An Alternative Full-Potential ELAPW Method

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Introduction

This new combination of the extended LAPW-***k·p*** method [1] with a plane-wave basis set [2] offers a scheme for self-consistent full-potential calculations alternative to the well-known FLAPW [3] technique.

The valence density is expanded in a Fourier series. The number of Fourier constituents retained depends upon the desired accuracy of the potential. By construction the potential is continuous everywhere in the unit cell.

To solve the Schrödinger equation the wave function is expressed in terms of APWs. In the ***k·p*** method, the matrix elements of the Hamiltonian are evaluated once for each iteration, which makes the algorithm fast.

In the usual full potential technique [3] the density is constructed directly out of the variational wave functions given in the APW representation. In contrast to this procedure we expand the density in a Fourier series and retain a finite number of Fourier components (FC's). Thus the representation of the density is independent from the representation of the wave functions and a reciprocal-space density cutoff G^d_{max} can be introduced depending upon the desired accuracy.

In constructing the Coulomb potential the G^d_{max} criterium is natural, as the true FC's of the density are limited, and the FC's of the potential decrease as G^{-2}. It should be noted that the FC's of the pseudo density, which are employed in the FLAPW, are not limited and consequently no cutoff can be introduced.

The augmented Fourier components method

The valence density is given by

$$\rho(\vec{r}) = F_0 + \rho^F(\vec{r}) + \rho^H(\vec{r}). \qquad (1)$$

$F_0 = \frac{N_{tot}}{\Omega}$ is the zeroth Fourier component of the density. The part of the crystal density given by a limited number of FC's is referred to as the *filtered density*:

$$\rho^F(\vec{r}) = \sum_{\vec{G}} \rho(\vec{G})\, e^{i\vec{G}\vec{r}}, \qquad 0 < |\vec{G}| \le G^d_{max}. \qquad (2)$$

The functions ρ^F and ρ^H represent electrically neutral density distributions.

The boundary values of the potential at the surfaces of the spheres are determined by the Fourier-filtered potential

$$V^F(\vec{r}) = 4\pi e \sum \frac{\rho(\vec{G})}{G^2}\, e^{i\vec{G}\vec{r}}. \qquad (3)$$

The effect of the higher FC's on the potential in the interstitial is neglected. Inside the sphere t the potential is augmented by replacing the component V^F_{00} in its angular momentum expansion by the true spherically averaged potential V_{00}.

$$\Delta V_{00}(r) = 4\pi e \rho_{00}(r), \qquad V_{00}(S_t) = V^F_{00}(S_t).$$

The components V^F_{lm} for $l > 0$ are not augmented, the non-spherical part of the potential is thought to be described by the plane waves (3).

Representation of the crystal density

AFC	**FLAPW**
A sum of the Fourier-filtered true density and the spherically symmetric density inside the MT spheres.	A sum of the extended interstitial Fourier representation (EIFR) given by its FC's and a density given by its *lm* expansion inside the spheres.
$\rho(\boldsymbol{r}) = \rho^F(\boldsymbol{r}) + \sum_t \rho^H_{t00}(r_t)$	$\rho(\boldsymbol{r}) = \rho_I(\boldsymbol{r}) + \sum_t [\rho_t(\boldsymbol{r}) - \rho_I(\boldsymbol{r})]\theta(\boldsymbol{r} \in S_t)$
The FC's of the true density are limited.	The FC's of the EIFR are not limited.
Higher FC's of the density are spherically averaged in the MT spheres.	An exact angular momentum decomposition of the density in the MT spheres is employed.
The boundary values of the spherical part of the potential at the sphere boundaries $V_{00}(S)$ are derived from the FC's of the true density.	The boundary values of the potential at the MT sphere radii $V_{lm}(S)$ are derived from the FC's of the pseudo density.
The boundary value problem for Poisson's equation is solved only for $l = 0$.	The boundary value problem for Poisson's equation is solved for all l,m.

Non-muffin-tin results

for a transition metal and a compound semiconductor

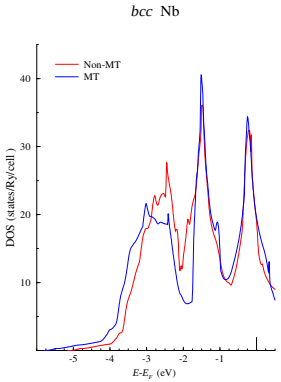


Fig. 3: Also for the transition metal Nb, which is thought to be very well described by the MT approximation, energy shifts of up to 0.3 eV are observed.

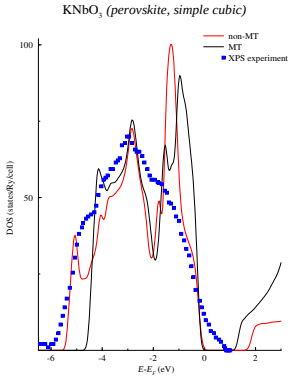


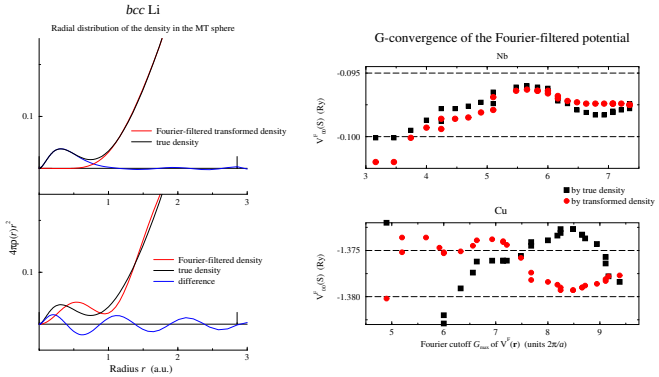
Fig. 4: The use of the non-MT potential visibly improves the self-consistent DOS for this perovskite with respect to the experiment [4].

Acceleration of the plane-wave convergence of the valence density

The Fourier constituents of the valence density decay rather slowly even for simple metals. The main contribution to the higher FC's, $\rho^H(r)$, comes from the close vicinity of the nucleus. There the valence density varies rather rapidly, but at the same time the density in this region can be considered spherical to a good approximation.

To accelerate the plane-wave convergence of the density we ''gouge out'' its rapidly varying part to arrive at the transformed valence density. The latter coincides with the original density everywhere in the unit cell, except for small spheres ($r \sim 1$ a.u.) where the density is smoothed and damped. The gouged density is then added to the core density.

Convergence properties of the gouge transformation



Figs. 1 and 2: The gouge transformation yields a great acceleration in the convergence of the density (left) and the potential (right). This is true even for the ''plane-wave'' metal Li.

Advantages of the AFC method

The potential is continuous everywhere in the unit cell.

The effect of the approximations involved is easily monitored, and the parameters of the method can be chosen to balance the desired accuracy with available computational power.

Calculations of quantities which have no physical meaning is avoided.

Limitations

The method is not designed to precisely calculate the density given by the variational wave functions.

Being applied within a non-***k·p*** formulation of the eigenvalue problem the method would result in rather time-consuming calculations.

The Program

1. Calculate the ELAPW-***k·p*** matrices for a self-consistent muffin-tin potential

2. For each ***k*** point
   - 2.1. Solve the Kohn-Sham equations
   - 2.2. Get the Plane-Wave Expansion
   - 2.3. Calculate the electron density

3. Integrate over the BZ to get the FC's of the density as well as its exact radial distribution inside the spheres

4. Solve Poisson's equation and determine the crystal potential (AFC method)

5. Calculate the Hamiltonian (full potential), overlap and momentum matrices in the APW representation for the next iteration.

6. Iterate 2. to 5. to self-consistency

Appendix

The AFC formalism enables us to exclude the angular momentum series from the representation of the density. We consider this to be an advantage of the method, because in the general case the effect of the L cutoff cannot be estimated *a priori*.

In the FLAPW method [3] the problem is avoided by taking into account all the L terms included in the basis functions. Fig. 5 shows that in the APW-like methods the l_{max} has to be taken unphysically large.

Thus in calculating observables a formalism not involving infinite L series might be advantageous.

How many *l* are **really** needed?

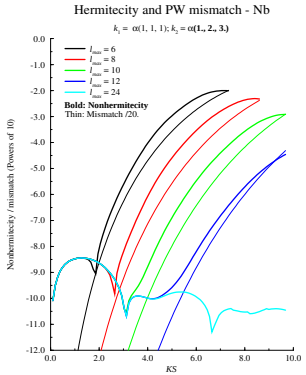


Fig. 5: The nonhermiticity $\frac{|<i|H|j> - <j|H|i>|}{|<i|H|j>| + |<j|H|i>|}$ and the plane-wave mismatch $m_{l_{max}}(KS) = 1 - \sum_l \tilde{c}^2_l(KS)(2l+1)$.

Conclusions

We have calculated the electronic structure of the Li, Nb, and Cu metals as well as the semiconducting oxide $KNbO_3$.

No non-muffin tin effect has been observed for Li; for Cu the effect has been found negligible.

The Coulomb potential in the Nb metal shows considerable deviation from the MT form: a shift of about 0.3 eV has been observed at the bottom of the valence band (see Fig. 3).

As expected the non-MT corrections are significant in complex oxides. For $KNbO_3$ the AFC calculation yields better agreement with XPS measurements.

References

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