§5.6 LAPW and LCAO methods

§5.6.1 LAPW method.

The Linearized Augmented Plane Wave (LAPW) method can be applied to simplify the solution of the corresponding Schrödinger equation (SE) for periodic (lattices) or non periodical (molecules) structures. The LAPW method was developed as a further development of Augmented Plane Wave (APW) method (Slater ,1937).

The eigenvalue problem for periodical potential is looks like this:

$$\hat{H} \cdot \Psi_j = E_j \cdot \Psi_j$$
 here the Hamiltonian $\hat{H} = \hat{T} + V$ (1)

here \hat{T} -kinetic energy operator, V - periodic potential energy, Ψ_j and E_j is corresponding eigenfunction and eigenvalue.

In periodic structures the wavefunction should satisfy to Bloch theorem it means that generally it can be presented in next form:

$$\Psi_{j}(\vec{r},\vec{k}) = u_{j}(\vec{r},\vec{k})e^{i\vec{k}\cdot\vec{r}}$$
⁽²⁾

here $u_j(\vec{r}, \vec{k}) = u_j(\vec{r} + \vec{R}_n, \vec{k})$ is a periodical part of the total wavefunction. Due to periodicity of $u_j(\vec{r}, \vec{k})$ it can be expanded to Fourier series by this way:

$$u_{j}(\vec{r},\vec{k}) = \sum_{\vec{b}_{g}} C_{j}^{\vec{k},\vec{b}_{g}} e^{i\vec{b}_{g}\vec{r}}$$
(3)

here $C_j^{\vec{k},\vec{b_g}}$ - coefficient of expantion and $\vec{b_g}$ - vector of translations for reciprocal lattice (see lecture 5.2.1). Another simplification can be applied to the method. This is the so-called Muffin-Tin approximation. Within this approximation, the potential V can be divided into two parts. The inner (I) part, where the potential is practically described by the potential of an isolated atom. And the interatomic region (MT), where the periodical function $u_j(\vec{r},\vec{k})$ can be described in the free electron approximation. The border between these two areas looks like a sphere (MT_{sp}) with radius some R_{MT}. For (2) in this case we have:

$$\Psi_{j}(\vec{r},\vec{k}) = \begin{cases} \sum_{\vec{b}_{g}} C_{j}^{\vec{k},\vec{b}_{g}} e^{i(\vec{b}_{g}+\vec{k})\vec{r}} \text{ for } \vec{r} \in MT_{sp} \\ \sum_{\vec{b}_{g}} C_{j}^{\vec{k},\vec{b}_{g}} \sum_{l=0}^{l_{max}} \sum_{m=-l}^{m=+1} a_{l,m}^{\vec{k},\vec{b}_{g}} R_{l} Y_{l,m} \text{ for } \vec{r} \text{ out of } MT_{sp} \end{cases}$$
(4)

here R_1 and $Y_{1,m}$ are hydrogen-like radial and angular wave functions and $\varphi_{\vec{k},\vec{b}_a}$ just additional function to simplify further calculations and include two last sums in equations (4). Formally, the energy of a quantum system can be calculated as follows:

$$E = \frac{\int \Psi^* \hat{H} \Psi \, d\nu}{\int \Psi^* \Psi \, d\nu} \tag{5}$$

After substitution (4) to (5) we get the system of linear equations for coefficients C (instead of differential equation (1)):

$$\sum_{\vec{b}_g} H_{\vec{b}_g, \vec{b}_g}^{\vec{k}} C_j^{\vec{k}, \vec{b}_g} = E_j^{\vec{k}} \sum_{\vec{b}_g} S_{\vec{b}_g, \vec{b}_g}^{\vec{k}} C_j^{\vec{k}, \vec{b}_g}$$
(6)

Here $H_{\vec{b}_g,\vec{b}_g}^{\vec{k}} = \int \varphi_{\vec{k},\vec{b}_g}^* \hat{H} \varphi_{\vec{k},\vec{b}_g} dv$ - matrix elements of Hamiltonian operator \hat{H} , and $S_{\vec{b}_g,\vec{b}_g}^{\vec{k}} = \int \varphi_{\vec{k},\vec{b}_g}^* \varphi_{\vec{k},\vec{b}_g} dv$ is so called overlap matrix. Problem (6) is a system of linear equations for unknown coefficients **C** and can be solved by standard methods of linear algebra. In pure LAPW approximation (2)+(3) the $\varphi(\vec{r})_{\vec{k},\vec{b}_g} = e^{i(\vec{b}_g + \vec{k})\vec{r}}$.

In real calculations on a computer, the high optimized LAPACK library is used for these purposes. There is a high effective and free realization of this library for Intel processors so called MKL library and library ACML for AMD peocessors.

This method is often used in various abinitio programs for searching for energy and wave functions of the electronic subsystem of crystals and molecules.

It makes sense to note that the number of terms in (3) should be quite large, up to tens of thousands. Such a large number is necessary for a more or less accurate representation of the wave function of electrons in crystals. In this case, solving problem (6) requires large computing resources and can be completed only using large computing clusters (supercomputers).

Often the calculated wave function is stored as a set of calculated coefficients C. This coefficients can be used to generate a wave function for specific values of the position vector (\vec{r}) and electron wave vector (\vec{k}) by using equations (2) and (3).

Important to emphasize that the knowing the wave function allows to calculate the physical properties of the crystal, such as optical, vibrational, elastic, magnetic, etc.

§5.6.2 LCAO approach.

The Linear Combination of Atomic Orbitals (LCAO) method can be represented as further development of the LAPW method and often used in quantum chemistry to calculate properties of molecules.