Improvements to Generalized Monkhorst-Pack Grids

Wiley S. Morgan, Jeremy J. Jorgensen, Brett C. Hess, Branton J. Campbell, Gus L. W. Hart
Department of Physics and Astronomy, Brigham Young University, Provo, Utah, 84602, USA
(Dated: July 28, 2017)

I. INTRODUCTION

High throughput materials design has become a effective route to material discovery with many successes already documented[1–6]. The creation of large material databases is central to the success of high throughput approaches. Computationally expensive electronic structure codes generate the data repositories that are analyzed in computational materials design and limit the extent to which data analysis tools, such as machine learning, can be applied. Any improvements in the efficiency of these codes have the potential to significantly increase the size of theoretical material repositories thus increasing the accuracy of material predictions.

All electronic structure codes perform numerical integrals over the Brillouin zone, which in the case of metals are exceedingly slowly convergent. Dense sampling of the Brillouin zone, required for high accuracy, is computationally expensive, especially when implementing hybrid functionals or pertubative expansions in density functional theory (DFT)[7]. The selection of **k**-points covering the Brilloun zone in programs running DFT haven't changed much since Monkhorst and Pack published their influential paper over 40 years ago[8]. Their method was quickly accepted by the community due it its simplicity and ability to generalize previous methods[9,10]. Methods that made improvements to Monkhorst-Pack grids are far less prevalent[11–13]. Resolving the issues pertaining to these improvements is the topic of this paper.

II. BACKGROUND

Over the past 40 years a variety of **k**-point selection methods have been investigated in the literature[8–13]. Many of these so-called special point methods focused on selecting points that accurately determined the mean value of a function defined over the Brillouin zone, since the integral of a periodic function over one period is simply its mean value. Other factors that were considered in developing special point methods were selecting the most uniform grids possible, and exploiting symmetry to the fullest extent possible.

Baldereschi introduced the mean-value point of the Brillouin zone[9], one of the first special point methods. He began by performing a Fourier expansion of the periodic, Brillouin zone function

$$f(\mathbf{k}) = \sum_n c_n e^{i\mathbf{k}\cdot\mathbf{R}_n} \tag{1}$$

whose integral over one period, the first Brillion zone (BZ), was given by the common result

$$\int_{\mathrm{BZ}} f(\mathbf{k}) = \frac{(2\pi)^3}{\Omega} c_0 \tag{2}$$

where Ω was the volume of the Brillouin zone and c_0 was the leading coefficient in the Fourier series. He explained that by choosing points that made as many as possible of the leading terms evauate to zero, he would obtain an accurate approximation of the leading Fourier coefficient and the integral he was after.

Chadi and Cohen extended the mean-value point by introducing sets of points whose weighted sum eliminated the contribution of a greater number of leading basis functions than that of the mean-value point[10]. Their grid of **k**-points could also be made as dense as required for a desired. Chadi and Cohen grids were equivalent to uniform grids within the Brillouin zone.

The most popular **k**-point selection method was created by Monkhorst and Pack[8]. They established a grid of points that generalized the mean-value point of Baldereschi and its extension by Chadi and Cohen, and were equivalent to points used by Janak et al.[14].

Froyen generalized Monkhorst-Pack points, which he called Fourier quadrature points, by eliminating the restriction that the vectors that defined the grid be parallel to the reciprocal lattice vectors[11]. However, he did require the grid to be commensurate with the reciprocal lattice and the have full point-group symmetry of the crystal.

Moreno and Soler introduced the idea of searching for the **k**-point grids with the fewest points for a given length cutoff—a parameter that characterized the quality of the grid and was closely related to the **k**-point density)[12]. These two conditions meant the grid was as uniform as possible and that the grid subcells were as spherical as possible. They argued that since there was no knowledge of how the function behaved beforehand, and hence no reason to sample one region over another, uniform grids were. Moreno and Soler further improved Brillouin zone sampling by finding the optimal offset of the origin that maximized the symmetry reduction of the **k**-points.

In a recent paper by Wisesa et al., they acknowledge that the lack of popularity with Moreno and Soler's approach is due to the expensiveness in calculating many Froyen grids—which they called generalized Monkhorst-Pack grids—and searching through them for the one with the highest symmetry reduction[13]. Their remedy involved precalculating the grids and searching through them for the ones with the highest symmetry reduction. These grids were stored in a database that had to be queried with every DFT calculation. They were able to

obtain the grid with the highest symmetry reduction in a fraction of a second[?] .

In a recent paper by Wisesa et al., a search through a **k**-point grid database was used to significantly accelerate DFT calculations[13]. The database contained grids that were commensurate with all possible types of lattices and were guaranteed to have the largest possible symmetry reduction. Their method of generating the grids was similar to that of Froyen as well as Moreno and Soler.

[1] Jeff Greeley, Thomas F Jaramillo, Jacob Bonde, IB Chorkendorff, and Jens K Nørskov. Computational high-throughput screening of electrocatalytic materials for hydrogen evolution. *Nature materials*, 5(11):909, 2006.

[2] Joseph J Hanak. A quantum leap in the development of new materials and devices. *Applied surface science*, 223(1):1–8, 2004.

[3] Martin L Green, Ichiro Takeuchi, and Jason R Hattrick-Simpers. Applications of high throughput (combinatorial) methodologies to electronic, magnetic, optical, and energy-related materials. *Journal of Applied Physics*, 113(23):9_1, 2013.

[4] XD Xiang, Xiaodong Sun, Gabriel Briceno, Yulin Lou, et al. A combinatorial approach to materials discovery. *Science*, 268(5218):1738, 1995.

[5] Bernd Jandeleit, Dieter J Schaefer, Timothy S Powers, Howard W Turner, and W Henry Weinberg. Combinatorial materials science and catalysis. *Angewandte Chemie International Edition*, 38(17):2494–2532, 1999.

[6] Selim M Senkan. High-throughput screening of solid-state catalyst libraries. *Nature*, 394(6691):350, 1998.

[7] Kristian Berland and Clas Persson. Enabling accurate first-principle calculations of electronic properties with a corrected k· p scheme. *Computational Materials Science*, 134:17–24, 2017.

[8] Hendrik J. Monkhorst and James D. Pack. Special points for brillouin-zone integrations. *Phys. Rev. B*, 13:5188–5192, Jun 1976.

[9] A. Baldereschi. Mean-value point in the brillouin zone. *Phys. Rev. B*, 7:5212–5215, Jun 1973.

[10] D. J. Chadi and Marvin L. Cohen. Special points in the brillouin zone. *Phys. Rev. B*, 8:5747–5753, Dec 1973.

[11] Sverre Froyen. Brillouin-zone integration by fourier quadrature: Special points for superlattice and supercell calculations. *Phys. Rev. B*, 39:3168–3172, Feb 1989.

[12] Juana Moreno and José M. Soler. Optimal meshes for integrals in real- and reciprocal-space unit cells. *Phys. Rev. B*, 45:13891–13898, Jun 1992.

[13] Pandu Wisesa, Kyle A. McGill, and Tim Mueller. Efficient generation of generalized monkhorst-pack grids through the use of informatics. *Phys. Rev. B*, 93:155109, Apr 2016.

[14] JF Janak. Gilat-raubenheimer methods for k-space integration. In *Computational Methods in Band Theory*, pages 323–339. Springer, 1971.