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Full Potential Augmented Plane Waves Method

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OUTLINE

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   - Representation of wave functions
   - Linear and non-linear methods
   - Slater's augmented plane wave method
2. Linear augmented plane wave method
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   - Electronic density and crystal potential
   - Relativistic calculations: Dirac equation and second variation
3. Accuracy and the extension of the radial basis set
   - Choice of energy parameters
   - Introduction of localized orbitals
4. $\mathbf{k} \cdot \mathbf{p}$ method
   - Localized orbitals beyond ϕ and $\dot{\phi}$
   - Inverse band structure problem and complex band structure

Bloch Functions by Variational Methods

- 3D infinite crystal
- 2D infinite crystal (slab)
- semi-infinite crystal

two ways to construct a Bloch function:

$$e^{i\,\mathbf{kr}}u^{\lambda}_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{R}} e^{i\,\mathbf{kR}}\,\phi^{\lambda}_{\mathbf{k}}(\mathbf{r}-\mathbf{R})$$

$$e^{i\,\mathbf{kr}}u^{\lambda}_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} \xi^{\lambda}_{\mathbf{k}+\mathbf{G}}(\mathbf{r})$$

variational methods: minimize $\dfrac{\langle\,\psi\,|\,\hat{H}\,|\,\psi\,\rangle}{\langle\,\psi\,|\,\psi\,\rangle}$

J.M. Ziman *The Calculation of Bloch Functions*, in Solid State Physics **26** Academic Press, New York (1971).

variational methods of band theory $H\Psi = E\Psi$

	crystal momentum (plane waves)	angular momentum (orbitals)	
		structure constants	tight-binding
non-linear methods	APW (1937)	KKR (1949)	screened KKR
linear methods	LAPW (1975)	LMTO (1975) ASW (1978)	tight-binding LMTO
Potential independent basis	plane waves		Gaussian, Slater orbitals

The methodology is distributed as commercial or public domain codes

Vanderbilt Ultra-Soft Pseudopotential
CASTEP
CPMD Program
DOD-Plane Wave
VASP
FHImd
ABINIT Software Project
PWSCF
Siesta
Conquest
LMTO
ASW
WIEN2k
FLEUR
DOD-Parallel Tight-Binding Molecular Dynamics
CAMPOS
PsiMag Software Repository
Octopus
CASINO
FPLO
Wien2K
CPMD
TranSIESTA
Crystal
Band

Augmented Plane Waves

The wave function of Bloch vector $\mathbf{k}$ and band number λ is a linear combination of basis functions satisfying the Bloch boundary conditions, e.g., plane waves:

$$\psi_{\mathbf{k}\lambda}(\mathbf{r}) = \sum_{\mathbf{G}} C_{\mathbf{G}}^{\mathbf{k}\lambda} \exp[i(\mathbf{k}+\mathbf{G})\mathbf{r}],$$

$\mathbf{G}$ are reciprocal lattice vectors, and $C_{\mathbf{G}}$ are variational coefficients.

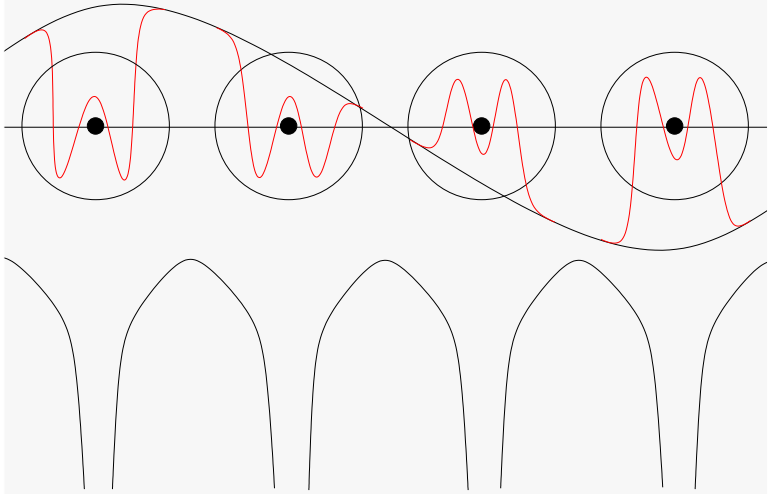
This works only for *pseudopotentials*, and not for the potential with a singularity $1/r$ at the nucleus.

Slater: introduce non-overlapping muffin-tin spheres and replace the Bessel functions $j_l(Kr)$ in the Rayleigh decomposition of the plane wave inside the sphere with exact radial solutions $\phi_l(E, r)$.

Augmented Plane Waves

J.C. Slater *Wave Functions in a Periodic Potential*
Phys. Rev. **51**, 846 (1937)

For the special case of muffin-tin potential the Bloch function may be determined with any desired accuracy without having a complete basis set.



inside the muffin-tin spheres

$j_l(Kr) \rightarrow \phi_l(E,r)$

This leads to a non-linear equation:

$\hat{H}(E)\Psi = E\hat{O}(E)\Psi$

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Augmented Plane Waves

Radial solutions $\phi_l(E,r)$ satisfy the *radial Schrödinger equation*

$$(\hat{H}_r - E)\,\phi_l(r) = 0, \qquad \hat{H}_r = -\frac{1}{r}\frac{d^2}{dr^2}r + \frac{l(l+1)}{r^2} + V(r),$$

and match the Bessel functions at the sphere only in value.

$$\exp(i\mathbf{Kr}) = \sum_{lm} 4\pi i^l j_l(Kr) Y^*_{lm}(\hat{\mathbf{K}}) Y_{lm}(\hat{\mathbf{r}}), \qquad \mathbf{K} = \mathbf{k} + \mathbf{G},$$

augmentation means $\quad j_l(Kr) \;\rightarrow\; \phi_l(E,r),$

or, more general, $\quad j_l(Kr) \;\rightarrow\; \Phi_l(K,r).$

In the latter case $\Phi_l(K,r)$ may deviate from the exact solution in order to match $j_l(Kr)$ at the sphere both in value and in slope.

Augmented Plane Waves

Inside the sphere located at $\mathbf{r} = 0$ the APW reads

$$\xi(\mathbf{K}, \mathbf{r}) = \sum_{lm} 4\pi i^l \Phi_l(K, r) Y^*_{lm}(\hat{\mathbf{K}}) Y_{lm}(\hat{\mathbf{r}}),$$

where $\mathbf{K} = \mathbf{k} + \mathbf{G}$, and the trial function is

$$\psi_{\mathbf{k}\lambda}(\mathbf{r}) = \sum_{\mathbf{G}} C^{\mathbf{k}\lambda}_{\mathbf{G}}\, \xi_i(\mathbf{k} + \mathbf{G}, \mathbf{r}).$$

In Slater's APW the trial function is *flexible*: the radial function can be varied independently from the set of $\{C^{\mathbf{k}\lambda}_{\mathbf{G}}\}$.

If $\Phi_l(K, r)$ depends only on K the trial function is *rigid*: the coefficients $\{C^{\mathbf{k}\lambda}_{\mathbf{G}}\}$ uniquely determine the trial function in the spheres.

Linear Augmented Plane Waves Method

In order to be able to use linear algebra one needs a fixed basis set:
APWs $\rightarrow$ energy independent APWs $\rightarrow \hat{H}\Psi = E\hat{O}\Psi$

$$\xi(\mathbf{K},\mathbf{r}) = \sum_{lm} 4\pi i^l \Phi_l(K,r) Y^*_{lm}(\hat{\mathbf{K}}) Y_{lm}(\hat{\mathbf{r}}).$$

There exist many ways to construct Φ_l: rigid schemes [1-5] and flexible schemes [6-9], where Φ_l have some variational freedom after the matching conditions have been fulfilled.

1. O.K. Andersen, Phys. Rev. B **12**, 3060 (1975).
2. D.D. Koelling and G.O. Arbman, J. Phys. F **5**, 2041 (1975).
3. T. Takeda and J. Kubler, J. Phys. F **9**, 661 (1979).
4. D.J. Shaughnessy, G.R. Evans, and M.I. Darby, J. Phys. F **17**, 1671 (1987).
5. D.D. Koelling, Phys. Rev. B **2**, 290 (1970).
6. H. Bross *et al.*, Phys. Rev. B **2**, 3098 (1970).
7. D. Singh, Phys. Rev. B **43**, 6388 (1991).
8. E.E. Krasovskii, Phys. Rev. B **56**, 12866 (1997).
9. E. Sjöstedt, L. Nordström, and D.J. Singh, Solid State Commun. **114**, 15 (2000).

Linear Augmented Plane Waves Method

In the majority of implementations the radial functions Φ_l are linear combinations of a number of solutions of the radial Schrödinger equation $\phi_{\nu l}(E_{\nu l}, r)$ and their energy derivatives $\dot{\phi}_{\nu l}(E_{\nu l}, r)$

$$\begin{aligned}
(\hat{H}_r - E_{\nu l})\,\phi_{\nu l}(E_{\nu l}, r) &= 0, \\
(\hat{H}_r - E_{\nu l})\,\dot{\phi}_{\nu l}(E_{\nu l}, r) &= \phi_{\nu l}(E_{\nu l}, r), \\
\left\langle\, \dot{\phi}_{\nu l} \mid \phi_{\nu l} \,\right\rangle &= 0.
\end{aligned}$$

$E_{\nu l}$ are called energy parameters of the method.

Only two functions for each l are needed to match an APW in both value and slope at the sphere.

1. O.K. Andersen, Phys. Rev. B **12**, 3060 (1975).
2. D.D. Koelling and G.O. Arbman, J. Phys. F **5**, 2041 (1975).

The logarithmic derivative parametrization

To fulfill the matching conditions: $\Phi_l(K) \rightarrow \Phi_l(D(K))$

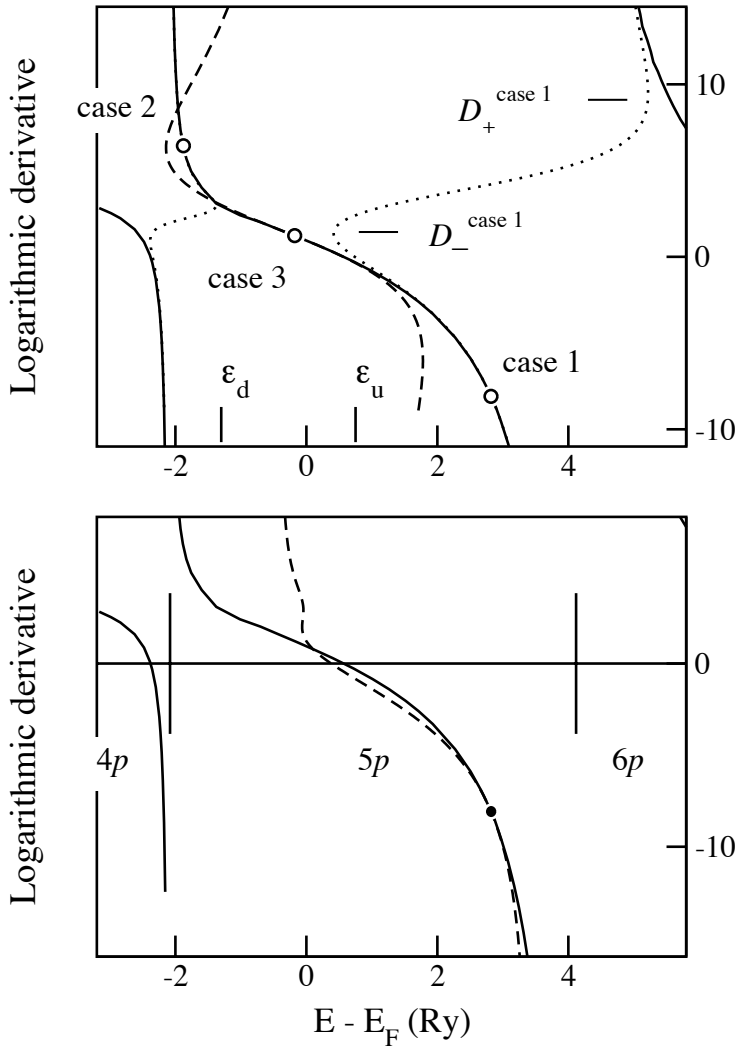
$$\Phi_l(D) = \phi_{\nu l}(E_{\nu l}) + \omega(D)\dot{\phi}_{\nu l}(E_{\nu l})$$

Compare the exact energy dependence of the logarithmic derivative,

$$D^{\mathrm{true}}(E) = S\,\frac{\phi_l'(E,r)}{\phi_l(E,r)}\bigg|_S,$$

to the energy parametrization curve

$$E_{\mathrm{par}}(D) = \langle\, \Phi_l(D) \mid \hat{H}_r \mid \Phi_l(D)\,\rangle.$$



Accuracy and convergence

1. Continuity of the basis functions:

   in the sphere $\sum_{lm}^{l_{\max}} 4\pi i^l \Phi_l(K,r) Y^*_{lm}(\hat{\mathbf{K}}) Y_{lm}(\hat{\mathbf{r}})$ must match

   the plane wave $\sum_{lm}^{\infty} 4\pi i^l \; j_l(\,Kr\,)\; Y^*_{lm}(\hat{\mathbf{K}}) Y_{lm}(\hat{\mathbf{r}})$ in the interstitial

   A rule of thumb: truncate the lm series at $l_{\max} > KS$.

2. Convergence of the plane wave expansion in the interstitial: $KS \gtrsim 8$

3. Choice of the radial functions: energy parameters $E_{\nu l}$ to define $\Phi_l(D(K),r)$ and local orbitals (extension of the radial basis set). Choose the energy parameters $E_{\nu l}$ close to the eigenenergy to be determined.

D.J. Singh, *Plane waves, Pseudopotentials and the LAPW Method*, Kluwer, Boston (1994).

Crystal density and crystal potential

Coulomb potential: to solve the Poisson equation it is convenient to have a Fourier representation of the crystal density $|\psi_{\mathbf{k}\lambda}(\mathbf{r})|^2$:

1. Analytically continue the plane-wave representation of the density in the interstitial into the spheres $\Rightarrow$ *extended interstitial density* $\rho^I(\mathbf{r})$.

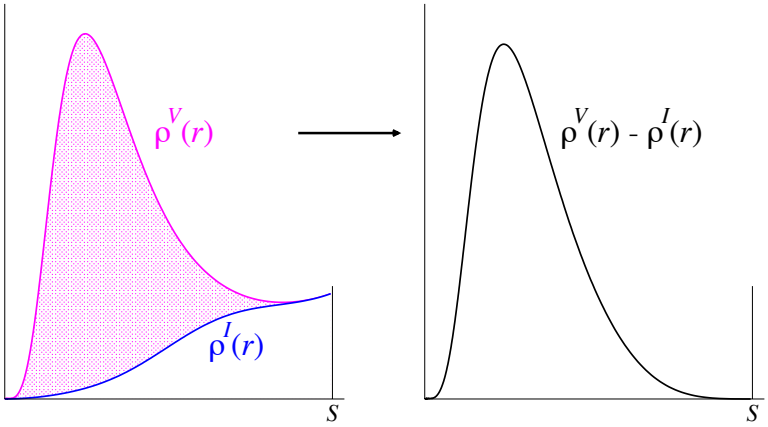
$$\begin{aligned} \text{in the interstitial} \quad \psi_{\mathbf{k}\lambda}(\mathbf{r}) &= \sum C_{\mathbf{G}}^{\mathbf{k}\lambda} \exp[i(\mathbf{k}+\mathbf{G})\mathbf{r}] \quad \Rightarrow \rho^I(\mathbf{r}), \\ \text{inside the sphere} \quad \psi_{\mathbf{k}\lambda}(\mathbf{r}) &= \sum R_{lm}^{\mathbf{k}\lambda}(r) Y_{lm}(\hat{r}) \qquad\qquad \Rightarrow \rho^V(\mathbf{r}). \end{aligned}$$

2. In the spheres subtract ρ^I and replace it with the true density ρ^V.
3. To calculate the Coulomb potential instead of performing a Fourier expansion of the densities, construct the Fourier expansion of the pseudodensities $\tilde{\rho}^I$ and $\tilde{\rho}^V$ with the same multipole momenta as ρ^I and ρ^V but smooth.

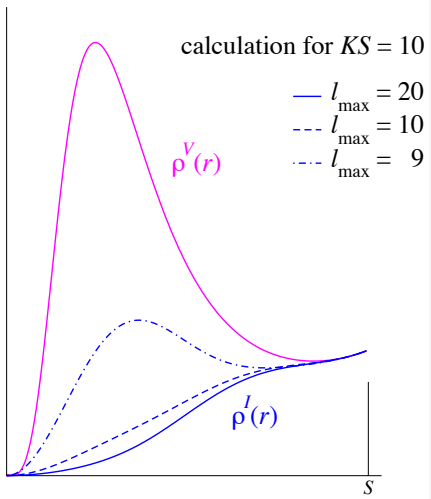
Crystal density and crystal potential

$\rho^V - \rho^I$ is localized in spheres, thus, can be replaced by a pseudodensity $\tilde{\rho}^V - \tilde{\rho}^I$ having a rapidly convergent Fourier expansion.

ρ^I is exactly given by a finite number of Fourier components, but the Fourier expansion of the function $\tilde{\rho}^V - \tilde{\rho}^I$ has to be truncated, as well as the lm expansion of $\tilde{\rho}^I$ and $\tilde{\rho}^V$.



$\rho^I(\mathbf{r})$ has no physical meaning:
if the matching of the basis functions at the sphere is not perfect it may behave rather weirdly →



1. M. Weinert, J. Math. Phys. **22**, 2433 (1981).
2. E. Wimmer, H. Krakauer, M. Weinert, and A.J. Freeman, Phys. Rev. B **24**, 864 (1981).

Dirac equation for the four-component function

$$\left[c \begin{pmatrix} 0 & \vec{\sigma} \\ \vec{\sigma} & 0 \end{pmatrix} \cdot \hat{\vec{p}} + mc^2 \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} + V(\vec{r}) \right] \psi = \epsilon \psi$$

Solutions for a spherical potential are labeled by κ and μ:

$$\phi_{\kappa\mu}(\vec{r}) = \begin{pmatrix} g_\kappa(r) \mid & \kappa\mu \rangle \\ \mathrm{i} f_\kappa(r) \mid & -\kappa\mu \rangle \end{pmatrix},$$

$\mid \kappa\mu \rangle$ are the two-component spin-angular functions,
κ are the eigenvalues of the operator $\hat{\vec{\sigma}} \cdot \vec{l} + 1$

$$\mid \kappa\mu \rangle = \sum_{s=\pm\frac{1}{2}} C(l\frac{1}{2}j; \mu - s, s) Y_l^{\mu-s} \chi^s, \quad \text{for} \quad j = l + \frac{1}{2} \rightarrow \kappa = -l - 1,$$

$$\text{for} \quad j = l - \frac{1}{2} \rightarrow \kappa = l.$$

Fully relativistic radial equation

For a given energy E the radial solution $g_\kappa(r)$ (large component) and $f_\kappa(r)$ (small component) satisfy the set of the radial Dirac equations:

$$\begin{aligned}\left(\frac{d}{dr}+\frac{1-\kappa}{r}\right)cf_\kappa(r)+[\,E-V(r)\,]\,g_\kappa(r) &= 0,\\ \left(\frac{d}{dr}+\frac{1+\kappa}{r}\right)g_\kappa(r)-\left[1+\frac{E-V(r)}{c^2}\right]cf_\kappa(r) &= 0.\end{aligned}$$

The formalism is implemented in non-linear APW and KKR, and LMTO:

1. T.L. Loucks, Phys. Rev. **139**, A1333 (1965).
2. V.V. Nemoshkalenko, A.E. Krasovskii, V.N. Antonov, Vl.N. Antonov, U. Fleck, H. Wonn, and P. Ziesche, Phys. Status Solidi B **120**, 283 (1983).

Two-component Koelling-Harmon formalism

Express the large components in terms of small components to arrive at a second order equation:

$$\left[-\frac{1}{r}\frac{d^2}{dr^2}r + \frac{l(l+1)}{r^2} + V(r) - H_{\rm R}(E)\right]\phi_l(r) = E\,\phi_l(r)$$

Now average $H_{\rm R}(E)$ over the two values of $\kappa = l$ and $-l-1$:

$$H_{\rm R}(E) = \frac{1}{2mc^2 + E - V(r)}\frac{dV}{dr}\frac{d}{dr} + \frac{[E-V(r)]^2}{c^2}.$$

The *scalar relativistic approximation*: radial functions $\phi_l(r)$ are the solutions of the equation $H_{\rm R}(E)\phi_l = E\phi_l$.

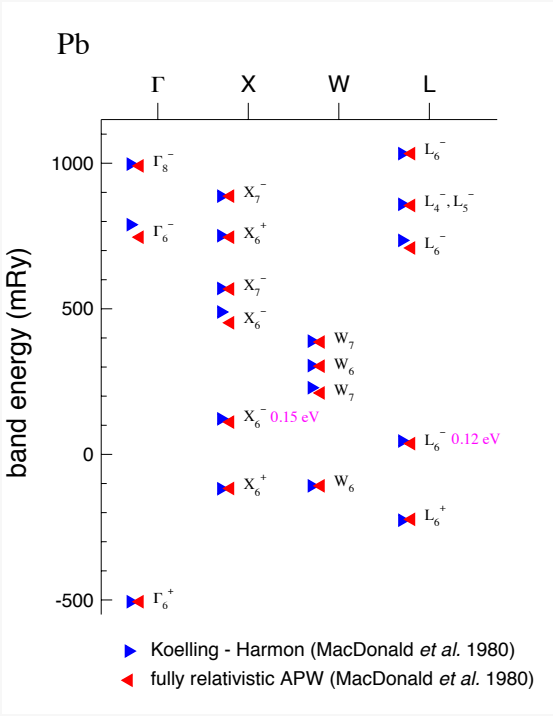
Still, the relativistic term $H_{\rm R}(E)$ depends explicitly on the energy E.

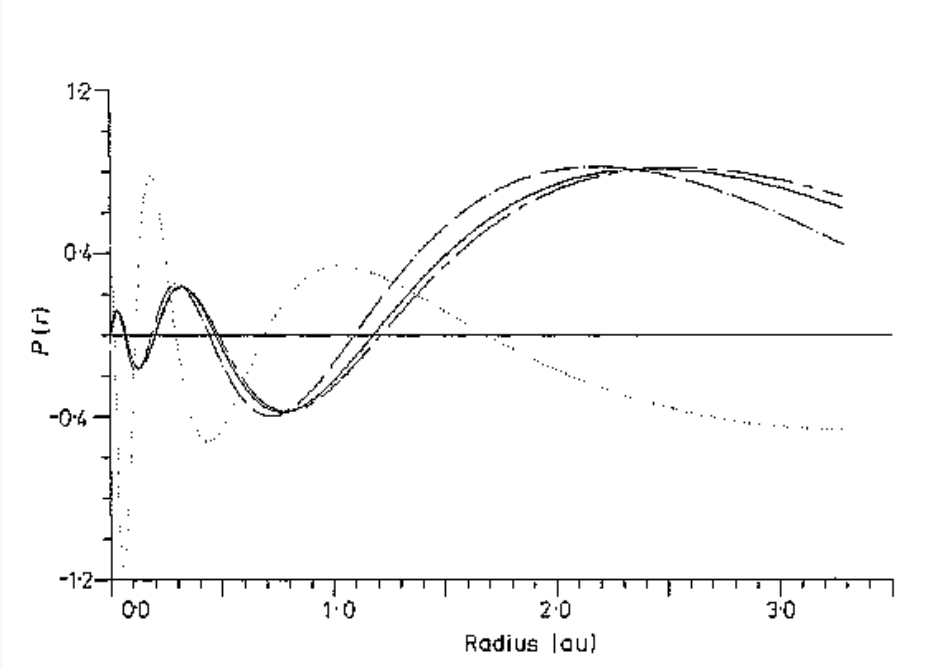
Spin-orbit coupling by second variation

The spin-orbit contribution is restricted to atomic spheres:

$$\frac{1}{4c^2}\left[m+\frac{E-V(r)}{2c^2}\right]^{-2}\frac{1}{r}\frac{dV(r)}{dr}\,\hat{\vec{\sigma}}\cdot\hat{\vec{L}}.$$

The dependence of $\phi(r)$ on κ is neglected. The largest error occurs for p states because the radial functions for $p_{1/2}$ and $p_{3/2}$ are rather different.





Systematic improvement of the basis set

$\phi_l(E_\nu, r)$ with the same logarithmic derivative D_0 form a complete orthogonal set for D_0.

$$\dot{D} = S \left.\frac{\dot{\phi}_l'(E_\nu, r)}{\dot{\phi}_l(E_\nu, r)}\right|_S \neq S \left.\frac{\phi_l'(E_\nu, r)}{\phi_l(E_\nu, r)}\right|_S$$

A function with arbitrary D can be represented by a convergent series

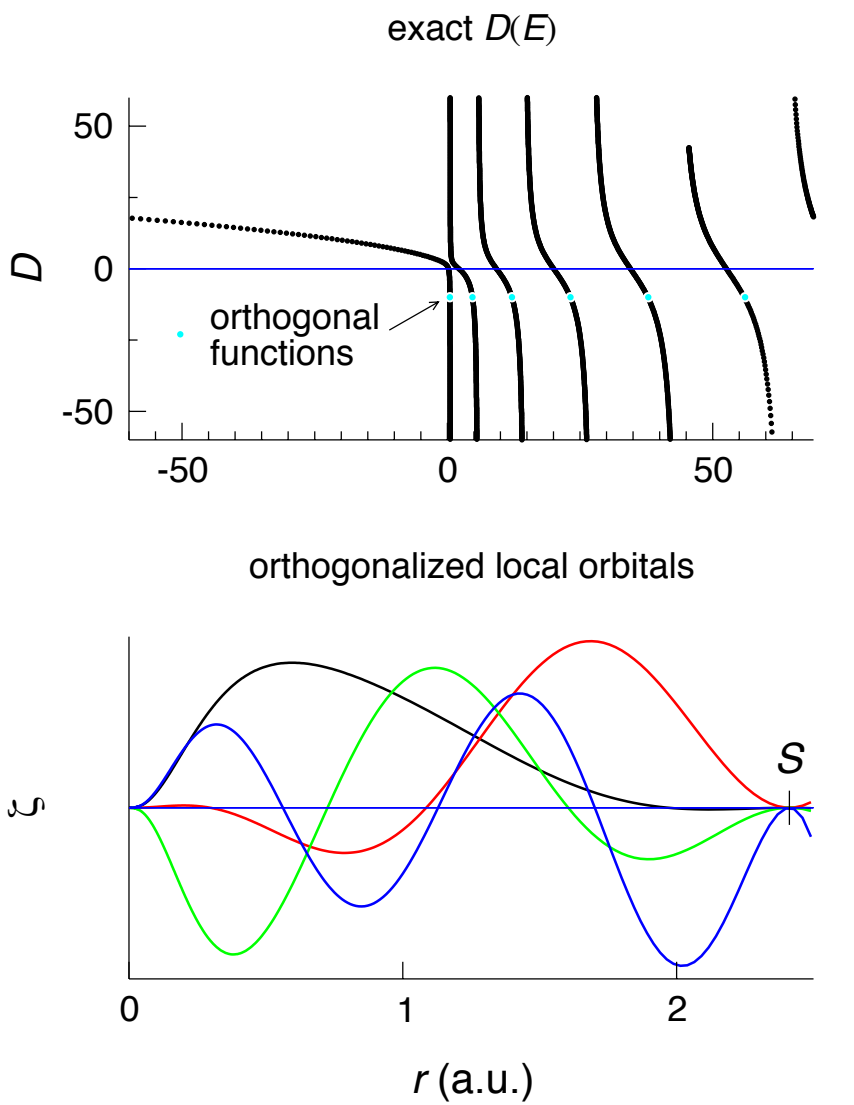
$$R_{lm} = \dot{\phi}_{\nu_0 l} + \sum_\nu a_\nu \phi_{\nu l}.$$

In terms of local orbitals

$$\zeta_{\nu l}(S) = \zeta_{\nu l}'(S) = 0$$

the matching term separates out:

$$R_{lm} = \phi_{\nu_0 l} + \omega(D)\dot{\phi}_{\nu_0 l} + \sum_\nu \alpha_\nu \zeta_{\nu l}$$



Accuracy of the radial basis set

Approximate $\phi_l(E,r)$ by a function $\Phi_l(D,r)$ with the same logarithmic derivative.

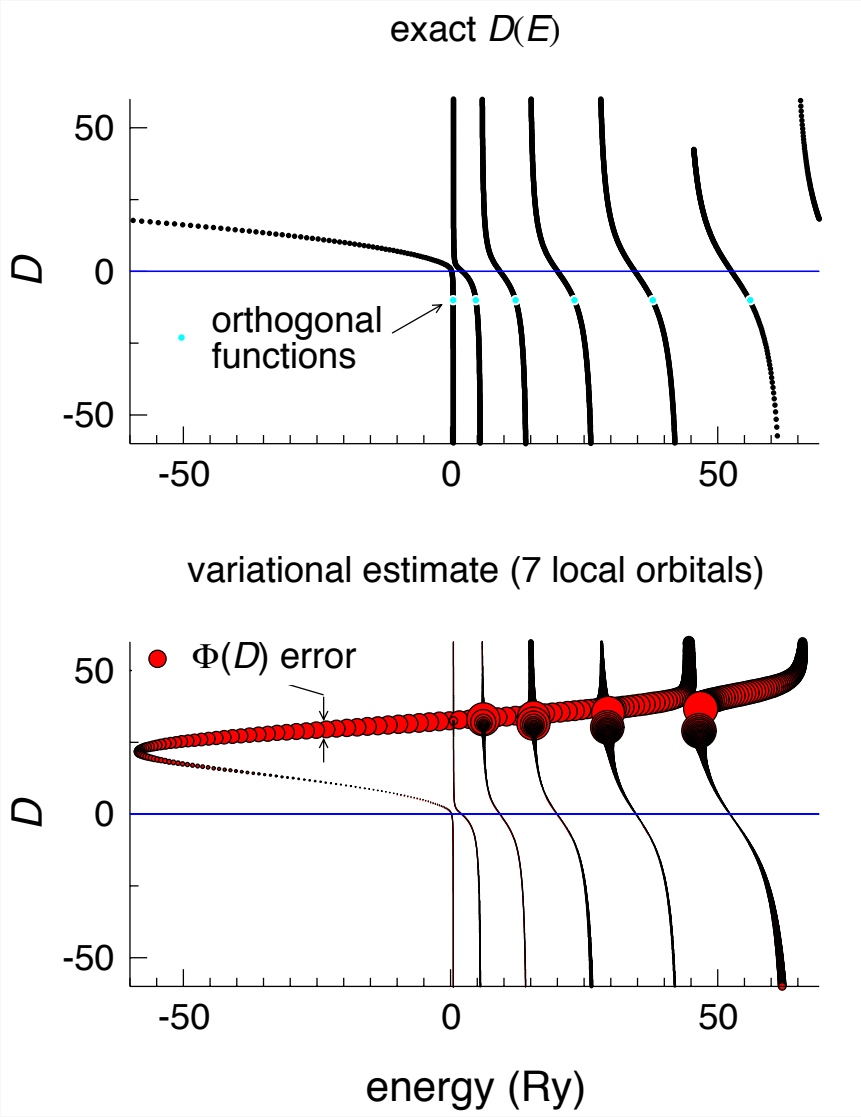
Apply the variational method:

$$\min \frac{\langle\, \Phi_l(D) \mid \hat{H}_r \mid \Phi_l(D)\,\rangle}{\langle\, \Phi_l(D) \mid \Phi_l(D)\,\rangle} = E(D)$$

with

$$\Phi_l(D) = \phi_{\nu_0 l} + \omega(D)\dot{\phi}_{\nu_0 l} + \sum_\nu \alpha_\nu \zeta_{\nu l}$$

In a certain range of D the stationary solution is wrong.



Accuracy of the radial basis set

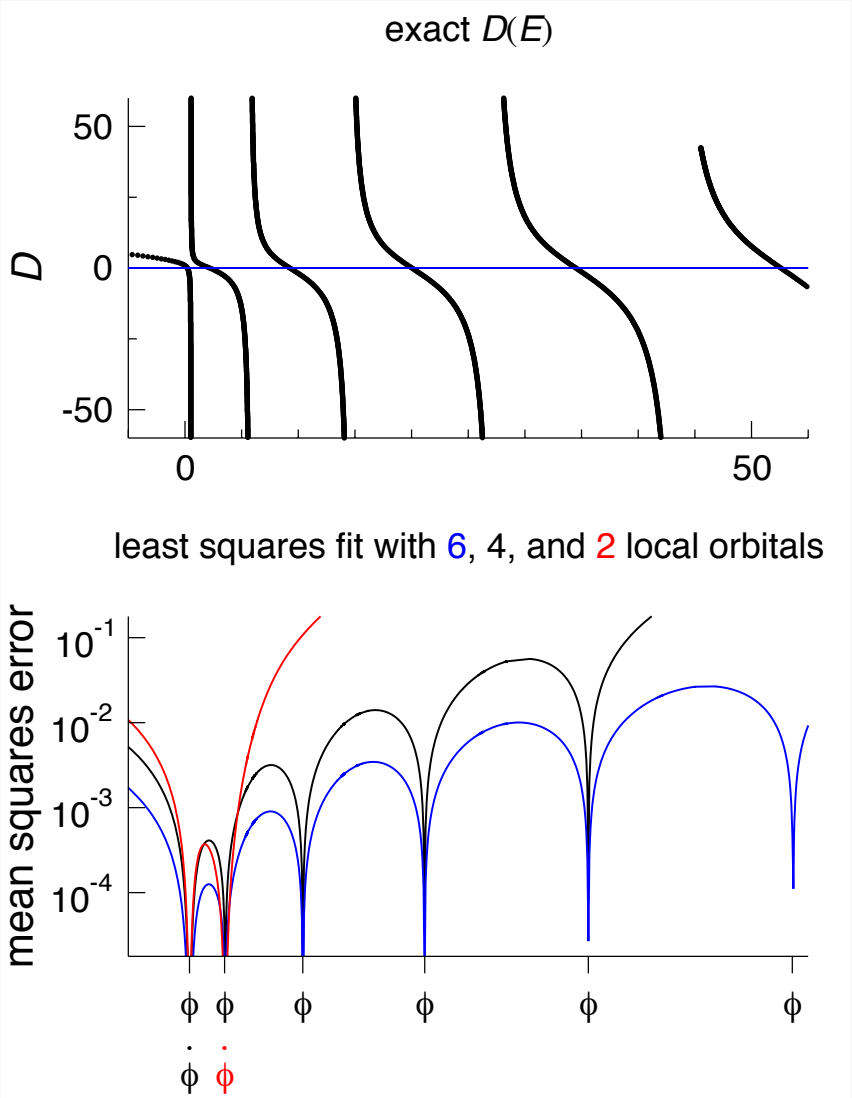
What is the best choice of the additional radial functions (local orbitals)?

The least squares fit (with a free boundary) $\Phi \approx \phi(E)$

$$\Phi = a\phi_{\nu_0} + b\dot{\phi}_{\nu_0} + \sum \alpha_\nu \zeta_\nu$$

mean squares error $= ||\phi_l(E) - \Phi||$

When $\dot{\phi}$ is included the basis set performs much better. Still, the error is very unevenly distributed over the energy region of interest.



Extended linear APW $-$ $\mathbf{k}\cdot\mathbf{p}$ method

$\mathbf{k}$ point independent basis set: for a reference point $\mathbf{k}_0$ construct the APWs; the wave function for a Bloch vector $\mathbf{k}$ is

$$\Psi(\mathbf{k},\mathbf{r}) = \exp[\, i(\mathbf{k}-\mathbf{k}_0)\cdot\mathbf{r}\,] \sum C_n(\mathbf{k})\; \psi_n^{\mathbf{k}_0}(\mathbf{r})$$

The eigenvalue problem reads

$$\left\{ \hat{H}^{\mathbf{k}_0} + 2\Delta\mathbf{k}\cdot\hat{\mathbf{p}}^{\mathbf{k}_0} + [\Delta\mathbf{k}^2 - E_\lambda(\mathbf{k})]\; \hat{O}^{\mathbf{k}_0} \right\} \vec{C}_\lambda(\mathbf{k}) = 0,$$

$\mathbf{k}$ may be complex $\Rightarrow$ complex band structure of the semi-infinite crystal.
The matrices do not depend on $\mathbf{k}$:

$$\begin{aligned} H_{ij}^{\mathbf{k}_0} &= \left\langle \psi_i^{\mathbf{k}_0} \left| \hat{H} \right| \psi_j^{\mathbf{k}_0} \right\rangle , \\ O_{ij}^{\mathbf{k}_0} &= \left\langle \psi_i^{\mathbf{k}_0} \mid \psi_j^{\mathbf{k}_0} \right\rangle , \\ \mathbf{p}_{ij}^{\mathbf{k}_0} &= \left\langle \psi_i^{\mathbf{k}_0} \left| -\mathrm{i}\nabla \right| \psi_j^{\mathbf{k}_0} \right\rangle . \end{aligned}$$

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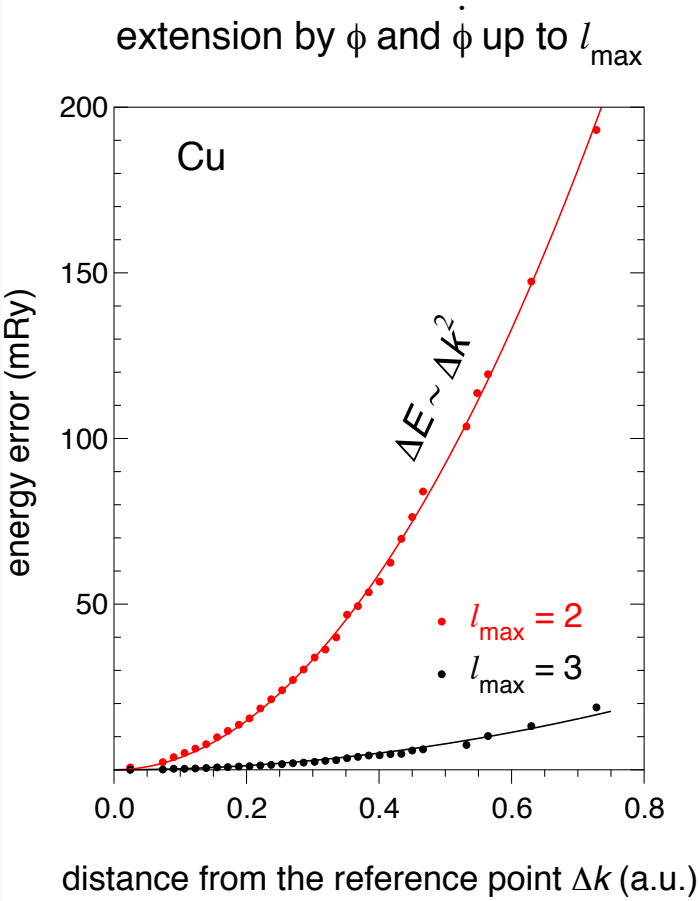
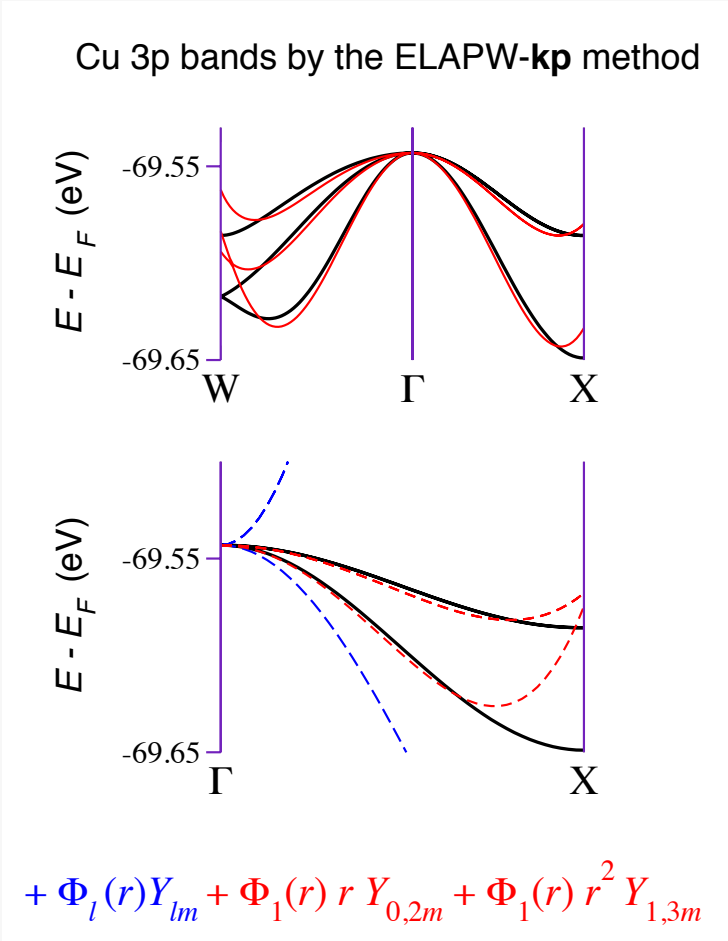
Extended LAPW – $\mathbf{k}\cdot\mathbf{p}$: accuracy

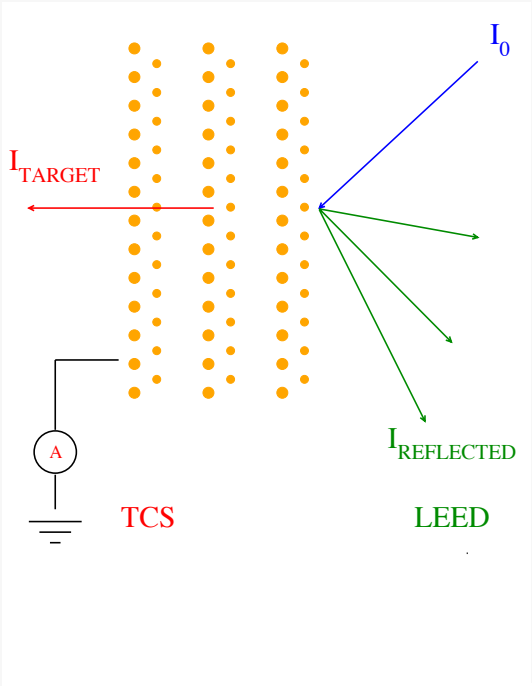




To ensure a high accuracy, the radial basis set has to be extended by functions $r\phi_{l\pm1}(r)$, $r\dot{\phi}_{l\pm1}(r)$, $r^2\phi_{l\pm2}(r)$, etc.

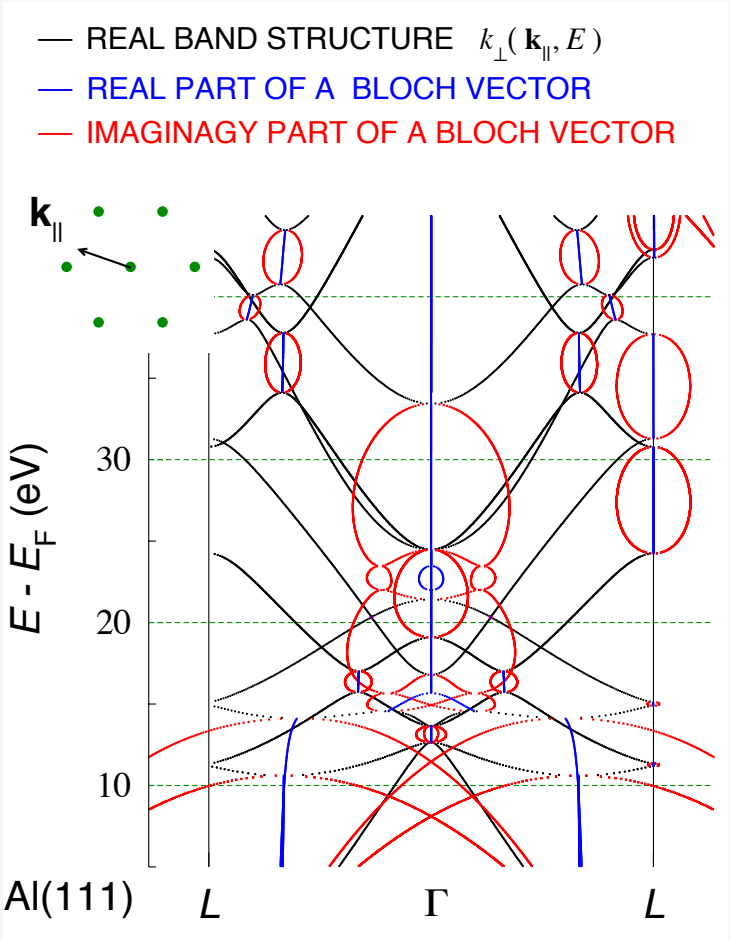
1. E.E. Krasovskii and W. Schattke, Solid State Commun. **93**, 775 (1995).
2. E.E. Krasovskii and W. Schattke, Phys. Rev. B **63**, 235112 (2001).

Electronic structure of semi-infinite crystals



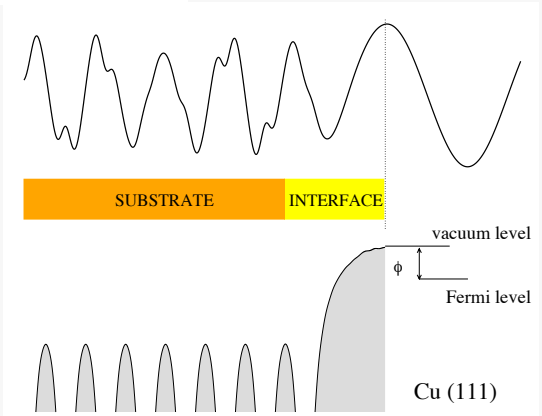
LEED

photoemission



scattering

problem



Solve the Schrödinger equation for a given asymptotics in vacuum.

Inverse ELAPW - $\mathbf{k}\cdot\mathbf{p}$ Method

Given $\mathbf{k}_{\|} = (k_x, k_y)$, and the energy E,
find the $k_\perp$ (real and complex) of propagating and evanescent waves.

A $\mathbf{k}\cdot\mathbf{p}$ method leads to a matrix equation of twice the dimension:

$$\begin{pmatrix} 0 & \hat{H} - E\hat{O} \\ \hat{I} & 2\hat{P}_\perp \end{pmatrix} \begin{pmatrix} \vec{D} \\ \vec{C} \end{pmatrix} = \Delta k_\perp \begin{pmatrix} \hat{I} & 0 \\ 0 & -\hat{O} \end{pmatrix} \begin{pmatrix} \vec{D} \\ \vec{C} \end{pmatrix}.$$

Here $\vec{C}$ is the eigenfunction, and $\vec{D} = -(2\hat{P}_\perp + \Delta k_\perp \hat{O})\vec{C}$

The solutions are orthogonal in the sense that at the plane $z = \text{const}$ the non-diagonal elements of the current operator vanish:

$$\int_S \left[\left(-i\frac{d}{dz}\Psi_n \right) \Psi^*_{n'} - \left(-i\frac{d}{dz}\Psi^*_{n'} \right) \Psi_n \right] \, d\vec{\rho} = 0.$$

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Conclusions and remaining problems

1. With LAPW the Bloch wave function can be obtained with any desired accuracy, but. . .
2. the basis set of energy independents APWs is incomplete,
3. and at the same time the basis set is overcomplete $\Rightarrow$
   the eigenvalue problem may be unstable, especially at $KS \to \infty$.
   - How to optimize the APW basis in the interstitial?
4. Accuracy can be systematically improved by local orbitals.
   - How to optimally construct the local orbitals?
5. The basis functions – APWs – are neither intuitive, nor are they eigenfunctions of any reasonable operator.
   - Can we construct an equivalent basis set, but more physical?
6. - May LAPW be faster?