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Analytic quadratic integration over the two-dimensional Brillouin zone

Frank E Harris

Department of Physics, University of Utah, Salt Lake City, UT 84112, USA
and
Quantum Theory Project, University of Florida, PO Box 118435, Gainesville, FL 32611, USA

E-mail: harris@qtp.ufl.edu

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Abstract

Brillouin-zone (BZ) integrations in systems with two-dimensional periodicity are discussed in the context of a method wherein the BZ is divided into simplices (triangles), and band energies and properties contributions are represented by quadratic interpolations based on six data points on the edges of each simplex. This paper describes a straightforward and easily implemented algorithm for identifying the paths bounding the occupied portion(s) of each simplex, and (in contrast to earlier work by others) provides completely analytic expressions, in closed form, for evaluating properties integrals over the occupied regions.

1. Introduction

Questions associated with the choice and use of Brillouin-zone (BZ) points ('$\boldsymbol{k}$-points') for periodic-structure calculations have received considerable attention in the scientific literature. These points are generally used for two types of calculation: (1) those involving summations over the occupied single-particle states, to obtain quantities such as band occupancies, energies, and forces; and (2) those involving energy-resolved properties, such as densities of states (DOS). A recent paper by Pickard and Payne [1] has called attention to the operational differences between these two computational problems, and, at least for DOS calculations, advocates and describes an 'extrapolative' approach in which the behaviour in the integration cell surrounding a $\boldsymbol{k}$-point is estimated from data at that point alone rather than derived interpolatively using also data from neighbouring points.

The present paper is focused on calculations of the first type (as defined above), for which interpolative methods have provided reasonably successful results. Many of the interpolative computations thus far reported have been based on the use of 'special points' designed to minimize calculational error; procedures of this kind apply best when the band occupancy is complete, but have also provided satisfactory results for more complex occupancy patterns

such as are encountered in metals. The special-points approach is illustrated by contributions such as that of Chadi and Cohen [2] and the frequently cited work of Monkhorst and Pack [3].

An alternative to the use of special points most naturally arises when the BZ is described as an assembly of simplices, with an interpolative optimum-integration procedure applied using a set of points in each simplex. Early work in this direction used linear interpolations of the band energies and other properties [4]. However, more accurate methods based on simplices have since been studied, and, in an article with the same title as this communication, Wiesenekker *et al* [5] reported an algebraic method for the integration of quadratically interpolated quantities for systems with two-dimensional periodicity.

The work by Wiesenekker *et al* compares quadratic methods both with linear methods [6,7] and with an earlier attempt at a quadratic method by Methfessel *et al* [8]. For the history of this problem, we refer the reader to several significant earlier contributions [9–13]; for an extension to three dimensions we cite another contribution from the Baerends group: [14]. The method of Wiesenekker *et al* is quadratic in its treatment of both the band energy and property quantities, and in that approximation includes analytical formulae for integrals restricted to a single band energy (such as the DOS). However, these authors only succeeded in proposing numerical (as opposed to analytical) methods for the final evaluation of quantities described as two-dimensional integrals (such as band occupancies), and these numerical methods must be implemented carefully to avoid instabilities associated with the existence of van Hove singularities [15]. The rapid convergence of the quadratic method (with respect to the number of $\boldsymbol{k}$-points) makes it desirable to improve the computational efficiency by eliminating the final numerical steps.

The present paper deals with the completely analytic evaluation of integrals of the type

$$J_n(E) = \int f_n(\boldsymbol{k})\theta(E - \epsilon_n(\boldsymbol{k}))\,\mathrm{d}\boldsymbol{k} \tag{1}$$

where $f_n(\boldsymbol{k})$ is the value of a quantity associated with energy band n at two-dimensional reciprocal-space point $\boldsymbol{k}$, θ is the Heaviside function (unity for positive values of its argument, zero otherwise), $\epsilon_n(\boldsymbol{k})$ is the energy of band n at $\boldsymbol{k}$, E is the Fermi energy, and the integration is by a quadratic method based on simplices for the irreducible wedge of the BZ. Much of the discussion also applies to integrals of the type

$$I_n(E) = \int f_n(\boldsymbol{k})\delta(E - \epsilon_n(\boldsymbol{k}))\,\mathrm{d}\boldsymbol{k} \tag{2}$$

where δ is the Dirac delta function, but we give no formulae for complete evaluation of $I_n(E)$ because these may be found in the work of Wiesenekker *et al* [5].

The essential contributions of the present communication are (1) a simpler and more straightforward way of evaluating $J_n(E)$ and $I_n(E)$ for partially occupied bands, and (2) the presentation of completely analytical formulae for all the quantities involved in the evaluation of $J_n(E)$. A computer program illustrating the method is available on the Web [16].

2. Quadratic integration scheme

Following Wiesenekker *et al*, the irreducible wedge of the BZ is divided into simplices (in this two-dimensional case, triangles), and values of f_n and ϵ_n (for all n) are assumed to be available at the vertices and the midpoints of the sides of each triangle. There is no requirement that the triangles have specific angles or relations among their dimensions, nor that the various simplices of the irreducible wedge be similar. In fact, it is not even required that the same division into simplices be used for different bands.

For each simplex and band, the six values of f suffice to define a quadratic approximation $\bar{f}$, applicable throughout the simplex; similarly, from the six ϵ-values, one may define a quadratic approximation $\bar{\epsilon}$. We are no longer using symbols to designate particular bands; the formulae to be obtained apply to any band and simplex. In general terms, the procedure to be followed for $J_n(E)$ will be (1) to construct $\bar{\epsilon}$ from the six input data points of the simplex; (2) to determine the path(s) in the simplex on which $\bar{\epsilon} = E$, thereby also identifying the occupied portion of the simplex (that for which $\bar{\epsilon} < E$); (3) to integrate over the occupied part of the simplex the six monomials used in $\bar{f}$; and (4) to convert the results of step (3) into weights with which the individual f-points are to be combined. Alternatively to step (3), one could perform monomial integrations along the simplex paths, thereby obtaining the building blocks needed for the integrals $I_n(E)$; we need not do so explicitly, as those results are contained in previous work [5].

It is easiest to carry out the procedure indicated above for a 'standard' simplex with convenient geometry; for this purpose we take a right triangle, with sides of unit length along the x- and y-directions of a Cartesian coordinate system. An arbitrary triangle can be transformed to the standard simplex by a linear transformation with Jacobian equal to the constant value $2A$, where A is the area of the untransformed triangle. Since vertices and side midpoints remain such under the transformation, one can work out integration formulae for the standard simplex, and use them unchanged (except for a scale factor $2A$) for simplices of arbitrary dimensions [17].

In addition to the benefits arising from a quadratic (as opposed to a linear) method, the scheme of Wiesenekker *et al* has two practical advantages, of which the first is that all the evaluation points (except some on the boundary of the irreducible wedge) are common to several simplices. A second advantage is that the integration can be refined by inscribing in each triangle another triangle whose vertices are at the side midpoints of the original triangle. This means that all points used at a given level of approximation can be reused at all subsequent stages of refinement.

3. Detailed procedure

3.1. Quadratic representation of ϵ

The first main step of the integration procedure is to obtain a representation of ϵ in the coordinates x, y of the standard simplex, as was done by Wiesenekker *et al* [5]. Writing

$$\bar{\epsilon}(x, y) = q_1 + q_2 x + q_3 y + q_4 x^2 + q_5 xy + q_6 y^2 \tag{3}$$

the coefficients q_1–q_6 are obtained by the matrix multiplication

$$\begin{pmatrix} q_1 \\ q_2 \\ q_3 \\ q_4 \\ q_5 \\ q_6 \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ -3 & -1 & 0 & 4 & 0 & 0 \\ -3 & 0 & -1 & 0 & 0 & 4 \\ 2 & 2 & 0 & -4 & 0 & 0 \\ 4 & 0 & 0 & -4 & 4 & -4 \\ 2 & 0 & 2 & 0 & 0 & -4 \end{pmatrix} \begin{pmatrix} \epsilon(0,0) \\ \epsilon(1,0) \\ \epsilon(0,1) \\ \epsilon(1/2,0) \\ \epsilon(1/2,1/2) \\ \epsilon(0,1/2) \end{pmatrix}. \tag{4}$$

Here $\epsilon(0, 0), \epsilon(1, 0), \ldots$ refer to the ϵ-values at the points of the input simplex that correspond to the points $(0, 0), (1, 0), \ldots$ of the standard simplex. For later reference, the 6×6 matrix in equation (4) will be denoted as **G**.

3.2. Paths bounding integration region

The second major step of the integration procedure is to identify the path(s) bounding the portion of the standard simplex for which $\bar{\epsilon}(x, y) < E$.

We start the path identification by using the representation provided by equation (3) to find the points, if any, where $\bar{\epsilon}(x, y) = E$ intersects the standard simplex. We require: (1) the solutions between $y = 0$ and 1, if any, of $q_1 + q_3 y + q_6 y^2 = E$; these describe points $(0, y)$; (2) the solutions between $x = 0$ and 1, if any, of $q_1 + q_2 x + q_3(1-x) + q_4 x^2 + q_5 x(1-x) + q_6(1-x)^2 = E$; these describe points $(x, 1-x)$; and (3) the solutions between $x = 0$ and 1, if any, of $q_1 + q_2 x + q_4 x^2 = E$; these describe points $(x, 0)$. These intersection points, and the vertices (0, 0), (0, 1), and (1, 0) of the standard simplex, are then arranged in the order in which they would be encountered in a clockwise circuit of that simplex. This ordered set of points (which we call the 'simplex list') will be thought of as defining the straight-line segments connecting its successive points, including a segment from the last point to the first.

We next find the rotation and translation needed to bring the curve described by $\bar{\epsilon}(x, y) = E$ (the 'curve'; it is a conic section or a degenerate form thereof) to a standard form permitting the easy identification of its type and the locations, if any, of its critical points (bifurcation points for y viewed as a function of x; double-valued square roots change sign when passing on the curve through such points). The standard form will place conic sections symmetrically with respect to the origin and with foci on a coordinate axis; degenerate conics are transformed into lines parallel to the y-axis.

We apply the above-identified transformation to the intersection points, and then arrange the intersection points and any critical points in the order in which they would be encountered in a clockwise circuit of the curve (as seen from the origin of the transformed coordinates). An algorithm for ordering the points is straightforward when the curve is in a standard form. The ordered set of points (which we call the 'curve list') will be thought of as defining the curve sections connecting its successive points, including that from the last point to the first.

Since it will be our plan to surround each included portion of the standard simplex by a boundary to be traversed in the clockwise direction, we determine, and use henceforth, the direction of travel in the curve list that places the included region on the right-hand side. Thus, if in the transformed coordinates $\bar{\epsilon}(0, 0) < E$, the curve list will be traversed in the forward direction, otherwise, in reverse.

Clockwise paths enclosing the occupied portion of the standard simplex (in the transformed coordinates) may now be constructed as follows: starting from the first segment of the simplex list in which $\bar{\epsilon} < E$, proceed forward in the simplex list until an intersection point is reached; then proceed on the curve list from that intersection point until another intersection is reached; then from there forward on the simplex list to the next intersection, alternating the use of the two lists in this way until returning to the start point. If all the simplex list segments with $\bar{\epsilon} < E$ have not yet been used, find another such segment of the simplex list and repeat the process. If there were no intersections, traverse the entire simplex list or none of it (depending upon whether or not $\bar{\epsilon} < E$). If the curve $\bar{\epsilon}(x, y) = E$ is entirely within the simplex, then also traverse the entire curve list (which in that case must describe an ellipse). In all cases, retain the information needed to fully identify the paths (including vertex and bifurcation points).

3.3. Integration of monomials

The next step in our analysis is to integrate, in the transformed coordinate system, the monomials 1, x, y, x^2, xy, and y^2 over the portions of the standard simplex bounded by the paths that we found in the preceding section. A relatively simple way of doing this is

based on relations between integrals over an area and line integrals for the boundary path. For example, the integral of 1 (the area) is given by

$$J_1 = \int_A \mathrm{d}A = \int_C y\,\mathrm{d}x \tag{5}$$

where the path C runs clockwise around the boundary of the area A, and the subscript to J refers to the monomial (in this case, 1). To evaluate J_1, we write

$$\begin{aligned} J_1 &= \int_{x_1}^{x_2} y\,\mathrm{d}x + \int_{x_2}^{x_3} y\,\mathrm{d}x + \cdots + \int_{x_{n-1}}^{x_n} y\,\mathrm{d}x + \int_{x_n}^{x_1} y\,\mathrm{d}x \\ &= \eta_{12}[j_1(x_2) - j_1(x_1)] + \eta_{23}[j_1(x_3) - j_1(x_2)] \\ &\quad + \cdots + \eta_{n-1,n}[j_1(x_n) - j_1(x_{n-1})] + \eta_{n1}[j_1(x_1) - j_1(x_n)] \end{aligned} \tag{6}$$

where $x_1, x_2, \ldots, x_n, x_1$ are the successive x-values along path C, and $j_1(x)$ is the indefinite integral $\int^x y\,\mathrm{d}x$ for the y appropriate to the path section being integrated, and with y, if double valued, on its upper branch. Each coefficient η_{ij} is +1 unless the path section from x_i to x_j is on the lower branch of a double-valued function, in which case $\eta_{ij} = -1$.

Equations analogous to equation (5) can be written for the remaining monomials:

$$J_x = \int_A x\,\mathrm{d}A = \int_C xy\,\mathrm{d}x \tag{7}$$

$$J_y = \int_A y\,\mathrm{d}A = \int_C \tfrac{1}{2}y^2\,\mathrm{d}x \tag{8}$$

$$J_{xx} = \int_A x^2\,\mathrm{d}A = \int_C x^2 y\,\mathrm{d}x \tag{9}$$

$$J_{xy} = \int_A xy\,\mathrm{d}A = \int_C \tfrac{1}{2}xy^2\,\mathrm{d}x \tag{10}$$

$$J_{yy} = \int_A y^2\,\mathrm{d}A = \int_C \tfrac{1}{3}y^3\,\mathrm{d}x. \tag{11}$$

The evaluation of J_x, J_{xx}, and J_{yy} will be by equations similar to equation (6); the formulae for J_y and J_{xy} will differ from an analogue of equation (6) by omission of the η_{ij}-factors—in these last two line integrals y occurs to an even power. We will therefore also need the indefinite integrals $j_x(x) = \int^x xy\,\mathrm{d}x$, $j_y(x) = \frac{1}{2}\int^x y^2\,\mathrm{d}x$, $j_{xx} = \int^x x^2 y\,\mathrm{d}x$, $j_{xy} = \frac{1}{2}\int^x xy^2\,\mathrm{d}x$, and $j_{yy}(x) = \frac{1}{3}\int^x y^3\,\mathrm{d}x$.

We now need to evaluate the various indefinite integrals for the different curve types involved: parabola, ellipse, hyperbola, and straight line. All the integrals reduce to elementary functions.

Parabola. Assumed functional form: $y = ax^2 + b$;

$$j_1(x) = \tfrac{1}{3}ax^3 + bx \tag{12}$$

$$j_x(x) = \tfrac{1}{4}ax^4 + \tfrac{1}{2}bx^2 \tag{13}$$

$$j_y(x) = \tfrac{1}{2}aj_{xx}(x) + \tfrac{1}{2}bj_1(x) \tag{14}$$

$$j_{xx}(x) = \tfrac{1}{5}ax^5 + \tfrac{1}{3}bx^3 \tag{15}$$

$$j_{xy}(x) = \tfrac{1}{12}a^2x^6 + \tfrac{1}{4}abx^4 + \tfrac{1}{4}b^2x^2 \tag{16}$$

$$j_{yy}(x) = abj_{xx}(x) + \tfrac{1}{21}a^3x^7 + \tfrac{1}{3}b^3x. \tag{17}$$

Ellipse or hyperbola. Assumed functional form: $y = (ax^2 + b)^{1/2}$;

$$j_1(x) = \frac{x}{2}(ax^2 + b)^{1/2} + \frac{bW(x)}{2|a|^{1/2}} \tag{18}$$

$$j_x(x) = \frac{(ax^2 + b)^{3/2}}{3a} \tag{19}$$

$$j_y(x) = \tfrac{1}{6}ax^3 + \tfrac{1}{2}bx \tag{20}$$

$$j_{xx}(x) = \frac{x(ax^2 + b)^{3/2}}{4a} - \frac{b}{4a}j_1(x) \tag{21}$$

$$j_{xy}(x) = \tfrac{1}{8}ax^4 + \tfrac{1}{4}bx^2 \tag{22}$$

$$j_{yy}(x) = \tfrac{1}{3}bj_1(x) + \tfrac{1}{3}aj_{xx}(x). \tag{23}$$

For the ellipse,

$$W(x) = \sin^{-1}\left(\frac{|a|^{1/2}x}{b^{1/2}}\right). \tag{24}$$

For the hyperbola,

$$W(x) = \log(|a|^{1/2}x + (|a|x^2 + b)^{1/2}). \tag{25}$$

Straight line. Assumed functional form: $y = ax + b$;

$$j_1(x) = \tfrac{1}{2}ax^2 + bx \tag{26}$$

$$j_x(x) = \tfrac{1}{3}ax^3 + \tfrac{1}{2}bx^2 \tag{27}$$

$$j_y(x) = \tfrac{1}{2}aj_x(x) + \tfrac{1}{2}bj_1(x) \tag{28}$$

$$j_{xx}(x) = \tfrac{1}{4}ax^4 + \tfrac{1}{3}bx^3 \tag{29}$$

$$j_{xy}(x) = \tfrac{1}{2}aj_{xx}(x) + \tfrac{1}{2}bj_x(x) \tag{30}$$

$$j_{yy}(x) = \tfrac{1}{3}a^2j_{xx}(x) + \tfrac{2}{3}abj_x(x) + \tfrac{1}{3}b^2j_1(x). \tag{31}$$

Note: These integrals vanish for lines parallel to y-axis (i.e. given by $x = c$).

We ultimately need the monomial integrals in the original (untransformed) coordinate system of the standard simplex, so the final step of this section is to apply to them the inverse of the transformation used to bring the curve to standard form. For details see Wiesenekker *et al* [5].

3.4. Integration weights for f

If we assume that f has a quadratic expansion in the coordinates of the standard simplex, of the form

$$\bar{f}(x, y) = p_1 + p_2x + p_3y + p_4x^2 + p_5xy + p_6y^2 \tag{32}$$

then the integral of $\bar{f}$ will be a corresponding linear combination of the integrals of its monomials. Letting $J_1, J_x, \ldots$ stand for these integrals over the occupied portion(s) of the standard simplex in the original (untransformed) coordinates, we have

$$\int_A \bar{f}(x, y)\,\mathrm{d}A = p_1J_1 + p_2J_x + p_3J_y + p_4J_{xx} + p_5J_{xy} + p_6J_{yy}. \tag{33}$$

Writing this equation in matrix form, and introducing a formula analogous to equation (4) to relate p_1–p_6 to $f(0,0)$, $f(1,0)$, ..., we obtain

$$\int_A \bar{f}\,\mathrm{d}A = (\,J_1 \quad J_x \quad J_y \quad J_{xx} \quad J_{xy} \quad J_{yy}\,)\,\mathbf{G}\begin{pmatrix} f(0,0) \\ f(1,0) \\ f(0,1) \\ f(1/2,0) \\ f(1/2,1/2) \\ f(0,1/2) \end{pmatrix} \tag{34}$$

where **G** is the matrix in equation (4). This equation shows that $\int_A \bar{f}\,\mathrm{d}A$ can be written as a weighted sum of the values $f(0,0)$, $f(1,0)$, ...:

$$\begin{aligned}\int_A \bar{f}\,\mathrm{d}A = {} & w_1 f(0,0) + w_2 f(1,0) + w_3 f(0,1) \\ & + w_4 f(1/2,0) + w_5 f(1/2,1/2) + w_6 f(0,1/2)\end{aligned} \tag{35}$$

with

$$(\,w_1 \quad w_2 \quad w_3 \quad w_4 \quad w_5 \quad w_6\,) = (\,J_1 \quad J_x \quad J_y \quad J_{xx} \quad J_{xy} \quad J_{yy}\,)\,\mathbf{G}. \tag{36}$$

As observed by Wiesenekker *et al*, the integration weights depend upon $\bar{\epsilon}$ but not upon $\bar{f}$.

4. Discussion

When the method of the foregoing section is implemented computationally, a number of programming issues arise, including the following:

(1) When a simplex–curve intersection occurs at a vertex of the simplex, the curve may or may not, depending upon its direction, enter the simplex. The simplest way to avoid problems from such intersections is to move them a negligible amount away from the vertices by making small changes in the coefficients of the expansion for $\bar{\epsilon}$ before undertaking the analysis of section 3.

(2) As each successive section of a boundary path is identified, we need to set a marker showing whether it is a curve or a straight-line section, and if the curve of a double-valued function whether the section is on the upper or lower branch. Each individual straight-line section will have its own coefficients a and b, but all curve sections will have common parameters which can be determined when transforming the curve to standard form.

(3) Often, as for example during the successive iterations of a self-consistent-field process, the only property to be evaluated will be the band occupancy, which is simply J_1. Because J_1 is invariant under the rotation–translation transformation, it will in this case be unnecessary either to calculate $J_x, \ldots, J_{yy}$ or to explicitly carry out the inverse transformation. It will increase efficiency to recognize this situation with an input flag.

An issue that, in contrast to the case for the work of Wiesenekker *et al*, does not arise here is the effect of van Hove singularities. Those authors used numerical quadrature to evaluate $J(E)$ as the integral of an appropriate $I(\epsilon)$ over the ϵ-range $(\epsilon_{\min}, E)$. Such a procedure will be sensitive to singularities in the density of states, i.e. the van Hove singularities (which must always exist [15]). We avoid this problem here because we are working with closed analytical expressions. It goes without saying that the replacement of a numerical quadrature by relatively compact closed formulae will also translate into a substantial gain in computing efficiency.

5. Illustrative calculations

Both to validate our methods and to illustrate their use, we present a few sample calculations, computed using a FORTRAN 90 program that we prepared for that purpose. We do not provide an extensive evaluation because the present method is simply an improved way of carrying out the process already studied in detail by Wiesenekker *et al* [5]. Our test program is available on the World Wide Web [16], and it can easily be modified to carry out any further tests that may be desired.

All calculations are either for a square BZ or for a triangular irreducible wedge thereof (assuming fourfold symmetry). For the irreducible wedge, the coarsest grid was the entire wedge: a triangle with vertices at $(k_x, k_y) = (0, 0)$, $(0, 1)$, and $(1, 0)$. For the entire zone, the coarsest grid consisted of two triangles: one with vertices $(-1, -1)$, $(1, -1)$, and $(1, 1)$; the other with vertices $(1, 1)$, $(-1, 1)$, and $(-1, -1)$. Finer grids were generated by connecting the midpoints of all triangle sides of the next coarser grid. We designate the number of times this subdivision has been carried out by n; a triangle that has been subdivided in this way n times will consist of 2^{2n} smaller triangles, and an integration by our method for this subdivided triangle will utilize $(2^{n+1} + 1)(2^n + 1)$ distinct $\boldsymbol{k}$-points.

Values of the band energy $\epsilon(\boldsymbol{k})$ at the data points were generated from one of the following three formulae (referred to in the tables by the subscripts shown here):

$$\epsilon_1(\boldsymbol{k}) = k_x^2 + k_y^2 \tag{37}$$

$$\epsilon_2(\boldsymbol{k}) = \frac{k_x^2 + k_y^2}{1 + 0.2\cos 4\phi} \tag{38}$$

$$\epsilon_3(\boldsymbol{k}) = 0.4(k_x - 0.65)^4 + 0.2(k_y - 0.33)^4 \tag{39}$$

where $\phi = \tan^{-1}(k_y/k_x)$ is the polar angle in $\boldsymbol{k}$-space. The energy profile ϵ_1 will (for any Fermi energy) produce an integration region that our method will represent exactly, consisting of circular arcs and straight-line segments. Profile ϵ_2, while consistent with fourfold symmetry, will (for Fermi energies corresponding to a partially occupied band) yield a boundary curve that we will only be able to represent approximately. Profile ϵ_3 will, for certain values of the Fermi energy, produce a closed integration boundary requiring approximate representation, located asymmetrically entirely within the BZ.

Values of the functions $f(\boldsymbol{k})$ to be integrated were generated at the data points from one of the following formulae:

$$f_1(\boldsymbol{k}) = 1 \tag{40}$$

$$f_2(\boldsymbol{k}) = k_x^2 + k_y^2 \tag{41}$$

$$f_3(\boldsymbol{k}) = (k_x^2 + k_y^2)^{1/2} \tag{42}$$

$$f_4(\boldsymbol{k}) = \cos(2\pi k_x) + \cos(2\pi k_y). \tag{43}$$

Functions f_1 (the area) and f_2 (a kinetic energy integral) are exactly representable in our method and should give exact results when integrated over an exactly representable region. Function f_3, which is simply the magnitude of $\boldsymbol{k}$, is only representable approximately by a quadratic form, and function f_4 will only have a reasonable quadratic approximation when the grid is not too coarse.

Some representative calculations for the irreducible wedge are presented in table 1. At the Fermi energy chosen, the integration region for ϵ_1 will be that within a circular arc, while for ϵ_2 it will be a complicated shape in part delimited by the zone boundary. When both ϵ and f are represented exactly, we obtain a result that is independent of the grid subdivision and also agrees with analytic evaluations of the same integrals. When either the integration

Table 1. Irreducible wedge integrations, at grid subdivision n. All calculations are for Fermi energy $E = 1.0$, and for the indicated energy profiles ϵ_k and functions f_k. For a more detailed specification, see the text.

n	ϵ_1, f_1	ϵ_1, f_2	ϵ_1, f_3	ϵ_2, f_1	ϵ_2, f_2	ϵ_2, f_3
0	0.392 6991	0.196 3495	0.266 5848	0.374 4011	0.179 7432	0.249 0470
1	0.392 6991	0.196 3495	0.262 4176	0.374 1209	0.179 8731	0.244 9184
2	0.392 6991	0.196 3495	0.261 8752	0.373 9700	0.179 7480	0.244 2391
3	0.392 6991	0.196 3495	0.261 8088	0.373 9695	0.179 7493	0.244 1728
4	0.392 6991	0.196 3495	0.261 8006	0.373 9701	0.179 7499	0.244 1652
5	0.392 6991	0.196 3495	0.261 7996	0.373 9701	0.179 7488	0.244 1642

Table 2. BZ integrations, at grid subdivision n. All calculations are for Fermi energy $E = 0.1$ and energy profile ϵ_3, and for the indicated functions f_k. For a more detailed specification, see the text.

n	f_1	f_2	f_3	f_4
0	1.488 305	0.888 579	0.902 719	2.976 610
1	0.650 129	0.411 442	0.509 705	−0.518 516
2	0.681 187	0.415 919	0.512 468	−0.149 305
3	0.644 110	0.407 013	0.493 677	−0.186 966
4	0.645 208	0.406 250	0.493 677	−0.186 920
5	0.645 301	0.406 145	0.493 625	−0.187 105

boundary or the function are only approximately represented, we note a rapid convergence with grid subdivision.

Table 2 presents a few results for partial occupancy of the entire BZ. The grids for these calculations span eight times the area of those for the irreducible wedge, but for given n have only twice as many points. The main purpose of this table is to illustrate results for an integration region that is a closed curve entirely within the BZ and centred asymmetrically. The very poor result for f_4 on the coarsest grid reflects the fact that the values of this oscillatory function on the zone boundary give no information about its behaviour at interior points.

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