



Imaging from atomic structure to electronic structure

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ABSTRACT

This paper discusses the possibility of retrieving the electron distribution (with highlighted valence electron distribution information) of materials from recorded HREM images. This process can be achieved by solving two inverse problems: reconstruction of the exit wave and reconstruction of the electron distribution from exit waves. The first inverse problem can be solved using a focal series reconstruction method. We show that the second inverse problem can be solved by combining a series of exit waves recorded at different thickness conditions. This process is designed based on an improved understanding of the dynamical scattering process. It also explains the fundamental difficulty of obtaining the valence electron distribution information and the basis of our solution.

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1. Introduction

According to density functional theory (Hohenberg and Kohn, 1964; Kohn and Sham, 1965), the ground state electron distribution of a material provides all the physical properties of the materials. The innermost electrons (core electrons) which tightly surround the nucleus, define the atomic structure while the outmost electrons (valence electrons), delocalized around neighboring atoms, provide the bonding, electronic structure information. Although the electron density of the valence electrons is smaller, their influence on the properties of the materials is largest. Therefore it would be of great value for chemistry, physics and materials science if one could determine the valence electron distribution experimentally. However, this is a very difficult problem because the density of valence electrons is much lower than that of core electrons (lower by three or four orders). The usual way of obtaining valence electron distribution is to measure the total electron density or the directly related electrostatic potential by using X-rays (Coppens, 1997; Koritsanszky and Coppens, 2001) or electron diffraction (Zuo et al., 1999; Zuo, 2004; Zhu and Taftø, 1997; Wu et al., 2004) and then probing the minute details of the valence electron distribution. In this way, the total electron density must be measured with a very high accuracy so as to

extract the information of the valence electron density from the tails of the core electron density and from the noise (Coppens, 1997). Moreover, diffraction experiments only measure the averaged structure information of materials whereas direct imaging may have the advantage of providing the local structural information.

High resolution electron microscopy enables direct imaging of materials. It has played an important role in obtaining the atomic structure of materials in the last 30 years. The development of aberration corrected electron microscopes has improved the resolution of imaging down to sub-angstrom level such that it has become relatively easy to obtain atomic structural imaging (Haider et al., 1998; Jia et al., 2003; Urban, 2008) and opens new opportunities and challenges (Muller et al., 2008; Jannik et al., 2011). Revealing the electron distribution, especially the valence electron distribution of materials would be such a challenge. It has been known for a long time that the valence electron distribution influences the contrast of HREM images. However, this effect was usually considered to be weak and hardly interpreted. It is now possible to deduce information from the valence electron distribution from accurate fitting of the HREM images with those obtained from DFT calculations (Deng and Marks, 2006; Deng et al., 2007; Ciston et al., 2011). However, this trial-and-error method highly relies on the DFT calculation, and is not a completely independent experimental tool. It would be much more powerful if we could develop a method to reconstruct the (valence) electron distribution directly from the recorded HREM images which will have a huge advantage for analyzing materials that are difficult to predict from theoretical calculations, for instance, strong correlated

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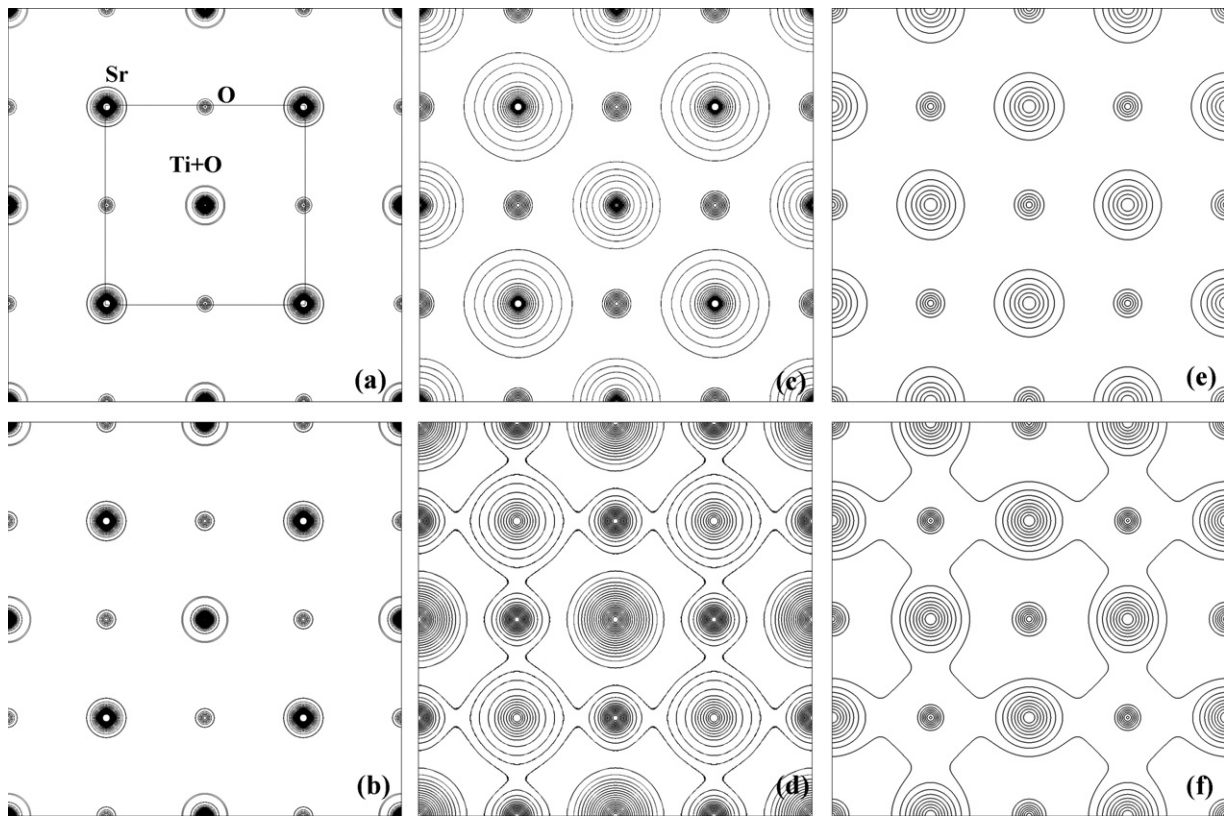


Fig. 1. Electron density and rescaled electron density viewed along 100 direction. (Square frame outlining the unit cell and the atomic column types are indicated only in (a) for simplicity). (a) The total electron distribution contour maps of the SrTiO₃ model ignoring bonding effects; (b) the total electron distribution contour maps for the structure model taking bonding effects into account. The contour map of (a) and (b) are generated using 200 equal-density lines with constant energy interval. The contour map of the rescaled electron distribution (c and d), are obtained from structure models without and with the bonding effects. The rescaling of (c and d) is carried by the superposition of the logarithm scaled core electron density and the normal linear scaled valence electron density; (e and f) show another type of rescaled electron distribution of the same structure. They are reconstructed from a series of exit waves and the rescaling scheme is indicated by the orange line plot in Fig. 2. The contour maps of (c–f) are generated using only 50 lines equal-density lines with constant energy interval. The valence electron distribution can be easier visualized in (c–f) where even less contour-lines are used.

materials. However, this is a very challenging task. In this paper, we discuss the main difficulties and possible solutions for such a method.

2. Projected electron distribution and rescaled electron density

HREM provides only two-dimensional images which cannot be directly linked to 3-dimensional properties (for instance 3D distribution of electrons), but would rather provide projected structure information of the sample. Hence we will limit our discussion to the retrieval of the projected (valence) electron distribution of the object from the HREM images (though it might be possible to obtain 3-dimensional electron distribution information in future by applying a tomographic scheme). In order to obtain the most accurate information of the projected electron density, one has to investigate the sample precisely along a low order zone axis. At this condition, the highly peaked, positively charged nuclei are arranged in columns, and their overlap with the projection of the electron distribution will be minimal. Since the valence electron density is much lower than the core electron density (as low as three orders or even lower) one has:

$$\rho_v(r) \ll \rho_c(r) \quad (1.1)$$

$$\rho(r) = \rho_c(r) + \rho_v(r) \doteq \rho_c(r) \quad (1.2)$$

where $\rho_v(r)$, $\rho_c(r)$ respectively denote the valence electron density and core electron density. Due to this huge density difference, it

is therefore very difficult to extract the features of the projected valence electron distribution directly from the total projected electron density map which is mainly dominated by the core electron density.

For example, Fig. 1A and B shows the total electron density contour maps of SrTiO₃ projected along [100] for two different types of valence electron distributions respectively: (1) all atoms are regarded as isolated atoms; the bonding induced by the valence electron redistribution is ignored so that the electron distribution of each atom maintains the spherical symmetry; (2) the interaction between neighboring atoms is included and the non-spherical valence electron distribution is described by using multipole models (Hansen and Coppens, 1978; Lippmann et al., 2003). Thus, apart from the valence electron distribution these two structure models are almost the same. And as expected no evident difference can be distinguished from the projected total electron distribution. In order to measure or visualize the valence electron distribution, one needs to develop an imaging scheme in which the recorded information of valence electron density is enhanced with respect to that of the core electron density. For instance, Fig. 1C and D shows the contour map of the rescaled electron density, as shown in Eq. (1.3), created by superimposing the two respective images: one representing the logarithm of the core electron density ρ^c and the other representing the valence electron density ρ^v of the corresponding structure model.

$$I_{rescaled}^{tot} = I(\log(\rho^c)) + I(\rho^v) \quad (1.3)$$

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