

I. INTEGRATION

We have seen that in crystals the Kohn-Sham eigenvalues need to be found which are self-consistent solutions of a \vec{k} -dependent Hamiltonian

$$H(\vec{k})\phi_{\vec{k}}(\vec{r}) = \epsilon_i(\vec{k})\phi_{\vec{k}}(\vec{r}). \quad (1)$$

The total energy is then given through an integration over the first Brillouin zone. In numerical practice we convert this integral into a sum over discrete points in \vec{k} -space. We then have

$$E_e = \frac{1}{N_k} \sum_{\vec{k}, i} \left[\epsilon_i(\vec{k}) + \sum_{\vec{G}} \epsilon_{xc}(\vec{G}) n(\vec{G}) + 2\pi \sum_{\vec{G}} \frac{n(\vec{G})^2}{G^2} \right] \quad (2)$$

In principle if we manage to choose a dense enough \vec{k} -grid over which to perform the summation, it makes little difference how many \vec{k} -points we have in our sum or the manner in which they are chosen. However, since each new \vec{k} -point means a new self-consistent Kohn-Sham system it's crucial to maximize the accuracy while reducing the size of the \vec{k} -point set as much as possible.

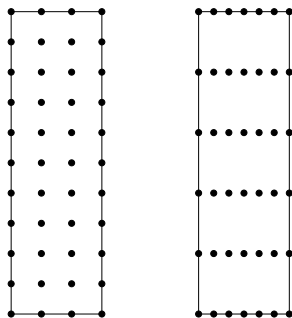
Since all functions having the symmetry of the crystal (such as the density) repeat beyond the first Brillouin zone, the \vec{k} -points are also constrained to this area. According to a widely-used procedure proposed by Monkhorst and Pack (see *Physical Review B*, **13**, 5188) a uniform set of points may be determined using the formula

$$\vec{k}_{n_1, n_2, n_3} = \sum_i^3 \frac{2n_i - N_i - 1}{2N_i} \vec{b}_i \quad (3)$$

where \vec{G}_i are the primitive reciprocal lattice vectors, $n_i = 1, \dots, N_i$ and N_i determines the number of \vec{k} -points to be chosen in each direction.

A. Choosing kpoints

There are several considerations while choosing kpoints.



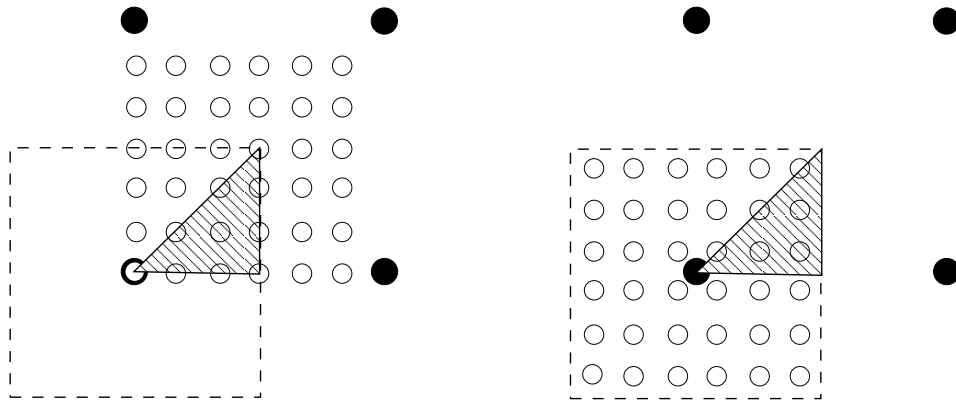
B. Uniformity

As discussed in the illuminating paper by Moreno and Soler (*Physical Review B*, **45**, 24), mesh points that are uniformly distributed are preferred over those that have different densities in different dimensions. Let's assume that we have a crystal that whose BZ is longer in one dimension than the other as seen in the figure to the left. Although the two meshes illustrated in the figure have more or less the same number of points, the one on the right resolves even small oscillation in one direction while leaving the other direction inadequately sampled. In the one on the left, however, the resolution in either direction is equally uniform and thus this is preferred over

the one on the right since there is no reason to expect oscillations particularly in one direction.

C. Symmetry

While summing a function over kpoints in the BZ, it reduces the calculation time by a several factors if we make use of the symmetry of the crystal in question. Points in the reciprocal space grid generated for the BZ integration are usually connected to each other by symmetry operations. Using these operations, the points to be used in the integration may be reduced to what is known as the *irreducible BZ*.



Integrals over the BZ may be interchanged with integrals over the IBZ

$$\bar{f}_i = \sum_{\vec{k}}^{\text{IBZ}} w_{\vec{k}} f_i(\vec{k}) \quad (4)$$

where $w_{\vec{k}}$ are the relative weights.

II. INSULATORS VS METALS

What differentiates between an insulator and a metal is the presence of a gap and the location of the Fermi level. The Fermi level is the energy of the highest occupied state and if it falls inside a gap in the band structure, then the crystal is said to be an insulator. If on the other hand it falls on a point where there is a finite density of states, it is a conductor. In terms of \vec{k} -integration, the insulators are well-behaved in the sense that the density of states goes to zero smoothly before the gap and the integration of a smooth function usually does not cause problems. For metals on the other hand, the functions to be integrated need first to be multiplied by a sharp Fermi occupation, which makes their resolution in planewaves very hard.

$$I = \int_{\text{BZ}} f(\vec{k}) [1 - \theta(E(\vec{k}) - E_F)] d\vec{k} \quad (5)$$

In order to overcome the difficulty we introduce an artificial smearing to the problem. There are several schemes for this smearing, each with their advantages and disadvantages. First we recast the integral into a form with a delta-function (as suggested in the paper by Methfessel and Paxton *Physical Review B*, **40**, 3616) which yields for Eq. 5

$$I = \int_{-\infty}^{\infty} [1 - \theta(E(\vec{k}) - E_F)] \int_{\text{BZ}} f(\vec{k}) \delta(\epsilon - E(\vec{k})) d\epsilon \quad (6)$$

Next, we replace the delta function by a smearing function which makes the integrand smoother. Several methods have been proposed for this smoothing procedure. Each method, while improving the \vec{k} -point convergence, causes the answer to converge to the wrong value. Among the methods available we seek those that minimize this error.

- **Fermi-Dirac function :** This introduces an artificial temperature into the system by approximating the step function by a Fermi-Dirac distribution

$$f(E) = \frac{1}{e^{(E-E_F)/kT} + 1} \quad (7)$$

which as $T \rightarrow 0$ approaches the step-function. This approach has a drawback however that the reduced occupation probability in the states with energies smaller than the Fermi energy are not compensated by the occupation probability of the newly introduced states with energies higher than the Fermi energy.

- **Methfessel-Paxton** : The Methfessel-Paxton scheme aims to overcome this shortcoming by introducing a smearing scheme that can progressively be improved. They first propose an approximation scheme to the delta-function and then integrate it to obtain an approximation to the step function. The form they propose is an expansion in terms of *Hermite functions* which are simply Hermite polynomials multiplied by Gaussians.

$$\delta(x) \approx D_N = \sum_n^N A_n H_{2n} e^{-x^2} \quad (8)$$

where A_n are suitable coefficients. They use Hermite polynomials of even order only since the delta function is even. The delta function obtained by integrating D_N in the following way

$$\delta(x) \approx S_N = 1 - \int_{-\infty}^x D_N(t) dt \quad (9)$$

Using recursion properties of Hermite functions, we arrive at

$$S_0 = \frac{1}{2}(1 - \text{erf}(x)) \quad (10)$$

$$S_N = S_0(x) + \sum_{n=1}^N A_n H_{2n-1}(x) e^{-x^2} \quad (11)$$

$$(12)$$

Here S_0 corresponds to the Fermi-Dirac smearing whereas the other terms serve to correct errors introduced.

A drawback of the Methfessel-Paxton smearing is that we encounter negative occupation values which are unrealistic and cause problems in such procedures as visualizing the density of states.

- **Gaussian** : Approximate delta function by a Gaussian obtain delta-function by integration.
- **Marzari-Vanderbilt** : The Marzari-Vanderbilt approach has been proposed in order to amend the negative occupancies introduced by the Methfessel-Paxton method. The delta-function this time is approximated by a Gaussian multiplied by a first order polynomial

$$\tilde{\delta}(x) = \frac{1}{\sqrt{\pi}} e^{-[x-(1/\sqrt{2})]^2} (2 - \sqrt{2}x) \quad (13)$$

where

$$x = \frac{\mu - \epsilon}{\sigma} \quad (14)$$

with width σ .