

Extrapolative approaches to Brillouin-zone integration

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A highly efficient extrapolative Brillouin-zone integration scheme is presented that requires a very low \mathbf{k} -point sampling density for spectral integrations. It is important to use an extrapolative approach, since at low sampling densities interpolative schemes are hindered by problems associated with band crossing, which introduce spurious singularities in the density of states (DOS). The information for the extrapolation is obtained using second-order $\mathbf{k}\cdot\mathbf{p}$ perturbation theory within a set of subcells of the Brillouin zone, which can be chosen to make full use of symmetry. The resulting piecewise quadratic representation of the band structure is converted directly to a DOS using an analytic approach. It is also shown that this method can be successfully applied even in the linear extrapolative case. [S0163-1829(99)06807-1]

I. INTRODUCTION

Most electronic properties of real systems in the solid state depend on sums over a computationally intractable number of electronic levels. Bloch's theorem transforms the electronic structure problem from one of calculating an infinite number of electronic states (for an infinite periodic system) to one of calculating for a finite number of bands at an infinite number of \mathbf{k} points within the Brillouin zone of the system. Calculations of the properties of a given system then require some form of integration over these \mathbf{k} points. Straightforward weighted sums over the states—e.g., for the total energy and forces—are usually performed using a special point scheme¹ and a modest number of \mathbf{k} points. Recent developments of sampling approaches led to accurate values for these integrated quantities even in the difficult cases of metals.^{2,3} However, energy-resolved spectral properties, such as densities of states (DOS), require more careful integrations.

On examining experimental spectral data, one is led to the conclusion that Brillouin-zone integrations are, in many cases, only required to produce features at a finite-energy resolution—a limit placed, for example, by the energy-broadening effects introduced by core hole lifetimes in core-level spectroscopies⁴ and the finite lifetimes of the final quasiparticle states in optical spectroscopy.⁵ Thus it is not physically meaningful to calculate at higher resolutions. Further, from a practical perspective, all experiments have a finite-energy resolution and frequently concentrate on the shifts, distortions, and changes in weight in the spectral features. Looking at calculated band structures, it is clear that the bands are essentially smoothly varying objects in \mathbf{k} space. Detailed investigation of the wave functions show that they also vary smoothly in \mathbf{k} space.⁶ It might therefore be hoped that only a sparse sampling of the Brillouin zone would be required to obtain a good representation of the bands and hence the DOS. However, any interpolative sparse sampling scheme has to confront the band crossing problem described in Sec. II. In the past the approach taken has been to acknowledge this problem and calculate the DOS at the very high density of \mathbf{k} points required to alleviate its effects, and then smear the resulting spectrum to the experimental resolution. This is clearly computationally wasteful, but is offset by the fact that many of the electronic structure ap-

proaches used to predict spectra used require only small basis sets that allow rapid matrix diagonalization of the resulting Hamiltonian and hence a small computational cost for each \mathbf{k} point. However, minimal basis set approaches are necessarily restricted as to how far they can predict spectra into the conduction band, and they are not intrinsically as accurate as the more expensive plane-wave pseudopotential methods⁷ or other methods that include the full basis set. It is clear that if resources can be saved in the Brillouin-zone integrations then the savings can be “spent” on using plane waves, larger supercells, or more elaborate theory. In this paper a Brillouin-zone integration scheme is described that exploits the essential smoothness of the bands and avoids the band crossing problem.

II. BAND CROSSING PROBLEM

The band crossing problem is a well-known impediment to the rapid convergence of interpolative methods.^{8,9} The simple one-dimensional example shown in Fig. 1 illustrates the kind of changes that can occur in the DOS given different band allocations for the interpolation. At a general \mathbf{k} point it is more likely that the bands do not actually cross as a result of small interactions between the bands that break the degeneracy—rather they can be described as “kissing” (see Fig. 2), getting very close at a given point, but both the upper and lower bands remaining individually continuous although the character of the bands is exchanged across the “kissing” point. It is unclear as to whether any connection of the bands between \mathbf{k} points will lead to the correct topology of the band structure in three dimensions.

III. CURRENT METHODS

Many Brillouin-zone integration techniques have been developed over recent years. Some common ones are briefly described below, with particular emphasis placed on their performance for predicting spectral properties.

A. Gaussian broadening

This is the simplest approach to Brillouin-zone spectral integrations. \mathbf{k} points are distributed as evenly as possible

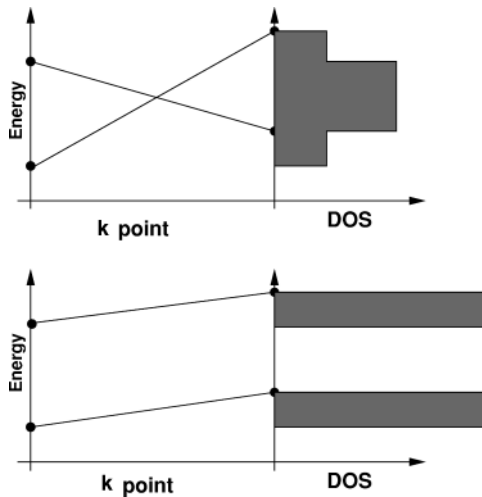


FIG. 1. A simplified one-dimensional example of the band crossing problem. An incorrect allocation of bands can cause dramatic changes in the calculated DOS.

throughout the Brillouin zone (either regularly or randomly as in a Monte Carlo method), and the DOS $D(E)$ is formed according to

$$D(E) = \frac{1}{\sqrt{2\pi}\sigma} \sum_i e^{-(E-E_i)^2/2\sigma^2}, \quad (1)$$

where the sum is performed over the states i , E_i are the corresponding energy levels, and σ is the energy broadening parameter. This method actually converges at van Hove singularities¹⁰ faster than the linear method described below.¹¹ However, this only applies at the limit of full convergence, which is rarely required or achieved. The Gaussian broadening method is, in practice, less accurate than the linear interpolative method for most purposes, but it is the method of choice for work that simply requires a rough idea of where the electronic states lie. It clearly does not suffer from the band crossing problem, since no topology of the bands is assumed.

B. Linear interpolative tetrahedron method

The linear tetrahedron method¹² is the staple Brillouin-zone integration technique for the electronic structure community. Indeed, recently Blöchl *et al.*⁸ have published an “improved” method. It is a relatively straightforward approach and, hence, very attractive. The scheme is applied by dividing the irreducible wedge of the Brillouin zone into approximately equally volumed tetrahedra, then by calculating the band energies at each apex a linear representation of the band is constructed within the tetrahedron. From this, contributions to the DOS can be evaluated analytically. However, the method suffers from the band crossing problem and a poor representation of van Hove singularities due to the absence of second-order band information.¹¹

C. Quadratic interpolative tetrahedron method

A series of papers by Methfessel and co-workers^{11,13,14} demonstrate the superior convergence properties of a method based on a piecewise quadratic representation of the Brillouin zone.

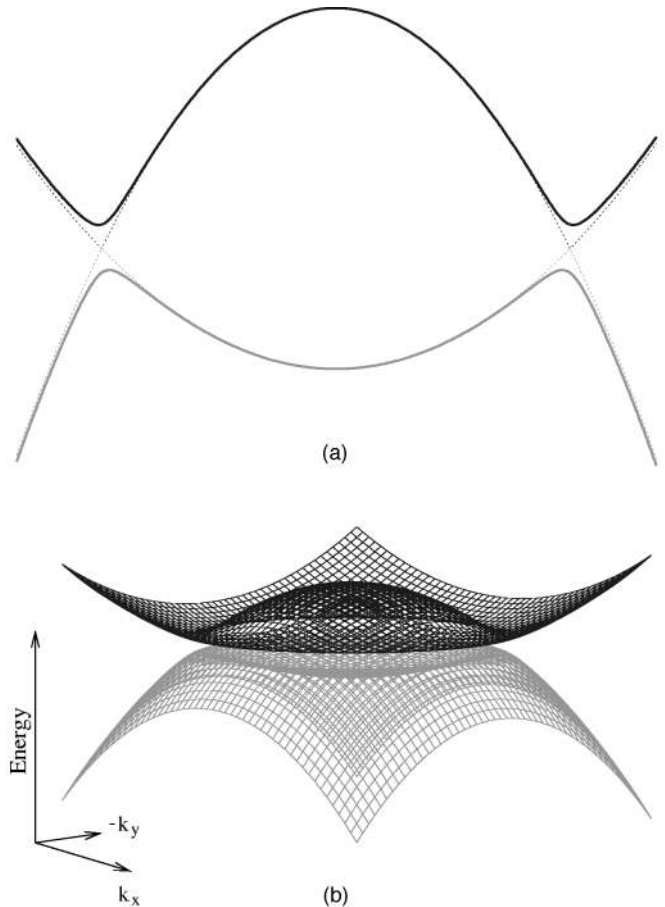


FIG. 2. An example of one kind of frequently encountered band “kissing,” for which there is some hope of dealing with in the extrapolative method. This example consists of two quadratically dispersive bands intersecting each other and a repulsion occurring along the curve of intersection. Two- and three-dimensional projections are shown (with two and one reciprocal space dimensions removed, respectively).

louis zone. This method converges more rapidly than both the Gaussian broadening and linear tetrahedron methods due to the more accurate treatment of the van Hove singularities, which occur when $|\nabla E(\mathbf{k})|=0$. To accurately describe these points, $E(\mathbf{k})$ must be known to at least second order in \mathbf{k} . However, this methodology does not appear to have been widely applied by the community. A probable reason for this is that this method is particularly susceptible to the band crossing problem because it is a higher-order interpolative scheme. So, while convergence for a single band is impressive, the method becomes relatively expensive in real systems since a high \mathbf{k} -point sampling density is required to overcome the band crossing problem and the extra effort is not justified. It is, however, one of the building blocks for the scheme developed below.

D. Linear extrapolative method

The vast majority of Brillouin-zone integration schemes use an interpolative approach. However, an alternative is to extrapolate from a single point within the subcell of integration. This removes the need to allocate bands, circumventing the band crossing problem completely. This approach has

been used by Müller and Wilkins⁹ who developed a linear extrapolative method. They demonstrated the improvement over conventional schemes by calculating a free-electron DOS using both linear interpolative and linear extrapolative schemes. Using 256 tetrahedra the extrapolative scheme is close to convergence, while the interpolative one is a mess of spurious features.

IV. OBTAINING THE QUADRATIC REPRESENTATION

If we are to employ an extrapolative scheme, we need a technique for evaluating the quadratic representation of a band within a given cell from information available at a single \mathbf{k} point in that cell. $\mathbf{k}\cdot\mathbf{p}$ perturbation theory⁶ provides a technique for doing just this. Knowledge of the wave functions and energy eigenvalues at the \mathbf{k} point concerned allows information about neighboring \mathbf{k} points to be extracted. In principle, a second-order expansion of the energy requires a perturbation sum over matrix elements between all states in the eigenspectrum. This has consequences for a plane-wave approach that depends on iterative diagonalization. The summation is necessarily restricted to those few bands actually evaluated.

Alternatively, numerical differentiation might be used to evaluate the second-order expansion of the band energies. However, the problem of band crossing is reintroduced as the bands must be allocated to enable the differentiation. In tests of this approach it was found that numerical differentiation fails completely near any degeneracies in the band structure and so a general scheme based on this could not be produced.

In this work the quadratic representation of the band structure is obtained using an extension of $\mathbf{k}\cdot\mathbf{p}$ perturbation theory, modified to work to second order and with nonlocal pseudopotentials, as will be described in a future paper.¹⁵

V. AN OUTLINE FOR A NEW INTEGRATION SCHEME

To summarize, the prevalent scheme for spectral Brillouin-zone integrations is currently the interpolative linear tetrahedron method. A low-order interpolation fails to describe van Hove singularities efficiently but is relatively simple. Since high \mathbf{k} -point sampling densities are required for convergence, the band crossing problem is not extreme. Other schemes have been presented in the literature, but none of them have made a significant impact. The second-order $\mathbf{k}\cdot\mathbf{p}$ approach of Wang and Callaway¹⁶ did not correctly implement Lowdin perturbation theory (as clarified by Loehr¹⁷). It was thought of as an interpolative scheme, the DOS was evaluated by resampling and using a linear method, and as a result the scheme required a very large number of sampling points (1357 in the irreducible wedge). Müller and Wilkins⁹ used an extrapolative first-order $\mathbf{k}\cdot\mathbf{p}$ scheme, clearly recognizing the band crossing problem. The restriction of $\mathbf{k}\cdot\mathbf{p}$ theory to local potentials, and the problem of incomplete local basis sets, noted by Boykin,¹⁸ may have reduced its use. The current work removes this restriction.

In light of previous arguments, the essential features of the method are as follows.

Extrapolative. Extrapolating away from a single point alleviates the worst of the band crossing or “kissing” problems.

Piecewise quadratic. To correctly treat the van Hove singularities, at least a second-order expansion is required.

$\mathbf{k}\cdot\mathbf{p}$ perturbation theory. Allows access to band information around a selected \mathbf{k} point, and hence gives the required quadratic expansion of the bands.

Brillouin-zone division. The Brillouin zone is divided into arbitrary polyhedra of approximately equal volumes. The full symmetry of the system can be utilized (Sec. VII).

Analytic quadratic. The work of Methfessel and co-workers^{11,13,14} permits a direct conversion of the piecewise quadratic representation to a contribution to the DOS, avoiding the need for resampling (Sec. VIII).

Many of the individual elements of this proposed method are not new. However, they have never previously been brought together as a single technique. Some components (the treatment of “kissings,” second-order $\mathbf{k}\cdot\mathbf{p}$ perturbation theory with nonlocal pseudopotentials,¹⁵ and the Brillouin-zone division) are novel developments. Technical details of the method are now described.

VI. BAND “KISSING”

As mentioned in Sec. II, one of the remaining problems of Brillouin-zone integrations is what to do when bands cross, or get very close to each other—“kiss.” For interpolative approaches, this manifests itself as a problem of band ordering, and it is not clear whether in general it is a soluble one. While the band ordering problem is eliminated by adopting an extrapolative method, problems arise when sampling points land at or near kissing points (which are the points where bands do not quite cross because there are small interactions between the approaching bands that repel the bands as shown in Fig. 2). At these points the curvature of the bands can be very large, and the radius of convergence of the Taylor expansion is much reduced. Thus the piecewise quadratic method fails at these points because the extrapolation sends states to a wide range of incorrect energies in some cases leading to the closure of band gaps. Clearly, if there is to be any hope of a sparse sampling high-order extrapolative approach to Brillouin-zone integrations, the problems associated with the kissings must be overcome.

There are many complex ways in which one could imagine three-dimensional sheets in four dimensions crossing, or kissing, each other. In our case these sheets are the bands. Given such a situation, it may appear to be an intractable problem to develop any scheme for reducing their effect on the Brillouin-zone integration. However, on looking at some representative band structures some generalizations can be made. As mentioned above, the kissing problem is revealed at points with extreme curvatures—the kissing bands get close to each other but rapidly turn away at the kissing point. The points where this occurs in the band structures can be easily located by looking for those bands at any particular \mathbf{k} point that exhibits extreme curvatures. Those bands that both curve strongly and lie close to each other in energy might be expected to be kissing. Following this detection it becomes clear that a vast majority of the kissings that occur are of the simplest kind—shown in Fig. 2. These involve pairs of bands that kiss as if they cross as simple sheets. This is most clearly illustrated by the fact that the pairs of bands with extreme curvatures and similar energies frequently have parallel di-

TABLE I. Curvature information indicating a simple band “kissing.” i is the band index and E_i the band energy. $B_{1,2,3}$ are the curvatures in the principal-axis directions of the curvature tensor and the vector $\mathbf{k}_{x,y,z}$ is the direction of greatest curvature. It is proposed that bands 18 and 19 participate in a band kissing. The band energies are close, the curvatures are extreme, and the directions of greatest curvature are approximately parallel.

i	\mathbf{k}_x	\mathbf{k}_y	\mathbf{k}_z	B_1	B_2	B_3	E_i
16	-0.22	0.48	0.84	-38.7	-0.1	84.5	59.9
17	-0.76	-0.36	-0.53	-37.3	-9.7	-1.1	66.0
18	0.81	-0.49	0.28	-1495.5	-101.6	41.4	67.4
19	0.85	-0.42	0.29	-69.2	34.5	1507.9	67.5
20	0.43	0.88	-0.17	-37.2	8.7	136.3	69.0

rections of greatest curvature, as would be expected if two three-dimensional planes in four dimensions kiss. The upper one (in energy) curves strongly upwards, the lower downwards. An example is presented numerically in Table I. The scheme now presented is capable of dealing with these simplest kissings. However, in real systems the situation is occasionally more complex. In many cases nearly degenerate triplets of bands with extreme curvatures are found that cannot be treated as a combination of the simple kissings. Dealing with these more complex cases is an area of current research.

The scheme

This method for Brillouin-zone integration is designed for efficient calculation of experimentally observed spectral properties where experimental and lifetime broadenings place a limit on the resolution required. It is clear that many of the band kissings observed will produce spectral features at too fine a resolution to have any experimental consequence. As a result, a scheme is presented that deals with the more common kissings detailed above—the straightforward sheet kissings. The approach taken is to make these true crossings, thus keeping the spectral weight in approximately the correct position, but ignoring the fine structure related to the band repulsion (i.e., a small change in the spectral weight due to the opening of a band gap).

The simple kissings that will be treated are dominated by two interacting bands, the remaining bands playing a much weaker role. Since the second-order Taylor expansion is insufficient in the region of the kissing, higher-order information about the behavior of the bands is required. This is provided by a restricted form of Lowdin perturbation theory—see Kane⁶ for a review. Historically it has been common practice to use Lowdin perturbation theory to describe strongly interacting or degenerate bands in a $\mathbf{k}\cdot\mathbf{p}$ approach.¹⁹ However, it has often been incorrectly applied leading to the problem being described by non-Hermitian submatrices¹⁶ as pointed out by Loehr.¹⁷ It is likely that this error went unnoticed due to the large number of \mathbf{k} points used in earlier $\mathbf{k}\cdot\mathbf{p}$ methods (1357 in $\frac{1}{16}$ of the Brillouin zone in Wang and Callaway’s¹⁶ nickel band-structure calculation). With the low sampling density used in the present scheme, these errors must be avoided.

The fundamental problem in the present approach is that of the band ordering within the subcell in which the kissing

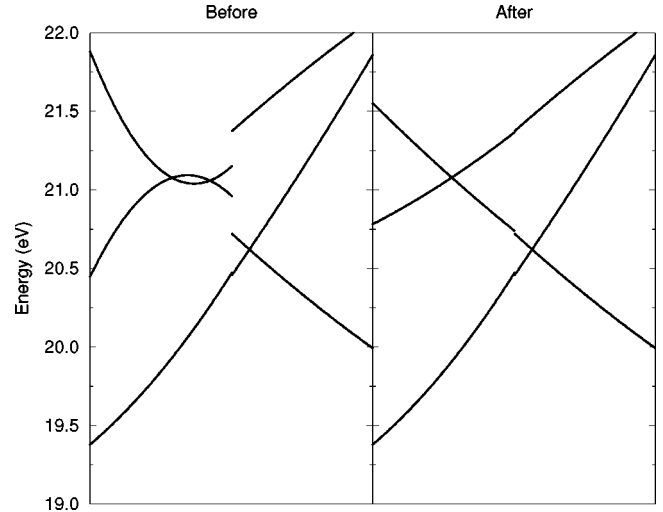


FIG. 3. An example of the scheme at work. The crossing procedure described in the text clearly works well for this particular band “kissing” situation—the bands which were presumably previously kissing are forced in this scheme to truly cross. This example is for the conduction band of silicon, where such situations are common. The curves are produced from the piecewise quadratic representation before and after the treatment for kissing. As can be seen from the discontinuities in the bands, there are two \mathbf{k} points along the slice presented, the \mathbf{k} points are not shown since the slices do not pass through them.

occurs. This can only be done simply if we assume the bands effectively cross only in one dimension. This can be a good approximation if the subcells are small compared to the local curvatures of the bands. In such a case, a three-dimensional crossing can be tracked along the direction of high curvature. If the approximation is good, the directions will be the same for both bands, and this is one of the conditions for detecting the treatable kissings. The band ordering then becomes a one-dimensional problem, and the two bands may be unambiguously crossed as shown in Fig. 3 and Taylor expansions for the two bands are constructed, using the higher-order information from the Lowdin perturbation calculation. A more detailed recipe for carrying out the procedure is as follows.

- (i) Look at the stack of bands for each \mathbf{k} point.
- (ii) Calculate the $\mathbf{k}\cdot\mathbf{p}$ expansion at each point.
- (iii) Diagonalize the curvature tensor, and note the direction of greatest curvature.
- (iv) The treatable kissings will consist of pairs of high curvature bands (see Table I). For both bands the direction of high curvature will be close (modulo a sign), and one will curve positively and the other negatively due to the sign change in the energy denominator of the perturbation sum.
- (v) Having found a candidate kissing, the bands are crossed by finding band energies either side of the suspect kissings using Lowdin perturbation theory (as corrected by Loehr¹⁷) on the two bands concerned.
- (vi) The new curvature in the high curvature direction is found by evaluating the band energies using Lowdin perturbation theory assuming the new crossed allocation, and this replaces the old curvature. The same is done with the gradient in that direction.

(vii) The gradients and curvatures are rotated back to the original coordinate frame.

(viii) Having looked through all bands and \mathbf{k} points the procedure can be repeated, since there may be several kissings mixed together.

Clearly, criteria are required as to what constitutes a strong curvature, and how close the high curvature directions must be. Setting these thresholds will determine the tolerance to kissings, and thus appropriate values for these thresholds will depend on the resolution required in the final spectrum. At present, the treatment of this threshold remains rather crude, and is based on a weighted sum of numbers representing the closeness of the directions and strength of the curvatures.²⁰

VII. BRILLOUIN-ZONE DIVISION

So far the expansion of the band structure of a given system about any point in the Brillouin zone has been discussed. This expansion is to second order only, and in anything other than the case of a free electron, it will be valid only about a finite region surrounding the expansion point. Therefore it is necessary to divide the Brillouin zone into a set of subcells within which the expansion holds to the accuracy required. Thus, from the information in every subcell a piecewise quadratic representation of the band structure is constructed. The total DOS for a given band can therefore be written,

$$D_{tot}(E) = \sum_i D_i(E), \quad (2)$$

where $D_i(E)$ is the DOS contribution of the i th subcell.

It should be noted that, in contrast to interpolative methods, this piecewise quadratic band structure is not continuous across the subcell boundaries. This is a necessary feature of the extrapolative approach. Any attempt to join the bands at the cell edges amounts to an interpolation, and the band ordering problem is reintroduced. In the example of Fig. 6 the oscillatory errors caused by these discontinuities are visible. Clearly, as the size of the subcells are decreased so do the magnitude of these errors.

To produce an efficient integration scheme we have to divide the Brillouin zone in the most efficient way, with an emphasis on good coverage of the Brillouin zone even at very low \mathbf{k} -point sampling.

A. Commensurate subcells

One approach is to divide the Brillouin zone into commensurate subcells. This can be done by forming a grid of points in terms of multiples of integer fractions of reciprocal-lattice vectors, keeping only those falling within the first Brillouin zone and constructing Wigner-Seitz proximity subcells about each point that is retained. For example, if $\mathbf{G}_{1,2,3}$ are reciprocal-lattice vectors, then a point in the new grid is given by

$$\mathbf{k}_{\alpha\beta\gamma} = \alpha \frac{\mathbf{G}_1}{l} + \beta \frac{\mathbf{G}_2}{m} + \gamma \frac{\mathbf{G}_3}{n}, \quad (3)$$

where α , β , and γ are integers labeling the grid, and l , m , and n are fixed integers chosen to give an even distribution of \mathbf{k} points in reciprocal space (i.e., approximately spherical Wigner-Seitz proximity subcells). If l , m , or n are even, then the grid can be shifted to balance the points about the origin in the associated direction.

If the system concerned has any symmetry in addition to the inversion symmetry that will always be present, then the subcells may be symmetrized. However, it is clear that for low \mathbf{k} -point density the symmetry will not be well used. Also, the grids produced by this method tend to have points along high-symmetry directions, making band kissings more common. Naively shifting the grid produces problems with symmetrization. However, to overcome this problem one may keep the cells fixed and shift the \mathbf{k} point of expansion within the subcell.

B. Full use of symmetry

Although many modern electronic structure calculations concentrate on systems with ever larger unit cells and ever reduced symmetry, it is clear that there are still many problems that could benefit from the use of symmetry, for example, highly computationally intensive techniques such as the *GW* method for calculation of quasiparticle spectra.⁵ To this end, a technique for efficiently exploiting symmetry even at low \mathbf{k} -point densities is now presented.

(1) Find the first Brillouin zone for the system of interest using the Wigner-Seitz proximity cell definition for symmetry reasons.

(2) Find the irreducible wedge, assuming the full symmetry of the lattice type. This is constructed from the Brillouin zone by the introduction of a set of planes that are dependent on the lattice type.

(3) Decide how many times to recursively halve the volume of the subcells—starting with the irreducible wedge. For example, n times will produce 2^n subcells and \mathbf{k} points. There is considerable freedom as to how to halve each subcell. It is important to try to make each subcell as close to spherical as possible so as to avoid “long” directions in which the second-order Taylor expansion will be less well converged. So, the subcells are divided perpendicular to the “long” direction, which is defined by consideration of the moment of inertia tensor of the cells if they are treated as uniform solids. The division is applied at a point where there is equal volume on either side of the cut.

(4) Having constructed the subcells, the \mathbf{k} points are placed at the center of mass of each cell (again treated as a uniform solid).

(5) So far, full lattice symmetry has been assumed. In the case of a reduction in lattice symmetry that can occur as atoms are placed on the lattice, it is necessary to determine which symmetry operations generating the star remain after symmetrization. The irreducible wedge (already divided in subcells) is then repeated for each symmetry operation, which results in distinct points in the Brillouin zone given the symmetry of the system of interest.

Examples of the application of the procedure outlined above are shown in Fig. 4. It is clear that this approach makes full use of the system’s symmetry. In the limit of a single \mathbf{k} point for a system with full symmetry, the one cell

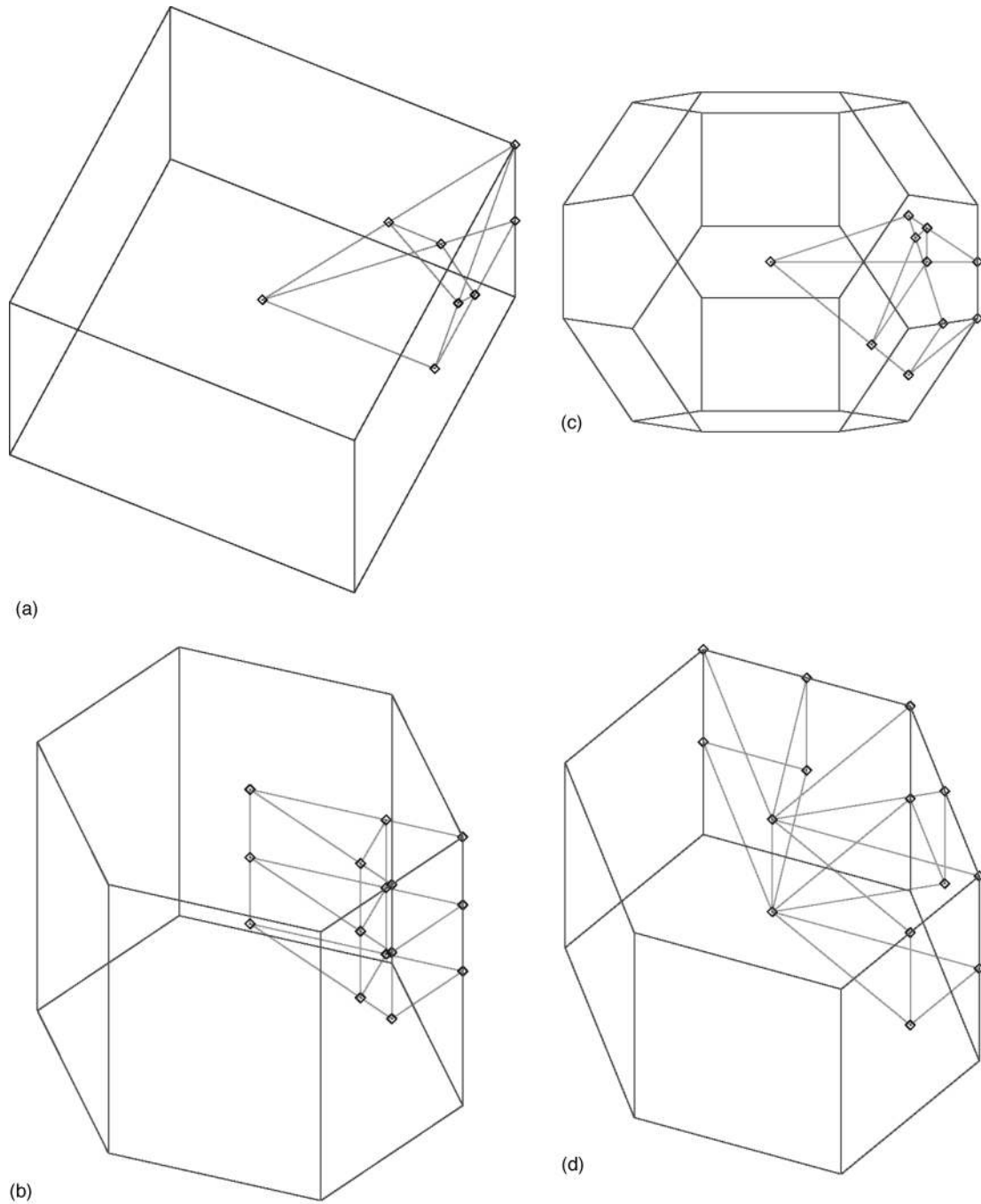


FIG. 4. (a) A simple cubic Brillouin zone, with the full symmetry irreducible wedge divided into two subcells. (b) Hexagonal Brillouin zone, with full hexagonal symmetry and the irreducible wedge halved twice. (c) fcc lattice Brillouin zone with full cubic symmetry. (d) A hexagonal Brillouin zone with reduced symmetry, with the irreducible wedge undivided.

generated is the irreducible wedge. It should be noted that for any integration routine based on interpolation it is impossible to contemplate the use of a single \mathbf{k} point. Also, in general, the \mathbf{k} points generated by this technique do not fall in directions of high symmetry, thus reducing the problems associated with band kissing and crossings. However, it should also be pointed out that this method is not particularly useful if high \mathbf{k} -point sampling densities are required as the polyhedra produced can get quite complex. Also, there is little gain due to symmetry at high density in comparison to the commensurate subcells described in Sec. VII A. The approach based on the division of the irreducible wedge is de-

signed for situations of high symmetry and for Brillouin-zone integrations requiring low \mathbf{k} -point sampling density.

VIII. ANALYTIC QUADRATIC DENSITY OF STATES

The final problem to be solved is to perform Brillouin-zone integrations for the DOS and other spectral properties from the piecewise quadratic representation of the band structure. Clearly, one could resample the representation to find the band energies on a finer grid and simply apply one of the standard methods for Brillouin-zone integration described in Sec. III. This is not appealing, since the correct

analytic form for the bands around the critical points is lost. Furthermore, it is a computationally costly route. The ideal approach would be to take the quadratic representation and turn it directly into a contribution to the total DOS. Since the DOS of a free electron (with its quadratic dispersion) has a well-known, and simple, analytic form this should be possible. The significant complication is that the contribution to the DOS comes from a finite region in reciprocal space (i.e., the subcells described in Sec. VII). An expression for the density of states for a given band is

$$D(E) = \int \delta(E(\mathbf{k}) - E) d^3\mathbf{k} = \int_S \frac{dS}{|\nabla_{\mathbf{k}} E(\mathbf{k})|}, \quad (4)$$

where S is a constant energy surface (CES) at energy E . For a spherical dispersion relationship $E(\mathbf{k}) = Bk^2$, $|\nabla E(\mathbf{k})| = 2Bk$, and, hence,

$$D(E) = \int_S \frac{dS}{|\nabla_{\mathbf{k}} E(\mathbf{k})|} = \frac{4\pi k^2}{2Bk} = \frac{2\pi\sqrt{E}}{\sqrt{B^3}}, \quad (5)$$

where spherical symmetry has been used to simplify the surface integral.

The problem must now be extended to the situation in which the surface integration is restricted to a finite volume in reciprocal space (bounded by a convex polyhedron). For simplicity consider a cube, with the origin at its center. Clearly, for small E the expression for the DOS will be unchanged. However, at some energy the CES must start to cut the polyhedron. At this energy and above, the DOS will be reduced (since the included surface is reduced). This energy is known as a *singularity*. Singularities occur when the CES strikes the faces, edges, and vertexes of the polyhedron. At some point the entire CES will be outside the polyhedron and the DOS will become zero. It may appear to be a difficult problem to track this change in the DOS, and indeed this problem has been called *impossible* by Lehmann and Taut.¹² But the work of Methfessel and co-workers^{11,13,14} presents a theoretical solution to this problem for tetrahedral volumes and a practical scheme for its implementation. For the purposes of the current approach the implementation of Methfessel and co-workers must be extended beyond tetrahedra to arbitrary polyhedra. This is described elsewhere.²¹

IX. EXAMPLES

Having described a new scheme for spectral Brillouin-zone integrations, we now give some examples that demonstrate the quality of Brillouin-zone integrations that are possible with this scheme. It should be noted that the technique is not designed for the ultimate in accuracy, but rather as a method for rapidly obtaining the general features of a spectrum. In the following examples, the DOS is presented in units of number of electrons per unit cell per unit of energy (electron volts in Figs. 5 and 8 and unity in Figs. 6 and 7).

A. Toy models

1. Free-electron dispersion

The Brillouin-zone integration method is applied after performing an electronic structure calculation with the ionic

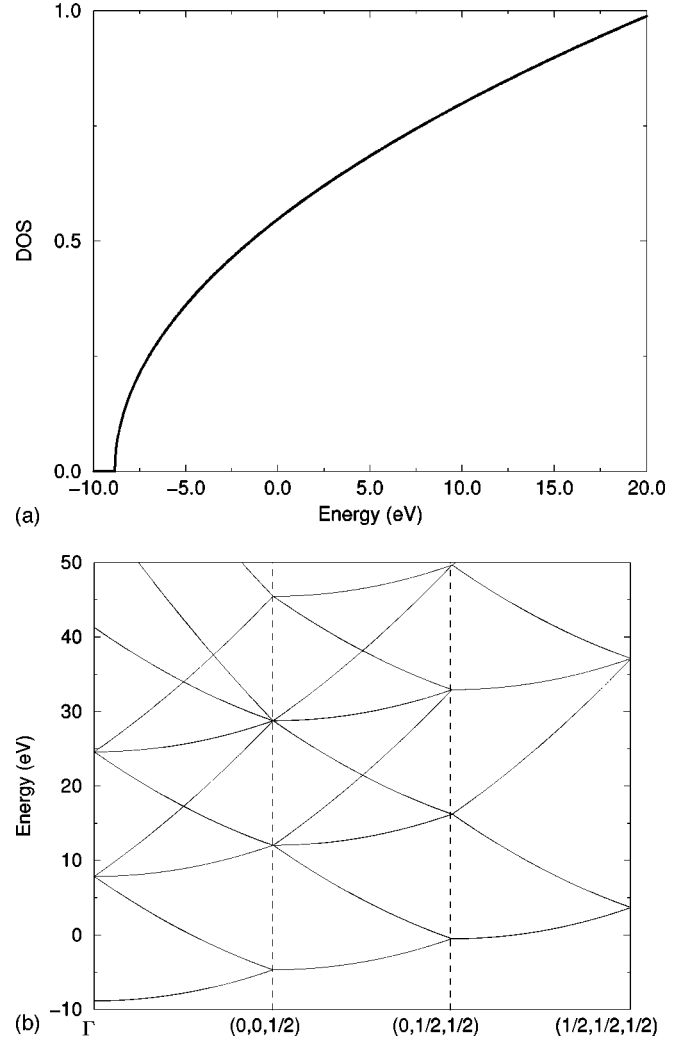


FIG. 5. Density of states for a free electron, calculated in a simple cubic cell using a single \mathbf{k} point, displaying the expected $(E - E_0)^{1/2}$ behavior and the corresponding free-electron band structure. The coordinates indicate points in the Brillouin zone in units of reciprocal-lattice vectors.

potentials set to zero. A simple cubic cell is used, and the single integration subcell is the irreducible wedge. As expected (since the free-electron dispersion is quadratic), the DOS is fully converged using a single \mathbf{k} point as can be seen in Fig. 5. A selection of bands are also shown that are also extrapolated from a single sample point. This is not an entirely trivial result, since in the case of an interpolative approach there would be problems with band crossings. This result should be compared to the linear extrapolative free-electron test of Müller and Wilkins,⁹ which required 256 tetrahedra for a similar level of convergence.

2. Simple cubic s -band test

The convergence of the new scheme is now examined for a simple cubic s band, the example discussed previously by Boon *et al.*¹¹ The dispersion relation for this system is

$$E(\mathbf{k}) = -\frac{1}{3}[\cos \pi k_x + \cos \pi k_y + \cos \pi k_z]. \quad (6)$$

The gradient and curvature information for the piecewise quadratic representation required for the new scheme is ob-

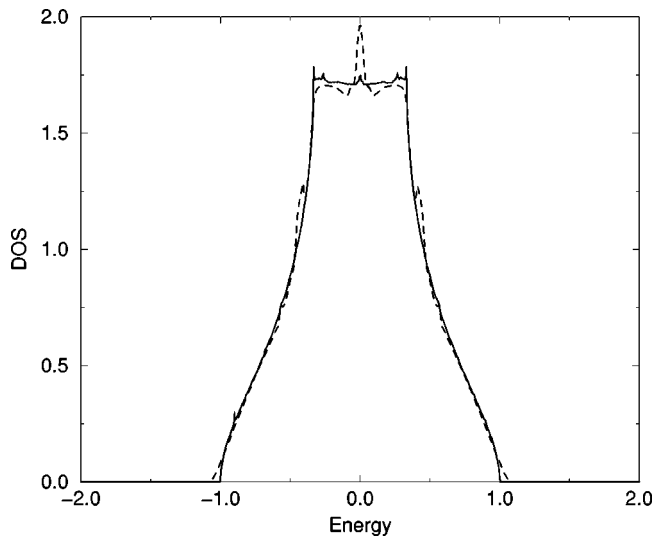


FIG. 6. s -band DOS with no smearing. The dashed curve is obtained using 8 k points in $\frac{1}{48}$ of the Brillouin zone, while the solid one is obtained with 128 k points. Note the poor convergence on the plateau.

tained directly from the dispersion relation. Boon *et al.*¹¹ looked at the extreme convergence properties and found the analytic quadratic method to work well, as it deals with the van Hove singularities. Here the emphasis is on the low sampling densities.

It is clear that, in comparison with the free-electron case, the convergence is slow, as shown in Figs. 6 and 7. This is to be expected—the dispersion relation contains terms to all orders. Particular problems are encountered on the plateau of the DOS—the spikes being due to overlap in energy of the piecewise quadratic bands due to an inadequacy of the second-order expansion. However, in keeping with the philosophy of the approach, the application of a Gaussian

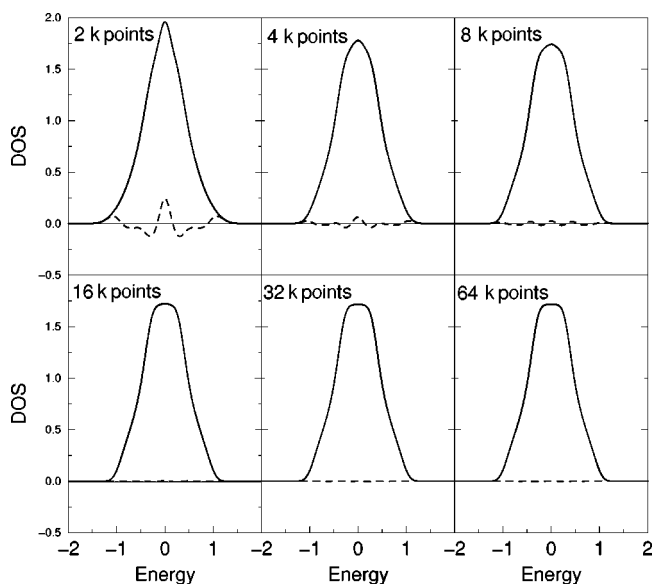


FIG. 7. Convergence of s -band DOS with smearing. A Gaussian smear of 0.1 is applied, producing the solid curves. The dashed curves are the differences of the unsmoothed DOS from one converged at 128 k points.

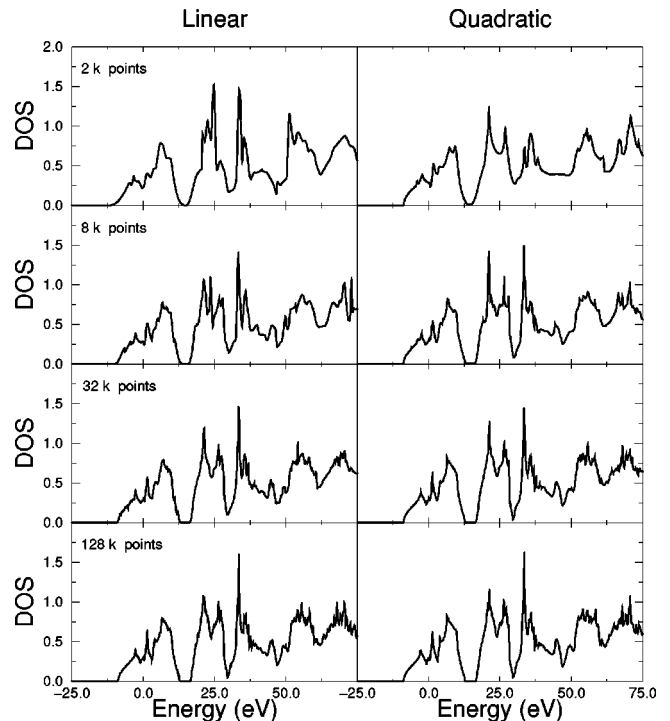


FIG. 8. Convergence of the DOS of diamond for linear and quadratic extrapolative approaches: two-atom diamond primitive cell, 40 bands, and an energy cutoff of 600 eV. No smearing is applied. The k points are contained within $\frac{1}{48}$ of the Brillouin zone.

smearing to the DOS results in good convergence at low k -point sampling densities.

B. Total density of states of diamond

Figure 8 shows a series of total DOS calculated for a two-atom primitive cell of diamond using an increasing number of k points in the irreducible wedge of the Brillouin zone. The calculations were performed using the local-density approximation, a plane-wave basis set, and optimized nonlocal pseudopotentials.⁷ The most important conclusion is that the essential features of the spectra are obtained for very low k -point densities and, somewhat surprisingly, for as few as two points in the irreducible wedge. Given the low resolution of many experimental spectra, it is clearly not necessary to push the calculations to very high sampling densities. It should be pointed out that any interpolative method would require more than a single sample point just to perform the interpolation, regardless of the quality of the integration.

X. LINEAR EXTRAPOLATIVE METHOD

It is straightforward to restrict the approach described above to the first order only, producing a linear extrapolative approach. The polyhedral subcells (see Sec. VII) can be divided into tetrahedra (each face can be divided into triangles and the fourth apex placed within the cell). Then the formula for the conversion of the first-order expansion of the bands into a DOS contribution given by Blöchl, Jepsen, and Andersen⁸ can be applied. A comparison of the results of this linear approach to the full quadratic scheme is shown in Fig. 8. It is clear that the linear extrapolative approach still allows

low \mathbf{k} -point sampling, but it can be seen that the behavior at the band thresholds is poor. However, an advantage of the linear approach is that it requires no perturbation summation, and hence the band truncation error mentioned above is avoided.

XI. SUMMARY

In summary, a second-order extrapolative approach to the integration of spectral properties has been developed. It exploits the smoothness of band structures seen through $\mathbf{k}\cdot\mathbf{p}$ perturbation theory and uses exactly this theory to generate a piecewise quadratic representation of the energy bands,

which is then converted analytically to a density of states. The Brillouin zone is efficiently divided into subcells to make full use of the symmetry of the system of interest. Tests of the scheme show that the essential features of spectra are obtained for very few \mathbf{k} points within this approach, and even a restriction to linear extrapolation gives rise to a useful scheme despite the poor treatment of the van Hove singularities.

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²⁰If $|\hat{\mathbf{k}}_a - \hat{\mathbf{k}}_b|^2 < 0.0075$ (where $\hat{\mathbf{k}}_{a,b}$ are the normalized vectors in the direction of maximum curvature for bands a and b , assumed parallel rather than antiparallel) and $\ln\{1/(1 - \gamma)[(\hat{\mathbf{k}} \cdot \mathbf{M}_{ab})^2/\Delta E_{ab}]^2\} > 1$ (where γ is the ratio between the maximum curvatures of the two bands—taken to be greater than unity, $\hat{\mathbf{k}}$ is the normalized direction of maximum curvature—now assumed to be the same for both bands, ΔE_{ab} is the energy difference between the two bands in electron volts, and \mathbf{M}_{ab} is $\langle \phi_a | \nabla | \phi_b \rangle$ in units of inverse angstroms) the bands a and b are taken to be kissing.
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