

4.7 Applying the LCAO method to s-band electrons

We now evaluate Eq. (4.40) for one atomic s-orbital with the energy E_s . Therefore we define the integrals

$$\beta = - \int dV \Delta U(\vec{r}) |\psi(\vec{r})|^2 \quad (4.44)$$

$$\alpha(\vec{R}) = - \int dV \psi^*(\vec{r}) \psi(\vec{r} - \vec{R}) \quad (4.45)$$

$$\gamma(\vec{R}) = - \int dV \psi^*(\vec{r}) \Delta U(\vec{r}) \psi(\vec{r} - \vec{R}) \quad (4.46)$$

Using this integrals we find

$$\epsilon(\vec{k}) = E_s - \frac{\beta + \sum \gamma(\vec{R}) e^{i\vec{k}\vec{R}}}{1 + \sum \alpha(\vec{R}) e^{i\vec{k}\vec{R}}} \quad (4.47)$$

The integrals (4.44)-(4.46) can be simplified extremely taking into account the symmetries of s-orbitals: Since we only discuss s-levels, we can always choose $\Phi(\vec{r})$ real and it's value depends only on the length r . Consequently we find

$$\alpha(-\vec{R}) = \alpha(\vec{R}) \quad (4.48)$$

The inversion symmetry of the Bravais lattices gives

$$\Delta U(-\vec{r}) = \Delta U(\vec{r}) \quad (4.49)$$

leading to

$$\gamma(-\vec{R}) = \gamma(\vec{R}) \quad (4.50)$$

Neglecting even in a further approximation α completely and summing only over nearest neighbor (n.n.-) atoms we find

$$\epsilon(\vec{k}) = E_s - \beta - \sum_{n.n.} \gamma(\vec{R}) \cos(\vec{k}\vec{R}) \quad (4.51)$$

Example: In an fcc-lattice each atom has 12 nearest neighbors at

$$\vec{R} = \frac{a}{2}(\pm 1, \pm 1, 0), \quad \vec{R} = \frac{a}{2}(\pm 1, 0, \pm 1), \quad \vec{R} = \frac{a}{2}(0 \pm 1, \pm 1) \quad . \quad (4.52)$$

For $\vec{k} = (k_x, k_y, k_z)$ we find for the 12 values of the scalar product

$$\vec{k}\vec{R} = \frac{a}{2}(\pm k_i \pm k_j) \quad i, j = x, y; y, z; z, x \quad (4.53)$$

Since $\Delta U(\vec{r}) = \Delta U(x, y, z)$ displays the full cubic symmetry, we find no changes in the argument when permutating the parameters x , y , and z . In addition we have the radial dependence $\Phi(\vec{r}) = \Phi(r)$ leading to $\gamma(\vec{r}) = \gamma$ for all permutations of the indices. Summing up we find (after some trivial but time consuming calculations)

$$\epsilon(\vec{k}) = E_s - \beta - 4\gamma \left\{ \cos\left(\frac{a}{2}k_x\right) \cos\left(\frac{a}{2}k_y\right) + \cos\left(\frac{a}{2}k_y\right) \cos\left(\frac{a}{2}k_z\right) + \cos\left(\frac{a}{2}k_z\right) \cos\left(\frac{a}{2}k_x\right) \right\} \quad (4.54)$$

and

$$\gamma = - \int dV \Phi^*(x, y, z) \Delta U(x, y, z) \Phi\left(x - \frac{a}{2}, y - \frac{a}{2}, z\right) \quad . \quad (4.55)$$

Equation (4.55) demonstrates

The characteristics of the "Tight-Binding" approach

- The band width (distance between the minimal and maximal energy of a band) is proportional to the (small) overlap integral γ . Thus we describe "narrow" bands.
- For small values of ka we can simplify Eq. (4.54) to

$$\epsilon(\vec{k}) = E_s - \beta - 12\gamma + \gamma k^2 a^2 \quad (4.56)$$

i.e. in the fcc crystal the planes with constant energies for small momentum values are spherical (as in the case of free electrons).

- A universal result for narrow bands is the coupling between the band width and the overlap integral

$$\gamma_{ij}(\vec{R}) = - \int dV \psi_i^*(\vec{r}) \Delta U(\vec{r}) \psi_j(\vec{r} - \vec{R}) \quad . \quad (4.57)$$

- For small overlap integrals we find correspondingly narrow bands. With increasing energy the range of atomic orbitals increases, leading to an enlarged overlap integral; therefore typically the band width increases for orbitals with increasing n (energy). For metals we find very broad bands for the highest occupied orbitals, since the range of these orbitals is comparable to the lattice parameter. For metals the approximation of "narrow" band is often inadequate.
- The mean velocity of an electron in a Bloch state is defined by

$$v = \frac{1}{\hbar} \frac{\partial \epsilon}{\partial k} \quad (4.58)$$

If ϵ is independent of k we find $v = 0$. This is consistent with the model of isolated atoms and electrons which are coupled strongly to that atom. If on the other hand the overlap integral is not vanishing, $\epsilon(k)$ will show a k dependence and the electron will move through the solid. The velocity is proportional to the overlap integral. This may be equivalently described by an electron which is bound to the atom but by tunneling can hop to a neighboring atom. The larger the overlap integral the higher is the probability for tunneling.

- All the calculations in this chapter neglected the interaction between electrons. This interaction can be included into the "narrow band approximation" by a lattice periodic average of the electron density. In many cases this is not enough to describe the physical properties of solids correctly (e.g. in magnetic materials or in high temperature superconductors HTSC).

3) The quantum mechanical point of view

- The exact quantum mechanical problem could not be solved.
- We therefore simplified the Hamiltonian until we could calculate it exactly.
- In the next chapter we will learn about another simplification where we take the exact Hamiltonian but use a variational approach to get a "simple" approximation for the solution of the Hamiltonian.
- The above calculations for energy bands used the single electron approximation, i.e. we calculated the states of a single electron within a solid which is coupled strongly to an atom. To solve the many particle problem we have to answer several questions:
- Electrons are charged; which consequences does the Coulomb interaction between electrons have for our calculations?
- Electrons are quantum mechanical particles - Fermions - ; which consequences does the Pauli principle have for the occupation of the energy levels with electrons?
- Electrons have a spin which is an additional quantum number to distinguish electronic states; what are the consequences for the occupation of the energy levels with electrons?
- The spins as well as the rotational momenta generate magnetic fields within the solid; when do we have to take these effects into consideration?

Only after we have answered all these questions we can calculate the ground state of a solid, i.e. the properties of the ideal undisturbed solid when no forces and excitations are applied. We need concepts to decide when and how to use energy bands as a starting point for additional forces applied to our system.