Excited State Properties

Abstract The phenomenological theory of optical properties of materials is presented. The general theory of calculations of optical properties from first principles theory is given, with special emphasis on the implementation in the FP-LMTO method. Numerical examples of semi-conductors as well as metals are presented. Interband and intraband transitions are discussed, as are maneto-optical effects. The chapter ends with a description of the theory of x-ray magnetic circular dichroism, and how its calculation is made possible in the FP-LMTO method.

With RSPt, it is possible to calculate optical and magneto-optical spectra as well as X-ray absorption (XAS) and X-ray magnetic circular dichroism XMCD. The implementation is based on the dipole approximation. Furthermore, the usual DFT underestimation of the energy band gap is dealt with using the scissors operator. This very simple model makes the calculations fast. More elaborate, alternative ways of computing excited states within DFT involve the GW approximation, the two-particle Dyson equation, or time-dependent DFT. In this chapter, we give details on our implementation and its limitations and strengths and we discuss the physical reasons as to why the simple dipole approximation combined with the scissors operator give such good results. We also present some general background theory for these types of excitation spectra and give examples of calculated spectra.

13.1 Phenomenology

Let us introduce the subject of calculating excitation spectra by briefly reviewing the macroscopic theory of optical and magneto-optical properties. The interaction of electromagnetic radiation with a magnetic medium is described classically by Maxwell’s equations [125]. For linear materials the electric displacement $D$ is related to the total electric field $E$ and the polarization $P$ as
\[ \mathbf{D} = \epsilon_0 \mathbf{E} + \mathbf{P} = (1 + \chi_e)\epsilon_0 \mathbf{E} - \epsilon \mathbf{E}. \quad (13.1) \]

Similarly, the magnetic field \( \mathbf{B} \) is related to \( \mathbf{H} \) and the magnetization \( \mathbf{M} \) according to
\[ \mathbf{B} = \mu_0 (\mathbf{H} + \mathbf{M}) = (1 + \chi_m)\mu_0 \mathbf{H} = \mu \mathbf{H}. \quad (13.2) \]

Here, \( \epsilon_0, \mu_0, \chi_e, \) and \( \chi_m \) are the vacuum permittivity, the vacuum permeability, the electric susceptibility, and the magnetic susceptibility, respectively. \( \epsilon \) is the dielectric function and \( \mu \) the magnetic permeability. A third fundamental equation is Ohm’s law, which connects the macroscopic current density \( \mathbf{J} \) with the electric field \( \mathbf{E} \) according to
\[ \mathbf{J} = \sigma \mathbf{E}, \quad (13.3) \]

where \( \sigma \) is the conductivity. Equations (13.1), (13.2), and (13.3) are known as the material equations. They characterize the *response functions of the medium to external excitations*. In general the dielectric function is a function of both spatial and time variables that relate the displacement field \( \mathbf{D}(\mathbf{r}, t) \) to the total electric field \( \mathbf{E}(\mathbf{r}', t') \) according to
\[ \mathbf{D}(\mathbf{r}, t) = \int_{-\infty}^{t} \int_{\mathbf{r}'} \epsilon(\mathbf{r}, \mathbf{r}', t') \mathbf{E}(\mathbf{r}', t') dt' d\mathbf{r}'. \quad (13.4) \]

In the following we neglect the spatial dependence of the dielectric function and consider only its frequency dependence \( \epsilon(\omega) \). Usually, the effect of the magnetic permeability \( \mu(\omega) \) on optical phenomena is small and we therefore assume from now on that \( \mu(\omega) = \mu_0 \mathbf{I} \) where \( \mathbf{I} \) is a unit tensor. It should be stressed also that \( \epsilon \) and \( \mu \) may depend on the field strength. In such cases higher order terms in a Taylor expansion of the material parameters lead to the appearance of non-linear effects [34]. Using the material equations and Maxwell’s equations it can be shown that the dielectric function and the conductivity are connected according to
\[ \epsilon = \frac{1}{\epsilon_0} \left( 1 + i \frac{\sigma}{\omega} \right). \quad (13.5) \]

The real part of the dielectric function \( \epsilon \) is often denoted \( \epsilon^{(1)} \) or \( \epsilon_1 \) and the imaginary part is denoted \( \epsilon^{(2)} \) or \( \epsilon_2 \). Similar notation for the conductivity \( \sigma \) is also in use.

For non-magnetic materials with cubic structure, the form of the dielectric tensor becomes particularly simple. The three diagonal components of the dielectric tensor are then equal, the off-diagonal components are zero, and thus we can write
\[ \epsilon(\omega) = \epsilon(\omega) \mathbf{I}. \quad (13.6) \]

With a macroscopic magnetization \( \mathbf{M} \) directed along the \( z \)-axis, the symmetry is lowered and \( \epsilon(\omega) \) becomes [135]