

4.6 General solution of LCAO

1) The quantum mechanical point of view

- The formerly stable atomic states are disturbed by the lattice potential, leading to a mix of atomic states.
- Since the atomic states are only disturbed slightly, the mixture of atomic states is small as well.
- Only states with nearly the same energy will mix; otherwise these mixed states would relaxate very quickly.
- For the calculation we only must take into account atomic states with energies near the Fermi level.
- Since the crystal lattice continuously disturbs the atomic states, the mixture of this states is stable.
- The calculation of the coefficients is nothing but the unitary transformation into the new Eigenvectorsystem of the Hamiltonian of the solid.
- This demonstrate that the unitary transformation will consist of only a few non diagonal elements.
- The mathematical effort is minimized by this approach.

Hint: the above considerations hold for all perturbation approaches in quantum mechanics.

We multiply the Schrödinger equation of the solid

$$H\psi(r) = (H_{at} + \Delta U(r))\psi(r) = \epsilon(k)\psi(r) \quad (4.36)$$

with the atomic wave function $\psi_m^*(r)$, integrate over the complete space by taking into account

$$\int \psi_m^*(r)H_{at}\psi(r)dV = E_m \int \psi_m^*(r)\psi(r)dV \quad (4.37)$$

Thus we find

$$(\epsilon(k) - E_m) \int \psi_m^*(r)\psi(r)dV = \int \psi_m^*(r)\Delta U(r)\psi(r)dV \quad (4.38)$$

Including Eq. (4.35) and using the orthogonal relation

$$\int \psi_m^*(r)\psi_n(r)dV = \delta_{mn} \quad (4.39)$$

we get the Eigenvalue equation for the calculation of the coefficients $b_n(k)$ and the band energies $\epsilon(k)$:

$$\begin{aligned} (\epsilon(k) - E_m)b_m = & -(\epsilon(k) - E_m) \sum_n \left(\sum_{R \neq 0} \int \psi_m^*(r)\psi_n(r-R)e^{ikR}dV \right) b_n \\ & + \sum_n \left(\int \psi_m^*(r)\Delta U(r)\psi_n(r)dV \right) b_n \\ & + \sum_n \left(\sum_{R \neq 0} \int \psi_m^*(r)\Delta U(r)\psi_n(r-R)e^{ikR}dV \right) b_n \end{aligned} \quad (4.40)$$

2) The quantum mechanical point of view

- The integration corresponds to the scalar product.
- We therefore calculate the matrix element which belong to the (disturbed) solid state Hamiltonian.
- Without any perturbation the right hand side of Eq. (4.40) is zero and the Eigenvalue equation is trivial.
- Including the lattice perturbation and following the above considerations only a few Eigenvectors are needed for the diagonalization.

Let us estimate the right hand side of Eq. (4.40):

The first term:

$$\left\| \int \psi_m^*(r) \psi_n(r-R) e^{ikR} dV \right\| \leq \int \|\psi_m^*(r) \psi_n(r-R)\| dV \quad (4.41)$$

Fig. 4.1 demonstrates that for well localized states the right hand side of Eq. (4.41) should be quite small, since atomic wave functions of different lattice points are multiplied.

The second term:

$$\int \psi_m^*(r) \Delta U(r) \psi_n(r) dV \quad (4.42)$$

Since we assume a small perturbation for the atomic wave function, we find an anticorrelation between the regions where the wave function is large and the regions where $\Delta U(r)$ is large. Thus the term of Eq. (4.42) is small as well.

This considerations hold again for the third term.

Consequently the right hand side of Eq. (4.40) is small, i.e.

$$\text{for } b_m \gg 0 \quad \text{we find} \quad (\epsilon(k) - E_m) \approx 0 \quad (4.43)$$

- Thus only those atomic wave functions add strongly to the state of a solid whose atomic energies are nearly the same and show values near the band energy (Fermi energy).
- This verifies the former results which followed directly from general quantum mechanical considerations.
- If Eq. (4.43) would hold absolutely, i.e. if we describe the atomic limit, all states would again be independent of k .

We take benefit from the above considerations in Eq. (4.41) - (4.43) to get a good approximation for the band energies $\epsilon(k)$ by

1. taking into account only atomic levels n which have energies close to the Fermi energy,
2. taking into account only neighboring lattice sites when summing up lattice vectors,
3. using the integrals of the form (4.41) partly as fit parameters.

This approximations simplify the numerical and analytical effort in several ways:

- The system of linear equations for the calculation of the coefficients b_n has a small dimension.
- Only very few integrals have to be calculated.
- We have only a small number of fit parameters which have to be adapted to experimental data.

Examples:

- For a one atomic basis of atoms with s-electrons which are not degenerated, we do not need to solve a set of linear equations at all.
- For a one atomic basis of p-states we have to calculate a 3x3 Eigenvalue-problem in addition to the integrals.
- For a one atomic basis of d-states we have to calculate a 5x5 Eigenvalue-problem; e.g. for many transition metals the d-states and the s-state of the next orbital are almost degenerated; so we have to solve a 6x6-Eigenvalue equation.

This are the typical sizes of LCAO-approximations; if more states are necessary for a good description of the system, normally the overlap between the states is so large that an expansion into plane waves is more appropriate.