Ab Initio Band Structure Calculations

(Written by J.-M. Wagner; first draft: February/March 2021)

Advanced

▮ ***Ab initio*** (written in italics just because it is Latin, not English) roughly means "from scratch" – in the sense of not using any information from experiment except for the chemical composition of the material and its (possible) crystal structure(s). All further input comes from basic physical principles (as, e.g., conservation laws or symmetry considerations) and fundamental equations.

- Since the desired band structure is nothing but the collection of all "allowed" energy values of electrons inside the crystal, all we have to do is to solve the *Schrödinger equation for this crystal*. (How that equation looks like in this case one can see, e.g., [here](#).)

- However, this is impossible to do because there are **too many electrons** involved – "too many" in the sense of "more than can be handled numerically" (estimate the relevant order of magnitude yourself, e.g. by considering the number of silicon atoms in a cubic centimeter of bulk crystalline material).

- Also, the **electron–electron interaction** makes the problem intrinsically intricate: Analytic solutions of the Schrödinger equation are only known for *single-electron* systems.

▮ Nowadays there are many different approaches to deal with these problems. Here I will focus on only one of them (and I will mention another one briefly). Beforehand, however, I will consider some **basic aspects** that are of **general relevance** in the context of many-electron systems.

- The intention here is that you have heard of these basic aspects and that you have a rough idea of what they mean. It is not necessary that you understand them in full detail; however, you should understand *why* those things come into play.

- On the other hand, when you are just interested in doing the calculations (which is the final step in answering the initial question, "how the band structures of real-world materials can be obtained"), you may skip all this and go directly to the [list of quantum chemistry and solid-state physics software](#) that I will turn to in the end anyway; just be prepared that you won't understand anything about how to use such software when you go there directly.

▮ The basic aspects I want to consider are these two:

Exchange and Correlation

▮ Since the full problem is too big to be solved directly, approximations need to be made. There are several aspects that motivate a *single-particle approach* for trying to solve the Schrödinger equation of the crystal in an approximative manner:

- The Schrödinger equation can be solved much easier for a single electron than for many electrons.

- The resulting energy eigenvalues can be interpreted much easier for a single electron than for a many-electron system.

▮ In fact, all that we have considered so far (and almost all that is still to come in this lecture; the only exception being excitons) are **single-particle states** and **single-particle energies**.

- This way, it is very easy to understand, for example, the absorption of a photon: The energy of the photon is completely taken up by a single electron that thereby jumps up in the band structure by the relevant amount.

▮ On the other hand, it is immediately clear that this approach is rather absurd, because a single-particle solution of the Schrödinger equation (or a combination thereof) can never behave like a many-particle solution.

- This is so because such a many-particle solution is a *single* wavefunction for *all* electrons, which means that, at least in principle, single electrons cannot be identified anymore.

- Remember that $|\Psi|^2$ gives the **probability density** for finding the particle(s) described by this wavefunction at (a) certain location(s). A many-particle density is fundamentally different from a combination of single-partilce densities because the latter refer to independent particles, whereas in the many-particle wavefunctions there are no independent particles.

▮ This intrinsically non-classical property of a many-particle system whose state is described quantum-mechanically by a single wavefunction, that the particles aren't independent, is also expressed by saying that the particles are *correlated*.

- **Correlation** means that there is a "link" between the particles which is beyond their direct interaction, which here is Coulomb interaction; correlation effects would also be present if there were no Coulomb interaction.

- A typical example for such (possible) correlation effects among electrons is the phenomenon of **high-temperature superconductivity** occurring in some transition-metal oxides.

- Another important example for electronic correlation is the recently found explanation of ### **benzene ring molecule** ###

It is clear *per se* that in any single-particle approach, these correlation effects will be absent. Since, however, correlation may also influence the energy eigenvalues, it must nevertheless still be be taken into account.

- The only possibility to include the contribution of correlation effects to the single-particle energy eigenvalues is to add an *effective correlation energy term* in the single-particle Hamiltonian (for which the Schrödinger equation will be solved instead of the many-particle one).
- How such an effective correlation energy term looks like and how it can be determined so that the resulting single-particle energies are (more or less) identical to the many-particle ones will be discussed below.

We now turn to the second basic aspect mentioned above, **exchange**.

- To understand what it means and where it comes from, we take a closer look at how the single-particle description is obtained, starting from the many-particle wavefunction.

In fact, ###

- The ###
- The pre-exponential factor, which was $(1/L)^{3/2}$, now changes to $(1/V)^{1/2}$.

Since all relevant quantities are usually expressed as densities, i.e. divided by *V*, and the quantization of *k* is usually given up in favor of a continuous range of *k*'s, we may just as well stick to the more simple description of a crystal with equal sides - the results are the same.