

Augmented wave ab initio EFG calculations: some methodological warnings

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Abstract

We discuss some accuracy aspects inherent to ab initio electronic structure calculations in the understanding of nuclear quadrupole interactions. We use the projector augmented wave method to study the electric-field gradient (EFG) at both Sn and O sites in the prototype cases SnO and SnO₂. The term ab initio is used in the standard context of the also called *first principles* methods in the framework of the Density Functional Theory. As the main contributions of EFG calculations to problems in condensed matter physics are related to structural characterizations on the atomic scale, we discuss the “state of the art” on theoretical EFG calculations and make a brief critical review on the subject, calling attention to some fundamental theoretical aspects.

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1. Introduction

The interaction of a nucleus with its surroundings gives rise to the so-called hyperfine interactions. It can be used to label different sites in a given sample. Experimental techniques like Mössbauer spectroscopy, nuclear quadrupole resonance (NQR), perturbed angular correlations (PAC), etc. [1] can probe the effect of the chemical environment on the nuclear energy levels. This information, however, is given as a product between a nuclear and an extra-nuclear quantity. It is also usual to further separate it according to being magnetic or electric hyperfine interactions. The extra-nuclear quantities come from the electronic charge and spin densities which can be theoretically obtained by state of the art electronic structure calculations. If we know the nuclear quantity, by performing a theoretical electronic structure calculation we can compare the results with measurements and study local properties like location of defects and impurities, determine structural parameters, impurity energy levels,

etc. [2]. On the other hand, if we do not know the nuclear quantity but have a precise theoretical electronic structure calculation and precise experimental results, we can determine the nuclear quantity in this case [3–5]. In the case of electric hyperfine interactions the nuclear quantity is the nuclear quadrupole moment Q , characteristic of a given nuclear state of spin I , which interacts with the electric-field gradient (EFG) at the nuclear position, and the experimental information is given as the nuclear quadrupole coupling constant [1].

In former times the EFG in solids was divided in two main contributions: an electronic contribution due to the electrons near the nucleus and a lattice contribution due to the rest of the system. The electronic contribution was until recently very difficult to be obtained since it basically depends on very small differences (of the order of 0.01 or less) between the occupations of electron orbitals with different symmetries around a given nucleus. In consequence, a realistic calculation of the EFG electronic contribution requires a very good description of the electronic structure of the system under consideration. Due to this fact, and in the absence of more realistic descriptions, the interpretation of the (indirect) EFG

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measurements has been done using empirical models that assume that the electronic contribution is somehow proportional to the lattice contribution [6,7]. The lattice contribution is obtained, in this case, using a simple “point-charge model” and can include a term modulated by a so called “Sternheimer factor”, to take the eventual core electrons polarization into account [8]. This is the oldest, most popular, and still in use model to interpret the experimental data. Nevertheless it has been shown that the results obtained in this way can be non-conclusive and also lead to erroneous interpretation of the experimental results. This is specially true in metallic systems where the attribution of a localized point charge may not be valid due to the itinerant character of the electrons. In insulators and semiconductors the point-charge model may work sometimes, but the physical insight is limited due to the parameterized character of the approach. In 1985, Blaha and co-workers presented a methodology to calculate the EFG based on the full-potential linearized augmented plane wave (FP-LAPW) method [9]. They applied it first to study the EFG at Li_3N [10] and in 1988 to HCP metals [11]. The charge density for the infinite system is calculated directly from the full potential, which is obtained without any shape restriction in all regions of the solid. The charge density used to calculate the EFG in this case is obtained in a self-consistent ab initio or *first-principles* calculations in the framework of the Kohn–Sham (K–S) scheme of the density functional theory (DFT) and no empirical factor has to be used. The large success achieved by this approach has brought a quality jump in the field: previously, the reproduction of the “order of magnitude” of the measured EFG was considered satisfactory; the FP-LAPW brought this agreement to a few percents. In the last 20 years the FP-LAPW method became the “bench mark” in EFG calculations and has been applied to many different systems. This was mostly due to the fact that it became popular and available to everyone interested in its implementation in a user friendly computer package: the Wien code [12]. In turn, the large impulse in the area of ab initio electronic structure calculations was due to the fact of the development of fast computers that allows the performance of calculations for larger and more complicated systems. It was then natural that other electronic structure methods were also applied to calculate EFGs in solids. The main requirement in this case is that the method can describe accurately both the bonding region between the atoms and the region near the nucleus. This is a challenge for a given method since the wave function behavior in these two regions is very different and poses numerical difficulties.

In 1998 the projector augmented wave (PAW) method [13] together with the Car-Parrinello approach (CP-PAW code) has been tested against the FP-LAPW Wien code and experimental results in a variety of systems by one of us [14]. It has been shown that they agree very well and both are state of the art methods to obtain total energies and EFGs. Due to the fundamentally different architectures of

the CP-PAW and Wien code they are better suited for some different applications, depending on computer efficiency. Also other methods like, e.g., the full-potential linear muffin-tin orbital method (FP-LMTO) [15] and the discrete variational method (DVM) [16], among others, have been successfully applied to calculate the EFG.

Together with the benefit brought by the introduction of state of the art ab initio EFG calculations the impulse of this area has introduced many new researchers and nonexperts into the field. It is the aim of the present paper to call the attention of the community to some fundamental aspects of the EFG calculations, which are known for the experienced researcher, but not so much to the broad new comers in the field. Due to its very high sensitivity to the probe environment concerning both chemical species and structural position, EFG has been claimed as an important fingerprint tool to identify different sites in a given sample. We shall show here that careful tests have to be performed before we arrive at a conclusive EFG result. We use, for the first time, the PAW method as embodied in the CP-PAW code to study the EFG at Sn and O sites in tin oxides SnO and SnO₂. Due to the relevant technological applications, these systems are very well studied in the literature by different experimental [17,18] and theoretical [19] approaches and the EFG at the Sn site has been recently studied using the Wien code by one of us [20]. Using these results and the measurements at the Sn site as benchmarks we also study here for the first time the EFG at the O site. Whenever necessary to analyze a specific situation and to compare with the PAW results, we also perform FP-LAPW calculations with the Wien code.

2. Theoretical approach

The EFG is a traceless symmetric tensor of rank two whose components are defined by the second derivative (with respect to the spatial coordinates) of the Coulomb potential V at the position of the nucleus, located for simplicity at the origin of coordinates:

$$V_{ij}(\vec{r} = 0) = \left. \frac{\partial^2 V}{\partial^2 x_i x_j} \right|_{\vec{r}=0}. \quad (1)$$

The potential can be determined from the total charge density in the crystal by solving Poisson’s equation. In this scheme, the EFG can be determined straightforwardly once the total charge distribution has been calculated. After changing the reference system of axis to the so called “principal” system of axis where the tensor is diagonal, the EFG tensor is completely defined by two numbers which are usually chosen as the largest component (named V_{ZZ}) and the asymmetry parameter η (which varies from zero to one), defined as

$$\eta = \frac{V_{XX} - V_{YY}}{V_{ZZ}}. \quad (2)$$

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