Structure Factor: Plane Wave Expansion

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Abstract

Given a list of plane wave coefficients in Fourier space, how can we reconstruct the wavefunction, the charge density, and the structure factor.

I. ELECTRONIC WAVEFUNCTIONS

The solution is in Bloch's theorem, where we can write a single-electron wavefunction as

$$\psi_{n,k}(\vec{r}) = u_{n,k}(\vec{r})e^{i\vec{k}\cdot\vec{r}} \tag{1}$$

The Bloch waves, $u_{n,k}(\vec{r})$, have the symmetry of the lattice. We can expand them in a plane wave basis, essentially taking the discrete Fourier transform. This allows us to write the wavefunction in terms of plane wave coefficients.

$$\psi_{n,k}(\vec{r}) = \sum_{\vec{G'}} C_{n,k}(\vec{G'})e^{i(\vec{k}+\vec{G'})\cdot\vec{r}} \tag{2}$$

II. REAL SPACE CHARGE DENSITY

The assumption that goes into forming the charge density, $\rho(\vec{r})$, is that the wavefunctions for electrons of different bands do not interfere - they are separable. This is a direct result of the wavefunctions being solutions to the Hartree-Fock equations.

$$\begin{aligned}
\rho(\vec{r}) &= \sum_{n,k} |\psi_{n,k}(\vec{r})|^2 \\
&= \sum_{n,k}[\sum_{\vec{G'}} C_{n,k}(\vec{G'})e^{i(\vec{k}+\vec{G'})\cdot\vec{r}}][\sum_{\vec{G}} C^*_{n,k}(\vec{G})e^{-i(\vec{k}+\vec{G})\cdot\vec{r}}] \\
&= \sum_{n,k}\sum_{\vec{G'},\vec{G}} C_{n,k}(\vec{G'})C^*_{n,k}(\vec{G})e^{i(\vec{G'}-\vec{G})\cdot\vec{r}} \qquad (3)
\end{aligned}$$

III. STRUCTURE FACTOR

The structure factor is the Fourier transform of the real space charge density.

$$
\begin{aligned}
S(\vec{Q}) &= \int \mathrm{d}^3 r \;\rho(\vec{r}) e^{-i(\vec{Q}\cdot\vec{r})} \\
&= \sum_{n,k} \sum_{\vec{G}',\vec{G}} C_{n,k}(\vec{G}') C^*_{n,k}(\vec{G}) \int \mathrm{d}^3 r \; e^{i(\vec{G}'-\vec{G}-\vec{Q})\cdot\vec{r}} \\
&= \frac{1}{(2\pi)^3} \sum_{n,k} \sum_{\vec{G}',\vec{G}} C_{n,k}(\vec{G}') C^*_{n,k}(\vec{G}) \delta^3(\vec{G}'-\vec{G}-\vec{Q}) \\
&\propto \sum_{n,k} \sum_{\vec{G}} C_{n,k}(\vec{Q}+\vec{G}) C^*_{n,k}(\vec{G})
\end{aligned} \tag{4}
$$

The delta function collapses one of the sums over reciprocal lattice vector. Thus, the structure factor can be represented (up to factors of 2π and the unit cell volume) by a simple sum over plane wave coefficients. This sum is a convolution in Fourier space.