8.0.1 Functionals

A functional can be defined as a rule for going from a function to a number or it enables a function to be mapped to a number and is usually written using square brackets. Thus:

$$F[f] = \int g(f(r))dr$$  \hspace{1cm} (8.1)

where function $g(x)$ is a well-defined function. Also area under the curve which takes a function $f^2(r)$ (integral from point $a$ to $b$):

$$F[f(r)] = \int_{a}^{b} f^2(r)dr$$  \hspace{1cm} (8.2)

In the case of DFT the function $g(x)$ depends upon the electron density, which would make $F$ a functional of $n(r)$; in the simplest case $g(r)$ would be equivalent to the density (i.e. $g(r) \equiv n(r)$).

8.0.2 Bloch’s theorem

Bloch’s theorem states that in a periodic solid, each electronic wave function can be written as the product of a cell periodic part and a wave like part,

$$\Psi_i(r) = \exp^{ikr} f_i(r)$$  \hspace{1cm} (8.3)

The cell periodic part of the wave function can be expanded using a basis set consisting of a discrete set of plane waves whose wave vectors are reciprocal lattice vectors of the crystal,

$$f_i(r) = \sum_{G} c_{iG} \exp^{iG \cdot r}$$  \hspace{1cm} (8.4)

where the reciprocal lattice vectors $G$ are defined by

$$G.l = 2\Pi m$$  \hspace{1cm} (8.5)
for all \( l \) where \( l \) is a lattice vector of the crystal and \( m \) is an integer. Therefore, each

electronic wave function can be written as a sum of plane waves,

\[
\Psi(l)(r) = \sum_{G} c_{l,k+G} \exp[i(k+G)
\]

(8.6)

The Bloch theorem changes the problem of calculating an infinite number of
electronic wave functions to one of calculating a finite number of electronic wave functions
at an infinite number of \( k \) points. The occupied states at each \( k \) point contribute to the
electronic potential in the bulk solid so that, in principle, an infinite number of calculations
are needed to compute this potential. However, the electronic wave functions at
\( k \) points that are very close together will be almost identical. Hence it is possible to
represent the electronic wave functions over a region of \( k \) space by the wave functions at
a single \( k \) point. So the electronic states at only a finite number of \( k \) points are required
to calculate the electronic potential and hence determine the total energy of the solid.