Goethe-Universität Frankfurt
Fachbereich Physik

Lehrende: Prof. Dr. Roser Valentí, Raum 01.130
Übungsgruppenleitung: Karim Zantout, Room 01.142

Frankfurt, 16.04.2019

# Theorie zu Magnetismus, Supraleitung und Elektronische Korrelation in Festkörpern

Sommersemester 2019

## Blatt 3

(Abgabe: 07.05.2019)

**Aufgabe 1** (**Some basis functions in density functional theory**) (10=5+5 Punkte)

In order to solve the Kohn-Sham equations [Eq. (1.39) in the lecture notes] in practice, one expands the single-electron wavefunctions[1] $\psi_i(\vec{r})$ in terms of some simple known functions $\phi_p(\vec{r})$ called *basis* functions:

$$\psi_i(\vec{r}) = \sum_{p=1}^{P} c_p^i \phi_p(\vec{r}) \tag{1}$$

Here, the basis set size, which in principle should be infinite, has been truncated to a finite value $P$ for practical reasons. Given (1), the Kohn-Sham equations can be written in a matrix form as

$$\begin{pmatrix} \langle\phi_1|H_{KS}-\epsilon_i|\phi_1\rangle & \langle\phi_1|H_{KS}-\epsilon_i|\phi_2\rangle & \cdots \\ \langle\phi_2|H_{KS}-\epsilon_i|\phi_1\rangle & \langle\phi_2|H_{KS}-\epsilon_i|\phi_2\rangle & \cdots \\ \vdots & \vdots & \ddots \quad \langle\phi_P|H_{KS}-\epsilon_i|\phi_P\rangle \end{pmatrix} \begin{pmatrix} c_1^i \\ c_2^i \\ \vdots \\ c_P^i \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ \vdots \\ 0 \end{pmatrix} \tag{2}$$

and solved by performing numerical diagonalization.

(a) **(Plane waves)** In a periodic solid environment, a natural choice of basis functions are *plane waves*:

$$\psi_i(\vec{r}) = \sum_{p=1}^{P} c_p^i \phi_p(\vec{r}) \quad \Rightarrow \quad \psi_{n\vec{k}}(\vec{r}) = \sum_{\vec{K}} c_{\vec{K}}^{n\vec{k}} \phi_{\vec{k}\vec{K}}(\vec{r}) \tag{3}$$
$$\phi_{\vec{k}\vec{K}}(\vec{r}) = e^{i(k+\vec{K})\vec{r}}$$

where $K$ is a reciprocal lattice vector. The expansion is limited to reciprocal lattice vectors $K$ for which $|K| \leq K_{max}$. Now, let us consider Ca crystallized in a face-centered-cubic structure with a conventional lattice constant of 3 Å. Estimate the number of plane waves required to describe the electrons residing on the Ca $3s$ states (Fig. 1), whose structure is roughly preserved in a solid. How realistic would it be to perform density functional theory calculations in this case using the plane-wave basis?

(*Hint*: $K_{max}$ depends on the smallest relevant length scale $d_{min}$ as $K_{max} \approx \frac{2\pi}{d_{min}}$. )

(b) **(Augmented plane waves)** From part (a) it should be clear that the plane-wave basis set size blows up mainly due to the need to describe the rapidly varying electron density in the close vicinity

[1] We assume a non-spin polarized case and omit the spin index $\sigma$.

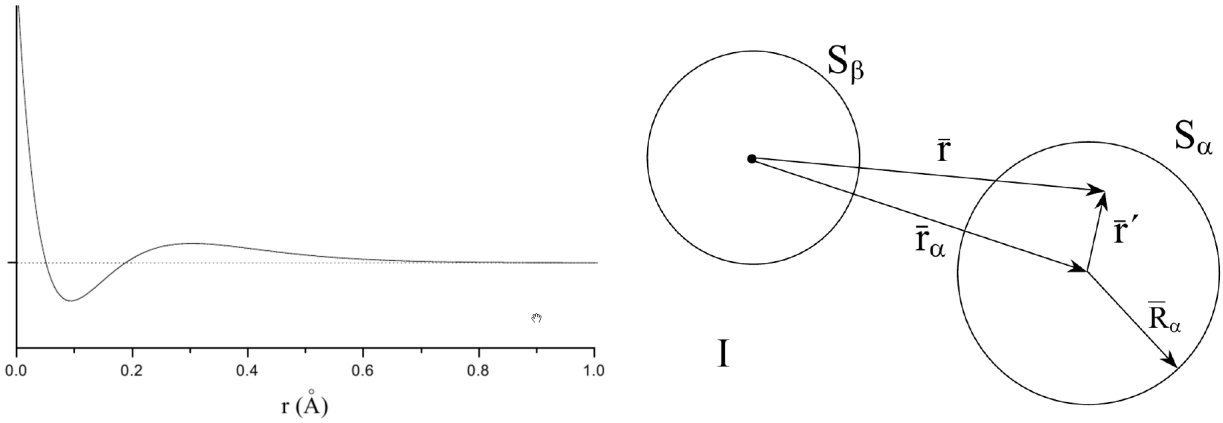


Figure 1: **Left:** Radial part of the Ca $3s$ wavefunction. **Right:** Partitioning of a unit cell in the augmented plane waves method.

of a nucleus. In order to (substantially) reduce the basis set size, alternative basis functions can be used, such as, for instance, the augmented plane waves:

$$\phi_{\vec{k}\vec{K}}(\vec{r},E) = \begin{cases} \frac{1}{\sqrt{V}} e^{i(\vec{k}+\vec{K})\vec{r}} & \vec{r} \in \mathrm{I} \\ \sum_{lm} A_{lm}^{\alpha,\vec{k}+\vec{K}} u_l^{\alpha}(r',E) Y_m^l(\hat{r}') & \vec{r} \in \mathrm{S}_\alpha \end{cases} \tag{4}$$

which are defined in terms of normalized plane waves in the interstitial region I and in terms of atomic-like functions inside the so-called muffin-tin spherical regions around atoms $\mathrm{S}_\alpha$ (see Fig. 1). In Eq. (4), $V$ is the unit cell volume, $u_l^\alpha(r',E)$ are solutions to the radial part of the Schrödinger equation for a free atom $\alpha$ at energy $E$, the $Y_m^l(\hat{r}')$ are spherical harmonics, and expansion coefficients $A_{lm}^{\alpha,\vec{k}+\vec{K}}$ are chosen such as to ensure the continuity of the wavefunction through the muffin-tin sphere boundary; other variables are explained in Fig. 1. The expansion over the spherical harmonics is limited to some $l_{max}$. Determine the number of augmented plane waves sufficient to perform density functional theory calculations for the crystallized Ca from the requirement that the shortest plane-wave period (which depends on $K_{max}$) should match the finest nodal structure of the atomic-like functions at the surface of the Ca muffin-tin spheres (which depends on $l_{max}$ and the Ca muffin-tin radius $R_{\alpha=\mathrm{Ca}}$). Take $l_{max} = 8$ and $R_{\alpha=\mathrm{Ca}} = 1.06$ Å.

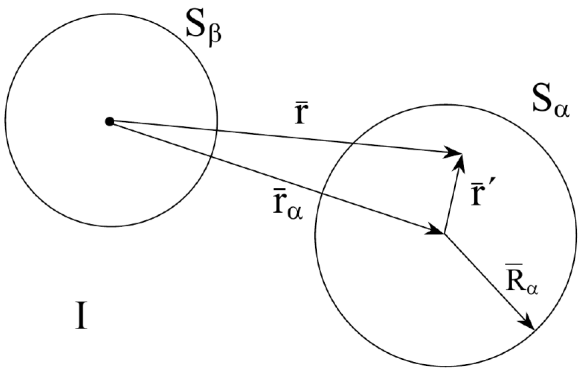


Figure 2: Partitioning of a unit cell in the augmented plane waves method.