

# *Ab initio* methods in solid state physics

Przemek Piekarz and Paweł T. Jochym

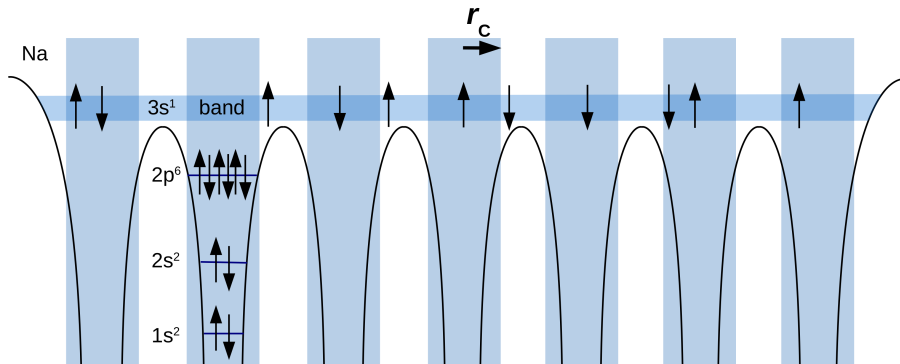
Computational Materials Science  
Institute of Nuclear Physics  
Polish Academy of Sciences  
Kraków

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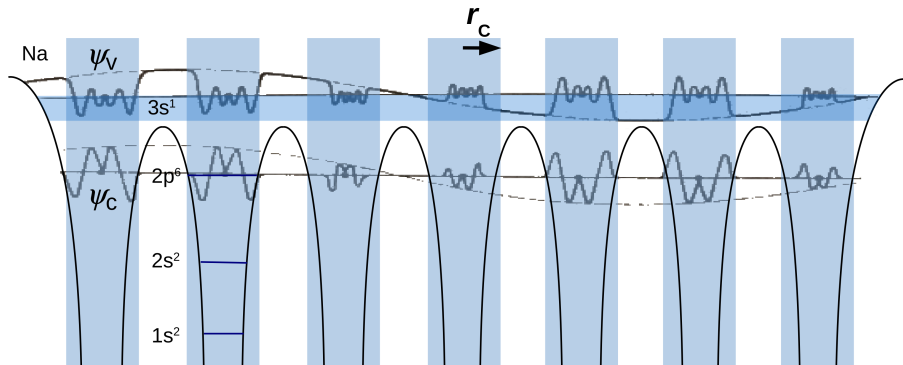
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# Core and valence electrons



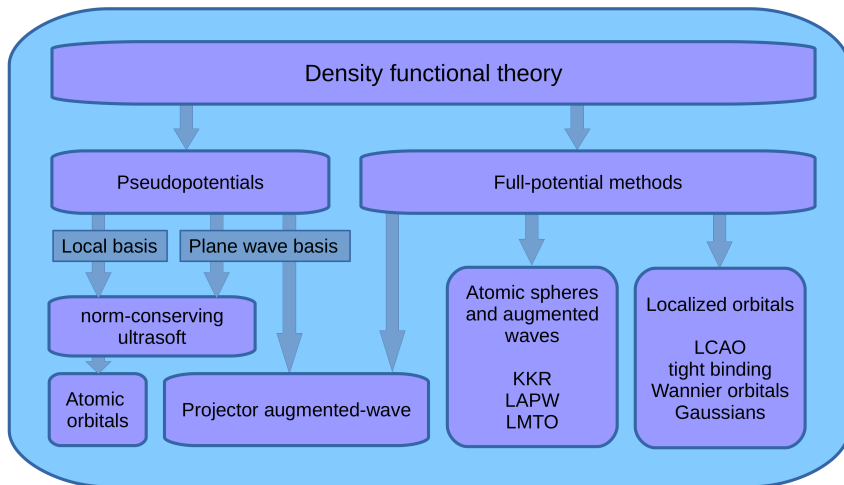
**Figure :** The core states and valence band in the Na crystal.  $r_c$  is the core cut-off radius.

# Core and valence electrons

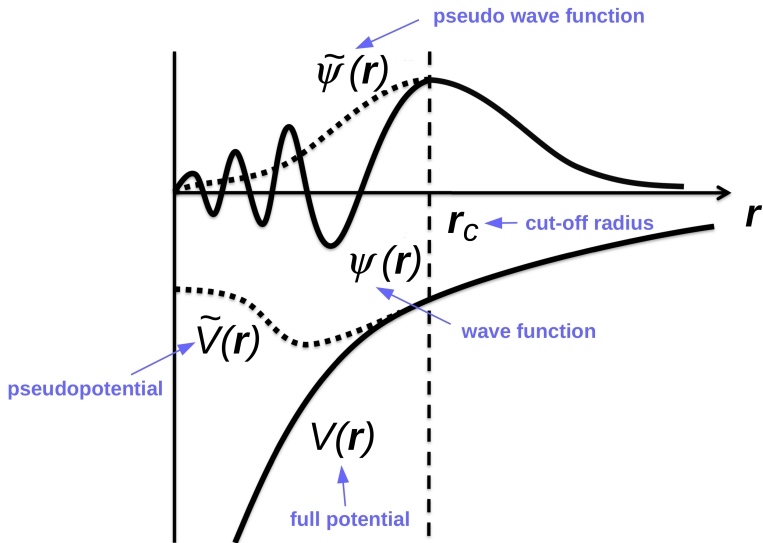


**Figure :** Bloch functions of the core  $\psi_c$  and valence  $\psi_v$  states in the core and interstitial regions.

# Electronic structure calculation methods



# Pseudopotential and pseudo wave function



# Pseudopotential and pseudo wave function

- C. Herring, Phys. Rev. **57**, 250 (1940) - orthogonalized plane waves (OPW).  
E. Antoncik, Czech. J. Phys. **4**, 439 (1954).  
J. C. Philips and L. Kleiman, Phys. Rev. B **116**, 287 (1959).

We consider the valence states  $|\psi_v\rangle$  and core states  $|\psi_c\rangle$ , which are the eigenvectors of the Hamiltonian  $H = T + V$  with eigenenergies  $\varepsilon_v$  and  $\varepsilon_c$ . The valence state, which is orthogonal to core states, can be expressed by the pseudo wave function  $\tilde{\psi}_v$

$$|\psi_v\rangle = |\tilde{\psi}_v\rangle + \sum_{\alpha,c} a_\alpha |\psi_{\alpha c}\rangle, \quad (1)$$

where summation is over atoms  $\alpha$  and core states  $c$ . The coefficients  $a_\alpha$  are obtained from the orthogonality condition  $\langle\psi_{\alpha c}|\psi_v\rangle = 0$

$$a_\alpha = -\langle\psi_{\alpha c}|\tilde{\psi}_v\rangle. \quad (2)$$

Using the equation  $H|\psi_v\rangle = \varepsilon_v|\psi_v\rangle$  we obtain

$$H|\tilde{\psi}_v\rangle + \sum_{\alpha,c} a_\alpha \varepsilon_{\alpha c} |\psi_{\alpha c}\rangle = \varepsilon_v |\tilde{\psi}_v\rangle + \sum_{\alpha,c} a_\alpha \varepsilon_v |\psi_{\alpha c}\rangle. \quad (3)$$

# Pseudopotential and pseudo wave function

Finally we get Schrödinger-type equation

$$(H + \sum_{\alpha, c} (\varepsilon_v - \varepsilon_{\alpha c}) |\psi_{\alpha c}\rangle \langle \psi_{\alpha c}|) |\tilde{\psi}_v\rangle = \varepsilon_v |\tilde{\psi}_v\rangle. \quad (4)$$

with the additional core potential

$$V_c = \sum_{\alpha, c} (\varepsilon_v - \varepsilon_{\alpha c}) |\psi_{\alpha c}\rangle \langle \psi_{\alpha c}| \begin{cases} > 0 & r \leq r_c, \\ = 0 & r > r_c. \end{cases} \quad (5)$$

When we add this potential to the original full potential  $V$ , we obtain a new Hamiltonian  $\tilde{H} = T + \tilde{V}$  with the pseudopotential  $\tilde{V} = V + V_c$ .

In the interstitial region, the pseudopotential  $\tilde{V}$  is equal the full potential  $V$ . Within the core region, the strongly varying negative potential  $V$  is weakened by the positive potential  $V_c$ . It enables to expand the pseudo wave function in the plane wave basis in the entire crystal – in core and interstitial regions.



# Hard and soft pseudopotentials

Pseudopotentials and cut-off radius  $r_c$  depend on the quantum number  $l$  and they have non-local character. Generally, we can divide it into the local and non-local parts

$$V_l(r) = V_{\text{loc}}(r) + \delta V_l(r). \quad (6)$$

The nonlocal part exists only in the core region,  $\delta V_l(r) = 0$  for  $r > r_c$ , and all long-distance effects depend only on  $V_{\text{loc}}(r)$ .

Good pseudopotentials should be universal and transferable to other systems. Possibility of choosing  $r_c$  gives flexibility in constructing different pseudopotentials.

Hard pseudopotentials: more exact and universal pseudopotentials with smaller values of  $r_c$  but require more plane waves in the basis (larger cut-off energy).

Soft pseudopotentials: larger  $r_c$ , smaller cut-off energy, and smoother pseudo wave functions.

# Norm-conserving pseudopotentials

D. R. Hamann, M. Schlüter, and C. Chiang, Phys. Rev. Lett. **43**, 1494 (1979).

The norm-conserving pseudopotentials fulfil the following conditions:

- 1 The exact and pseudo wave functions should be equal,  $\psi_i(r) = \tilde{\psi}_i(r)$ , for  $r > r_c$ .
- 2 Their eigenenergies for valence electrons should be equal.
- 3 The exact charge and pseudocharge should be equal in the core region  $r \leq r_c$  (norm conserving)

$$\int_0^{r_c} dr r^2 |\psi_i(r)|^2 = \int_0^{r_c} dr r^2 |\tilde{\psi}_i(r)|^2. \quad (7)$$

- 4 Logarithmic derivative of the exact and pseudo wave functions should be equal at  $r_c$

$$\frac{1}{\psi_i(r)} \frac{d\psi_i(r)}{dr} = \frac{1}{\tilde{\psi}_i(r)} \frac{d\tilde{\psi}_i(r)}{dr}. \quad (8)$$

# Ultrasoft pseudopotentials

D. Vanderbilt, Phys. Rev. B **41**, 7892 (1990).

Pseudo wave functions are solutions of the generalized eigenequation

$$H|\tilde{\psi}_i\rangle = \varepsilon_i S|\tilde{\psi}_i\rangle, \quad (9)$$

where Hamiltonian has the form

$$H = -\frac{\hbar^2}{2m}\nabla^2 + V_{\text{loc}} + \delta V_{\text{NL}}, \quad (10)$$

with the overlap operator

$$S = 1 + \sum_{i,j} Q_{ij} |\beta_i\rangle \langle \beta_j|, \quad (11)$$

which defines the generalized condition of normalization  $\langle \tilde{\psi}_i | S | \tilde{\psi}_j \rangle = \delta_{ij}$ . Macierz  $Q_{ij}$  opisuje różnicę w normalizacji funkcji i pseudofunkcji falowych

$$Q_{ij} = \int_0^{r_c} dr Q_{ij}(\mathbf{r}) = \int_0^{r_c} dr r^2 [\psi_i^*(\mathbf{r}) \psi_j(\mathbf{r}) - \tilde{\psi}_i^*(\mathbf{r}) \tilde{\psi}_j(\mathbf{r})]. \quad (12)$$

# Ultrasoft pseudopotentials

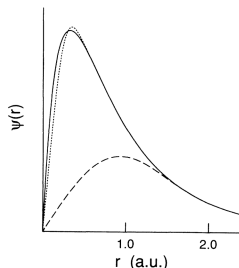
Local functions, which vanish for  $r > r_c$ , are obtained from pseudo wave functions,

$$|\beta_i\rangle = \sum_j (B^{-1})_{ij} |\chi_j\rangle = \sum_j (B^{-1})_{ij} (\varepsilon_i + \frac{\hbar^2}{2m} \nabla^2 - V_{\text{loc}}) |\tilde{\psi}_j\rangle \quad (13)$$

Nonlocal part of the potential is obtained from  $\delta V_{\text{NL}} = \sum_{ij} D_{ij} |\beta_i\rangle \langle \beta_j|$ , where  $D_{ij} = B_{ij} + \varepsilon_j Q_{ij}$ . Total electron density is equal

$$n_v(\mathbf{r}) = \sum_i \tilde{\psi}_i^*(\mathbf{r}) \tilde{\psi}_i(\mathbf{r}) + \sum_{i,j} \sum_k \langle \beta_i | \tilde{\psi}_k \rangle \langle \tilde{\psi}_k | \beta_j \rangle Q_{ij}(\mathbf{r}). \quad (14)$$

Comparison of the exact wave function of the  $2p$  orbital in oxygen (solid line) with the norm-conserving (dotted line) and ultrasoft pseudopotential (dashed line). Cut-off radius for the ultrasoft pseudopotential ( $r_c \approx 1.5$  a.u.) is much larger than for the norm-conserving pseudopotential ( $r_c \approx 0.5$  a.u.).



# Projector augmented-wave (PAW) method

P. E. Blöchl, Phys. Rev. B **50**, 17953 (1994).

The main advantage of the PAW method is that the exact wave function can be obtained from the pseudo wave function using the linear transformation

$$|\psi_v\rangle = \mathcal{T}|\tilde{\psi}_v\rangle = (1 + \sum_m \mathcal{T}_m)|\tilde{\psi}_v\rangle, \quad (15)$$

where linear operators  $\mathcal{T}_m$  act in core regions  $r \leq r_c$  at atomic positions  $\mathbf{R}_m$ . We expand both functions in the core region using local bases  $|\phi_m\rangle$  and  $|\tilde{\phi}_m\rangle$

$$|\psi_v\rangle = \sum_m c_m |\phi_m\rangle, \quad (16)$$

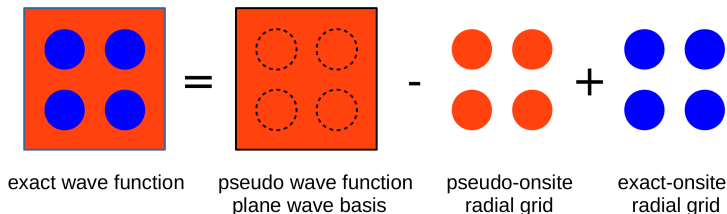
$$|\tilde{\psi}_v\rangle = \sum_m c_m |\tilde{\phi}_m\rangle, \quad (17)$$

with the same coefficients  $c_m$ , so they are connected by the same transformation  $|\phi_m\rangle = (1 + \sum_m \mathcal{T}_m)|\tilde{\phi}_m\rangle$ , and they are equal  $|\phi_m\rangle = |\tilde{\phi}_m\rangle$  for  $r > r_c$ .

# Projector augmented-wave (PAW) method

$|\phi_m\rangle$  are solutions of the Schrödinger equation for the exact atomic potential, orthogonal to the core states. To each  $|\phi_m\rangle$  state corresponds one pseudo state  $|\tilde{\phi}_m\rangle$ . Subtracting (16) and (17) we get

$$|\psi_v\rangle = |\tilde{\psi}_v\rangle - \sum_m c_m |\tilde{\phi}_m\rangle + \sum_m c_m |\phi_m\rangle. \quad (18)$$



# Projector augmented-wave (PAW) method

Operator  $\mathcal{T}$  is linear provided that coefficients  $c_m$  are linear functionals of  $|\tilde{\psi}_v\rangle$

$$c_m = \langle \tilde{p}_m | \tilde{\psi}_v \rangle, \quad (19)$$

where  $\langle \tilde{p}_m |$  are projectors dual to pseudo states  $\langle \tilde{p}_m | \tilde{\phi}_n \rangle = \delta_{mn}$ , with the condition  $\sum_m |\tilde{\phi}_m\rangle \langle \tilde{p}_m| = 1$ . Introducing (19) to (18) we get

$$|\psi_v\rangle = |\tilde{\psi}_v\rangle + \sum_m (|\phi_m\rangle - |\tilde{\phi}_m\rangle) \langle \tilde{p}_m | \tilde{\psi}_v \rangle = [1 + \sum_m (|\phi_m\rangle - |\tilde{\phi}_m\rangle) \langle \tilde{p}_m |] |\tilde{\psi}_v\rangle, \quad (20)$$

from which we obtain the linear operator

$$\boxed{\mathcal{T} = 1 + \sum_m \mathcal{T}_m = 1 + \sum_m (|\phi_m\rangle - |\tilde{\phi}_m\rangle) \langle \tilde{p}_m|.} \quad (21)$$

Expectation values can be expressed using the exact or pseudo wave functions

$$\langle A \rangle = \sum_n f_n \langle \psi_n | A | \psi_n \rangle = \sum_n f_n \langle \tilde{\psi}_n | \tilde{A} | \tilde{\psi}_n \rangle, \quad (22)$$

where  $f_n$  are occupations of states  $n$ , and  $\tilde{A}$  is pseudo operator calculated from

$$\tilde{A} = \mathcal{T}^\dagger A \mathcal{T} = A + \sum_{i,j} |\tilde{p}_i\rangle (\langle \phi_i | A | \phi_j \rangle - \langle \tilde{\phi}_i | A | \tilde{\phi}_j \rangle) \langle \tilde{p}_j|. \quad (23)$$

# Projector augmented-wave (PAW) method

We can apply it to density operator  $n = |\mathbf{r}\rangle\langle\mathbf{r}|$ , obtaining

$$n(\mathbf{r}) = \tilde{n}(\mathbf{r}) + n^1(\mathbf{r}) - \tilde{n}^1(\mathbf{r}), \quad (24)$$

where

$$\tilde{n}(\mathbf{r}) = \sum_n f_n \langle \tilde{\psi}_n | \mathbf{r} \rangle \langle \mathbf{r} | \tilde{\psi}_n \rangle = \sum_n f_n |\tilde{\psi}_n(\mathbf{r})|^2, \quad (25)$$

$$n^1(\mathbf{r}) = \sum_{n,i,j} f_n \langle \tilde{\psi}_n | \tilde{p}_i \rangle \langle \phi_i | \mathbf{r} \rangle \langle \mathbf{r} | \phi_j \rangle \langle \tilde{p}_j | \tilde{\psi}_n \rangle, \quad (26)$$

$$\tilde{n}^1(\mathbf{r}) = \sum_{n,i,j} f_n \langle \tilde{\psi}_n | \tilde{p}_i \rangle \langle \tilde{\phi}_i | \mathbf{r} \rangle \langle \mathbf{r} | \tilde{\phi}_j \rangle \langle \tilde{p}_j | \tilde{\psi}_n \rangle, \quad (27)$$

where the summations are over the valence and core states. PAW belongs to the most accurate and effective methods. It is implemented in Vienna Ab Initio Simulation Package (VASP) and Quantum Espresso.



# Recipe for electronic band structure

- 1 Optimize the electronic and crystal structure using the pseudo wave function expanded in the plane wave basis

$$\tilde{\psi}_{kj}^{\sigma}(\mathbf{r}) = \sum_m \tilde{c}_{jm}^{\sigma}(\mathbf{k}) e^{i(\mathbf{k} + \mathbf{G}_m)\mathbf{r}}, \quad (28)$$

by solving the KS eigenequation

$$\sum_n H_{mn} \tilde{c}_{jn}^{\sigma}(\mathbf{k}) = \varepsilon_{j\sigma}(\mathbf{k}) \tilde{c}_{jm}^{\sigma}(\mathbf{k}). \quad (29)$$

- 2 For the relaxed crystal structure, calculate the charge density  $n(\mathbf{r})$  within the self-consistent electronic loop.
- 3 Using this precalculated charge density, obtain the KS energies  $\varepsilon_{j\sigma}(\mathbf{k})$  by solving Eq. (29) for selected points (paths) in the reciprocal space. This is non-self-consistent calculation, in which the charge density and potential are kept fixed.

# Example: band structures of iron and cobalt

A. Kobiałka, P. Piekarz, A. M. Oleś,  
and A. Ptok, Phys. Rev. B **100**,  
205143 (2020).

Quantum Espresso

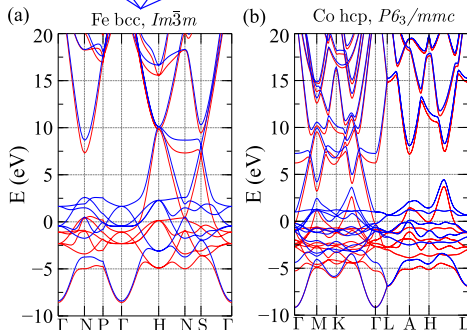
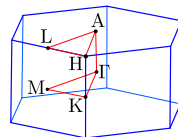
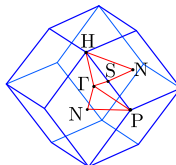
GGA-PBE, MP  $k$ -point grids:

Fe  $12 \times 12 \times 12$

Co  $12 \times 12 \times 4$

First Brillouin zones and band  
structures of the Fe and Co crystals.  
Red and blue colors denote states  
with spin up and down.

Fermi level is located at zero energy.



# Electronic density of states

The electronic density of states (DOS) for  $\sigma$  spin component is calculated by summation over the (irreducible) Brillouin zone

$$\rho_{\sigma}(E) = \frac{1}{N_k} \sum_{j,\mathbf{k}} \delta(\varepsilon_{\mathbf{k}j}^{\sigma} - E), \quad (30)$$

and the total DOS is equal to  $\rho(E) = \sum_{\sigma} \rho_{\sigma}(E)$ . DOS can be calculated using the Monkhorst-Pack grid but usually we use the tetrahedron method, in which the Brillouin zone is divided into tetrahedra and summation is performed over the points  $\mathbf{k}$  being the corners of tetrahedra. The energies at other points are obtained by the linear interpolation.

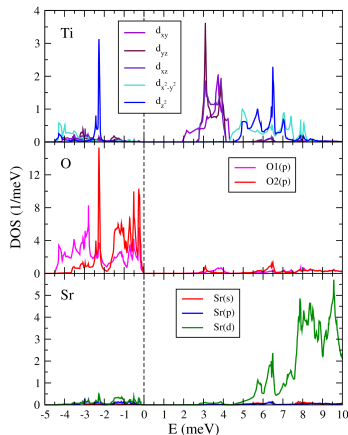
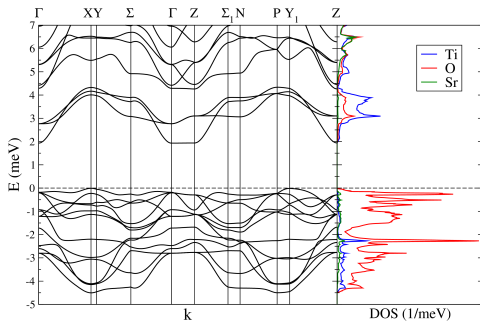
The projected/partial density of states is the relative contribution of a particular atom or orbital  $\phi_n$  to the total DOS

$$\rho_{n\sigma}(E) = \frac{1}{N_k} \sum_{j,\mathbf{k}} |\langle \phi_n | \psi_{\mathbf{k}j} \rangle|^2 \delta(\varepsilon_{\mathbf{k}j}^{\sigma} - E). \quad (31)$$

# Example: $\text{Sr}_2\text{TiO}_4$

K. Rościszewski, P. Piekarz, A. M. Oleś, Phys. Stat. Sol. B **254**, 1700022 (2017).

VASP, GGA-PBE, MP grid:  $10 \times 10 \times 10$ .



# Local orbitals: Wannier representation

Wannier function is a Fourier transform of the Bloch function

$$w_{j\sigma}(\mathbf{r} - \mathbf{R}_n) = \frac{1}{\sqrt{N}} \sum_{\mathbf{k}} e^{-i\mathbf{k}\mathbf{R}_n} \psi_{\mathbf{k}j}^{\sigma}(\mathbf{r}). \quad (32)$$

Wannier functions centered on different atoms are orthogonal

$$\begin{aligned} \int d\mathbf{r} w_{j\sigma}^*(\mathbf{r} - \mathbf{R}_n) w_{j\sigma}(\mathbf{r} - \mathbf{R}_m) &= \frac{1}{N} \sum_{\mathbf{k}, \mathbf{k}'} e^{i(\mathbf{k}\mathbf{R}_n - \mathbf{k}'\mathbf{R}_m)} \int d\mathbf{r} \psi_{\mathbf{k}j}^{\sigma*}(\mathbf{r}) \psi_{\mathbf{k}'j}^{\sigma}(\mathbf{r}) \\ &= \frac{1}{N} \sum_{\mathbf{k}, \mathbf{k}'} e^{i(\mathbf{k}\mathbf{R}_n - \mathbf{k}'\mathbf{R}_m)} \delta_{\mathbf{k}\mathbf{k}'} = \frac{1}{N} \sum_{\mathbf{k}} e^{i\mathbf{k}(\mathbf{R}_n - \mathbf{R}_m)} = \delta_{mn}. \end{aligned} \quad (33)$$

They also fulfil the condition of completeness

$$\sum_n w_{j\sigma}^*(\mathbf{r} - \mathbf{R}_n) w_{j\sigma}(\mathbf{r}' - \mathbf{R}_n) = \delta^3(\mathbf{r} - \mathbf{r}'), \quad (34)$$

therefore they create the set of localized basis functions.

# Tight binding model

Energies in band  $j$  can be obtained within the tight binding model

$$\begin{aligned}\varepsilon_{kj}^{\sigma} &= \int d\mathbf{r} \psi_{kj}^{\sigma*}(\mathbf{r}) H \psi_{kj}^{\sigma}(\mathbf{r}) = \frac{1}{N} \int d\mathbf{r} \sum_{n,m} e^{ik(\mathbf{R}_m - \mathbf{R}_n)} w_{j\sigma}^*(\mathbf{r} - \mathbf{R}_n) H w_{j\sigma}(\mathbf{r} - \mathbf{R}_m) \\ &= \frac{1}{N} \sum_n \int d\mathbf{r} w_{j\sigma}^*(\mathbf{r} - \mathbf{R}_n) H w_{j\sigma}(\mathbf{r} - \mathbf{R}_n) \\ &\quad + \frac{1}{N} \sum_{n \neq m} e^{ik(\mathbf{R}_m - \mathbf{R}_n)} \int d\mathbf{r} w_{j\sigma}^*(\mathbf{r} - \mathbf{R}_n) H w_{j\sigma}(\mathbf{r} - \mathbf{R}_m). \quad (35)\end{aligned}$$

It can be written in shorter form introducing on-site energies  $\varepsilon_n$  and hopping parameters  $t_{nm}$

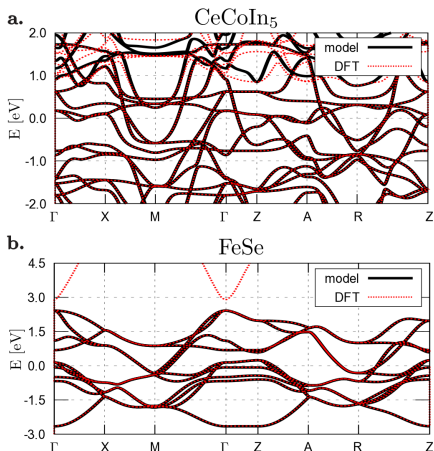
$$\varepsilon_{kj}^{\sigma} = \frac{1}{N} \sum_n \varepsilon_n^{\sigma} + \frac{1}{N} \sum_{n \neq m} e^{ik(\mathbf{R}_m - \mathbf{R}_n)} t_{nm}^{\sigma}. \quad (36)$$

# Example: tight binding model vs DFT

A. Ptok, K. J. Kapcia, P. Piekarz,  
and A. M. Oleś, New J. Phys. **19**,  
063039 (2017).

Quantum Espresso, GGA  
MP grid:  $10 \times 10 \times 10$   
The tight binding model  
in the basis of the maximally  
localized Wannier functions:

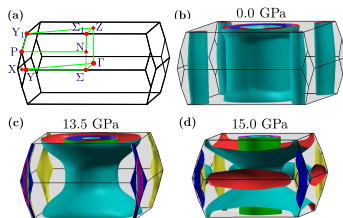
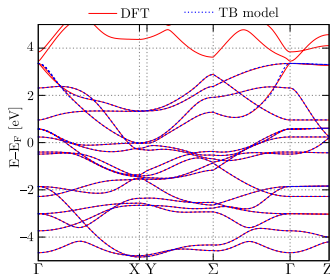
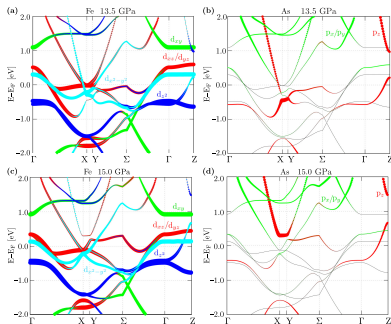
Wannier90 software  
A. A. Mostofi *et al.*,  
Comput. Phys. Commun. **178**  
685 (2008)



# Example: $\text{KFe}_2\text{As}_2$ superconductor

A. Ptok, M. Sternik, K. J. Kapcia, and P. Piekarz Phys. Rev. B **99**, 134103 (2019).

VASP, GGA-PBE, MP grid:  $16 \times 16 \times 8$





# Local orbitals: Gaussian basis

Gauss functions are very convenient because integrals can be calculated analytically. The matrix elements of the Hamiltonian are calculated for the basis

$$G_{ijk}(\mathbf{r}, \alpha, \mathbf{R}_n) = N(x - x_n)^i (y - y_n)^j (z - z_n)^k e^{-\alpha(\mathbf{r} - \mathbf{R}_n)^2}, \quad (37)$$

where  $\alpha$  are variational parameters, which enable to optimize the basis for specific atoms,  $\mathbf{R}_n = (x_n, y_n, z_n)$  are vectors defining the centers of functions, and  $N$  is normalization. The orbital quantum number fulfils the condition  $l = i + j + k$ . The multiplication of two  $s$  functions ( $l = 0$ ) centered at  $\mathbf{R}_n$  and  $\mathbf{R}_m$  gives

$$G_s(\mathbf{r}, \alpha, \mathbf{R}_n) G_s(\mathbf{r}, \beta, \mathbf{R}_m) = e^{-\gamma(\mathbf{R}_n - \mathbf{R}_m)^2} G_s(\mathbf{r}, \kappa, \mathbf{R}_p), \quad (38)$$

where

$$\kappa = \alpha + \beta, \quad \gamma = \frac{\alpha\beta}{\alpha + \beta}, \quad \mathbf{R}_p = \frac{\alpha\mathbf{R}_n + \beta\mathbf{R}_m}{\alpha + \beta}, \quad (39)$$

and  $\mathbf{R}_p$  is a vector centering a new resulting Gauss function. In a general case, the multiplication of two Gauss functions can be written in the form

$$G_{i_1 j_1 k_1}(\mathbf{r}, \alpha, \mathbf{R}_n) G_{i_2 j_2 k_2}(\mathbf{r}, \beta, \mathbf{R}_m) = N e^{-\gamma(\mathbf{R}_n - \mathbf{R}_m)^2} e^{-\kappa(\mathbf{r} - \mathbf{R}_p)^2} \\ \times (x - x_n)^{i_1} (x - x_m)^{i_2} (y - y_n)^{j_1} (y - y_m)^{j_2} (z - z_n)^{k_1} (z - z_m)^{k_2}. \quad (40)$$

# Linearized augmented plane wave (LAPW)

J. C. Slater, Phys. Rev. **51**, 846 (1937) – Augmented plane wave (APW).

O. K. Andersen, Phys. Rev. B **12**, 3060 (1975) – LAPW.

In the LAPW method, wave functions

$$\psi_{\mathbf{k}j}^{\sigma}(\mathbf{r}) = \sum_{\mathbf{G}} c_{\mathbf{G}j}^{\sigma} \phi_{\mathbf{k}+\mathbf{G}}(\mathbf{r}), \quad (41)$$

are expanded in two different bases for the core and interstitial regions

$$\phi_{\mathbf{k}+\mathbf{G}}(\mathbf{r}) = \begin{cases} e^{i(\mathbf{k}+\mathbf{G})\mathbf{r}} & r > r_c \\ \sum_{lm} [A_{lm}(\mathbf{k} + \mathbf{G}) u_l(r, E_l) + B_{lm}(\mathbf{k} + \mathbf{G}) \dot{u}_l(r, E_l)] Y_{lm}(\theta, \varphi) & r \leq r_c, \end{cases} \quad (42)$$

where  $A_{lm}$  and  $B_{lm}$  are coefficients obtained from the conditions of continuity of wave functions and their derivative at  $r_c$ ,  $Y_{lm}(\theta, \varphi)$  are spherical harmonics, while  $u_l(r, E_l)$  and  $\dot{u}_l(r, E_l) = \partial u_l / \partial E$  are solutions of the equations

$$\left[ -\frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} + V(r) - E_l \right] r u_l(r, E_l) = 0, \quad (43)$$

$$\left[ -\frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} + V(r) - E_l \right] r \dot{u}_l(r, E_l) = r u_l(r, E_l). \quad (44)$$

# Linearized augmented plane wave (LAPW)

Potential  $V(r)$  can be approximated by the *muffin-tin* (MT) potential, in which the core part is spherically symmetric and the interstitial part is constant ( $V(\mathbf{r}) = V_0$ ). Within the self-consistent method, the full potential is calculated in the core and interstitial regions using two basis

$$V(\mathbf{r}) = \begin{cases} \sum_{\mathbf{G}} V_{\mathbf{G}} e^{i\mathbf{G}\mathbf{r}} & r > r_c \\ \sum_{lm} V_{lm} Y_{lm}(\theta, \phi) & r \leq r_c. \end{cases} \quad (45)$$

The LAPW method can take into account the pseudo-core states by including additional local orbitals (lo) in the basis for  $r \leq r_c$ . This approach is called the APW+lo method [D. Singh, Phys. Rev. B **43**, 6388 (1991)].

The derivative of the radial function  $\dot{u}_l$  is removed from the main basis and attach to lo in the form

$$\chi_L^{lo}(\mathbf{r}) = [a_{lm}^{lo} u_l(r, E_l) + b_{lm}^{lo} \dot{u}_l(r, E_l)] Y(\theta, \varphi), \quad (46)$$

where coefficients  $a_{lm}^{lo}$  and  $b_{lm}^{lo}$  are chosen in this way that lo vanish at the sphere. The orbital quantum number is restricted here to  $l \leq 3$ .