{x})\, d\mathbf{x} \approx A(f) \equiv \sum_{i=1}^{N} f(\mathbf{x}_i)\, w_i. \tag{1.1}$$

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In Gaussian-type formulas, to which class also our method belongs, the function f is implicitly approximated by A as a finite expansion in (as a rule) polynomials over the region of integration. The *degree* (of precision) of A is d if A is exact for all polynomials of degree $\leqslant d$, and not exact for at least one polynomial of degree $d+1$. The *practical* precision depends then on whether the integrands of interest have rapidly converging expansions in polynomials.

Although the general theory of Gaussian formulas, i.e., the relations between their degrees and the (minimum) numbers of points needed, the location of these points and the common zeros of systems of orthogonal polynomials, is fairly well developed [2–6], its practical usefulness is limited.

In one dimension the problem can be considered solved since the points and weights of a formula of any degree for an interval can routinely be computed by well-established standard procedures. In two dimensions formulas of rather high degrees have been published for regular polygons [6–8], the square and the triangle [9, 10], the circle [11], and the surface of the unit sphere [12–15]. However, the *computation* of these formulas is far from straightforward, and in practice one has to store the points and weights as fixed data in the program, thus limiting the application to the few available degrees. Moreover, for regions that are not affinely related to those mentioned, a different solution has to be found. In three and more dimensions the situation is even worse: only for a small number of special regions, like the n-simplex, the n-cube, and the n-sphere, a few formulas are known [11].

Regions not belonging to one of the "standard" ones may be handled by either one of the following two techniques, or a combination of them. First the region may be split in subregions,

$$\int_V d\mathbf{x} = \int_{V_1} d\mathbf{x} + \int_{V_2} d\mathbf{x} + \cdots \int_{V_n} d\mathbf{x}, \tag{1.2}$$

such that for each V_i a formula is known. Second we may invoke *product* formulas, writing the nD integral as a sequence, or product, of lower dimensional integrations. A 3D integral, for instance, may be written as

$$\int_{V^3} f(x, y, z)\, dx\, dy\, dz = \int_{z_1}^{z_2} g(z)\, dz \tag{1.3a}$$

$$g(z) = \int_{V^2(z)} f(x, y, z)\, dx\, dy \tag{1.3b}$$

and we need a formula for the interval (z_1, z_2) to integrate $g(z)$, and a formula for the 2D region $V^2(z)$. It depends on the regions in 3D and 2D space, of course, and on the integrand, whether such a reduction is possible and sensible. If the size and form of the region $V^2(z)$ do not vary smoothly with z, this will show up as a non-polynomial feature in the function $g(z)$ and hamper the accurate evaluation of (1.3a) by Gaussian quadrature. In case the non-smoothness of $V^2(z)$ occurs only at a single point $z = z_0$ such a problem may be solved by splitting the integral (1.3a) in two subintegrals (cf. (1.2)) and apply suitable formulas to integrate $g(z)$ separately over (z_1, z_0) and (z_0, z_2). Problems with product formulas and the ensuing partitioning into subregions are often related to the boundary functions, i.e., the form of the total region.

Not only the form of the *region*, but also particular features of the *integrand* may necessitate the use of product formulas and/or a subdivision into smaller regions. In polyatomic systems the integrands have cusps (wave functions) or singularities (coulomb potential) at the positions of the nuclei. This leads to the introduction of atomic spheres and naturally the use of (local) spherical coordinates for the integration. The remaining interstitial region is partitioned by defining atomic cells (polyhedra), each containing thus an atomic sphere. Except in crystals, there remains a part of the space outside the atomic cells denotes as the "outer region." This again is treated as a separate subregion.

Polyatomic systems can be classified according to their translational symmetry: crystals (periodic in three dimensions), slabs or films (two dimensions), chains (one dimension), and molecules (no periodicity at all). We thus will sometimes speak of n-dimensional crystals, by which we understand 3D systems that are periodic in n directions, $n = 0, 1, 2, 3$. The cartesian coordinate system is taken such that the translational symmetry is exhibited in the first n coordinates.

Since we will deal exclusively with integrands that have the translational symmetry of the system, the integral over R^3 can be reduced to the integration over a unit cell, which is bounded in the n directions of periodicity and infinite in the remaining $(3-n)$ ones.

By systematically applying product formulas and, where necessary, divisions into subregions, the total integral is reduced to a sequence of fundamental integrals over (1D) finite intervals and/or (2D) spherical surfaces. For the interval we employ either the goniometric formula, consisting of equidistant points and equal weights [16] (if the integrand is periodic) or Gauss–Legendre quadrature (non-periodic integrands). In the latter case the points, that is the zeros of the appropriate Legendre polynomial, and the associated weights are routinely and efficiently generated for any desired degree.

The spherical surface may be treated with a product formula, thereby reducing it to the 1D case

$$\int d\Omega\, f(\Omega) = \int_{-1}^{1} d\cos\theta \int_0^{2\pi} d\phi\, f(\phi, \theta) \tag{1.4}$$

with a goniometric formula for the inner integral and a Legendre scheme for the outer one. It proves to be advantageous, however, as we will discuss later, to have a formula with octahedral (or icosahedral) point group symmetry. For this reason our package contains the data of a number of special formulas for the spherical surface. Some of these have been taken from [11]. Those with higher precision, up to degree 29, are from [13–15]. Although formulas of this type are thus limited in degree, this is immaterial in practice as higher degrees are never needed.

In the following section we discuss the application of our approach to (three-dimensional) crystals, i.e., the treatment of the atomic spheres and the polyhedra. In Section 3 the outer regions (for molecules, chains, and slabs) are examined. Formulas that exhibit the same symmetry as the polynuclear system offer important advantages; in Section 4 we deal with the symmetry property of the integration scheme. Finally we present results in Section 5, together with a discussion of efficiency and optimizations; some remarks on the use of the program and integration parameters are included. The package (in Fortran 77) is available on request.

2. CRYSTALS

The integration procedure is *cellular* in nature. Space is divided in atomic *Voronoy polyhedra.* The Voronoy polyhedron around an atom is the part of space closer to that atom than to any other. Computationally it may be defined as the region bounded by the planes that orthogonally bisect the line segments joining the atom with all other atoms. (In [1] it was remarked that these boundary planes need not necessarily be chosen halfway between the *atoms*, with the suggestion to position them halfway between the *spheres.* This is, in general, incorrect. According to that procedure some regions in space might belong to more than one atomic polyhedron at the same time, or to none at all.)

Voronoy polyhedra of different atoms are by definition non-overlapping and the conjunction of them fills all space exactly. In particular, the set of polyhedra corresponding to the atoms in the central unit cell defines a proper unit cell, which can be used as the region of integration. In the case of one atom per unit cell the polyhedron is precisely the well-known Wigner–Seitz cell.

For a particular polyhedron, the origin of the (local) coordinate system is chosen at the atom and an atomic sphere is introduced inside the polyhedron, both to isolate the very localized core functions and to handle adequately the problematic features of integrands containing a cusp (wavefunctions) or singularity (coulomb potential) by using spherical coordinates. The integration is thus separated into one over the sphere and one over the remaining part of the polyhedron. The latter is conceptually split into a sum of (truncated) pyramids, each having its top at the atom and as its base one of the faces of the polyhedron:

$$\int_{\text{polyhedron}} f(\mathbf{r})\,d\mathbf{r} = \int_{\substack{\text{atomic}\\ \text{sphere}}} f(\mathbf{r})\,d\mathbf{r} + \sum_{\text{faces}} \int_{\substack{\text{trunc}\\ \text{pyramid}}} f(\mathbf{r})\,d\mathbf{r}. \quad (2.1)$$

Atomic Sphere

Several special point formulas have been published for numerical integration over the solid sphere in three dimensions [11]. Their maximum degree is rather limited. Furthermore, as far as they implicitly expand the integrand in *cartesian* polynomials they will fail to give good results for cusps and the coulomb singularity at the origin. Besides, the radial and angular variations of the integrands may differ appreciably in complexity. So it is sensible to separate the variables and use the product form

$$\int_{\text{sphere}} f(\mathbf{r})\,d\mathbf{r} = \int_0^R g(r)\,r^2\,dr \quad (2.2a)$$

$$g(r) = \int_{\substack{\text{spherical}\\ \text{surface}}} f(r, \Omega)\,d\Omega. \quad (2.2b)$$

For the angular integral (2.2b) the special formulas of Lebedev are used, or a product formula in the standard spherical coordinates; the choice between these depends on symmetry considerations (Section 4). The radial integral (2.2a) is evaluated with a Legendre scheme. The Jacobian r^2 is included into the integrand, so that $r^2 g(r)$, rather than $g(r)$ itself, is implicitly approximated by a polynomial. In our case $g(r)$ varies much more rapidly near $r = 0$ than near $r = R$, and it may even be divergent. The factor r^2 suppresses the problematic behaviour of $g(r)$, and, in particular, removes the $1/r$ singularity of the coulomb potential.

The integrands are usually matrix elements of the one-electron hamiltonian in the basis of some set of atomic functions. Due to the presence of both steep core functions and relatively smooth valence functions, a large variation in radial behaviour exists among these integrands. Roughly speaking we are faced with the problem to integrate a set of functions of the form $r^n e^{-\alpha r}$ with very different values for the decay parameters α and the polynomial exponents n. In these cases it is much more efficient to make a logarithmic subdivision of the interval in two (three, four) smaller intervals and to generate N-point formulas for each of them, than to use one $2N$ ($3N$, $4N$)-point formula for the whole interval. A typical partitioning of the unit interval (0, 1) would for instance be (0, 0.04), (0.04, 0.2), (0.2, 1). In molecular and solid state calculations with light atoms a subdivision in two radial intervals gives good results. For heavier atoms with steeper core functions, $Z > 25$ say, three intervals are advisable, and the very heavy elements are best treated with four.

In this case a division in subregions is thus dictated by peculiarities of the integrands, rather than by the form of the region of integration.

Pyramids of the Voronoy Polyhedra

For the pyramids a threefold product formula is used. Three parameters u, v, w are defined to map the truncated pyramid onto the unit cube $(0,1)\times(0,1)\times(0,1)$. u and v parametrize the base as well as the spherical surface cut out by the pyramid; they define points $\mathbf{Q}(u,v)$ and $\mathbf{P}(u,v)$ on these regions. The third parameter w parametrizes the connection line **PQ**.

The base is a polygon and may have any number of vertices. Product formulas for quadrangles and triangles are easily written down. To treat a general polygon with more than four vertices we repeatedly split off a quadrangle (Fig. 1) and deal with that part until a quadrangle or triangle remains (depending on the total number of polygonal vertices being even or odd). So a final further splitting in subregions is performed, writing the pyramid as a sum of pyramids with each a quadrangular (or triangular) base.

(a) *Quadrangular base.* The base is parametrized by u and v, such that a general point **Q** of the base is

$$\mathbf{Q}(u,v)=(1-u)(1-v)\mathbf{A}+u(1-v)\mathbf{B}+uv\mathbf{C}+(1-u)\,v\mathbf{D}. \tag{2.3}$$

A, **B**, **C**, and **D** are the vertices of the base. The parametrization defines a (bilinear) map from a general quadrangle to the unit square, which can then be treated with a product formula (in u and v).

To deal with the appropriate part of the spherical surface we first introduce two auxiliary angular coordinates, in the following way (Fig. 2). Let S_1 be the common line of the planes ABO and CDO, and S_2 the common line of ADO and CBO; **O** is the top of the pyramid; α is the angle between S_1 and S_2. Choose the cartesian coordinate system such that S_1 and S_2 are in the xy-plane, and S_2 is the x-axis. Consider the set of half planes through S_1 and define coordinate ϕ_1 as

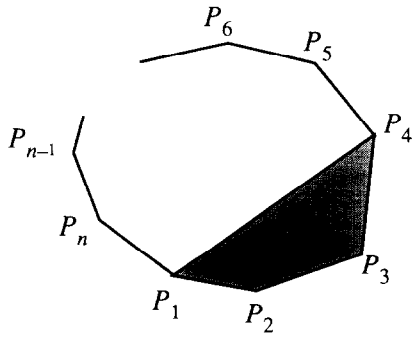

FIG. 1. A general polygon $P_1\cdots P_n$, split into a quadrangle $P_1\cdots P_4$ and a remaining $(n-2)$-gon $P_1, P_4, P_5\cdots P_n$.

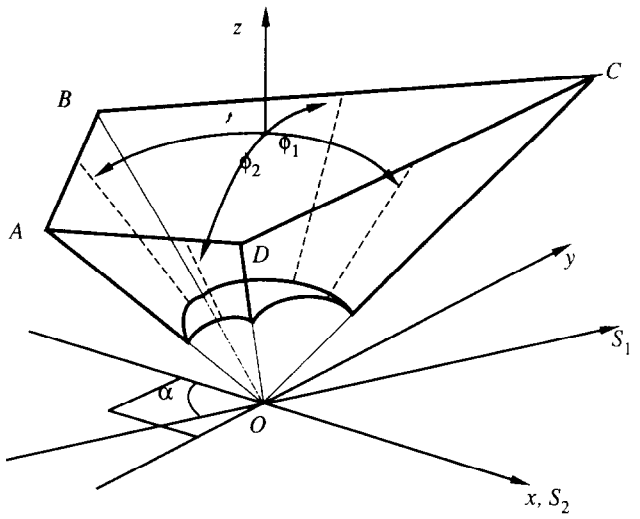

FIG. 2. Truncated pyramid with quadrangular base $ABCD$.

the angle of such a plane with the z-axis, such that the half plane containing the positive x-axis has $\phi_1=\pi/2$ and the plane containing the negative x-axis has $\phi_1=-\pi/2$. ϕ_2 is similarly defined for the set of half planes through S_2.

The spherical surface inside the pyramid is a rectangle in the ϕ_1, ϕ_2-coordinates. The relations between (ϕ_1, ϕ_2) and the cartesian coordinates (x, y, z) for points on the unit sphere with radius R are

$$\begin{aligned} x &= \frac{z}{\sin\alpha}(\operatorname{tg}\phi_1+\operatorname{tg}\phi_2\cos\alpha)\\ y &= z\operatorname{tg}\phi_2\\ z &= \sqrt{(R^2-x^2-y^2)}\\ &= R\Big/\sqrt{\frac{1}{\cos^2\phi_2}+\frac{(\operatorname{tg}\phi_1+\cos\alpha\operatorname{tg}\phi_2)^2}{\sin^2\alpha}}. \end{aligned} \tag{2.4}$$

Turning back to the parameters u and v, we define them to parametrize the intervals for ϕ_1 and ϕ_2,

$$\begin{aligned} \phi_1(u) &= \phi_{1,\max}+u(\phi_{1,\min}-\phi_{1,\max})\\ \phi_2(v) &= \phi_{2,\max}+v(\phi_{2,\min}-\phi_{2,\max}). \end{aligned} \tag{2.5}$$

The signs and orderings have been chosen to let the parametrizations of the base and the sphere respectively correspond in orientation. A point $\mathbf{P}(u,v)$ on the sphere is thus given by (2.4) with ϕ_1 and ϕ_2 depending on u and v via (2.5).

The third parameter w describes the line segment **PQ** from the sphere to the base, and for a general point in the region of integration we have

$$\mathbf{X}(u,v,w)=\mathbf{P}(u,v)+w(\mathbf{Q}(u,v)-\mathbf{P}(u,v)). \tag{2.6}$$

The integration operator is then written as

$$\int_{\text{trunc. pyramid}} dx\, dy\, dz = \int_0^1 \int_0^1 \int_0^1 du\, dv\, dw\, J(u, v, w). \quad (2.7)$$

The jacobian $J(u, v, w)$ of the transformation is determined by the partial derivatives $\partial \mathbf{X}/\partial u$ etc.,

$$\begin{aligned} \partial \mathbf{X}/\partial w &= \mathbf{Q}(u, v) - \mathbf{P}(u, v) \\ \partial \mathbf{X}/\partial u,\, v &= (1-w)\, \partial \mathbf{P}(u, v)/\partial u,\, v + w \partial \mathbf{Q}(u, v)/\partial u,\, v. \end{aligned} \quad (2.8)$$

From (2.3),

$$\begin{aligned} \partial \mathbf{Q}/\partial u &= (1-v)(\mathbf{B}-\mathbf{A}) + v(\mathbf{C}-\mathbf{D}) \\ \partial \mathbf{Q}/\partial v &= (1-u)(\mathbf{D}-\mathbf{A}) + u(\mathbf{C}-\mathbf{B}). \end{aligned} \quad (2.9)$$

For the derivatives of $\mathbf{P}$ define

$$\begin{aligned} a &= \frac{\operatorname{tg}\phi_1 + \operatorname{tg}\phi_2 \cos\alpha}{\sin\alpha}, & b &= \frac{1}{1/\cos^2\phi_2 + a^2} \\ d_1 &= \phi_{1,\max} - \phi_{1,\min}, & d_2 &= \phi_{2,\max} - \phi_{2,\min}. \end{aligned} \quad (2.10)$$

Then we obtain from (2.4) and (2.5)

$$\begin{aligned} \partial \mathbf{P}_z/\partial u &= d_1 \mathbf{P}_z \frac{ab}{\sin\alpha \cos^2\phi_1} \\ \partial \mathbf{P}_x/\partial u &= \frac{d_1 \mathbf{P}_z}{\sin\alpha \cos^2\phi_1}(ab-1) \\ \partial \mathbf{P}_y/\partial u &= \frac{d_1 \mathbf{P}_z}{\sin\alpha \cos^2\phi_1} ab \operatorname{tg}\phi_2 \end{aligned} \quad (2.11)$$

and

$$\begin{aligned} \partial \mathbf{P}_z/\partial v &= d_2 \mathbf{P}_z (\cos\alpha \operatorname{tg}\phi_1 + \operatorname{tg}\phi_2) \frac{b}{\sin^2\alpha \cos^2\phi_1} \\ \partial \mathbf{P}_x/\partial v &= a\, \partial \mathbf{P}_z/\partial v - \mathbf{P}_z \frac{d_2 \cos\alpha}{\cos^2\phi_2 \sin\alpha} \\ \partial \mathbf{P}_y/\partial v &= \operatorname{tg}\phi_2\, \partial \mathbf{P}_z/\partial v - \mathbf{P}_z \frac{d_2}{\cos^2\phi_2}. \end{aligned} \quad (2.12)$$

For each integration point $\mathbf{X}(u_i, u_j, w_k)$ the partial derivatives of its components x, y, z with respect to u, v, w are easily evaluated and the determinant of the 3×3 matrix, i.e., the jacobian, is then computed straightforwardly.

(b) *Triangular base.* This case is analoguous to the previous one. **A**, **B**, and **C** are the vertices (Fig. 3). Parametrize the triangle by u and v as

$$\mathbf{Q}(u, v) = (1-u)\mathbf{A} + u(1-v)\mathbf{B} + uv\mathbf{C}(2.14). \quad (2.13)$$

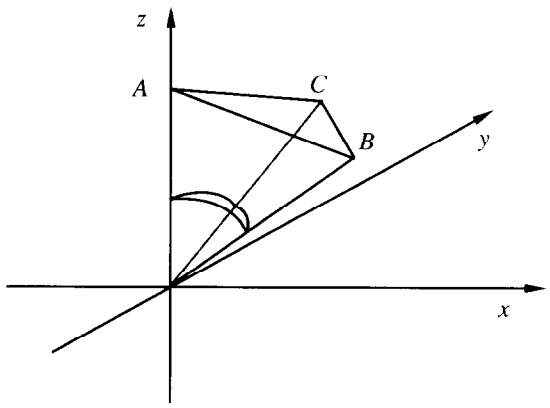

FIG. 3. Truncated pyramid with triangular base ABC: A on the z-axis, B in the xz-plane.

For the parametrization of the spherical surface choose the z-axis along **OA** and **B** in the xz-plane. Let ϕ and θ be the usual spherical coordinates, $\phi_{\max}$ the θ-direction of plane OAC, $\theta_{\max}(\phi)$ the θ-value of the common line of plane OBC, and the halfplane defined by ϕ; u and v parametrize this as

$$\begin{aligned} \phi &\equiv \phi(v) = v\phi_{\max} \\ \theta &\equiv \theta(u, v) = u\theta_{\max}(\phi) = u\theta_{\max}(v\phi_{\max}). \end{aligned} \quad (2.14)$$

A general point $\mathbf{X}$ in the interior of the pyramid is

$$\mathbf{X}(u, v, w) = \mathbf{P}(u, v) + w(\mathbf{Q}(u, v) - \mathbf{P}(u, v)), \quad (2.15)$$

where $\mathbf{P}$ is a point on the spherical surface. The partial derivatives entering the jacobian are then

$$\begin{aligned} \partial \mathbf{X}/\partial w &= \mathbf{Q}(u, v) - \mathbf{P}(u, v) \\ \partial \mathbf{X}/\partial u,\, v &= (1-w)\, \partial \mathbf{P}/\partial u,\, v + w\, \partial \mathbf{Q}/\partial u,\, v \end{aligned} \quad (2.16)$$

with

$$\begin{aligned} \partial \mathbf{Q}/\partial u &= -\mathbf{A} + (1-v)\mathbf{B} + v\mathbf{C} = \mathbf{B} - \mathbf{A} + v(\mathbf{C}-\mathbf{B}) \\ \partial \mathbf{Q}/\partial v &= u(\mathbf{C}-\mathbf{B}) \end{aligned} \quad (2.17)$$

and

$$\begin{aligned} \partial \mathbf{P}_x/\partial u &= \theta_{\max} R \cos\theta \cos\phi \\ \partial \mathbf{P}_y/\partial u &= \theta_{\max} R \cos\theta \sin\phi \\ \partial \mathbf{P}_z/\partial u &= -\theta_{\max} R \sin\theta \end{aligned} \quad (2.18)$$

and

$$\begin{aligned} \partial \mathbf{P}_x/\partial v &= R(-\phi_{\max} \sin\theta \sin\phi + \cos\theta \cos\phi\, u\, \partial\theta_{\max}/\partial v) \\ \partial \mathbf{P}_y/\partial v &= R(\phi_{\max} \sin\theta \cos\phi + \cos\theta \sin\phi\, u\, \partial\theta_{\max}/\partial v) \\ \partial \mathbf{P}_z/\partial v &= -R \sin\theta\, u\, \partial\theta_{\max}/\partial v. \end{aligned} \quad (2.19)$$

To evaluate $\partial\theta_{max}/\partial v$ consider the spherical triangle cut out by the pyramid, with vertices **A'**, **B'**, and **C'**. Let α be the arc $A'B'$ and β the spherical angle $A'B'C'$, which is equal to the angle between the planes $OA'B'$ and $OB'C'$. Then, from spherical geometry we have the relation

$$\theta_{max} = \mathrm{tg}^{-1}\left(\frac{\sin\alpha\sin\beta}{\cos\alpha\sin\beta\cos\phi + \cos\beta\sin\phi}\right). \quad (2.20)$$

Hence,

$$\partial\theta_{max}/\partial v = \partial\theta_{max}/\partial\phi, \qquad \partial\phi/\partial v = \phi_{max}\,\partial\theta_{max}/\partial\phi \quad (2.21)$$

We conclude the treatment of the truncated pyramids with a few remarks. The present way to generate a product formula, i.e., the specific coordinate transformations (parametrizations) chosen, is by no means the only one possible. It has been selected after extensive experimentation with a variety of other transformations. The most straightforward alternatives are (referring for concreteness to the quadrangular case)

1. Use the auxiliary coordinates ϕ_1 and ϕ_2 (2.4) to integrate over the spherical surface. One may then apply the classical radial coordinate for the outward integration to the base

$$\int_{\substack{\text{truncated}\\ \text{pyramid}}} d\tau = \int d\Omega \int r^2\,dr$$

$$= \iint d\phi_1\,d\phi_2\,J(\phi_1,\phi_2)\int r^2\,dr. \quad (2.22)$$

   This is the method presented in [1].

2. Start with a cartesian integration over the base, with the discussed parametrization for the quadrangle. For each base point obtained in this manner one may integrate radially inward towards the sphere. This procedure was proposed in [1] for truncated pyramids with a triangular base. It has also been applied to the quadrangular case [17].

Both schemes have disadvantages that become pronounced in extreme geometries, that is, for pyramids with a large solid angle. Using a 2D analogue this can be understood as follows: Scheme 1 gives the integration in the usual polar coordinates (r, ϕ) (see Fig. 4a, where we put the lower bound of the angular interval $\phi_1 = 0$ for convenience)

$$I_1 = \int_{\phi_1}^{\phi_2} d\phi \int_R^{x_0/\cos\phi} f(r,\phi)\,r\,dr. \quad (2.23)$$

Integrating, for instance, the area ($f \equiv 1$), one obtains for the ϕ-integration the integrand $1/\cos^2\phi$, which is singular

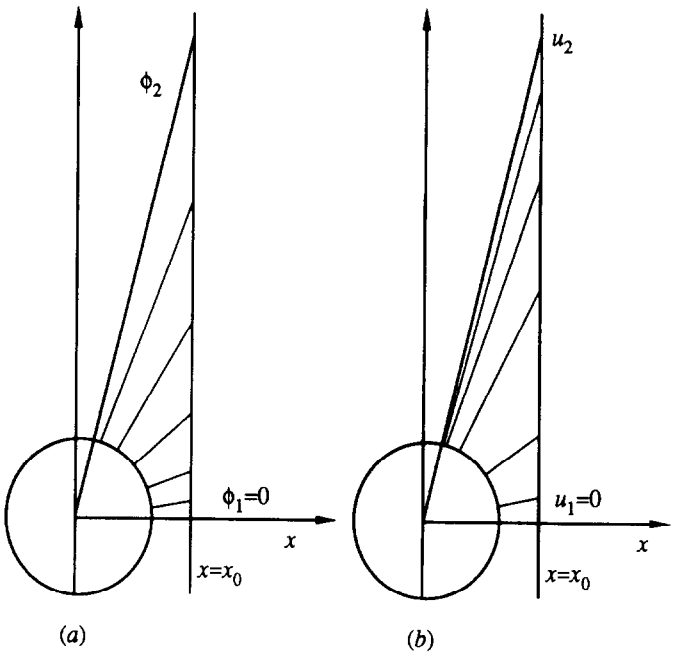

FIG. 4. Two methods for the distribution of integration points: (a) normal distribution on the "sphere"; (b) normal distribution on the base.

for $\phi \to \pi/2$. In scheme 2 one uses, instead of ϕ, the coordinate $u = x_0\,\mathrm{tg}\,\phi$ which parametrizes the base line $x = x_0$ (see Fig. 4b):

$$I_2 = \int_{u_1}^{u_2} \frac{x_0}{u^2 + x_0^2} \int_R^{\sqrt{(u^2+x_0^2)}} r\,dr. \quad (2.24)$$

With the second scheme the integration of the area converges rapidly but it breaks down for spherical harmonics (i.e., the functions $e^{-\alpha r}\cos(n\phi)$ in the 2D case). This can be analyzed by considering the behaviour of the occurring integrands on the large intervals (u_1, u_2) that result when $\phi \to \pi/2$.

The basic flaws of schemes 1 and 2 can also be understood intuitively by considering the integration grids. The integrations over the radial coordinate r are analoguous and do not present a problem. For the "angular" (ϕ- or u-) integrations we consider the distribution of mesh points on the lower ($r = R$) and upper ($x = x_0$) boundaries. Using Gauss-Legendre integration in ϕ and u respectively, the first scheme generates a normal distribution over the first boundary but clusters the points too much in the region near $\phi = 0$ on the second boundary (Fig. 4a). The other scheme on the contrary concentrates the points too much near $u = u_2$ on the first boundary. Accordingly functions that vary predominantly in the region near $r = R$ will be integrated better with scheme 1, while method 2 should be

used when the function is characterized mainly by its behaviour near $x = x_0$.

One might say that the first method is best for "atomic" one-center functions located on the (local) origin, while the other is suitable for (tails of) "atomic" functions on another site, plane waves, and so on. Extensive experimentation has shown that the problems of either scheme become severe for wide angles $\phi_2 > 80°$.

Our approach can be interpreted as a hybrid, distributing the points correctly over both boundaries and connecting the corresponding points. The "radial" integration lines, when extended, do not pass through the origin then, in contrast with the two methods above; this is not relevant, however. Our findings are that, on the average, the hybrid scheme gives superior results.

3. SLABS, CHAINS, AND MOLECULES

For systems with periodicity in $n < 3$ directions, like a slab with translational symmetry in the xy-plane, or a molecule, we wish to apply basically the same method as for 3D crystals. For the atoms in the interior of the system this is straightforward. Their polyhedra are defined by the planes between the atom under consideration and the surrounding nuclei. For an atom at the outside, however, the polyhedron, defined in this way, is not bounded.

This is solved by the introduction of a set of boundary planes encompassing all atoms. For a slab, for instance, we use two boundary planes, parallel to the xy-plane, one above the slab and one underneath. In the construction of all atomic polyhedra these boundary planes are also taken into account, together with the usual orthogonally bisecting planes. This yields a set of non-overlapping atomic polyhedra that completely fill the region enclosed by the boundary planes. The integration over this *inner* region is performed as described in the previous section. What remains is the part outside the boundary planes. The integration over this *outer region* is the main subject of this section. Although the outer region does in principle extend to infinity, this is not so in practice. All functions and integrands fall off more or less rapidly far away from the atoms. At a distance R_∞, say, they have become negligible and the region of integration can be limited accordingly.

The outer region is different for 2D periodic systems (slabs), 1D periodic systems (chains), and nonperiodic systems (molecules). We will treat these cases separately because the technical details differ substantially. The principle is nevertheless the same for all of them. A set of boundary planes is defined around the atoms, a distance R_∞ is determined as the outward limit of the outer region, and a formula is constructed for this empty space, where no atoms are located, but where the contribution to the various integrals is still significant.

Slabs

The system is periodic in the xy-plane. Let all atoms be contained between z_0 and z_1, i.e., z_0 and z_1 are the minimum and maximum z-values of the atomic positions. Choose a distance d for the boundaries, so that the two boundary planes parallel to the xy-plane have z-values $(z_0 - d)$ and $(z_1 + d)$, respectively; d is of the order of the nearest neighbour distance in the system, a few atomic units. The integration over the "outside" region between $z = z_1 + d$ and $z = z_1 + R_\infty$ (and similarly between $z = z_0 - d$ and $z = z_0 - R_\infty$) is easy. Due to the absence of nuclei a straightforward product formula can be applied:

$$\int_{\text{outside}} f(\mathbf{r})\, d\mathbf{r} = \int_{\substack{\text{unit cell} \\ \text{in } xy\text{-plane}}} dx\, dy\, g(x, y) \tag{3.1a}$$

$$g(x, y) = \int_{z_1 + d}^{z_1 + R_\infty} dz\, f(x, y, z). \tag{3.1b}$$

For (3.1b) Legendre integration is used. Experiments with Gauss–Laguerre, and Gauss–Hermite integration, taking $R_\infty = \infty$ and using various values for the exponential decay constants that underly such integration formulas, produced inferior results. This is probably due to the large variation in the exponential decay constants of the actual integrands. For the same reason it is advisable in the Legendre integration to subdivide the interval $(z_1 + d, z_1 + R_\infty)$ into two or three subintervals (in a logarithmic way, as we did for the atomic spheres). This is more efficient, presumably because some functions, which are rather (but not too) localized around atoms, may have significant tails extending over a relatively short distance into the outer region. There they behave as very localized functions, analogous to the core functions in the atomic spheres, and a high number of "outward" integration points would be needed to achieve accurate results if the subdivision were not applied.

For (3.1a) the standard technique for periodic functions is used: goniometric integration with equidistant points (and equal weights) along the lattice vectors that describe the translational symmetry in the xy-plane. Note that the implicit choice of the form of the unit cell here is different from that employed for the integration inside the slab, between the boundary planes.

Chains

Let the unit cell extend from x_0 to x_1 along the direction of translational symmetry. Again it is in principle infinite in y and z, but "infinity" may be located at some distance R_∞ from the chain. We distinguish two situations, according to the presence or absence of infinite rotational symmetry around the x-axis. This particular symmetry occurs when all atoms have the same y-coordinates and the same

z-coordinates, say zero. We denote these systems as linear and non-linear chains respectively.

(a) *Linear Chains.* As a consequence of the continuous rotational symmetry the natural approach is to use cylindrical coordinates; the boundary planes are cylindrical surfaces, and the integration formulas are products of the angular integration around the axis, and a 2D integral. So there are no 3D atomic polyhedra, but (truncated) triangles in the 2D region. In this particular case the integration in the interior region is different from all other cases. We therefore treat here the integration in both the interior and the outer regions. Let ϕ be the angle of rotation around the x-axis; then, in cylindrical coordinates,

$$\int f(\mathbf{r})\, d\mathbf{r} = \int_{x_0}^{x_1} dx \int_0^{R_\infty} \rho\, d\rho\, g(x, \rho) \tag{3.2a}$$

$$g(x, \rho) = \int_0^{2\pi} d\phi\, f(x, \rho \cos\phi, \rho \sin\phi); \tag{3.2b}$$

(3.2b) is integrated with equidistant points. This angular integral does not present any problem, irrespective of x and ρ, since all nuclei have $\rho = 0$. The difficulties associated with the positions of the nuclei appear only in the 2D integral (3.2a).

The 2D region is divided into atomic regions *I* (half circles), an interstitial part *II*, and the outer region *III* (Fig. 5).

I. The integration for the atomic circles is performed by a product rule in polar coordinates, where for each atom the (local) origin of the coordinate system is the center of the circle:

$$\int_{\text{halfcircle}} \rho\, dx\, d\rho\, g(x, \rho) = \iint \rho r\, dr\, d\theta\, g(r, \theta)$$

$$= \int_{-1}^{1} d(\cos\theta) \int_0^R r^2\, dr\, g(r, \theta). \tag{3.3}$$

Combining this with (3.2b) we find that in fact a three fold product formula is employed for the atomic sphere.

II. Considering the integration in the interstitial region *II* in the xy-plane, we note that all interatomic "planes" are lines parallel to the ρ-axis, between the atomic spheres. The boundary plane is a line parallel to the x-axis. Region *II* is the 2D analogue of the truncated polyhedron of the previous section.

We make a division in truncated triangles II^a, II^b, and II^c (2D pyramids) (Fig. 5). Product formulas for each of them (from (3.3)) are derived from a parametrization in analogy with that for 3D pyramids. We will work this out for II^a, the other two being similar. Let u parametrize both the angular

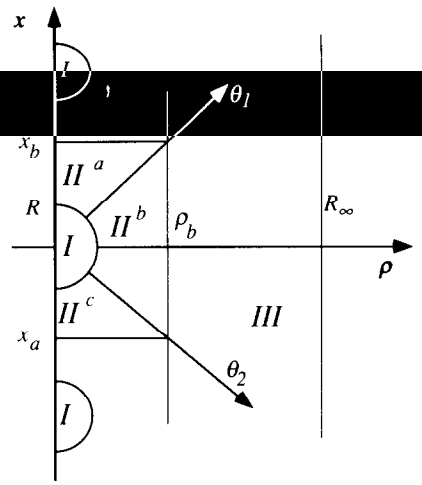

FIG. 5. Two-dimenstional region of integration for linear chains, divided into the atomic spheres (*I*), the interatomic region (*II*), and the outer region (*III*).

θ-interval $(0, \theta_1)$ and the ρ-interval $(0, \rho_b)$; R is the radius of the circle; $\mathrm{tg}(\theta_1) = \rho_b / x_b$. Then define

$$\begin{aligned} \mathbf{P}_x(u) &= R \cos(u\theta_1) \\ \mathbf{P}_\rho(u) &= R \sin(u\theta_1) \end{aligned} \tag{3.4}$$

and

$$\begin{aligned} \mathbf{Q}_x(u) &= x_b \\ \mathbf{Q}_\rho(u) &= u\rho_b; \end{aligned} \tag{3.5}$$

v is the second parameter, defining a general point

$$\mathbf{X}(u, v) = \mathbf{P}(u) + v(\mathbf{Q}(u) - \mathbf{P}(u)). \tag{3.6}$$

In (u, v) the region is the unit square, so that a product formula is applicable. The jacobian $J(u, v)$ from the partial derivatives is straightforward.

III. For the outer region (*III*) the approach is like that for the slab: an equidistant integration in x times a Legendre integration in ρ; the latter is again preferably subdivided in two or three subintervals.

(b) *Non-linear chains.* In contrast with the linear chains, the non-linear chains present a fully 3D problem. The boundaries are planes, parallel to the x-axis, enclosing the system in a prism. The polygonal projection of this prism onto the yz-plane is defined as follows: Project all atoms onto the yz-plane and determine the smallest convex polygon enclosing all the resulting points, the minimal polygon. The requirement that the polygon be convex implies that some of the projection points are "inner" points and these are discarded; the "outer" points are the corners

of the polygon and its sides represent a set of planes. Each of them is shifted a distance d outwards in the direction perpendicular to the plane itself. The resulting planes are the required boundary planes; d is a few atomic units.

Inside the boundary we have the familiar atomic polyhedra. The integral over the region outside the prismal envelope of the chain is performed by a product of a 1D periodic integration in x, by a goniometric formula, times a 2D integration in y and z.

The first hull, defined above, is a polygon in the yz-plane, the sides of which are characterized by a distance d from the outermost atoms. Let R_∞ be the distance where all functions have become negligible and set an outer hull by shifting all sides of the inner one outwards over a distance $(R_\infty - d)$. The region of integration between these two polygons is now in a natural way divided into trapezia. The parallel sides of each trapezium are the corresponding sides of the inner and the outer polygon, respectively, and the four vertices are the intersections with the appropriate neighbouring sides. The integral over a trapezium is easily written in product form.

Molecules

The minimal convex hull is a polyhedron. The planes describing it are obtained by the following procedure. For each distinct triplet of atoms that are not on one line, consider the plane through them. If all atoms lie at one side of it, or in it, it is a boundary plane; otherwise it is rejected.

Like in the other situations already discussed, the integration outside the inner hull of a molecule is not performed over all space, but an outermost hull is defined, consisting of the same planes as the inner one, all shifted over $R_\infty - d$. The integration between the inner and the outer hull is written in product form: a 1D outward integral over the distance z from the inner hull, ranging from zero to $R_\infty - d$, times a 2D integration over the polyhedral surface corresponding to the current distance value,

$$\int_{\text{region}} d\mathbf{r}\, f(\mathbf{r}) = \int_0^{R_\infty - d} dz\, g(z); \tag{3.7}$$

$g(z)$, the integral over the polyhedral surface at distance z from the inner polyhedron, is split into a sum over the respective faces, each being some polygon, and for every polygon a formula is generated by splitting it into quadrangles (and possibly a triangle) as discussed above:

$$g(z) = \sum_{\text{faces}} \left(\int_{\text{polygon}(z)} d\tau\, f(\tau) \right). \tag{3.8}$$

The r.h.s. of (3.7) is evaluated by Legendre integration.

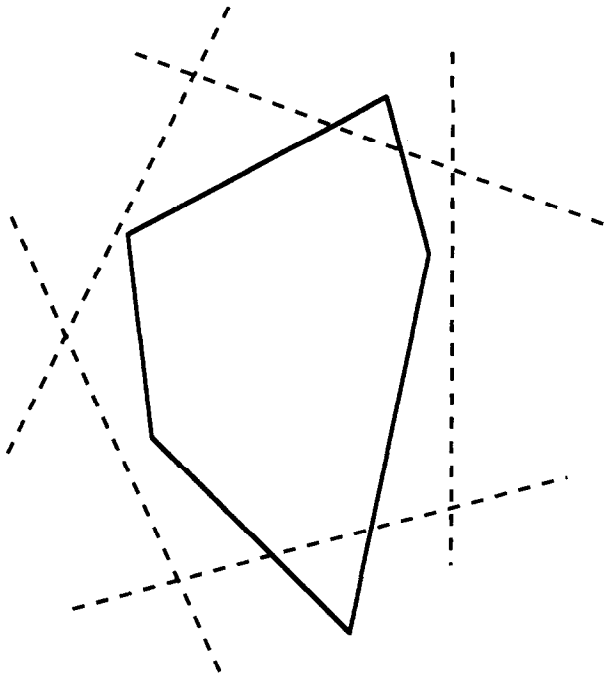

FIG. 6. The minimal convex polygon and the auxiliary planes; some of the auxiliary planes are redundant (see text).

Auxiliary Boundary Planes

The eveloping prism of the non-linear chain may have sharp angles at some of its edges. Similarly, sharp angles may occur at edges of the enveloping polyhedron of a molecule, as well as sharp points at its vertices. Such features are undesirable. In extreme cases one might imagine almost "degenerate" points and edges protruding to infinity. These will undoubtedly cause accuracy problems in the integration scheme, since the jacobian of the transformation from the ensuing pyramids to the unit cube eventually becomes singular. Therefore we introduce additional planes that cut off the sharp points and edges. This solution is automated by defining auxiliary boundary planes, one for each edge and (for a molecular polyhedron) also one for each vertex of the original hull. These are positioned at such a distance from the nearest atoms that the extreme features are indeed removed, while they do not change the hull when the corresponding edge or vertex is not so sharp. We do not go into the algorithmic technicalities here, but give in Fig. 6 a 2D exemplary polygonal hull with additional planes, some of which cut off a point and thus introduce an extra side of the polygon, while others turn out to be redundant.

4. SYMMETRY

The subject of this section is the aspects in the construction of the integration formulas that assure that they are symmetric. An integration formula is symmetric when it is mapped onto itself by each of the operators of the symmetry

group. The generator points, or *generators*, are any subset of the points of the formula that are not related to each other by symmetry *and* that yield all the other points by application of the symmetry operators.

The symmetry property of a formula offers various advantages, the most important of which in this context is the following: Assuming that the integrands can be organized such that they transform as the irreducible representations of the symmetry group, then the integration of all non-symmetric integrands is zero (analytically as well as numerically) and the numerical approximation of a symmetric integral can be evaluated by running over the generator points only. Obviously this may yield an appreciable saving in computer time, especially for systems with high symmetry, where the number of generators is only a small fraction of the total number of points.

The presented integration method has been implemented in our density-functional molecular (c.q. cluster-) program as well as in our density-functional bandstructure program. Both make use of symmetry in the numerical integration. While, of course, the advantage depends on the amount of symmetry present, it is reasonable to state that the disregard of symmetry would in many cases increase the cost of the calculations by one to two orders of magnitude. Clearly it is of utmost importance that the integration formulas be symmetric, even when this would imply a slight increase in the number of points compared to a non-symmetric formula with the same precision.

We will now demonstrate how symmetry is imposed on the formulas for each of the regions occurring in our method. In some cases a symmetric formula is constructed

unique subregion, the *irreducible wedge*, and the related points can be found by operation with all the symmetry operators.

The symmetry operators themselves are computed from the geometric data: the n lattice vectors for the n-dimensional crystal, the positions of the atoms, and their nuclear charges (to impose *in*equivalencies between the atoms which may not follow from their positions alone). The algorithm used for the calculation of the symmetry operators will not be discussed here; the software is incorporated in the integration package.

Polyhedra

As explained in Section 2 the integration over the polyhedra consists of a sum over the pyramids associated with their faces. By checking the set of symmetry operators of the system the *symmetry unique pyramids* are found in the polyhedra around the *symmetry unique atoms*. For each of these pyramids we need a symmetric formula for its base, since the radial integral from the base towards the atomic sphere has no bearing on the symmetry. The irreducible wedge of the base is constructed by selecting the symmetry unique edges of the polygon (and halving them when a particular reflection operator indicates such). We obtain a polygon, again, which then defines the pyramid for which a formula actually is computed.

Spheres

The radial integral is irrelevant as regards the symmetry, so here we are concerned only with integration over a spherical surface. The subgroup of the symmetry group of the system that leaves a particular atom invariant is a point group, the local group of that atom. The operators of this group are selected, analysed, and the group is classified as either octahedral, whenever it is a subgroup of O_h, or icosahedral, or axial. A formula of the correct symmetry type is then chosen. Of course this is done only for a set of symmetry unique atoms.

Outer Region

For 0-, 1-, and 2D crystals the regions outside the boundary planes have to be treated. For all of them, the outward, or radial, integration is again unimportant here, so we discuss formulas for the boundary planes themselves.

The boundary planes of a molecule define a polyhedron. Symmetric formulas for that polyhedron are similar to those for the atomic polyhedra and here again only the symmetry unique faces have to be considered. Each of them is a polygon. The irreducible wedge is determined, which is also a polygon. The irreducible wedge is determined, which is also a polygon (see above), and a formula for it is generated

cell. We take for it the parallelogram spanned by the lattice vectors $\mathbf{a}_1$ and $\mathbf{a}_2$. Since the integrands may be assumed periodic, a general integration scheme has all weights equal and has points

$$\mathbf{x}_{kl} = \mathbf{x}_0 + \frac{k}{N_1}\mathbf{a}_1 + \frac{l}{N_2}\mathbf{a}_2, \qquad k, l = \cdots, -1, 0, 1, 2, \ldots. \quad (4.1)$$

The points inside one unit parallellogram are those with N_1 consecutive values for k, and N_2 for l, e.g., $k = 0 \cdots N_1 - 1$, $l = 0 \cdots N_2 - 1$.

To investigate the symmetry property of set (4.1) in relation to the values of x_0, N_1, and N_2, we have to consider symmetry equivalencies between points. Since the set (4.1) has the periodicity of the lattice, it is sufficient to consider (only) the *generating* operators $\{\mathbf{t}_i; R_i\}_{i=1,n}$ of the planar space group. Combined with all Bravais translations they generate all operators of the complete group. Each $\{\mathbf{t}; R\}$ is an affine transformation

$$\mathbf{x}' = \{t; R\}\,\mathbf{x} = \mathbf{t} + (R\mathbf{x}), \quad (4.2)$$

$\mathbf{t}$ is a non-primitive translation, and R is a linear orthogonal transformation. Furthermore, R maps the Bravais lattice onto itself,

$$\mathbf{R}\mathbf{a}_i = \sum_j m_{ij}\mathbf{a}_j, \tag{4.3}$$

with *integer* matrix m. The set of generating operators is minimal in the sense that no two of them are related by a simple Bravais translation.

Denote by $C(\mathbf{x})$ the set of all distinct points that are symmetry equivalent with $\mathbf{x}$ *and* located in some chosen central unit cell. The number of points $\mathbf{c}_i \in C(\mathbf{x})$ is $M(\mathbf{x})$. For a general point $\mathbf{x}$ $M(\mathbf{x})$ will equal n, the number of generating operators. $M(\mathbf{x})$ may be lower, however, when $\mathbf{x}$ is located in a reflection plane or on some other symmetry element.

It is easily demonstrated that the symmetry requirement for set (4.1) implies

(a) as a rule $N_1 = N_2 (= N$, say)

(b) a *safe* choice for $\mathbf{x}_0$ is the geometric mean of a set $C(\mathbf{x})$ as defined above,

$$\mathbf{x}_0 = \frac{1}{M(\mathbf{x})} \sum_{\mathbf{c}_i \in C(\mathbf{x})} \mathbf{c}_i, \tag{4.4}$$

where $\mathbf{x}$ may be any point.

(c) a *good* choice for $\mathbf{x}_0$ is obtained with procedure (b) but with $\mathbf{x}$ as a high-symmetry point.

(d) $N (= N_1 = N_2)$ is (usually) an integer multiple of $M(\mathbf{x})$, the number of points in set $C(\mathbf{x})$.

This is shown as follows: Obviously it is necessary that all images of $\mathbf{x}_0$ are elements of (4.1). Assuming for the moment this to be the case,

$$\{\mathbf{t}; R\}\,\mathbf{x}_0 = \mathbf{x}_0 + \frac{k_0}{N_1}\mathbf{a}_1 + \frac{l_0}{N_2}\mathbf{a}_2; \tag{4.5}$$

then

$$\begin{aligned}\{\mathbf{t}; R\}\,\mathbf{x}_{kl} &= \mathbf{x}_0 + \frac{k_0}{N_1}\mathbf{a}_1 + \frac{l_0}{N_2}\mathbf{a}_2 + \frac{k}{N_1}R\mathbf{a}_1 + \frac{l}{N_2}R\mathbf{a}_2 \\ &= \mathbf{x}_0 + \left(\frac{k_0}{N_1} + \frac{km_{11}}{N_1} + \frac{lm_{21}}{N_2}\right)\mathbf{a}_1 \\ &\quad + \left(\frac{l_0}{N_2} + \frac{km_{12}}{N_1} + \frac{lm_{22}}{N_2}\right)\mathbf{a}_2. \end{aligned} \tag{4.6}$$

In general this is of the form (4.1) only if $N_1 = N_2$, proving assertion (a). Of course exceptions may occur for some symmetry groups, i.e., when all matrices m_{ij} have special forms. For simplicity we take $N_1 = N_2 = N$ from now on.

Next consider $\mathbf{x}_0$ itself. The image under some $\{\mathbf{t}; R\}$ is

$$\mathbf{x}_{0i} = \{\mathbf{t}; R\}\,\mathbf{x}_0. \tag{4.7}$$

For a general point $\mathbf{x}_0$ the difference vector $\mathbf{d}_i = \mathbf{x}_{0i} - \mathbf{x}_0$ does not necessarily have a rational expansion in the lattice vectors $\mathbf{a}_1$ and $\mathbf{a}_2$, i.e., it need not be of the form

$$\mathbf{d}_i = \frac{k_i}{N}\mathbf{a}_1 + \frac{l_i}{N}\mathbf{a}_2. \tag{4.8}$$

Hence $\mathbf{x}_0$ cannot be chosen at random. Let us now take some arbitrary point $\mathbf{x}$, determine the associated set $C(\mathbf{x})$, and set $\mathbf{x}_0$ equal to its geometric mean, in accordance with proposition (b); then

$$\begin{aligned}\mathbf{x}_{0i} = \{\mathbf{t}; R\}\,\mathbf{x}_0 &= \{\mathbf{t}; R\}\,\frac{1}{M(\mathbf{x})}\sum_{j=1}^{M(x)}\mathbf{c}_j \\ &= \frac{1}{M(\mathbf{x})}\sum_{j=1}^{M(x)}\{\mathbf{t}; R\}\,\mathbf{c}_j. \end{aligned} \tag{4.9}$$

$\{\mathbf{t}; R\}$ permutes the $\mathbf{c}_j$, but possibly with Bravais translations added:

$$\begin{aligned}\mathbf{x}_{0i} &= \frac{1}{M(\mathbf{x})}\sum_{j=1}^{M(x)}\{\mathbf{t}; R\}\,\mathbf{c}_j \\ &= \frac{1}{M(\mathbf{x})}\sum_{j'=1}^{M(x)}(\mathbf{c}_{j'} + \mathbf{T}_{j'}) = \mathbf{x}_0 + \frac{\mathbf{T}'}{M(\mathbf{x})}. \end{aligned} \tag{4.10}$$

To assure (4.10) to be of the form (4.1) it is sufficient to set N equal to an integer multiple of $M(\mathbf{x})$. This confirms points (b) and (d).

The different $\mathbf{T}'$ resulting from the various operators $\{\{\mathbf{t}; R\}$ may together constitute a set of vectors that renders the restriction on N even less severe. For instance we might find, on closer inspection of the $\mathbf{T}'$, that it is allowed to take N a multiple of $M(\mathbf{x})/2$. In our code this aspect is treated by analysis of all $\mathbf{T}'$ as rational expansions in the lattice vectors.

Assertion (c) follows from the consideration that the higher $M(\mathbf{x})$ is, the more restrictive is condition (d). We do not wish to be compelled to a high number of integration points only on grounds of symmetry. $M(\mathbf{x})$ is low if $\mathbf{x}$ is a point of high symmetry.

A simple, practical way to have a *small* set $C(\mathbf{x})$ is to take for the $\mathbf{c}_i$ the locations of the smallest set of symmetry equivalent atoms in the unit cell. A good, general alternative is a two-step process. Take any point $\mathbf{x}_a$, determine the set $C(\mathbf{x}_a)$, and define the associated geometric mean as $\mathbf{x}$, to start the usual procedure. The first step is then just a way to *find* a high symmetry point $\mathbf{x}$.

The above analysis is in no way restricted to two dimensions. With obvious adaptations in the references to set (4.1)

it is generaly applicable. To the 1D case, as regards the direction of periodicity, in three dimensions, if a goniometric, symmetric scheme is needed for a crystal unit cell.

For the boundary planes of a 1D crystal we have in the direction of periodicity, along the x-axis, a similar situation as for the 2D crystal: the equidistant points must constitute a symmetric set with respect to all operators of the space group. We proceed in the way described above to determine $\mathbf{x}_0$ and N. For linear chains this is all we have to do, since symmetry considerations are irrelevant for the outward integration away from the x-axis.

For non-linear chains the boundary consists of a set of rectangles parallel to the x-axis. The integration formula for such a rectangle is a product of equidistant points in the x-direction, dealt with above, and Legendre points in the perpendicular direction. The latter are automatically symmetric with respect to possibly present reflection planes containing the axis, and C_2-operators with the axis orthogonal to the x-axis; these are the only relevant symmetry operators. Naturally only the symmetry unique boundary planes are considered.

5. USE OF THE PROGRAM AND RESULTS

For a given crystal or molecule the global structure of the integration formula is determined by the geometry of the system, as discussed in the previous sections. The actual realization, that is, the number of points and the precision of the generated formula, depends on various parameters. Usually one is not interested in parameters, however, but rather in the total number of integration points and in the accuracy of the numerical integrations that have to be done with them. Therefore the program is organized such that the user has to input only the atomic positions and the required accuracy in the form of an accuracy parameter A. A corresponds to an accuracy 10^{-A}, so A is the number of significant digits of the numerical integrals. The program minimizes the numbers of points in the various subregions and checks the accuracy by integrating a set of test functions that are typical for electronic structure calculations: standard sets of exponential functions of the form $r^n e^{-\alpha r} Y_{lm}(\Omega)$ (and more-center products of them).

Of course, the precision defined in this way may not correspond to the intended application of the integration scheme. To provide for this the user can adapt the scheme by specifying different "accuracies" for the different main subregions (atomic spheres, atomic polyhedra, outer region); without instructions to the contrary the program sets all these accuracies at the same level. Some more technical parameters, such as the radii of the atomic spheres and the distances between the outermost atoms and the boundary planes, are automatically computed by the program from geometrical aspects (for instance, the distance to the nearest atom to determine the size of an atomic sphere). It has been made possible, however, to overrule the default determination and explicitly input such values; this may occasionally be useful for purposes of testing and analysis of possibly occurring (integration) problems.

Results

To illustrate the performance of the integration method a few data are presented for molecules. The results in crystals are similar. As integrands are chosen the diagonal elements of the overlap matrix of symmetry adapted combinations of Slater type basis functions $Y_{lm}(\Omega)\, r^n e^{-\alpha r}$, normalized analytically, so that the error is equal to the deviation of the numerical integral from unity. The function sets contain s, p, and d functions with varying exponential decay constants. The r.m.s. error over all functions is used for each entry in Table I and the only input parameter was the general accuracy parameter A.

The following 10 molecules have been selected to test the performance of the integration:

1. Cu_{11}, a regular linear chain of 11 Cu atoms. The symmetry group is $D_{\infty h}$.

2. C_5H_5, a regular pentagon. Symmetry D_{5h}.

3. Cu_7CO, a CO molecule adsorbed at the central top position on a Cu_7 cluster. The cluster is planar: a regular hexagon with a central atom. Symmetry C_{6v}.

4. $SiFCl_3$, a Si atom with an approximately tetrahedral coordination. Symmetry C_{3v}.

5. Oxalic acid, $(CO\,OH)_2$. The molecule is planar. Symmetry C_{2h}.

6. Oxalic acid with two water molecules; the water molecules stick out of the plane. Symmetry C_i.

7. $[Zr(C_5H_5)_2]_2\,(PH_2)_2$. Two Zr atoms bridged by two PH_2 groups. Each of the Zr atoms is coordinated by two C_5H_5 rings, and the bonds with the two rings and those with the PH_2 groups form roughly a tetrahedral system. Symmetry C_{2h}.

8. 4-amino-4′-nitro-stilbene, NO_2-C_6H_4-C_2H_2-C_6H_4-NH_2. The molecule is planar with C_s symmetry.

9. Dimaprit ([S-[3-(N,N-dimethylamino)propyl] isothiourea]), NH_2-NH-C-S-$(CH_2)_3$-N-$(CH_3)_2$. No symmetry.

10. Pd_6H_2, an octahedral Pd_6-cluster with two hydrogen atoms inside. Symmetry D_{4h}.

Table I shows the number of points M (in the irreducible wedge) and the r.m.s. error ε for several values of the accuracy parameter A. Figures 7 and 8 present the same data graphically. In Fig. 7 the errors are plotted as a function of A; we infer that the accuracy tests, used internally by

TABLE I

The Number of Points M and the r.m.s. Error ε for Several Values of A, the Accuracy Parameter

A	Mol. 1	Mol. 2	Mol. 3	Mol. 4	Mol. 5	Mol. 6	Mol. 7	Mol. 8	Mol. 9	Mol. 10	
1.5	670	326	963	1063	1471	6366	7827	6447	15307	608	M
	3.6e-3	9.9e-3	1.7e-2	1.2e-2	2.2e-2	1.2e-2	6.8e-3	1.2e-2	8.4e-3	5.7e-3	ε
2.0	802	535	1409	1444	2398	10043	12587	11627	25291	906	M
	9.8e-4	2.0e-3	3.2e-3	3.9e-3	3.3e-3	3.5e-3	3.3e-3	1.2e-3	3.8e-3	4.8e-3	ε
2.5	912	884	2071	2239	3762	16375	19387	16719	40081	1346	M
	3.4e-4	9.4e-4	1.5e-3	1.5e-3	1.5e-3	9.8e-4	1.2e-3	6.5e-4	1.5e-3	9.6e-4	ε
3.0	1124	1183	2810	3048	5128	22534	26722	23279	55755	1776	M
	8.9e-5	2.2e-4	5.8e-4	6.2e-4	8.4e-4	6.1e-4	1.1e-3	3.1e-4	7.9e-4	4.2e-4	ε
3.5	1309	1736	3910	4393	7668	33514	37345	33360	70683	2539	M
	6.7e-5	5.2e-5	3.9e-4	2.0e-4	3.0e-4	3.0e-4	7.0e-4	1.3e-4	4.9e-4	1.8e-4	ε
4.0	1539	2226	4890	5594	9775	42448	48410	42178	102884	3074	M
	1.3e-5	1.2e-5	5.5e-5	1.8e-4	3.8e-5	1.2e-4	2.2e-4	8.5e-5	2.3e-4	4.5e-5	ε
5.0	2017	3694	7835	9093	16288	71236	80063	69008	172186	5225	M
	1.4e-6	8.5e-7	6.3e-6	1.6e-5	4.6e-6	3.4e-5	5.0e-5	8.5e-6	4.7e-5	8.0e-6	ε
6.0	2544	5732	11894	13735	24767	110106	120370	104022	264799	7669	M
	1.8e-7	9.7e-8	9.9e-6	1.1e-6	6.9e-7	3.9e-6	3.9e-6	7.9e-7	7.7e-6	5.6e-6	ε

Note. The molecules 1 through 10 are discussed in the text.

the program, are reasonable. The relation between A and ε is roughly, as intended

$$A = -{}^{10}\log \varepsilon. \tag{5.1}$$

In practice it is more important to know how the errors behave as a function of the *number of points*; this is shown in Fig. 8. Except the linear chain Cu_{11} (where performance is better as a result from it being essentially a *two*-dimensional integration), all tested molecules display roughly the same convergence characteristics. It is expressed by the fitted relation

$$\frac{M(A+1)}{M(A)} = 1 + \frac{5}{2A} - \frac{1}{2A^2} \tag{5.2}$$

which gives the factor of increase in the number of points that are necessary to gain one more significant digit. This means relatively slow convergence for low accuracies: a factor of 3 to pass from one to two digits. It improves for higher accuracies: a factor of 1.5 to go from five to six digits.

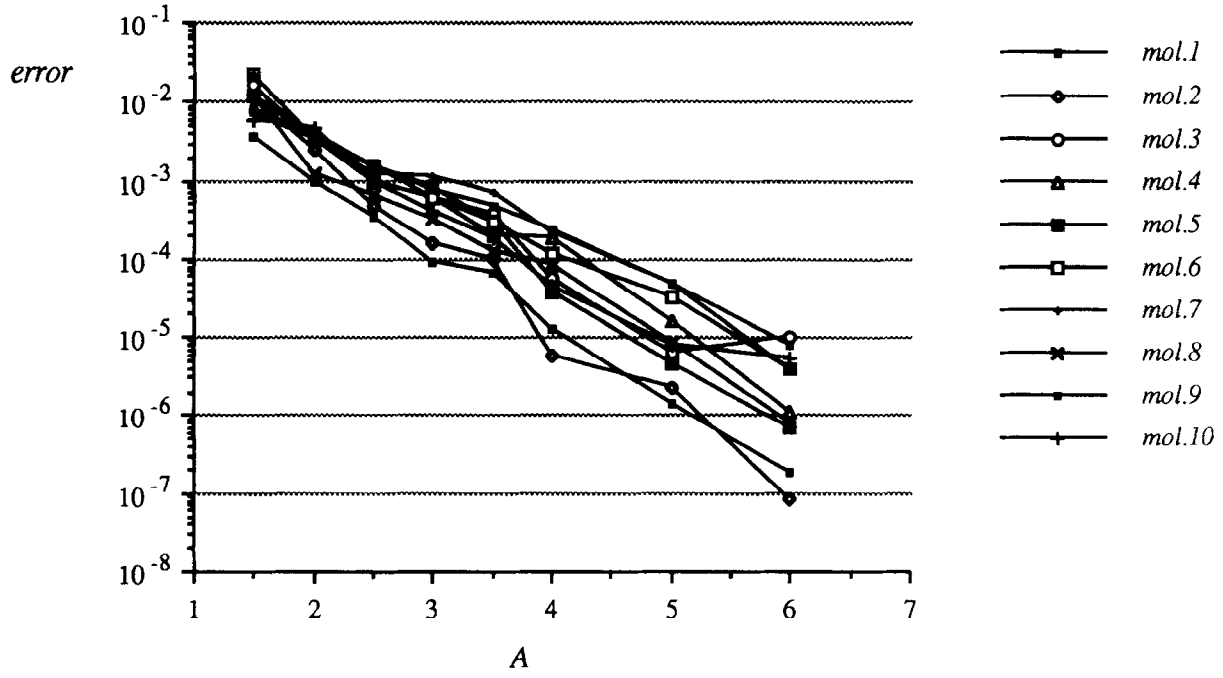

FIG. 7. Error vs. the accuracy parameter A, for a series of molecules.

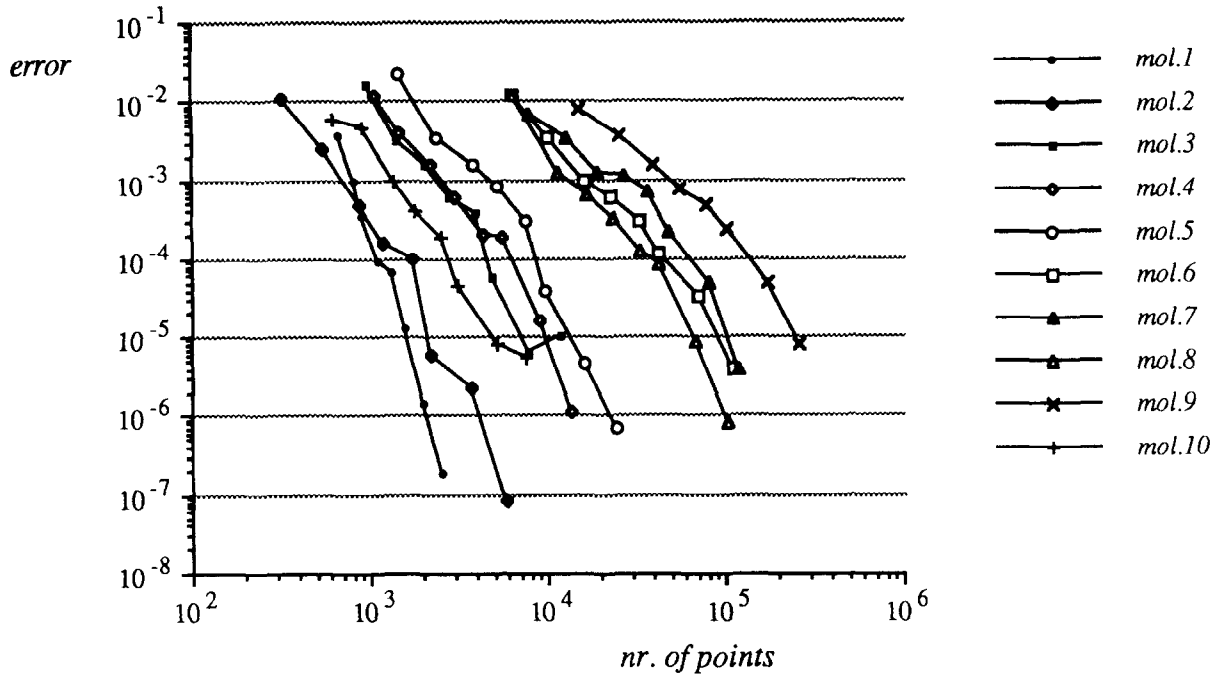

FIG. 8. Error vs. the number of integration points, for a series of molecules.

Comparison with (pseudo-)random methods may put these figures in perspective. Monte Carlo has theoretically (from statistics)

$$\varepsilon_{\mathrm{MC}} = cM^{-1/2}$$
$$\frac{M(A+1)}{M(A)} = 100. \tag{5.3}$$

The Diophantine method [18], which has been used in molecular as well as crystal DVM programs [19–21] claims an approximately linear convergence. So

$$\varepsilon_{\mathrm{DVM}} = cM^{-1}$$
$$\frac{M(A+1)}{M(A)} = 10. \tag{5.4}$$

It would be interesting to make a comparison with the elegant scheme proposed by Becke [22], which is, like ours, based on Gaussian integration. The convergence characteristics have not been examined in that paper in as much detail as we have done here. Our own findings with Becke's method indicate that it uses slightly more points than ours for moderate accuracies (10^{-3}); convergence to higher precision is much slower, in particular, for geometrically more complicated molecules. This may be due to the angular structure of the atomic weightfunctions [22]. We have not investigated the comparison systematically.

CONCLUSION

A Fortran program for numerical integration of both finite and infinite polyatomic systems has been presented and discussed. The scheme is based on a partitioning of the region of integration and subsequent application of Gaussian integration formulas, mostly of product type. The generated formulas are symmetric with respect to all symmetry operators of the polyatomic system; the operators are computed automatically from the geometric data. The numbers of points are optimized in each subregion, according to a prescribed accuracy defined in terms of a set of test function integrals. Convergence of accuracy with the number of points is fast, as it typical for Gaussian type methods.

Use of the program has been made easy: one needs to input only the atomic positions and the required general precision. At the other hand flexibility is retained since different accuracies can be imposed for the different main subregions (spheres, polyhedra, outer region). This is useful for special applications when the accuracy as defined in the program may not reflect the actual situation. Even some more technical parameters can by specified by the user, overruling the default determination by the program, for purposes of testing or for analysis of occurring integration problems.

The package is available on request: an extensive description with technical details of the implemented algorithms, serving as a user manual, is given in [23] and is available as well.

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