Calculations of Mössbauer parameters in solids by DFT bandstructure calculations

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Abstract. A short introduction to periodic bandstructure methods suitable for the calculation of Mössbauer parameters is presented. These methods are based on density functional theory (because we want to treat big and complicated systems) and must be accurate not only in the bonding region (like pseudopotential approaches), but also near the atomic nuclei since Mössbauer parameters depend crucially on the wave functions at/near the nucleus. A numerical basis set as in augmented plane wave (APW) based methods is very well suited for this purpose and the APW method is briefly sketched. The results for YBaFe$_2$O$_5$ are discussed in more detail and compared with experiment.

1. Introduction
The development of new and advanced materials requires both, experimental and theoretical support to gain deeper knowledge about the relationship between the desired materials properties and its atomic and electronic structure. Among the many experimental techniques, Mössbauer spectroscopy is rather outstanding because it can yield detailed local information about some atoms in the sample, even when no long range order exists or the concentration of that atom is very low. On the other hand, the interpretation of the obtained results (mainly the Mössbauer parameters for isomer shift (IS), quadrupole splitting (QS) and magnetic hyperfine field (HFF)) are not always straightforward and comparison with theory is highly desirable. The Mössbauer parameters are all linked to the electron (or spin-) density, which can be obtained from the wave functions after solving the quantum mechanical problem self-consistently.

Modern materials pose quite some challenges to theoretical approaches because of the more and more complex nature of these materials. Very often, the complexity comes from two facts: i) the composition of the material gets more and more complex (nanostructures with large unit cells and many atoms; disorder, non-stoichiometry, ...) ii) some specific atoms and their electronic structure is not so simple to describe by standard theoretical methods, since two or more electronic configurations may be very close in energy (low-spin vs. high-spin states, different ionicities, ...) and theory may not yield the correct ground state in all cases.

Theoretical methods can be classified in various ways. I will deal here only with periodic band structure approaches (contrary to finite cluster models), where the solid is described by a unit cell, which is repeated periodically in all three dimensions. In order to simulate surfaces, nanostructures, disorder or interfaces one has to create a supercell model, i.e. a larger unit cell which includes the relevant structural features and describes the real material as close as
possible. On modern computers such model structures can contain up to about 1000 atoms which is usually sufficient to build a reliable model of the specific material under investigation.

All theoretical methods considered here, try to describe the material by quantum mechanics and are based on Density Functional Theory (DFT)[1], which in principle is an exact theory, but the underlying functional is unknown and one has to make approximations. The most common approximations are the Local Density Approximation (LDA)[2] or the Generalized Gradient Approximation (GGA)[3], where just the local electron density (and its gradient) enters the equations for the exchange-correlation energy and potential. While these methods work pretty well for the vast majority of solids, they may fail severely for so-called correlated electrons in 3d transition metal oxides or 4f and 5f compounds. Unfortunately, the most important Mössbauer element, Fe, belongs often to this class of materials and the theoretical description of such Fe-compounds may not be so reliable as, for example, the electronic structure of Si in standard silicates. One has to go beyond LDA/GGA and use methods like hybrid-DFT[4], LDA+U[5] or DMFT[6], but this requires quite some advanced knowledge of both, the expected materials properties and these more complicated methods (and their applicability).

Besides the decision how to treat the electron-electron interaction, one also has to consider which particular magnetic order should be investigated (non-magnetic, ferromagnetic, various antiferromagnetic configurations, a disordered local moment approximation or even non-collinear magnetism[7]), and whether relativistic effects should be included (clearly, spin-orbit coupling is very important for 5f compounds, but even for Fe orbital contributions to the magnetic HFF can be significant in certain cases).

Most importantly, the specific electronic structure method must be suitable to calculate Mössbauer parameters, which requires an accurate description of the wave functions also in the core region of an atom. Thus the widely used plane wave (PW) pseudopotential methods[8] cannot be used here at all and also the popular Gauss basis functions of traditional quantum chemistry (LCAO methods) may not provide a very accurate description near/at the nucleus, in particular for heavier elements. On the other hand, methods with an adaptive numerical all-electron basis set are very well suited and I’ll describe the augmented plane wave methods in more detail. Once the electronic structure has been solved accurately, the Mössbauer parameters can be easily obtained from the corresponding wave functions as described below.

2. The augmented plane wave (APW) methods
One among the most accurate schemes for solving the DFT problem in solids is based on the APW method[9]. Much more information can be found in the book by Singh and Nordström[10] with many references and details. In APW based methods a basis set is introduced that is especially adapted to the problems in solids, where atomic like regions alternate with large empty space. Thus we divide the unit cell into non-overlapping atomic spheres (centered at the atomic sites) and an interstitial region and use different basis sets in the two types of regions. In the interstitial region a PW expansion is used

\[ \Phi_{k_n} = \frac{1}{\sqrt{\omega}} e^{i k_n r} \] (1)

where \( k_n = k + K_n \); \( K_n \) are the reciprocal lattice vectors, \( k \) is the wave vector inside the first Brillouin zone and \( \omega \) is the unit cell volume. While PWs are in principle a complete basis set, in praxis a PW expansion does not converge for the wave functions near the nucleus and we must augment them by atomic-like functions in every atomic sphere (of radius \( R_t \)). Thus we use inside the atomic spheres a linear combination of numerical radial functions \( u_l(r, E) \) times spherical harmonics \( Y_{lm}(r) \) (we omit the index \( t \)).

\[ \Phi_{k_n} = \sum_{lm} A_{lm} u_l(r, E) Y_{lm}(r) \] (2)
where \( u_l(r, E) \) is the (at the origin) regular solution of the radial Schrödinger equation for energy \( E \). This function depends on the energy (eigenvalues) leading to an expensive non-linear eigenvalue problem, but it can be linearized in various ways, either by using \( \dot{u}_l(r, E_l) \), the energy derivative of \( u_l \) (leading to the standard LAPW method introduced by Anderson\[11\]) evaluated at a fixed energy \( E_l \) (usually chosen at the center of bands with the corresponding \( l \)-like character), or by means of additional local orbitals\[12\] (APW+lo method, see below). The coefficients \( A_{lm} \) are functions of \( k_n \) and are determined by requiring that this basis function matches at \( R_t \) the corresponding PW (labeled with \( k_n \)) of the interstitial region. The accuracy of this method comes from the fact that \( u_l \) is the (numerical) exact solution for a given (spherical) potential.

In order to solve the problem of the energy dependence of \( u_l \), overcome linearization errors and to enhance the efficiency, Singh\[12\] introduced additional basis functions called “local orbitals” (LO), which look very similar to normal APWs, but the coefficients \( A_{lm} \) are not matched to plane waves, but set such that this additional basis function goes to zero at the sphere boundary (thus the name “local orbital”).

Such an optimized mixed basis set\[13\] forms the basis of the WIEN2k code\[14\], which has been developed in our group during the last two decades and is used worldwide by more than 1600 groups at universities and industrial laboratories.

The convergence of this basis set is controlled by a single cutoff parameter \( R_t K_{max} = 6 - 9 \), where \( R_t \) is the smallest atomic sphere radius in the unit cell and \( K_{max} \) is the magnitude of the largest \( K_n \) vector. Relativistic effects for core states are fully included, while by default the valence states are treated in a so called “scalar-relativistic” approximation\[10\], which includes mass velocity and Darwin s-shift terms, but neglects spin-orbit coupling. The latter can optionally be included in a second variational step and also radial basis functions for \( p_{1/2} \) states (which differ significantly from non-relativistic \( p \) or relativistic \( p_{3/2} \) functions) can be added\[15\]. WIEN2k comes with an (optional) user-friendly graphical user interface (“w2web”) and proved to be efficient and rather robust against user errors. For bigger systems an efficient parallelization on various levels (k-points or fine-grain mpi-based) is available and WIEN2k has been executed on 1000 cores in parallel, treating unit cells with more than 1000 atoms\[16\].

### 3. Calculation of Mössbauer parameters

The isomer shift of a given atom can be obtained by comparing its electron density at the nucleus \( (\rho_0) \) with a reference. For the most common Mössbauer element this is body centered cubic (bcc) \( \alpha \)-Fe. For this purpose bcc-Fe needs to be calculated with parameters as close as possible for the specific material under investigation. In particular the same \( R_t \), a comparable basis set cutoff \( (R_t K_{max}) \) and the same DFT functional (however, the GGA+U method cannot be used because it would yield wrong results for an itinerant metal) should be used. A magnetic metal requires a dense k-mesh (like 10000 k-points in the full Brillouin zone) and spin-orbit coupling should be enabled/disabled exactly as in the compound. The \( \rho_0 \) values are directly available from the calculations. The isomer shifts \( \delta \), which are always related to the 4s electron density and thus to ionicity, can be calculated using the following expression:

\[
\delta = \alpha (\rho_{0}^{\text{Sample}} - \rho_{0}^{\text{Reference}}),
\]

where \( \alpha \) is a proportionality constant that can be estimated through calibration. In recent DFT calculations by Wdowik et al.\[17\] \( \alpha \) was found to be \(-0.291 \text{a.u.}^3 \text{mm/s}\), which is slightly larger than the commonly used value of \(-0.27 \text{from the work of Duff}\[18\].

The quadrupole splitting \( \Delta = eQV_{zz} \) is proportional to the product of the nuclear quadrupole moment \( Q \) times the electric field gradient (EFG) \( V_{zz} \). In order to compare theory with experiment one needs a value for the nuclear quadrupole moment \( Q \), which was determined
by Dufek et al.[19] to be about 0.16 b (barn; 1 b = 10^{-28} m^2) by comparing theoretical and experimental data for a large number of Fe compounds. With this value the relation between EFG and quadrupole splitting is approximately EFG [10^{21} V/m^2] = 3\Delta [mm/s][20]. (Note that Q has limited accuracy and could also be about 10 % larger, which one should consider when comparing theory and experiment.) The EFG can be calculated directly from the electronic and nuclear charge distribution \(\rho(r)\)[21] by

\[
V_{zz} = \int \rho(r) \frac{2P_2(\cos\theta)}{r^3} dr,
\]

where \(P_2\) is the second-order Legendre polynomial which projects out the \(l = 2\) component of the charge density. In addition, the \(1/r^3\) factor weights non-spherical contributions near the nucleus much stronger. For further analysis, the integral can be decomposed spatially (into a sphere around the nucleus and the rest of space) or the density \(\rho\) can be decomposed into contributions from \(3p\) and \(4p\). The \(3p\) contribution can be large if these states get polarized by anions at short distances and a very anisotropic environment; the \(4p\) contribution originates mainly from the tails of neighboring atoms (e.g. oxygens) and is almost always very important, while the \(3d\) contribution is large when eg. in high-spin Fe\(^{2+}\) ions the single Fe-3d spin-down electron occupies one particular orbital (like \(d_{z^2}\) or \(d_{xy}\)), but is small if all d-orbitals have similar occupation (like eg. in high-spin Fe\(^{3+}\) ions). It should be noted that the EFG can be very sensitive to structural details and even small relaxations of some atomic positions may lead to very different EFGs[22].

In magnetic materials one can also calculate a magnetic hyperfine field \(B_{tot}\), which can be decomposed theoretically into the Fermi contact term \(B_{contact}\), the dipolar field \(B_{dip}\) (due to the dipole spin distribution) and the field associated with the orbital moment \(B_{orb}\) (this requires to include spin-orbit interactions in the Hamiltonian). Usually \(B_{contact}\) dominates and can be obtained from the spin-density at the nucleus

\[
B_{contact} = 8\pi/3[\rho_{\uparrow}(0) - \rho_{\downarrow}(0)],
\]

where the polarization of the core-orbitals due to the finite 3d moment accounts for a large fraction of \(B_{contact}\). Unfortunately, in many cases the contact term is underestimated by about 10 % in DFT.

4. Charge order and mixed valence state of \(YBaFe_2O_5\)

\(YBaFe_2O_5\) shows a Verwey transition slightly above room temperature from a low-temperature charge-ordered (CO) phase with two distinct Fe sites (with formal valencies of +2 and +3, respectively) into a high-temperature valence-mixed (VM) modification with just one nonequivalent Fe site (with a formal valency of +2.5 [23]. In addition the structure changes from a strongly distorted orthorhombic to a nearly tetragonal symmetry and also the type of antiferromagnetic ordering changes. The changes in symmetry and magnetic order can be seen in Figs. 1 and 2.

Details of the structural, magnetic and electronic properties above and below the Verwey transition have been presented elsewhere[24] and here I concentrate only on the changes of Mössbauer parameters. The results are summarized in tables 1 and 2. Comparison between experiment and theory immediately reveals that LDA or GGA calculations fail to describe the Mössbauer parameters. For instance the differences for the IS (\(\delta\)), quadrupole splitting (\(\epsilon QV_{zz}\)) or HFF (\(B_{tot}\)) between Fe\(^{2+}\) and Fe\(^{3+}\) sites in the CO phase are much too small. We need to consider on-site correlation effects as included in GGA+U and with a reasonable value of U (7 eV) rather good results are obtained in agreement with experiment. In particular for the CO-Fe\(^{2+}\) site significant dipolar and orbital contributions to the HFF lead to the relatively
Figure 1. The magnetic $1 \times 2 \times 1$ CO supercell. The arrows depict the direction of the magnetic moments.

Figure 2. The magnetic $2 \times 2 \times 2$ VM supercell. The arrows depict the direction of the magnetic moments.

Table 1. Theoretical and experimental[25, 26, 27] hyperfine fields $B$ (in Tesla), isomer shifts $\delta$ (mm/s) and quadrupole splittings $eQV_{zz}$ (mm/s) for the CO phase.

|                | exp. | GGA+U | LDA | GGA |
|----------------|------|-------|-----|-----|
| $U_{eff}$ [eV]| —    | 5     | 6   | 7   | 8   |
| Fe$^{2+}$      | —    |       |     |     |     |
| $B_{dip}$      | —    | -16.29| -16.49| -16.66| -16.83| -16.83| -16.83| -16.83| -12.67|
| $B_{orb}$      | —    | -6.73 | -6.90| -8.26| -8.65| -8.65| -8.65| -8.65| -6.34|
| $B_{contact}$  | —    | 32.25 | 32.23| 32.58| 32.60| 32.60| 32.60| 32.60| 31.58|
| $B_{tot}$      | $\sim$ 8 | 9.23 | 8.83 | 7.66 | 8.13 | 15.96 | 12.57 |
| $\delta$       | $\sim$ 1 | 0.92 | 0.94 | 0.96 | 0.99 | 0.74 | 0.79 |
| $eQV_{zz}$     | 3.6 – 4 | 3.66 | 3.74 | 3.81 | 3.89 | 3.89 | 3.89 | 3.89 | 2.60 |
| Fe$^{3+}$      | —    | -0.67 | -0.60| -0.52| -0.45| 1.29 | 0.39 |
| $B_{dip}$      | —    | -0.52 | -0.45| -0.37| -0.28| -7.96| -2.65|
| $B_{orb}$      | —    | 37.65 | 38.28| 38.15| 38.76| 29.64| 31.63|
| $B_{contact}$  | —    | 37.65 | 38.28| 38.15| 38.76| 29.64| 31.63|
| $B_{tot}$      | $\sim$ 50 | 36.46 | 37.24| 37.26| 37.12| 22.97| 29.37|
| $\delta$       | $\sim$ 0.4 | 0.33 | 0.30 | 0.28 | 0.25 | 0.50 | 0.47 |
| $eQV_{zz}$     | 1 – 1.5 | 1.46 | 1.50 | 1.51 | 1.52 | 1.04 | -0.30|

Small observed value. Of course, for the CO-$Fe^{3+}$ ion with a full $3d^7$ and empty $3d^1$ shell these contributions are very small. The EFG in the VM phase is very small, because the EFG contributions from the tails of the O-neighbors and the on-site $3d$ electrons cancel partially. For the CO-$Fe^{3+}$ ion $V^{3d}_{zz}$ is very small (the five $3d$ electrons lead to nearly spherical symmetry), while for the CO-$Fe^{2+}$ site a single $3d^1$ electron in the $3d_{xz}$ orbital leads to a large EFG.

5. Conclusions
Periodic bandstructure calculations based on DFT provide in most cases a very accurate description of Mössbauer parameters, provided one uses a method that is also accurate near the nucleus and the electron-electron interaction is described accurately. For so-called highly
Table 2. Theoretical and experimental[25, 26, 27] hyperfine fields $B$ (in Tesla), isomer shifts $\delta$ (mm/s) and quadrupole splittings $eQV_{zz}$ (mm/s) for the VM phase.

|        | exp. | GGA+U | LDA | GGA |
|--------|------|-------|-----|-----|
| $U_{eff}$ [eV] | — | 5 | 6 | 7 | 8 |
| $B_{dp}$ | — | -3.00 | -2.98 | -2.95 | -2.87 | -2.13 | -2.83 |
| $B_{orb}$ | — | -3.11 | -2.99 | -2.84 | -2.74 | -5.47 | -4.56 |
| $B_{contact}$ | — | 41.17 | 40.96 | 41.45 | 41.17 | 33.10 | 36.36 |
| $B_{tot}$ | ~30 | 35.06 | 34.98 | 35.67 | 35.56 | 25.50 | 28.98 |
| $\delta$ | ~0.5 | 0.53 | 0.52 | 0.51 | 0.49 | 0.60 | 0.60 |
| $eQV_{zz}$ | ~0.1 | 0.12 | 0.13 | 0.13 | 0.19 | 0.19 | -0.27 |

It is necessary to go beyond standard DFT and unfortunately in that case the ab initio character of the calculations is partially lost, but one can still learn a lot about the proper physics in such a system. It should be stressed, that such calculations not only produce a few numbers which can be compared with experiment, but provide the possibility to gain deeper understanding of the specific compound. Theory can easily test various geometric or magnetic structures (which are not accessible in experiment), calculate various spectra (from infrared to X-ray absorption or emission spectroscopy) and explain the electronic properties.

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