Electronic structure calculations of solids using the WIEN2k package for material sciences ☆

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Abstract

In studies of the electronic structure of solids, the augmented plane wave (APW) method is the basis for the solution of the Kohn–Sham equations of density functional theory (DFT). The different versions and developing steps are discussed in terms of linearization, full potential, local orbitals, mixed basis sets, relativistic effects and computational aspects, as employed in the WIEN2k code. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

The advanced technology in certain parts of material sciences involving condensed matter rely more and more on reducing the scale of the application and devices and thus getting closer to atomic dimensions. A fundamental understanding of such materials requires a quantum mechanical description of the related solids and thus relies on the calculation of the corresponding electronic structure. Such calculations are mainly done within density functional theory (DFT),

according to which the many-body problem of interacting electrons and nuclei is mapped onto a one-electron reference system that leads to the same density as the real system [1]. The corresponding Kohn–Sham (KS) equations must be solved iteratively till self-consistency is reached. The basic quantity is the electron density which is obtained by summing over the occupied KS orbitals. DFT includes both exchange and correlation effects, but in practice they are treated only approximately. Therefore, the form of the exchange and correlation energy and the related potential is crucial for the quality of DFT calculations. The first generation of DFT results was obtained using functionals based on the homogeneous electron gas, namely the local density approximation (LDA). Then corrections involving the gradient of the electron density became available in the form of the generalized gradient approximations (GGA) [2]. Recently, more sophisticated treatments of highly correlated systems were developed such as LDA+U [3].

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Once the DFT equations are defined in terms of the functional, there are several techniques to solve them, which shall not be summarized here. A natural basis for calculating the one-electron wave functions in periodic solids are plane waves (PWs) corresponding to Bloch functions labeled by the k-vector of the first Brillouin zone (BZ). PWs are, however, a very inefficient basis set for describing the rapidly varying wave functions close to the nuclei. In order to overcome this difficulty one can either eliminate these oscillations, due to the presence of the core electrons, as done in pseudopotential calculations or one can augment the PW basis set. One example of the latter approach has led to the linearized augmented plane wave (LAPW) method that is now established to be one of the most accurate schemes and thus will be the focus of the present work. Different versions of LAPW and their main developing steps are discussed below.

2. APW

In 1937 Slater [4] introduced augmented plane waves (APW) as basis functions for solving the one-electron equations, which now correspond to the Kohn–Sham equations within DFT. In the APW scheme the unit cell is partitioned into two types of regions: (i) spheres centered around all constituent atomic sites $\mathbf{r}_\alpha$ with a radius R_α, and (ii) the remaining interstitial region, abbreviated as I in this paper. In the latter the wave functions are expanded into PWs each of which is augmented by atomic solutions in the form of partial waves, i.e. a radial function times spherical harmonics. In the early work the muffin-tin (MT) approximation was adopted to the potential and the charge density, which were both assumed to be spherically averaged inside the atomic spheres and volume averaged in between. The APWs consist of

$$\phi_{\mathbf{K}}(\mathbf{r}) = \begin{cases} \sum_L a_L^{\alpha\mathbf{K}} u_l^\alpha(r', \epsilon) Y_L(\hat{\mathbf{r}}'), & r' < R_\alpha, \\ \Omega^{-1/2} \exp\big(i(\mathbf{k} + \mathbf{K}) \cdot \mathbf{r}\big), & r \in I, \end{cases}$$

where L is short for lm, Ω is the unit cell volume, $\mathbf{r}' = \mathbf{r} - \mathbf{r}_\alpha$ is the position inside sphere α with the polar coordinates r' and $\hat{\mathbf{r}}$, $\mathbf{k}$ is a wave vector in the irreducible Brillouin zone (IBZ), $\mathbf{K}$ is a reciprocal lattice vector and u_l^α is the numerical solution to the
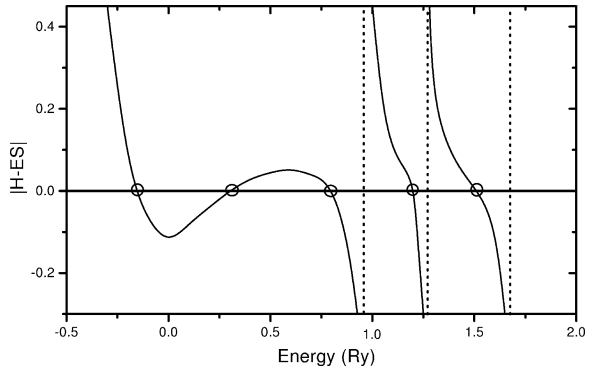

Fig. 1. Satisfying the secular equation $|H - ES| = 0$ in APW by numerically finding the zeros.

radial Schrödinger equation at the energy ϵ. The coefficients $a_L^{\alpha\mathbf{K}}$ are chosen such that the atomic functions for all L components match (in value) the PW with $\mathbf{K}$ at the MT sphere boundary. The KS orbitals $\psi_i(\mathbf{r})$ are expressed as a linear combination of APWs $\phi_{\mathbf{K}}(\mathbf{r})$. Inside the MT sphere a KS orbital can only be accurately described if ϵ in the APW basis functions is equal to the eigen-energy, ε_i. Therefore, a different energy-dependent set of APW basis functions must be found for each eigenenergy. This leads to a non-linear eigenvalue problem that is computationally very demanding. One had to choose an energy, solve the radial Schrödinger equation to obtain the APW basis and set up the matrix elements. Then the determinant $|H - ES|$ had to be computed, that should vanish according to the secular equation but did not. So one had to vary the trial energy to numerically find the zeros of this determinant (see Fig. 1), a procedure complicated by the presence of asymptotes. This was the main drawback of the APW scheme which at best works for simple systems with few eigenvalues only.

3. LAPW

Several improvements to solve the energy dependence of the basis set were tried but the first really successful one was the linearization scheme introduced by Andersen [5] leading to the linearized augmented plane wave (LAPW) method. In LAPW the energy dependence of each radial wave function inside the atomic sphere is linearized by taking a linear combination of a solution u at a fixed linearization energy
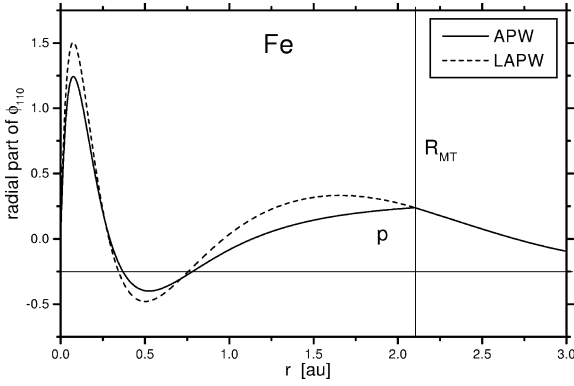
Fig. 2. Augmentation of a PW by a p-like partial wave inside the iron atomic sphere by APW (kink) or LAPW (smooth derivative).

and its energy derivative $\dot{u}$ computed at the same energy.

$$\phi_{\mathbf{K}}(\mathbf{r}) = \begin{cases} \sum_L \left[a_L^{\alpha\mathbf{K}} u_l^{\alpha}(r') + b_L^{\alpha\mathbf{K}} \dot{u}_l^{\alpha}(r') \right] Y_L(\hat{\mathbf{r}}'), \\ \qquad\qquad\qquad\qquad\qquad r' < R_{\alpha}, \\ \Omega^{-1/2} \exp\!\left(i(\mathbf{k}+\mathbf{K}) \cdot \mathbf{r} \right), \quad r \in I. \end{cases}$$

Each PW is joined continuously (in value and slope) to the one-center solution defining the relative weight of u and $\dot{u}$, i.e. the coefficients $a_L^{\alpha\mathbf{K}}$ and $b_L^{\alpha\mathbf{K}}$, see Fig. 2. The LAPWs provide a sufficiently flexible basis to properly describe eigenfunctions with eigenenergies near the linearization energy, which can be kept fixed. This scheme allows us to obtain all eigenenergies with a single diagonalization in contrast to APW.

Already in 1975 the first implementation was done by Koelling and Arbman [6] but only with the MT approximation and without going to self-consistency. In the following years it was extended to a full band structure code mainly by Freeman and co-workers [7,8], who developed the necessary algorithms and computer codes. In the 80s several groups improved this scheme and wrote their own programs. One among them was our group who has—during the last 20 years—developed the WIEN code [9] that is now used by more than 500 groups worldwide. A good summary of references concerning the LAPW method can be found in a book by Singh [10].

The LAPW basis set made it computationally attractive to go beyond the muffin tin approximation and to treat a crystal potential (and charge density) of general shape, making LAPW a full-potential scheme.

This became increasingly important for more complex materials with open structures or for surfaces, which can be treated by supercells using periodic boundary conditions (see, for example, Reuter and Scheffler [11]).

Another important quantity of interest was the forces acting on the atoms. Based on the formalism of Yu et al. [12] the calculation of forces was implemented [13] in the WIEN97 code [14] and allowed an efficient optimization of structural parameters. The general shape of the electron density (beyond MT) is important for the calculation of structure factors which can be compared with X-ray diffraction experiments (see, for example, [15]). A quantity related to the ground state density is the electric field gradient (EFG) tensor which is sensitive to the anisotropy of the charge density close to the nucleus and can be measured by nuclear quadrupole interactions [16].

The electronic states are classified into three categories, the core, semi-core and valence states. The core states are completely confined inside the corresponding atomic sphere and are treated in an atomic fashion (fully relativistically) as thawed core, i.e. the corresponding density is recalculated in each iteration cycle using the MT part of the actual crystal potential. The valence states are (partly) delocalized and are obtained by the LAPW method leading to the valence density. The semi-core states, however, are highly-lying core states with a principal quantum number one less than for the valence states (e.g., Ti-3p [17]). They are not completely confined inside the atomic sphere and thus need special attention. In 1991 Singh [18] has introduced the concept of local orbitals (LOs) which—in addition to an improvement in the variational flexibility—allow the efficient treatment of such semi-core states. An LO is constructed by the LAPW radial functions u and $\dot{u}$ at one energy ϵ_1 in the valence band region and a third radial function at ϵ_2 (e.g., around the semi-core state energy).

$$\phi_{LO}(\mathbf{r}) = \begin{cases} \left[a_L^{\alpha,LO} u_{1l}^{\alpha}(r') + b_L^{\alpha,LO} \dot{u}_{1l}^{\alpha}(r') \right. \\ \left. \quad + c_L^{\alpha,LO} u_{2l}^{\alpha}(r') \right] Y_L(\hat{\mathbf{r}}'), \quad r' < R_{\alpha}, \\ 0, \qquad\qquad\qquad\qquad\qquad r \in I. \end{cases}$$

The three coefficients are determined by the normalization and the requirement that the LO should have zero value and slope at the sphere boundary. Thus they are not connected to PWs in the interstitial. With

this scheme, which slightly increases the size of the basis set, all electrons (including semi-core states) can be treated accurately and the corresponding states are orthogonal to each other.

4. APW+lo

Recently, an alternative approach was proposed by Sjöstedt et al. [19], namely the APW+lo (local orbitals) method. Here the augmentation is similar to the original APW scheme but each radial wave function is computed at a fixed linearization energy to avoid the non-linear eigenvalue problem that complicated the APW method. Thus only the condition of continuity can be required and the basis functions may contain a kink at the sphere boundary (see Fig. 2). The missing variational freedom of the radial wave functions can be recovered by adding another type of local orbitals (termed lo in lower case to distinguish them from LO) containing a u and $\dot{u}$ term.

$$\phi_{lo}(\mathbf{r}) = \begin{cases} \left[a_L^{\alpha,lo} u_l^\alpha(r') + b_L^{\alpha,lo} \dot{u}_l^\alpha(r') \right] Y_L(\hat{\mathbf{r}}'), \\ \qquad r' < R_\alpha, \\ 0, \quad r \in I. \end{cases}$$

The los are evaluated at the same fixed energy as the corresponding APWs. The two coefficients are determined by the normalization and the condition that the lo has zero value at the sphere boundary. In this version the $\dot{u}$ is independent of the PWs, since it is only included for a few los and not associated with every PW. Recently it was demonstrated that this new scheme can reach the same accuracy as LAPW but converges faster in terms of number of PWs [20]. The highest efficiency was found for a mixed basis set in which the "physically important" l-quantum numbers are treated by APW+lo but the higher l by LAPW. It was shown in [20] that quantities such as the total energy, forces, or EFGs converge significantly faster with respect to the number of basis functions than with the pure LAPW procedure but reach the same values. This is illustrated in Fig. 3 for one component of the force acting on an oxygen atom in SES (sodium electro sodalite) containing 44 atoms per unit cell (see [20]). In LAPW the force changes sign and thus the atom would move in the wrong direction for a too small basis set, whereas in the
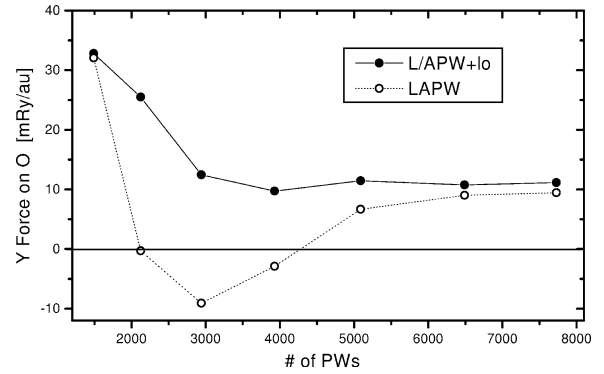

Fig. 3. Convergence of the force (Y-component) on oxygen in SES [20] vs. number of PWs.

APW+lo scheme the force converges smoothly and much faster. For large systems the matrix size N can be about halved and thus the computational cost can be an order of magnitude less, since the diagonalization scales with N^3.

The new scheme combines the best features of all APW-based methods available. The LAPW converges somewhat more slowly than the APW method as has already been pointed out by Koelling and Arbman [6], since the constraint of having differentiable basis functions makes LAPWs less optimally suited to describe the orbitals inside the sphere. This justifies going back to APW but the energy-independent basis introduced in LAPW is crucial for avoiding the non-linear eigenvalue problem and thus is kept, too. The local orbitals provide the necessary flexibility. Further details of the convergence and how to set up the matrix elements or compute terms such as the forces which require the inclusion of surface terms due to the kink in the basis functions are discussed in [20]. The APW+lo scheme has been implemented in the WIEN code and is the default option in the new WIEN2k version [21] (for further details see www.wien2k.at).

5. Relativistic effects

Another important aspect related to high accuracy is the treatment of relativistic effects. The standard procedure is a scalar relativistic version that includes the mass velocity and Darwin s-shift but omits spin-orbit coupling (SOC). The latter can efficiently be included by a second variational treatment [22]. In this
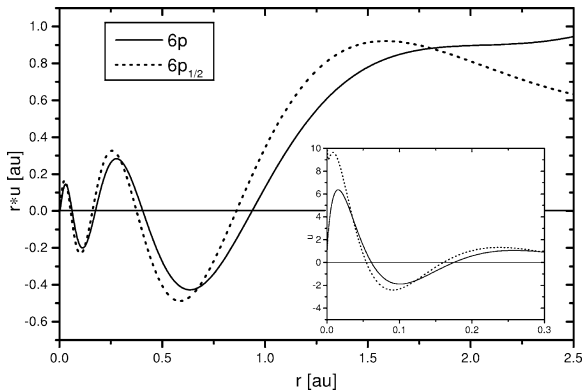
Fig. 4. The 6p radial semi-core function $r * u$ of thorium represented by the scalar relativistic version (full line) and by the additional local orbital (dashed line). The inset shows u (not $r * u$) close to the nucleus.

scheme the spin orbit term is set up in a subspace spanned by the scalar relativistic solution with about twice the number of the occupied orbitals but much less than the full basis. The proper treatment of SOC may require an improved basis set, in particular for semi-core states of heavy elements. The scalar relativistic basis contains, e.g., only one type of radial p-function that is very similar to the $p_{3/2}$ orbital. Now we add a local orbital with the $p_{1/2}$ function that has a different shape and nodal structure (Fig. 4) and is finite at the nucleus (see insert). Recently this scheme was demonstrated for Th [23]. Spin polarized calculations can provide both spin and orbital moments in magnetic materials [24].

6. Computational aspects

A modern computer code must combine several features to be widely used. We summarize considerations which were made in the development of the new WIEN2k package [21]:

– **Accuracy** is extremely important in the present case. It is achieved by the well-balanced basis set which contains numerical radial functions that are adapted in each iteration to changes due to charge transfer or hybridization. It is accurate near the nucleus (important for EFG) and satisfies the cusp condition. PW convergence can be controlled by one parameter, namely the cutoff energy. There is no dependence on selecting atomic orbitals or pseudopotentials. It is a full-potential and all-electron method. Relativistic effects (including SOC) can be treated with a quality comparable to solving Dirac's equation.

– **Efficiency and performance** should be as high as possible. The new mixed basis APW+lo/LAPW optimally satisfies this criterion. The smaller matrix size helps to save computer time or allows larger systems to be studied. Adapted algorithms can substantially speed up the performance as discussed, for example, in [25].

– **Parallelization.** The program can run in parallel, either in a coarse grain version where each k-point is computed on a single processor, or if the memory requirement is larger than that available on one CPU, a fine grain scheme is adopted in which the problem of one k-point is distributed to several CPUs. In the latter case special attention must be paid to the eigensolver, the most time consuming part. Both options, full and iterative diagonalization, are implemented to allow the selection of the most efficient routines.

– **Architecture.** The hardware in terms of processor speed, memory access, and communication is crucial. Depending on the given architecture, optimized algorithms and libraries are chosen during the installation of the program package.

– **Portability** requires the use of standards as much as possible, such as FORTRAN90, MPI, BLAS (level 3), SCALAPACK etc.

– **User friendliness** is achieved by a web based graphical user interface (w2web) and is complemented by an automatic choice of default options. In addition an extensive Users Guide is provided.

7. Conclusion

The improved convergence of APW+lo leads to a reduced matrix size but keeps the high accuracy already established in the WIEN97 code [14] which made it a benchmark code for solids. In combination with the many properties that can be calculated thanks to contributions from several groups, this new version of the solid state electronic structure package is a useful tool for studying materials problems.

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