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# How to analyse a density of states

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# ABSTRACT

The density of states of electrons is a simple, yet highly-informative, summary of the electronic structure of a material. Here, some remarkable features of the electronic structure that are perceptible from the density of states are concisely reviewed, notably the analytical E vs. k dispersion relation near the band edges, effective mass, Van Hove singularities, and the effective dimensionality of the electrons, all of which have a strong influence on physical properties of materials. We emphasize that appropriate parameters in electronic structure calculations are necessary to obtain even a sufficient-quality density of states exhibiting fine features of the electronic structure.

#### 1. Introduction

The density of states (DOS) is perhaps the most important concept for understanding physical properties of materials, because it provides a simple way to characterize complex electronic structures. Key aspects that underlie electrical and optical properties of materials are visually apparent from the DOS, including the band gap and effective masses of carriers. For this reason, the concept of DOS is typically mentioned in undergraduate Materials Science and Engineering [1], Inorganic Chemistry [2], and Physics [3,4] courses. The ability to compute a high-quality DOS that reflects the true electronic structure of a material greatly improves the ability to interpret and tune various material properties. DOS calculations are nowadays regularly performed thanks to the availability and ease of Density Functional Theory (DFT) calculations; yet, it is not uncommon for the DOS to inaccurately portray key characteristics of the electronic structure.

In this mini-tutorial, we briefly review some salient features of the electronic structure that are perceptible in a high-quality density of states. These topics are sometimes understated in instructional manuals for DFT calculations and even Chemistry or Materials Science courses, but they are nevertheless a direct consequence of elementary band theory in solids. We review key characteristics of the dispersion relation, Van Hove singularities, and indicators of low-dimensional electronic structures that are immediately discernible from a high-quality DOS. We discuss how appropriate computational settings and parameters are necessary to realize fine features of the electronic structure; for example, using the tetrahedron method [5] drastically improves the quality of the DOS compared to smearing methods. We note that although this method is widely recommended for accurate DOS calculations, it is not always used in practice perhaps because characteristics of a high-quality DOS are not illustrated frequently. The examples used in this manuscript can be found in the Materials Project database (https://materialsproject.org/) [6] under the following IDs: SrTiO<sub>3</sub> (mp-5229), PbS (mp-21276), CoSb<sub>3</sub> (mp-1317), and TiNiSn (mp-924130).

# 2. Band edge

The structure of the density of states at the band edge gives foremost insight into the electronic and optical properties of materials. It is therefore instructive to recognize the expected shape of the band edge before elaborating on unconventional band shapes encountered occasionally in materials.

An electron in a semiconductor can often be described by a kinetic energy  $E = \frac{p^2}{2m^*}$ , analogous to the classical picture where *p* is the momentum and  $m^*$  is the effective mass of the electron. In quantum mechanics, the momentum of an electron is given by  $p = \hbar k$ , where  $\hbar$  is

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**Fig. 1.** (a) The energy band dispersion and the density of states for parabolic (green) and Kane (purple) bands. The parabolic conduction and valence bands correspond to the  $g(E) \sim \sqrt{E}$  energy dependence of the density of states, whereas the linear character of the Kane bands far from the band edges correspond to a  $g(E) \sim E^2$  energy dependence. (b) The dispersion relation and density of states of a material with two separate parabolic bands. Each band contributes available electronic states  $g_1(E) \sim \sqrt{E}$  and  $g_2(E) \sim \sqrt{E}$  to the total density of states. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

the reduced Plancks constant and *k* is the wave vector. The resulting *E* vs. *k* is known as the dispersion relation, where  $E(k) = \frac{\hbar^2 k^2}{2m^*}$  for an electron in a parabolic band. In a semiconductor, electrons typically behave this way with an effective mass  $m^*$ , which is usually within an order of magnitude of the free electron mass.

The very observation that the energy depends on  $k^2$  implies the  $\sqrt{E}$  shape of the density of states. The analytical expression for the DOS of an electron, traveling in three dimensions in a parabolic energy band, is:

$$g(E) = \frac{(2m_{\text{DOS}}^*)^{3/2}}{2\pi^2\hbar^3}\sqrt{|E - E_b|}$$
(1)

where  $m_{\text{DOS}}^*$  is known as the DOS effective mass (i.e., the effective mass calculated from the DOS),  $E_b$  is the energy of the band edge, and g(E) is in units of states/(eV Å<sup>3</sup>). The magnitude of the DOS near the band edge is often used to estimate  $m_{\text{DOS}}^*$ , although it may be simpler to calculate the related Seebeck mass from the Seebeck coefficient [7,8].

The  $\sqrt{E}$  shape of the DOS in a conventional band leads to a sharp drop of the DOS at the band edge as shown by the green curves in Fig. 1a. This sharp demarcation of the band edge is important for confirming the magnitude of the band gap and location of the Fermi energy. The DOS of SrTiO<sub>3</sub> (Fig. 2a), PbS (inset of Fig. 2b), and CoSb<sub>3</sub> (inset of Fig. 2c)



Fig. 2. The electronic structures of cubic perovskite SrTiO<sub>3</sub>, rock-salt PbS, and skutterudite  $CoSb_3$ . (a) The Ti- $t_{2g}$  bands and their corresponding partial contributions to the density of states of SrTiO<sub>3</sub> are shown in red, blue, and yellow. The constant-energy Fermi surface of the blue  $\mathrm{Ti-t}_{\mathrm{2g}}$  band (where the blue dashed line denotes the constant energy slice) appears as three intersecting cylinders rather than a sphere. The cylindrical geometry is characteristic of a 2D electronic structure (D = 2), and the density of states of the parabolic band (n = 2) is therefore nearly energy independent  $g(E) \sim E^0$ . (b) Van Hove singularities appear as sharp peaks or abrupt changes of slope in the density of states. They arise in regions where the slope of E vs. k is zero, indicated by the red dashed lines. The inset shows the  $g(E) \sim \sqrt{E}$  trend expected at the band edges; however, the trend quickly changes curvature to  $g(E) \sim E^2$ , as described by linear or Kane bands. (c) Multiple bands in CoSb<sub>3</sub> contribute additively towards the number of states, indicated by the abrupt change in the energy dependence of the density of states. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



**Fig. 3.** Comparison of the density of states of TiNiSn calculated via the tetrahedron method using a  $21 \times 21 \times 21$  *k*-point mesh (red) and the Gaussian smearing method with  $3 \times 3 \times 3$  (orange) and  $21 \times 21 \times 21$  (blue) *k*-point meshes. The smearing width is set to 0.05 eV for calculations using Gaussian smearing methods. The inset magnifies the differences between the smearing methods at the band edge, a feature of the electronic structure necessary to interpret electrical transport measurements. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

show the Fermi energy at the sharp band edge. A poorly represented DOS with smeared band edges, which gives rise to a nonzero DOS at the Fermi energy, can incorrectly make an insulator or semiconductor look like a metal (see inset of Fig. 3).

# 3. Unconventional electronic structure

The density of states will sometimes deviate from the expected  $\sqrt{E}$  energy dependence away from the band edge. Features such as the effective dimension and non-parabolic bands are then expected to be discernible from the energy dependence of the DOS. The number of occupied electronic states *N* depends on the dimension *D* as  $N \sim k^D$ ; thus, electrons that are effectively constrained to *D* dimensions with an *E* vs. *k* dispersion relation  $E \sim k^n$  results in the DOS ( $g(E) = \frac{dN}{dE} = \frac{dN}{dk} \frac{dk}{dE}$ ) given by

$$g(E) \sim E^{\left(\frac{D}{n}-1\right)} \tag{2}$$

Consequently, the form of the energy band dispersion and dimensionality can be understood from the shape of the DOS and vice versa.

A form of a non-parabolic energy band found occasionally in 3D materials is a Kane band, which is parabolic (n = 2) at the band edge but linear (n = 1) away from the band edge [9,10]. As indicated by purple curves in Fig. 1a, as the band becomes more linear ( $E \sim k, n = 1$ ) away from the band edge, the DOS (in 3D) correspondingly follows a  $g(E) \sim E^2$  energy dependence. The electronic structure of the small band gap semiconductor PbS has Kane bands as shown in Fig. 2b, giving the DOS a  $\sqrt{E}$  energy dependence at the band edge with a change in curvature to an  $E^2$  energy dependence away from the band edge resulting in an inflection point that does not occur in a parabolic band. Kane bands tend to appropriately describe small band gap materials with low effective mass such as InSb [11] and PbSe [12].

Some materials may also exhibit multiple bands, indicated by an abrupt change in the energy dependence of the DOS. If the bands appear as separate ellipsoidal constant-energy Fermi surfaces in the Brillouin zone, then each band contributes additively to the total DOS, manifesting as a faster increase in the DOS when the second band appears along the energy axis (Fig. 1b). Such a multiband effect is exemplified by CoSb<sub>3</sub>, as shown in Fig. 2c.

Complex electronic structures are often parameterized by an effective mass  $m^*$ , where  $m^*$  changes with energy as measured by a Fermi level (or doping) dependence [8]. Changes in  $m^*$  are expected when the *E* vs. *k* dispersion relation deviates from a parabolic form [13,14] or if multiple bands are present [15]. Therefore, a change in  $m^*$  is the most direct indicator of a complex electronic structure [7,16]. Effective mass  $m^*$  is only expected to be a constant for a given doping, temperature, and measurement type (or definition) for 3D parabolic bands with specific electron scattering assumptions [8]. For example, the common definition of  $m^*$  based on band curvature ( $m^* = \hbar^2 \left(\frac{d^2E}{dk^2}\right)^{-1}$ ) will give very different values from Eq. (1) for non-parabolic [17] or warped (not isotropic) bands [18].

#### 4. Dimensionality and the Fermi surface

Occasionally, electrons in a material are constrained to fewer dimensions than the dimensionality of the crystal structure. In graphene for example, electrons are constrained to travel in two dimensions (D = 2) along bands that are linear (n = 1) [19]. By Eq. (2), this dimensional constraint is reflected in the DOS by scaling linearly with E, as opposed to the conventional  $\sqrt{E}$  energy dependence in bulk 3D materials.

Even in 3D materials, electrons can be effectively constrained to lower dimensions by the electronic structure, giving them different properties [20,21]. This is seen by the geometry of the constant-energy Fermi surface, which represents all wave vectors k of a band that have a particular electron energy. In SrTiO<sub>3</sub> for instance, the Fermi surface of one of the Ti-t<sub>2g</sub> bands looks like three interpenetrating cylinders (Fig. 2a), as opposed to a sphere for a typical 3D material [20,22]. The cylindrical constant-energy Fermi surface resembles that of a 2D system (D = 2), because the Fermi surface depends on only two of the three wave vector directions. Since the band has parabolic dispersion (n = 2), the DOS is nearly a constant with energy ( $g(E) ~ E^0$ ) as predicted by Eq. (2). Thus, an unconventional DOS alone may indicate dimensional constraints to the electronic structure.

### 5. Van hove singularities

Sharp, abrupt peaks are quite common in the density of states of many materials. Such peaks are usually due to a type of Van Hove singularity [23], which result from a vanishing slope in the E vs. k dispersion relation. Several appear in the DOS of PbS, indicated by red dashed lines in Fig. 2b. For example, a sharp, asymmetric peak at ~0.9 eV below the valence band edge corresponds to a flattening of the E vs. k dispersion at the W point.

Van Hove singularities are typically responsible for distinct features in the optical absorption spectra [24]. However, electronic structure calculations can show artificial peaks in a density of states plot that do not arise from a Van Hove singularity, as seen in Fig. 3. Often the peaks are artefacts due to the method of calculation intended for a purpose other than the analysis described above. Thus, in order to observe the effects of dimensionality, dispersion, and other important features in the DOS, the method of calculating the DOS needs to be considered.

#### 6. Calculating the density of states

Advancements in first-principles techniques for studying the electronic structures of materials [25] have made calculations of the density of states routine [6,26]; yet, some that are published do not exhibit the features described in this review. To calculate a sufficient-quality DOS, appropriate input parameters must be explicitly specified. For instance, the linear-tetrahedron method for Brillouin zone integration with Blöchl corrections [5] renders many salient features of the DOS with exceptional quality compared to smearing methods. To illustrate, in the half-Heusler compound TiNiSn, the expected  $\sqrt{E}$  energy dependence and the sharp drop at the valence band edge is clear from the tetrahedron method (see inset in Fig. 3), whereas the Gaussian smearing method smoothens the valence band edge even for dense *k*-point meshes. Using a coarse *k*-point mesh may show spurious DOS peaks that can be confused for Van Hove singularities. The true Van Hove peak at 0.7 eV below the valence band edge appears stark against the surrounding smooth portions of the DOS calculated using the tetrahedron method, whereas it looks similar to the spurious DOS peaks when using smearing methods.

It is tempting to assume that these essential features of a DOS will simply emerge from electronic structure calculations by considering more k-points. However, stark features such as Van Hove singularities and the band edge shape remain obscure even at higher k-point densities using smearing methods [27] while they appear clearly with the tetrahedron method, making the latter preferred. Although many in the community already follow these recommendations, they are important to re-emphasize as the user community of electronic structure methods grows.

#### 7. Conclusion

The density of states reveals striking features of an electronic structure that are often overlooked. This mini-tutorial should serve as a guide for interpreting the DOS of a real material. Not only can important material parameters like band gap and DOS effective mass (which may be derived from Seebeck coefficient measurements) be seen from a DOS, but new, unusual phenomena such as reduced dimensionality and unconventional band shapes can be identified from the shape of a DOS. Such phenomena can also exist deeper in the band, revealing potentially novel behavior of complex materials.

Smearing methods in electronic structure calculations can obscure these essential features and instead introduce artefacts that can be misidentified. These shortcomings can be remedied simply by using the tetrahedron method when computing the DOS and looking for these essential features of a DOS when assessing convergence of the calculation.

### **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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