Solid State Theory: Band Structure Methods

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Wed., 11:15-12:45

HS P3 (PH02112)

http://itp.tugraz.at/LV/boeri/ELE/

- DFT1+2: Hohenberg-Kohn Theorem and Kohn and Sham equations.
- DFT3+4: Solving K-S in practice; basis functions, augmented methods and psp theory.
- DFT5: Practical problems in DFT (k space integration, convergence etc)
- P1: EOS and band structure of silicon.
- ADV1+2: Linear Response theory (mostly for phonons).
- P2: Phonons of silicon
- ADV3: Wannier Functions and TB approximation.
- P3: Wannier Functions and BOM for silicon.

Main Concepts of Density Functional Theory:

The quantum-mechanical many-electron problem can be greatly simplified if we are only interested in its ground-state properties.

$$\Psi_0(\mathbf{r}_1\sigma_1, ..., \mathbf{r}_N\sigma_N) \quad \Rightarrow \quad n_0^\sigma(\mathbf{r}) = \sum_{\sigma_2 ... \sigma_N} \int d^3r_2 ... d^3r_N \, |\Psi_0(\mathbf{r}\sigma, ..., \mathbf{r}_N\sigma_N)|^2$$

Hohenberg-Kohn Theorem: The ground-state energy of a system of interacting electrons is a function of its ground-state density only. The complications induced by the electron-electron interaction are “dumped” into an effective exchange and correlation energy, whose exact form is unknown (but good approximation exists).

Kohn-Sham Equations: It is possible to find the ground-state density of the interacting system solving self-consistently a system of single-particle equations for the **auxiliary (effective) Kohn-Sham quasi-particles**.

Kohn-Sham Equations:

In the (spin-)density functional method, we seek the ground-state total energy E and the spin densities for a collection of N electrons which interact with each other, and with a given external potential (typically a sum of nuclear potentials). The energy and densities can be found **by self-consistent (scf) solution of a set of equations for the fictitious Kohn-Sham Orbitals and the ground state density.**

$$\left(-\frac{1}{2}\nabla^2 + v(\mathbf{r}) + u([n];\mathbf{r}) + v_{xc}^{\sigma}([n_\uparrow, n_\downarrow];\mathbf{r})\right)\psi_{\alpha\sigma}(\mathbf{r}) = \epsilon_{\alpha\sigma}\psi_{\alpha\sigma}(\mathbf{r})$$

$$n_\sigma(\mathbf{r}) = \sum_\alpha \theta(\mu - \varepsilon_{\alpha\sigma})\left|\psi_{\alpha\sigma}(\mathbf{r})\right|^2$$

1. **Start from a set of "guess functions".**
2. **Calculate the corresponding charge density.**
3. **Compute the Hartree and xc potentials**
4. **Insert into the Schoedinger equations.**

Iterate until the charge densities at step *t* and *(t+1) differ by less than a given threshold*

Please check the web page of the course for updated references!!!

Solving Kohn-Sham Equations in Practice (DFT 3-4):

- Charge self-consistency (mixing).
- Atoms: solution of the radial equations.
- Solids: Bloch Theorem.
- Basis functions and secular equations: Kohn-Sham equations for plane waves.

For these topics I will follow "A primer in Density Functional Theory" (Springer), chapters 6.

Kohn-Sham Equations:

$$\left(-\frac{1}{2}\nabla^2 + v(\mathbf{r}) + u([n];\mathbf{r}) + v_{xc}^{\sigma}([n_\uparrow, n_\downarrow];\mathbf{r})\right)\psi_{\alpha\sigma}(\mathbf{r}) = \epsilon_{\alpha\sigma}\psi_{\alpha\sigma}(\mathbf{r})$$

$$n_\sigma(\mathbf{r}) = \sum_\alpha \theta(\mu - \varepsilon_{\alpha\sigma})\,|\psi_{\alpha\sigma}(\mathbf{r})|^2$$

Iterate up to self-consistency, i.e. until the charge density (or the total energy) at iteration t and t+1 coincide.

In principle simple, BUT several practical problems arise:

1) How do we ensure the **stability** of the self-consistent loop?

2) How do we handle in practice the different terms of the K-S potential?

Convergence of the scf loop:

To start the self-consistent loop, we need a "good guess" for the charge density. For solids, this good be a sum of atomic densities:

$$n_0(\mathbf{r}) = \sum_\alpha n_\alpha(\mathbf{r} - \mathbf{R}_\alpha)$$

The self-consistent loop is stopped when:

$$\left|E^{t+1} - E^t\right| < \varepsilon_E$$

OR

$$\int d^3r \left|n^{t+1}(\mathbf{r}) - n^t(\mathbf{r})\right| < \varepsilon_n$$

If the exit criterion is not met, the scf loop is restarted. In principle one could use n^t as the new starting density; however this procedure is often **unstable**…

Mixing of the charge density:

To stabilize the scf loop, we can use a mixing of the charge density at the (t+1)-*th* and t-*th* iteration (**linear mixing**)…

$$n'^{(i+1)} = \alpha n^{(i+1)} + (1-\alpha) n^{(i)}$$

α is the **mixing parameter** (typically 0.2-0.3). Increases the mixing parameter increases the speed of convergence, but may lead to instabilities. Other mixing schemes (Broyden, Anderson) use a more refined schemes which take into account "older steps". Linear mixing is typically slower but more stable than these approaches.

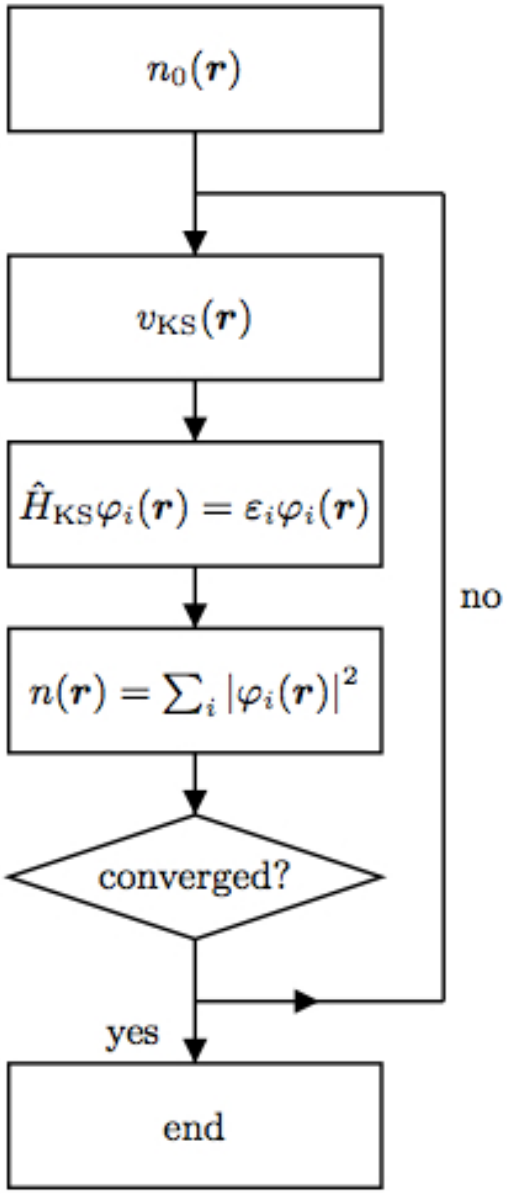


Fig. 6.1. Flow-chart depicting a generic Kohn-Sham calculation

Kohn-Sham Equations for Atoms:

Atoms are the only case in which K-S equations can be solved directly (i.e. integrating the differential equations). Even though DFT (LDA, GGA) is not particularly good for atoms, this is an important reference system since many approximations for solids are based on the solution of the atomic problem. One assumes that the charge density n(r) is spherically symmetric, and thus:

$$\varphi_i(\mathbf{r}) = Y_{nl}(\vartheta,\varphi)R_{nl}(r)$$

Y_{nl} are the spherical harmonics; for the **radia**l part, we obtain a second-order differential equation (1-d):

$$\left[-\frac{1}{2}\frac{d^2}{dr^2} - \frac{1}{r}\frac{d}{dr} + \frac{l(l+1)}{2r^2} + v_{KS}(r)\right]R_{nl}(r) = \varepsilon_{nl}R_{nl}(r)$$

Which is the usual equation for the hydrogenoid atoms, with $-Z/r \rightarrow v_{KS}(r)$.

Also in this case, the solution is not easy to obtain numerically; one exploits the fact that the asymptotic behaviours for large and small r are known:

$$R_{nl}(r) \underset{r\to 0}{\longrightarrow} Ar^{l}$$

$$R_{nl}(r) \underset{r\to \infty}{\longrightarrow} \exp\left(-\sqrt{-2\varepsilon_{nl}}r\right)$$

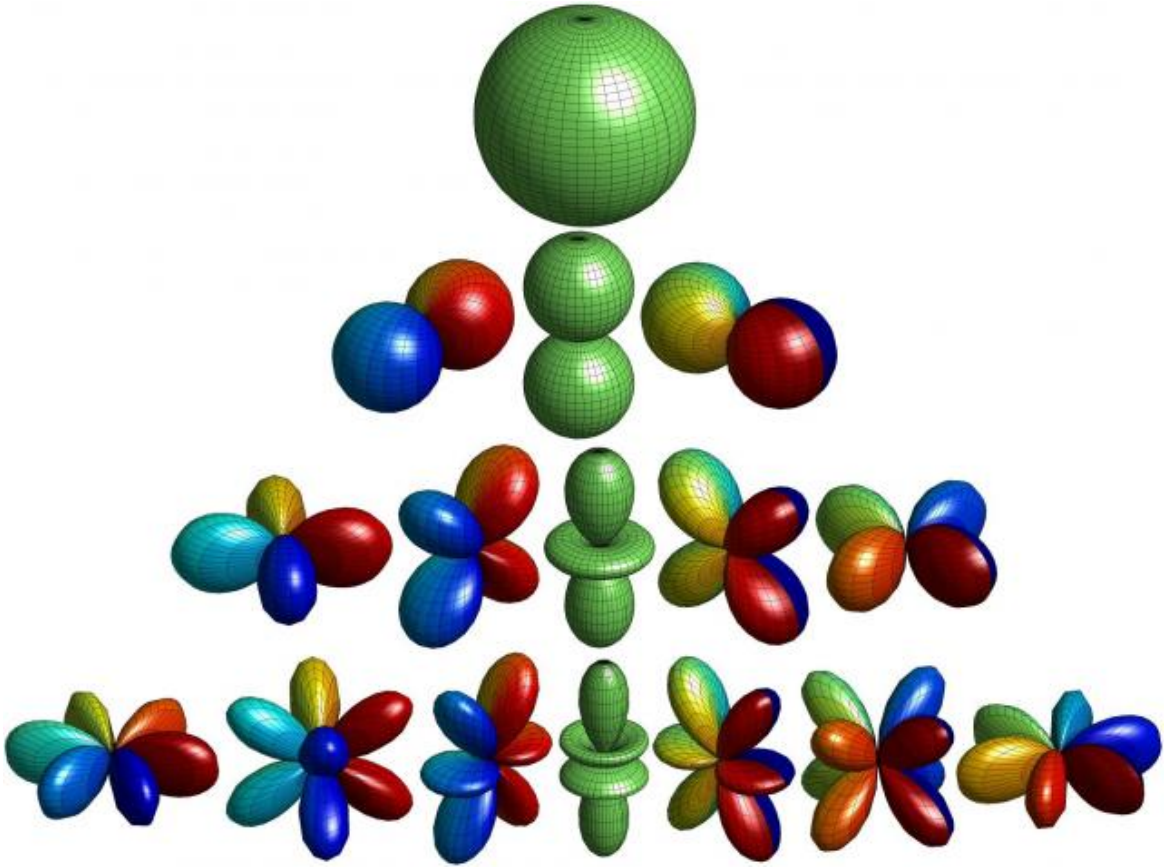
PROOF:

And looks for a function which interpolates in-between:

i) Choose an arbitrary value for ε_{nl} and $f_{nl}(r_\infty)$;
ii) Calculate $g_{nl}(r_\infty)$ using the boundary conditions (6.19);
iii) Integrate (6.17) from r_∞ to r_m (to get $f_{nl}^{\rm in}(r)$ and $g_{nl}^{\rm in}(r)$);
iv) Choose an arbitrary value for A, calculate $B = lA$, and use the boundary conditions (6.20) to get $f_{nl}(0)$ and $g_{nl}(0)$;
v) Integrate (6.17) from 0 to r_m (to get $f_{nl}^{\rm out}(r)$ and $g_{nl}^{\rm out}(r)$);
vi) Calculate $\gamma = g_{nl}^{\rm in}(r_m)/g_{nl}^{\rm out}(r_m)$ and scale $f_{nl}^{\rm out}(r)$ and $g_{nl}^{\rm out}(r)$ by this factor – now $g_{nl}(r)$ is continuous at the matching point ($\tilde{g}_{nl}^{\rm out}(r_m) \equiv \gamma g_{nl}^{\rm out}(r_m) = g_{nl}^{\rm in}(r_m)$) but $f_{nl}(r)$ is not;
vii) Compute $\delta(\varepsilon_{nl}) = f_{nl}^{\rm out}(r_m) - f_{nl}^{\rm in}(r_m)$: The zeros of this function are the eigenvalues, so one can find them using, e.g., the bisection method (one has to provide an educated guess for the minimum and maximum value of the eigenvalues).

Atoms: spherical harmonics

$$Y_{lm}(\vartheta,\varphi) = \alpha e^{im\varphi} P_l^m(\cos\vartheta)$$



Atoms: radial wavefunctions

$$R_{10} = 2\left(\frac{Z}{a_0}\right)^{\frac{3}{2}} e^{-Zr/a_0}$$

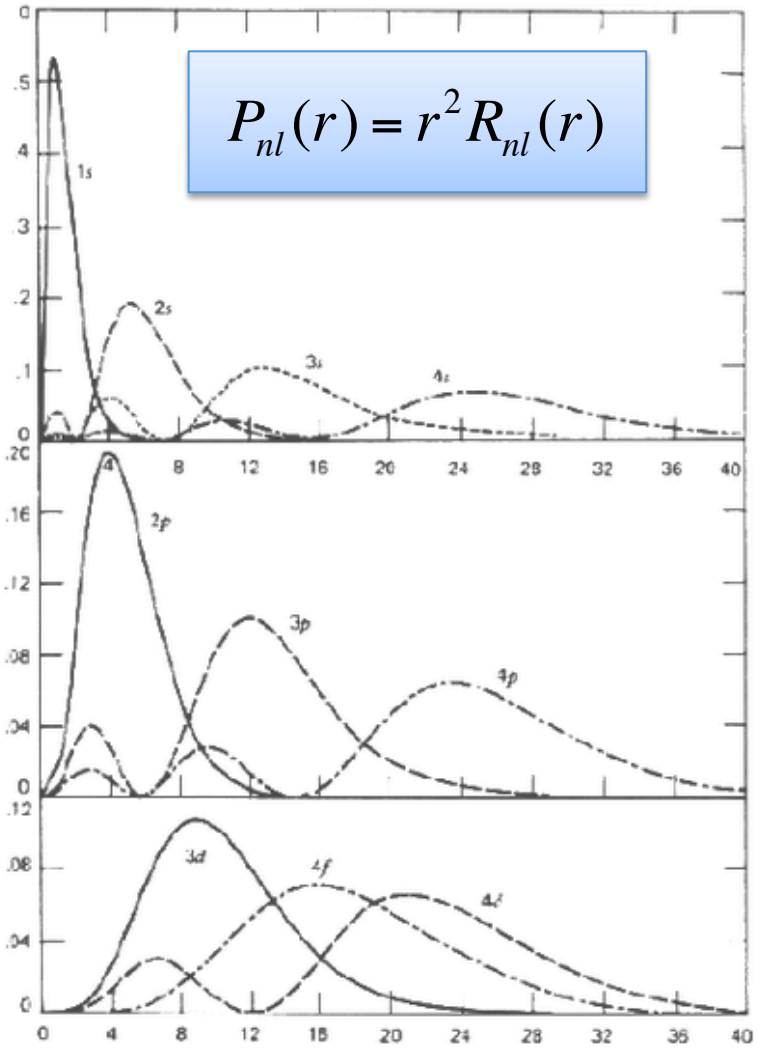
$$R_{21} = \frac{1}{\sqrt{3}}\left(\frac{Z}{2a_0}\right)^{\frac{3}{2}}\left(\frac{Zr}{a_0}\right) e^{-Zr/2a_0}$$

$$R_{20} = 2\left(\frac{Z}{2a_0}\right)^{\frac{3}{2}}\left(1-\frac{Zr}{2a_0}\right) e^{-Zr/2a_0}$$

$$R_{32} = \frac{2\sqrt{2}}{27\sqrt{5}}\left(\frac{Z}{3a_0}\right)^{\frac{3}{2}}\left(\frac{Zr}{a_0}\right)^2 e^{-Zr/3a_0}$$

$$R_{31} = \frac{4\sqrt{2}}{3}\left(\frac{Z}{3a_0}\right)^{\frac{3}{2}}\left(\frac{Zr}{a_0}\right)\left(1-\frac{Zr}{6a_0}\right) e^{-Zr/3a_0}$$

$$R_{30} = 2\left(\frac{Z}{3a_0}\right)^{\frac{3}{2}}\left(1-\frac{2Zr}{3a_0}+\frac{2(Zr)^2}{27a_0^2}\right) e^{-Zr/3a_0}$$



Kohn-Sham Equations for Solids:

For **solids**, the charge-density is generally non-symmetric, and one has to solve a differential equations in 3d. This is sometimes done in so-called **real space methods**, using **grids**. Real-space methods are generally powerful, but little used in practice because it is difficult to control the convergence of the calculation with the system size (and because they are typically expensive).

Most methods used in solid state physics exploit **Bloch's theorem** and **lattice periodicity** to work in **reciprocal space**.

Bloch's Theorem:

The excitations in a solid (infinite periodic array of atoms) are **Bloch waves** of the form:

$$\psi_{\tilde{n}}(\mathbf{r}) = \psi_{n\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}\varphi_{n\mathbf{k}}(\mathbf{r})$$

k is a Bloch vector (eigenvalue of the translation operator); φ is a lattice-periodic function:

$$\varphi_{n\mathbf{k}}(\mathbf{r}) = \varphi_{n\mathbf{k}}(\mathbf{r}+\mathbf{R})$$

$$\varphi_{n\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} e^{i\mathbf{G}\cdot\mathbf{R}} c_{n\mathbf{k}}(\mathbf{G})$$

Fourier Transforms of lattice-periodic functions only contain components corresponding to reciprocal lattice vectors!

Basis Functions:

The periodic part of the Bloch function is usually expanded on a basis function; Eigenvalues and Eigenvectors (K-S energies and orbitals) are then obtained solving a secular equation.

$$\varphi_{n\mathbf{k}}(\mathbf{r}) = \sum_{\alpha} c_{n\mathbf{k}}(\alpha) u^{\alpha}_{n\mathbf{k}}(\mathbf{r})$$

The three main sets of basis functions are: **Plane waves** (free-electron theory), **Localized orbitals** (tight-binding theory), **Augmented waves** (in-between). As we will see in the following, the choice of the basis set is also connected to the approximations made to represent the electron-ion potential (Plane wave: pseudopotential, augmented waves: Muffin Tin approximation).