Chapter 3
Electronic Structure Theory for X-Ray Absorption and Photoemission Spectroscopy

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Abstract The principles of X-ray absorption and photoemission spectroscopy calculations are introduced and the basics of electronic structure theory, including the Hartree–Fock approximation, density functional theory, its time-dependent version and quasiparticle theory are reviewed on an elementary level. Emphasis is put on polarization effects and the role played by electron correlation.

3.1 Introduction

In this chapter, the basic theory of X-ray absorption spectroscopy (XAS) and photoemission spectroscopy (PES) is introduced and popular computational methods are reviewed. Since XAS and PES mainly probe electronic excitations, a thorough understanding of electronic structure theory is mandatory. We shall review the standard theoretical methods for ground state electronic structure calculations, namely, Hartree–Fock (HF) and density functional theory (DFT). Among the various excited state theories, we focus on time-dependent DFT and briefly touch upon Green's function quasiparticle methods and the Bethe–Salpeter equation approach. We do not discuss ligand-field atomic multiplet theory, because this important method for transition metal L-edge calculations is covered in Chap. 4.

3.2 Light–Matter Interaction

As light is an electromagnetic wave, it interacts with all charged particles. In the visible to X-ray regime, the interaction with the electrons hugely dominates the interaction with the atomic nuclei. We shall therefore disregard the nuclear degrees

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of freedom in the following, focusing on the electronic state of the system. When an X-ray photon impinges on an atom it can be either absorbed or scattered, energy, momentum and spin being, of course, conserved in the whole process. In absorption, the photon vanishes: all its energy is transferred to an electron which is excited to an empty state above the vacuum level. In scattering, the energy of the photon can remain the same [elastic (Thomson) scattering]; it can also be partly transferred to the atom (inelastic scattering) as in Compton scattering, which leads to the ejection of an electron, or in a Raman-like scattering, in which the energy lost by the photon brings the atoms in an excited state, without any ionization. Neglecting relativistic effects and treating the X-ray field classically, the light–electron interaction is obtained by replacing, in the electronic Hamiltonian, the electron momentum operator $\mathbf{p}$ by $\mathbf{p} - e\mathbf{A}/c$, where $\mathbf{A}(\mathbf{r}, t)$ is the vector potential of the light [1]. In Coulomb gauge ($\nabla \cdot \mathbf{A} = 0$), the interaction Hamiltonian then becomes

$$H_{\text{int}} = -\frac{e}{mc}\mathbf{A} \cdot \mathbf{p} + \frac{e^2}{2mc^2}A^2 \ . \tag{3.1}$$

The first-order term in A describes light absorption and stimulated emission while the second-order term is responsible for (non-resonant) light scattering. Here we focus on the absorption process and neglect the generally much weaker A^2 term. First-order perturbation theory (Fermi golden rule) leads to the following expression for the absorption intensity from an initial state $|i\rangle$ of energy E_i:

$$I(\omega) \propto \sum_f |\langle f|\mathbf{A} \cdot \mathbf{p}|i\rangle|^2 \delta(\hbar\omega - E_f + E_i) \ , \tag{3.2}$$

where the sum runs over all possible final states $|f\rangle$ with energy E_f. It is common to make the dipole approximation, i.e. to neglect the spatial variation of the X-ray field $\mathbf{A}(\mathbf{r})$. We may also replace the transition operator $\mathbf{A} \cdot \mathbf{p}$, by $\mathbf{e} \cdot \mathbf{r}$, where $\mathbf{e} = \mathbf{A}/|\mathbf{A}|$ is the light polarization vector and the change from $\mathbf{p}$ to $\mathbf{r}$ is possible by exploiting commutation relations between $\mathbf{r}$, $\mathbf{p}$ and H, and the fact that $|i\rangle$ and $|f\rangle$ are energy eigenstates [2]. Equation (3.2) is often interpreted in a single-particle picture, in which case $|i\rangle$ is an atomic core state and $|f\rangle$ are unoccupied states above the Fermi level. However, electrons interact with each other through the Coulomb interaction, such that the excitation of one electron affects the motion of the others. Therefore, the correct use of (3.2) is in a many-particle sense, where $|i\rangle = |\Phi_g\rangle$ is the many-electron ground state, and $|f\rangle = |\Phi_f\rangle$ are many-electron excited states with a core hole. Putting the constants we have

$$I(\omega) = 4\pi^2\alpha\hbar\omega \sum_f |\langle \Phi_f|\mathbf{e} \cdot \sum_j \mathbf{r}_j|\Phi_g\rangle|^2 \delta(\hbar\omega - E_f + E_g) \ , \tag{3.3}$$

where $\alpha = e^2/\hbar c$ is the fine structure constant and j counts the electrons. Having established the expressions of the absorption intensity, the remaining task is to calculate the eigenstates of the (unperturbed) electronic system, $|\Phi_g\rangle$ and $|\Phi_f\rangle$, and their

energies. Thus, the main theoretical problem of XAS is the accurate description of the electronic structure of the system, both for the ground and core-excited states. We, therefore, start by reviewing the basics of (ground state) electronic structure theory before turning to the specific methods for handling core-excited states.

3.3 Ground State Electronic Structure Theory

Consider N electrons interacting with each other and the atomic nuclei. Following the Born–Oppenheimer approximation, we neglect the coupling between the nuclear and electronic dynamics. For the electronic problem, this means that the nuclei are at fixed positions and can be described by a static external potential $V_{ext}(\mathbf{r})$. The electronic Hamiltonian is then given by

$$H = T + V_{ext} + V_{ee} = \sum_i \frac{1}{2}\nabla_i^2 + \sum_i V_{ext}(\mathbf{r}_i) + \sum_{i<j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} , \qquad (3.4)$$

where i, j count the electrons and atomic units are used ($\hbar = m = e = 1$). The kinetic energy T and the external potential V_{ext} are one-particle operators whereas the electron–electron interaction V_{ee} is a two-particle operator. Because of V_{ee}, the electronic motion is correlated and the many-electron problem cannot be solved exactly (except for a few electrons). Drastic approximations need to be made. The most important ground state electronic structure methods are HF and DFT.

3.3.1 Hartree–Fock Approximation

Historically, the first accurate electronic structure method is the Hartree–Fock approximation (HFA) [3]. It is still widely used for single molecule calculations and as a starting point for more advanced schemes. The basic assumption of the HFA is that the many-electron ground state wave function is a Slater determinant, i.e. an antisymmetrized product of single-electron states (spin-orbitals). By applying the Rayleigh–Ritz variational principle, the HF equations are obtained, whose solutions are the HF orbitals $\phi_n(\mathbf{r})$ and energies ϵ_n. For convenience, we suppress the spin part of the single-particle wave functions. The HF equations are

$$\left(-\frac{1}{2}\nabla^2 + V_{ext}(\mathbf{r}) + V_H(\mathbf{r}) + V_X\right)\phi_n(\mathbf{r}) = \epsilon_n\phi_n(\mathbf{r}) . \qquad (3.5)$$

This is a one-electron Schrödinger equation where the pair-wise electron–electron interaction is replaced by an effective potential $V_H + V_X$.

$$V_{\mathrm{H}}(\mathbf{r}) = \sum_m^{\mathrm{occ}} \int d\mathbf{r}' \frac{|\phi_m(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} = \int d\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \tag{3.6}$$

is called the Hartree potential and corresponds to the classical electrostatic potential due to the electronic charge density $n(\mathbf{r}) = \sum_m^{\mathrm{occ}} |\phi_m(\mathbf{r})|^2$ of the occupied orbitals.

$$V_X \, \phi_n(\mathbf{r}) = - \sum_m^{\mathrm{same\ spin}} \int d\mathbf{r}' \frac{\phi_m^*(\mathbf{r}')\phi_m(\mathbf{r})\phi_n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \tag{3.7}$$

is the exchange potential which is due to the electron–electron interaction together with the antisymmetry of Slater determinants under permutation of two electrons. V_X is a non-local potential and has no classical analogue. Both V_{H} and V_X are static 'mean-field' potentials, obtained from the time-averaged orbital motion of the electrons. Dynamical effects are neglected. The exchange interaction induces some correlation between electrons of same spin, which avoid each other due to the Pauli principle. Correlation between electrons of opposite spin is completely absent in the HFA. By definition, the difference between the exact ground state and the HF ground state is called the electron correlation effect (even though mathematically speaking, there is correlation between same spin electrons in the HFA).

There are various methods to take account of electron correlation, often termed collectively as 'post-HF' methods in the chemical literature. The conceptually most simple way to include electron correlation is the configuration interaction (CI) method. In CI, a set of Slater determinants is generated from the HF ground state by (multiple) particle–hole excitations. The CI wave function is a linear combination of these many-electron basis states and the coefficients and total energy levels are determined variationally by diagonalizing the Hamiltonian in this sub-space. CI can be very accurate for atoms and small molecules, but cannot directly be applied to large molecules and materials because the number of Slater determinants grows exponentially with system size. For X-ray absorption spectra, CI effects, i.e. mixing between Slater determinants, are especially strong at transition metal L-edges and lanthanide M-edges, which correspond to excitations into the localized $3d$- and $4f$-orbitals. For these spectra, CI must be taken into account. This can be done with the ligand-field multiplet method which is based on CI of a single atom or a very small cluster (see Chap. 4 for details).

3.3.2 Density Functional Theory

Nowadays, most electronic structure methods are based on DFT [4, 5]. In DFT, one does not try to find approximations to the many-electron wave function. Instead, the idea is to directly find the exact electronic density $n(\mathbf{r})$ and total energy, which is expressed as a functional of the density. DFT is based on two theorems due to Hohenberg and Kohn [4] about the (non-degenerate) ground state of the interacting,

inhomogeneous electron gas. The first theorem states that the external potential V_{ext} is uniquely determined by the ground state electronic density $n(\mathbf{r})$ and that the total energy E (minus the external potential energy) is a unique and universal functional of n.[1] The consequence of the theorem is that knowledge of the ground state density alone is, in principle, sufficient to determine all properties of the system. The second theorem states that the exact ground state density $n_0(\mathbf{r})$ minimizes the total energy functional $E[n]$ in the space of all possible functions $n(\mathbf{r})$. Thus, approximations to E and n can be found variationally.

The Hohenberg–Kohn theorems are exact mathematical theorems. If the universal functional $E[n]$ were known, DFT would yield the exact total energy and electron density of the interacting electron system. But the exact functional $E[n]$ is unknown. Various approximate functionals have been proposed such as the local density approximation (LDA), generalized gradient approximations (GGA) and hybrid functionals, i.e. mixtures of GGA and HF exchange. In practical DFT calculations, Kohn–Sham theory is employed, which introduces an auxiliary, non-interacting system which, by definition, has the same electronic density as the real, interacting system. In the auxiliary system, the external potential is called Kohn–Sham potential V_{KS} and it is the sum of the true external (nuclei) potential and an effective one-electron potential which replaces the electron–electron interaction. The Kohn–Sham potential V_{KS} is given by the functional derivative of the total energy functional $E[n]$ with respect to the electron density. The effective electron–electron potential is written as the sum of the Hartree potential V_H and a rest, which is called exchange–correlation potential V_{XC}. As the exact energy functional $E[n]$ is unknown, so is V_{XC}, and the actual expression depends on the approximation used (LDA, GGA, hybrid).

As the Kohn–Sham auxiliary system is non-interacting, its eigenstates are Slater determinants made of orbitals ϕ_n that are solutions of the Kohn–Sham equations

$$\left(-\frac{1}{2}\nabla^2 + V_{ext}(\mathbf{r}) + V_H(\mathbf{r}) + V_{XC}\right)\phi_n(\mathbf{r}) = \epsilon_n\phi_n(\mathbf{r}) . \tag{3.8}$$

The Kohn–Sham equations (3.8) are similar to the HF equations (3.5) except that the exchange potential V_X is replaced by the exchange–correlation potential V_{XC} and the expression of the total energy as a function of the orbitals is different.

DFT takes account of electron correlation through V_{XC} and generally performs better than the HFA for ground state properties. This is, however, not necessarily true for excited states for which DFT should, in principle, not be used, because the Kohn–Sham orbitals and levels ϵ_n describe the auxiliary system and have, strictly speaking, no direct physical meaning for the real system. In practice, however, the orbitals and energy levels are used in the same way as the HF orbitals, namely, as a first-order approximation for the one-electron or one-hole excitations of the system.

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[1]The opposite is obvious because when V_{ext} is fixed, the Hamiltonian is known and so all properties, including the electronic density, are determined.

3.4 Absorption Spectra in the Independent Particle Approximation

Recalling (3.3), the absorption intensity is determined by the transition amplitude $M_{fg} = \langle \Phi_f | \mathbf{e} \cdot \sum_n \mathbf{r}_n | \Phi_g \rangle$. If both Φ_g and Φ_f are Slater determinants made of orbitals which are eigenstates of the same one-electron Hamiltonian, then it is easy to see that M_{fg} reduces to a one-particle transition matrix element between the core orbital $|\phi^c\rangle$ with energy ϵ_c and an unoccupied orbital $|\phi_k\rangle$ with energy ϵ_k and (3.3) simplifies to

$$I(\omega) = 4\pi^2 \alpha \hbar \omega \sum_k^{\epsilon_k > \epsilon_F} |\langle \phi_k | \mathbf{e} \cdot \mathbf{r} | \phi^c \rangle|^2 \delta(\hbar\omega - \epsilon_k + \epsilon_c) \ . \tag{3.9}$$

This is the basic equation of XAS in the independent particle approximation.

So far we have implicitly assumed that ϕ_k are the unoccupied orbitals of a ground state calculation. However, Φ_f is an excited state with a core hole. The core hole acts as a local positive charge which modifies the effective potential ($V_H + V_{X/XC}$) and so the best Slater determinant for Φ_f is made of a different set of orbitals $\tilde{\phi}_k$ than the ground state orbitals ϕ_k. Accordingly, better results are usually obtained with 'relaxed' orbitals $\tilde{\phi}_k$, corresponding to a constraint HF or DFT calculation with a core hole. As core holes are localized on one atomic site, the symmetry of the system is generally lowered in a core hole calculation and the computational cost increases. For crystals, in particular, a supercell calculation is needed in order to effectively separate the artificially repeated core hole sites. In the following, we shall write ϕ_k regardless for relaxed and unrelaxed orbitals.

3.4.1 Dipole Selection Rules and Density of States

For the calculation of the dipole transition matrix elements $\langle \phi_k | \mathbf{e} \cdot \mathbf{r} | \phi^c \rangle$, it is useful to expand the states $|\phi_k\rangle$ in a spherical harmonics basis centred at the atomic sites $\mathbf{R}_i$. By doing so, the dipole transition selection rules known from atomic physics can be exploited. This simplifies the calculation and yields an interpretation of the spectra in terms of projected density of states as we shall see. We write

$$\phi_k = \sum_{ilm} B^k_{ilm} \chi_{ilm} \ , \quad \chi_{ilm}(\mathbf{r}) = R_{il}(r_i) Y_{lm}(\mathbf{r}_i) \ , \tag{3.10}$$

where $\mathbf{r}_i \equiv \mathbf{r} - \mathbf{R}_i$, Y_{lm} are spherical harmonics, R_{il} radial functions and B_{ilm} complex coefficients. The core orbital is localized at some site (i_c). Therefore, only orbitals χ_{ilm} with $i = i_c$ give a non-zero contribution to the matrix element. Next we write the dipole operator as a spherical tensor product $\mathbf{e} \cdot \mathbf{r} = \sum_q (-1)^q e_{-q} r_q$, where $q = 0, \pm 1$ are the spherical components of a vector $\mathbf{a}$, given by $a_0 = a_z$,

$a_\pm = (\mp a_x - i a_y)/\sqrt{2}$. The angular integrals of the matrix elements can then be simplified with the help of the Wigner–Eckart theorem [2]

$$\langle n'l'm'|r_q|nlm\rangle = (-1)^{l'-m'} \begin{pmatrix} l' & 1 & l \\ -m' & q & m \end{pmatrix} \langle n'l'||r||nl\rangle , \qquad (3.11)$$

where $(\vdots\vdots\vdots)$ are Wigner-3j symbols and $\langle n'l'||r||nl\rangle$ are reduced matrix elements, which are independent of m, m', q. The Wigner-3j symbol is non-zero only for $l' = l \pm 1$ and $m' = m + q$. These are the dipole selection rules. For example, for K-edge spectra $l = m = 0$ and thus only $l' = 1$, i.e. p-type final states can be reached. If polarized light is used we further have $m' = q$, e.g. in z-polarization only p_z states are probed. We thus see that XAS is a local probe of the unoccupied electronic states, where different orbital symmetries can be projected out by appropriately choosing the absorption edge l value and the light polarization q.

Using the expansion (3.10) and the dipole selection rules (3.11), we find for the transition matrix elements from a core orbital ϕ_{ilm}^c

$$\langle \phi_k|r_q|\phi_{ilm}^c\rangle = \sum_\pm B_{i,l\pm1,m+q}^{k*} \langle \chi_{i,l\pm1,m+q}|r_q|\phi_{ilm}^c\rangle . \qquad (3.12)$$

The absorption intensity (3.9), dropping constants, from a core shell with angular momentum l, located at site i, for light polarization q becomes

$$I_q(\omega) = \sum_{km} \left| \sum_\pm B_{i,l\pm1,m+q}^{k*} \langle \chi_{i,l\pm1,m+q}|r_q|\phi_{ilm}^c\rangle \right|^2 \delta(\hbar\omega - \epsilon_k + \epsilon_c) . \qquad (3.13)$$

As defined in (3.10), the orbitals $R_{il}(r)$ and the expansion coefficients B are, in principle, energy dependent. This is the choice in multiple scattering theory which allows a minimal basis set (one orbital for each site and l). In the following, we neglect the slow energy dependence of the radial waves. We then obtain

$$I_q(\omega) \approx \sum_{m,a,b=\pm} M_{ilm,q}^{a*} M_{ilm,q}^{b} \sum_k B_{il_am+q}^k B_{il_bm+q}^{k*} \delta(\hbar\omega - \epsilon_k + \epsilon_c) , \qquad (3.14)$$

where $l_a, l_b = l \pm 1$ and $M_{ilm,q}^b = \langle \chi_{i,l_b,m+q}|r_q|\phi_{ilm}^c\rangle$. We introduce the local, orbital projected density of states matrix

$$\rho_{ilm,l'm'}(\epsilon) = \sum_k \langle \chi_{ilm}|\phi_k\rangle\delta(\epsilon - \epsilon_k)\langle\phi_k|\chi_{il'm'}\rangle = \sum_k B_{ilm}^k \delta(\epsilon - \epsilon_k) B_{il'm'}^{k*} . \qquad (3.15)$$

Note that the usual partial density of states (DOS) is given by the diagonal elements $(lm = l'm')$. So (3.14) can be written as

$$I_q(\omega) \approx \sum_{m,a,b=\pm} M_{ilm,q}^{a*} M_{ilm,q}^{b} \rho_{il_a m+q, l_b m+q}(\hbar\omega + \epsilon_c) \; . \tag{3.16}$$

We see that the absorption intensity is a weighted sum of a few partial DOS components with angular momentum $l_a = l \pm 1$. For high enough symmetry, the interference terms $a \neq b$ vanish, leaving only the diagonal, usual partial DOS. In some cases, e.g. for the linear dichroism at the sulphur $L_{2,3}$-edges in MoS_2, it was found that interference between $p \rightarrow s$ and $p \rightarrow d$ transitions is non-negligible [6]. For the special case of s-wave core states (K, L_1, M_1 edges) where $l = m = 0$, the selection rules (3.11) give $l' = 1, m = q$, such that the absorption spectrum for q-polarized light is directly proportional to the p_q-DOS (where $q = 0, \pm 1$ or $q = x, y, z$).

In this section, we have seen that in the independent particle and dipole approximation, the X-ray absorption spectra are approximately given by a weighted sum of partial DOS with momenta $l \pm 1, m + q$. The weighting factors are local transition matrix elements and reflect the light polarization and orbital symmetry. As a consequence, XAS can be used to probe the unoccupied DOS of the material in a site and orbital-resolved way, which gives detailed insight into the local bonding properties [7].

3.5 Absorption Spectra in Linear Response TDDFT

3.5.1 Time-Dependent Density Functional Theory

DFT is a ground state theory whose application to excited states is ill-founded. However, a large class of excitations can be computed using the time-dependent version of DFT. Time-dependent DFT (TDDFT) is the generalization of standard DFT to time-dependent external potentials $V_{ext}(\mathbf{r}, t)$. It was pioneered by Zangwill and Soven in 1980 [8], who developed a linear response theory for optical absorption spectroscopy of atoms using a time-dependent version of the LDA. In 1984, Runge and Gross [9] generalized the Hohenberg–Kohn theorems of DFT to the case of time-dependent systems, thus putting TDDFT on a rigorous theoretical ground. TDDFT has been applied to XAS of solids for the first time in 1998 by Schwitalla and Ebert [10] and to molecules in 2003 by Stener et al. [11].

The problem at hand is to find the time-dependent electron density $n(\mathbf{r}, t)$ of an interacting electron system subject to a time-dependent external field. In TDDFT, the exact time-dependent electron density $n(\mathbf{r}, t)$ can, in principle, be found from the knowledge of the external field, the universal energy functional $E[n(\mathbf{r}, t)]$ and the initial density $n(\mathbf{r}, 0)$. Linear response functions, including absorption coefficients, can be expressed as integrals over the electron density change induced by a time-dependent external field. Thus, if the exact functional $E[n(\mathbf{r}, t)]$ were known, TDDFT would allow to obtain exact absorption spectra. As in the case of time-independent

DFT, however, the exact functional is unknown. Moreover, finding good approximate functionals is even more difficult in TDDFT than in standard DFT.

3.5.2 Linear Response Theory

Here we shall outline the theory of absorption spectroscopy in linear response following Zangwill and Soven [8]. We consider an interacting electron system as described by the unperturbed Hamiltonian H in (3.4), and try to find its response to a time-dependent applied field $\varphi_{\text{ext}}(\mathbf{r}, t)$ such as the electromagnetic field of an X-ray beam. The perturbation Hamiltonian is written as

$$H'(t) = \int \varphi_{\text{ext}}(\mathbf{r}, t) n(\mathbf{r}, t) \mathrm{d}\mathbf{r} \,, \tag{3.17}$$

where $n(\mathbf{r}, t)$ is the electron density. It differs from the density of the unperturbed system $n^0(\mathbf{r})$ by the induced density

$$\delta n(\mathbf{r}, t) = n(\mathbf{r}, t) - n^0(\mathbf{r}) \,. \tag{3.18}$$

The fundamental assumption of *linear* response theory is that the response of the system, δn, is proportional to the applied field φ_{ext}, i.e.

$$\delta n(\mathbf{r}, t) = \int \mathrm{d}\mathbf{r}' \mathrm{d}t' \chi(\mathbf{r}, \mathbf{r}', t - t') \varphi_{\text{ext}}(\mathbf{r}', t') \,, \tag{3.19}$$

where χ, the response function, is an intrinsic property of the unperturbed system. In the frequency domain, this relation reads

$$\delta n(\mathbf{r}, \omega) = \int \mathrm{d}\mathbf{r}' \chi(\mathbf{r}, \mathbf{r}', \omega) \varphi_{\text{ext}}(\mathbf{r}', \omega) \,. \tag{3.20}$$

It can be shown that χ is given by the retarded density–density Green's function

$$\chi(\mathbf{r}, \mathbf{r}', t - t') = -i\theta(t - t')\langle 0|[\hat{n}(\mathbf{r}, t), \hat{n}(\mathbf{r}', t')]|0\rangle \,, \tag{3.21}$$

where $\hat{n}(t) = e^{iHt}\hat{n}e^{-iHt}$ is the density operator in Heisenberg representation, $|0\rangle$ is the exact ground state of H with energy E_0, $[\,,\,]$ denotes the commutator and $\theta(x)$ is the Heaviside step function $[\theta(x) = 1$ for $x > 0$ and $\theta(x) = 0$ for $x < 0]$. By inserting a complete set of excited states $\sum_m |m\rangle\langle m|$ and performing a time-frequency Fourier transformation, we obtain the following exact ('Lehmann') representation:

$$\chi(\mathbf{r}, \mathbf{r}', \omega) = \sum_m \frac{\langle 0|\hat{n}(\mathbf{r})|m\rangle\langle m|\hat{n}(\mathbf{r}')|0\rangle}{\hbar\omega - E_m + E_0 + i\eta} - \sum_m \frac{\langle 0|\hat{n}(\mathbf{r}')|m\rangle\langle m|\hat{n}(\mathbf{r})|0\rangle}{\hbar\omega + E_m - E_0 + i\eta} \,, \tag{3.22}$$

where $|m\rangle$ are excited states with energy E_m and η is an infinitesimal positive number. The exact eigenstates and energies of the interacting electron systems are unknown, so (3.22) cannot be evaluated directly. For a non-interacting electron gas, however, all eigenstates are Slater determinants, and (3.22) can be calculated. The only excitations which give non-zero matrix elements are single particle–hole excitations $|m\rangle = c_p^+ c_h |0\rangle$ with energy $\epsilon_p - \epsilon_h$, where p and h label states above and below the Fermi level, respectively. This gives the response function in the independent particle approximation

$$\chi_0(\mathbf{r}, \mathbf{r}', \omega) = \sum_{hp} \frac{\phi_h^*(\mathbf{r})\phi_p(\mathbf{r})\phi_p^*(\mathbf{r}')\phi_h(\mathbf{r}')}{\hbar\omega - \epsilon_p + \epsilon_h + i\eta} - [p \leftrightarrow h] . \tag{3.23}$$

If the electrons did not interact we would have $\chi = \chi_0$. But they do interact. In TDDFT, the interaction is handled as in DFT, by introducing an auxiliary, non-interacting system with the same electron density $n(\mathbf{r}, t)$ which corresponds to a time-dependent effective potential. In the real system, the density change $\delta n(\mathbf{r}, t)$ is induced by the external perturbation $\varphi_{\text{ext}}(\mathbf{r}, t)$. In the auxiliary system, however, the density $n(\mathbf{r}, t)$ corresponds to the sum of the Kohn–Sham potential V_{KS} and the perturbation φ_{ext}. As the Kohn–Sham potential depends on the density, a density change δn gives rise to an induced field $\varphi_{\text{ind}}(\mathbf{r}, t) = \delta V_{\text{KS}}[n(\mathbf{r}, t)]$. Thus, the density change $\delta n(\mathbf{r}, t)$ is due not only to the true external potential φ_{ext} but also to the induced field φ_{ind}. Note that there is a feedback effect: $\varphi_{\text{ext}} \rightarrow \delta n \rightarrow \varphi_{\text{ind}} \rightarrow \delta^2 n \rightarrow \delta\varphi_{\text{ind}} \ldots$, so we need to solve for δn and φ_{ind} self-consistently. Further, in linear response theory, a linear relation between the induced charge density and the induced field is assumed

$$\varphi_{\text{ind}}(\mathbf{r}t) = \int d\mathbf{r}' dt' K(\mathbf{r}t, \mathbf{r}'t') \delta n(\mathbf{r}'t') \tag{3.24}$$

which defines the interaction kernel K. We have $\varphi_{\text{ind}} \equiv \delta V_{\text{KS}} = \delta V_{\text{H}} + \delta V_{XC}$, where

$$\delta V_{\text{H}}(\mathbf{r}t) = \int d\mathbf{r}' \frac{\delta n(\mathbf{r}'t)}{|\mathbf{r} - \mathbf{r}'|} , \quad \delta V_{XC}(\mathbf{r}t) = \int d\mathbf{r}' dt' \frac{\delta V_{XC}(\mathbf{r}t)}{\delta n(\mathbf{r}'t')} \delta n(\mathbf{r}'t') . \tag{3.25}$$

The total time-dependent perturbation in the auxiliary system is often called the 'local field', $\varphi_{\text{loc}} = \varphi_{\text{ext}} + \varphi_{\text{ind}}$. As the electrons of the auxiliary system are independent, they respond to the perturbation φ_{loc} with the free response function χ_0, i.e. $\delta n(\mathbf{r}t) = \int d\mathbf{r}' dt' \chi_0(\mathbf{r}, \mathbf{r}', t - t') \phi_{\text{loc}}(\mathbf{r}'t')$. By construction, the charge densities of the real and auxiliary systems are the same, so we have

$$\chi \, \varphi_{\text{ext}} = \delta n = \chi_0 \, \varphi_{\text{loc}} = \chi_0(\varphi_{\text{ext}} + K\delta n) = \chi_0(1 + K\chi)\varphi_{\text{ext}} , \tag{3.26}$$

where arguments and integration symbols have been suppressed to simplify the notation. Since φ_{ext} is arbitrary, we have

$$\chi = \chi_0 + \chi_0 K \chi \quad \Leftrightarrow \quad \chi = (\chi_0^{-1} - K)^{-1} . \tag{3.27}$$

So the full response function χ can be calculated from free response function χ_0 and the kernel K, by iteration or inversion. Equivalently one can calculate the local potential directly by iteration of $\varphi_{\text{loc}} = \varphi_{\text{ext}} + K\chi_0\varphi_{\text{loc}}$ [8]. The problem is that the exchange–correlation part of the kernel

$$K_{XC}(\mathbf{r}t, \mathbf{r}'t') = \frac{\delta V_{XC}(\mathbf{r}t)}{\delta n(\mathbf{r}'t')} \tag{3.28}$$

is not known exactly. The adiabatic approximation consists in using a static exchange–correlation potential, which may be taken from standard time-independent DFT. In this case, $K_{XC} = [\delta V_{XC}(\mathbf{r})/\delta n(\mathbf{r}')]\delta(t - t')$ such that $\varphi_{\text{ind}}(t)$ changes instantaneously with $\delta n(t)$. As a result, $K(\mathbf{r}, \mathbf{r}', \omega)$ is frequency independent and dynamical screening is neglected. X-ray fields correspond to fast oscillations, so neglecting dynamical effects is questionable.

3.5.3 Absorption Spectra

The optical absorption coefficient is essentially the imaginary part of the response function χ as we shall show now. We consider an electromagnetic wave given by $\mathbf{E}(\mathbf{r}, t) = \mathbf{e}E_0 e^{i\mathbf{q}\cdot\mathbf{r} - i\omega t}$, where $\mathbf{e}$ is the light polarization vector, not to be confused with the electric charge e. The induced electrical polarization is $\mathbf{P}(\mathbf{r}, t) = -e\delta n(\mathbf{r}, t)\mathbf{r}$ and so the change in energy density is $-\mathbf{E} \cdot \mathbf{P} = e\mathbf{E} \cdot \mathbf{r}\delta n$. In the dipole approximation, $\mathbf{E}(\mathbf{r}, t) \approx \mathbf{e}E_0 e^{-i\omega t}$ and the perturbation in (3.17) is given by

$$\varphi_{\text{ext}}(\mathbf{r}, \omega) = eE_0 \mathbf{e} \cdot \mathbf{r} . \tag{3.29}$$

The total induced dipole moment is

$$\boldsymbol{\mu}(\omega) = -e \int \mathbf{r}\delta n(\mathbf{r}, \omega)\mathrm{d}\mathbf{r} = -e^2 E_0 \int \mathbf{r}\chi(\mathbf{r}, \mathbf{r}', \omega)\mathbf{e} \cdot \mathbf{r}'\mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}' , \tag{3.30}$$

and the absorbed energy is $\text{Re}\{\mathbf{E} \cdot \mathrm{d}\boldsymbol{\mu}/\mathrm{d}t\}$ or equivalently $\text{Im}\{\omega\mathbf{E} \cdot \boldsymbol{\mu}(\omega)\}$. The absorption coefficient $\sigma(\omega)$ is the absorbed energy divided by E_0^2, which yields

$$\sigma(\omega) = -4\pi\alpha\hbar\omega \int \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}'\mathbf{e} \cdot \mathbf{r} \, \text{Im}\chi(\mathbf{r}, \mathbf{r}', \omega)\mathbf{e} \cdot \mathbf{r}' . \tag{3.31}$$

This expression of the absorption coefficient is fully equivalent to (3.3). In the independent particle approximation, we put $\chi \to \chi_0$ and obtain from (3.23)

$$\sigma_0(\omega) = 4\pi^2\alpha\hbar\omega \sum_{hp} |\langle \phi_p | \mathbf{e} \cdot \mathbf{r} | \phi_h \rangle|^2 \delta(\hbar\omega + \epsilon_h - \epsilon_p) \tag{3.32}$$

in agreement with (3.9).

In summary, TDDFT with linear response provides a rigorous and efficient framework for calculating absorption spectra. Compared to the independent particle approximation, TDDFT takes the screening of the electromagnetic field into account by introducing the induced field $\varphi_{\text{ind}}(t)$ which is calculated self-consistently with the density change $\delta n(t)$. In practice, the problem is to find good approximations for the unknown exchange–correlation kernel K_{XC}. The Hartree part alone, i.e. putting $K_{XC} = 0$, yields the well-known random-phase approximation (RPA) [10]. Apart from the single particle–hole excitations included in χ_0, the RPA can describe plasmon excitations, i.e. collective oscillations of electron gas, which can be observed, for example, as satellite peaks in core-level photoemission spectra. The RPA kernel also gives rise to a redistribution of spectral weight between different transitions. This may strongly change the peak intensity ratio, e.g. between the L_2 and L_3 white lines in transition elements [10]. In adiabatic TDDFT, K_{XC} can be obtained from standard DFT [8], but such static approximations to K_{XC} do not improve much over the RPA [10, 12]. It appears that complex configuration mixing such as multiplet excitations cannot be described by the common, adiabatic kernels. Going beyond the adiabatic approximation is difficult, but some non-adiabatic kernels have been proposed and applied to the X-ray absorption problem [13].

3.6 Photoemission Spectroscopy

PES is probably the most direct way of probing the electronic structure of materials. In a PES, light is shone on a surface and the kinetic energy, and possibly exit angle and spin, of the emitted electrons is measured. In core-level PES, electrons from the inner atomic shells are excited. As these levels are element specific, core-level photoemission is a powerful tool for chemical analysis.

Angle-resolved core-level photoemission from crystal surfaces is known as X-ray photoelectron diffraction [14]. The photoelectron wave spreads from the core hole site and is diffracted by the neighbouring atoms. Analysis of the diffraction pattern gives precise information about the local structure around the atoms of a given chemical species. X-ray photoelectron diffraction can be well modelled with real-space single or multiple scattering theory on a finite cluster of atoms.

3.6.1 Angle-Resolved Photoemission Spectroscopy

Angle-resolved photoemission spectroscopy (ARPES) is the major method for measuring energy band dispersion (the 'band structure') of crystals. An intuitive picture of ARPES is provided by the three-step model [15]. The three steps are as follows:

1. Photon absorption in the bulk of the material resulting in an inter-band transition $|m\mathbf{k}\rangle \rightarrow |n\mathbf{k}\rangle$, with $\epsilon(n, \mathbf{k}) = \epsilon(m, \mathbf{k}) + \hbar\omega$. Here n, m are band indices and the

three-dimensional crystal momentum vector $\mathbf{k}$ is conserved up to a reciprocal lattice vector $\mathbf{G}$.

2. Propagation of the excited wave to the surface, with damping due to inelastic scattering.

3. Transmission through the surface by matching the Bloch wave $|n\mathbf{k}\rangle$ to a plane wave $\exp(i\mathbf{k}' \cdot \mathbf{r})$. The matching conditions are dictated by conservation of energy and the surface parallel component of $\mathbf{k}$, i.e. $\mathbf{k}'_{||} = \mathbf{k}_{||}$ and $k'^2_{\perp} = k^2_{\perp} + 2mV_0/\hbar^2$, where V_0 represents the surface potential barrier.

The three-step model is very useful for relating the photoemission data to the three-dimensional band structure of the material. However, for an accurate calculation of ARPES intensities, the one-step model should be used, where the photoelectron final state is calculated in all space (bulk, surface and vacuum) as a single wave function with proper boundary conditions (so-called 'time-reversed low-energy electron diffraction' boundary conditions). A suitable computational scheme is the layered Korringa–Kohn–Rostoker method [16].

The hole left behind in the photoemission process is not an independent particle, but it interacts with the electrons and the lattice, giving rise to various many-body effects, which are conveniently described using quasiparticle theory.

3.7 Quasiparticle Theory

In a photoemission experiment, an electron is ejected from the system, which becomes ionized. Neglecting the interaction between the photoelectron and the hole left behind, i.e. applying the so-called sudden approximation, the photoemission excitation is a one-electron removal process from the N-particle ground state to a $N - 1$ particle excited state. In the same fashion, inverse photoemission probes the one-electron addition process from the N-particle ground state to a $N + 1$-particle excited state. The true excitations are called quasiparticles. In the limit of vanishing electron interaction, the quasiparticle wave functions are the spin-orbitals of the ground state Slater determinant and the quasiparticle energies are the one-electron levels. In the independent particle approximation, the quasiparticles are taken as HF or Kohn–Sham orbitals. This neglects electron correlation and the interaction of the electrons with the lattice vibrations. These effects change the quasiparticle energies and wave functions. The quasiparticles are said to be renormalized or 'dressed' by the interaction. In particular, due to inelastic scattering at collective excitations such as phonons and plasmons, the one-electron quasiparticles will decay after a characteristic lifetime. As a result, compared to the delta-function-like photoemission peaks corresponding to the independent particle approximation, the true photoemission peaks are energy shifted and lifetime broadened. Moreover, some spectral weight of the main peak is lost to extra ('satellite') peaks, corresponding to some inelastic process.

3.7.1 Green's Functions

Quasiparticles can be described using many-body Green's function techniques. We introduce the retarded one-electron Green's function

$$G(\mathbf{r}, \mathbf{r}', t - t') = -i\theta(t - t')\langle 0|\{\Psi(\mathbf{r}t), \Psi^+(\mathbf{r}'t')\}|0\rangle, \qquad (3.33)$$

where $\Psi^+(\mathbf{r}t)$ is a Heisenberg field operator which creates an electron at point $\mathbf{r}$ and time t, and Ψ destroys one. $|0\rangle$ is the many-particle ground state and $\{A, B\} = AB + BA$ denotes the anti-commutator. Note that we have suppressed spin for convenience. This Green's function, or 'propagator', gives the probability amplitude for an electron to be found at $\mathbf{r}t$ if one was added at $\mathbf{r}'t'$. The one-electron removal and addition spectrum is given by the spectral function

$$A(\mathbf{k}, \omega) = -\frac{1}{\pi}\mathrm{Im}G(\mathbf{k}, \omega) , \qquad (3.34)$$

where $G(\mathbf{k}, \omega)$ is the space and time Fourier transform of (3.33). In the following, we focus on a perfect crystal and suppress the band index. The Hamiltonian of the non-interacting system is then given by $H_0 = \sum_{\mathbf{k}} \epsilon_{\mathbf{k}}\hat{n}_{\mathbf{k}}$, where $\mathbf{k}$ labels the Bloch eigenstates with energy $\epsilon_{\mathbf{k}}$ and $\hat{n}_{\mathbf{k}}$ is the corresponding occupation number operator. It is easy to see that in this non-interacting case, Green's and spectral functions are given by

$$G_0(\mathbf{k}, \omega) = (\omega - \epsilon_{\mathbf{k}} + i\eta)^{-1} , \quad A(\mathbf{k}, \omega) = \delta(\omega - \epsilon_{\mathbf{k}}) . \qquad (3.35)$$

Thus, the photoemission peaks are delta functions, meaning that Bloch states are exact excitations of energy $\epsilon_{\mathbf{k}}$ (band energy) and infinite lifetime. As mentioned above, due to electron interaction, the true photoemission peaks are shifted, broadened and may have satellite structures. In quasiparticle theory, these effects are described by the so-called self-energy Σ, which is essentially the difference between the inverses of the exact and the free Green's function. The self-energy is defined through the Dyson equation

$$G = G_0 + G_0\Sigma G \quad \Leftrightarrow \quad G^{-1} = G_0^{-1} - \Sigma . \qquad (3.36)$$

For a single band in a crystal, we have

$$G^{-1}(\mathbf{k}, \omega) = \omega - \epsilon_{\mathbf{k}} - \Sigma_{\mathbf{k}}(\omega) . \qquad (3.37)$$

It is clear from (3.35) and (3.37) that $\mathrm{Re}\Sigma$ describes a shift of the eigenvalues $\epsilon_{\mathbf{k}}$ (band energy) and $\mathrm{Im}\Sigma$ results in peak broadening, i.e. it reflects the finite lifetime $\tau = \hbar/\mathrm{Im}\Sigma$ of the quasiparticle. There are various methods to find (approximate) self-energies. For the electron correlation effect, two of the most popular methods are the so-called GW approximation and dynamical mean-field theory.

3.7.2 GW Approximation

The GW approximation was invented by Hedin in 1965 [17] and owes its name from the form of this self-energy, which is $\Sigma = iGW$, i.e. the product (or convolution) of Green's function (G) and the screened Coulomb interaction (W). The latter is given by [18]

$$W(\mathbf{r}, \mathbf{r}', \omega) = \frac{e^2}{4\pi\epsilon_0} \int d\mathbf{r}'' \frac{\epsilon^{-1}(\mathbf{r}, \mathbf{r}'', \omega)}{|\mathbf{r} - \mathbf{r}'|} , \tag{3.38}$$

where $\epsilon(\mathbf{r}, \mathbf{r}', \omega)^{-1}$ is the inverse dielectric function. This expression may be understood by analogy to the electrostatic energy between two electrons in a polarizable medium, which is given by $e^2/[4\pi\epsilon_0\epsilon_r|\mathbf{r} - \mathbf{r}'|]$, where ϵ_r is the relative dielectric permittivity. The dielectric function $\epsilon(\mathbf{r}, \mathbf{r}', \omega)$ generalizes ϵ_r to inhomogeneous media and dynamic screening effects. The GW approximation is most often used in a non-self-consistent way, i.e. as $\Sigma = iG_0W_0$ with the free Green's function G_0 instead of the full Green's function G. The GW approximation has been very successful for correcting band energies of weakly correlated systems. In particular, bandgaps of semi-conductors are very well reproduced in the GW approximation, while the values obtained in DFT (except for DFT-HF hybrid functionals) are systematically too small [19].

3.7.3 Bethe–Salpeter Equation

At this point, we briefly switch back to the problem of absorption spectroscopy. Since light absorption creates an electron–hole pair, absorption spectra are described with an electron–hole (i.e. a two-particle) Green's function G_{eh}. If the excited electron and the hole do not interact, G_{eh} is just the product of the one-particle removal (hole) Green's function G_h and the addition (electron) Green's function G_e. Electron–hole interaction leads to coupling of these two Green's functions, which may be expressed in a Dyson-type equation as [20]

$$\begin{aligned} G_{eh}(1, 2; 1', 2') &= G_e(1, 1')G_h(2, 2') \\ &+ \int G_e(1, 3)G_h(2, 4)K(3, 4; 5, 6)G_{eh}(5, 6; 1', 2')d3d4d5d6 , \end{aligned} \tag{3.39}$$

where 1 stands for all coordinates of particle 1 and K is the interaction kernel. In the Bethe–Salpeter equation (BSE) approach, (3.39) is solved with K given by the screened Coulomb interaction in (3.38) and the bare exchange interaction. The electron and hole Green's functions, G_e and G_h, are commonly computed in the GW approximation. The BSE approach is arguably the most accurate first-principles method for absorption spectroscopy in solids, but it is computationally very demanding. It was first applied to X-ray spectra by Shirley in 1998 [21]. It accounts well

for strong excitonic effects and features electron–hole multiplet coupling in L-edge spectra [22]. Let us note that the latter effect is also well described with multichannel multiple scattering theory [23, 24], where the electron–hole coupling is dealt by a CI calculation of the scattering matrix. However, at present, none of these particle–hole theories can fully account for the complex multiplet structure of L-edge spectra of open-shell transition metal compounds. These spectra are still best described with CI methods, either the semi-empirical ligand-field multiplet model (see Chap. 4) or the ab initio complete active space approach on small clusters [25].

3.7.4 Static and Dynamical Mean-Field Theory

In strongly correlated electron systems, e.g. $3d$ transition metal oxides and $5f$ elements, collective phenomena such as band magnetism, metal–insulator transition and high-T_c superconductivity are observed. These are genuine many-body effects that cannot be explained in the independent particle picture. Itinerant magnetism and the metal–insulator transition are due to the competition between the kinetic energy, which leads to delocalized band states, and strong local Coulomb repulsion which favours electron localization and formation of magnetic moments. The most simple model to study these problems is the (one-band) Hubbard model [26], whose Hamiltonian is given by

$$H = \sum_{k\sigma} \epsilon_k n_{k\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow} = \sum_{ij\sigma} t_{ij} c_{i\sigma}^+ c_{j\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow},$$

where lattice sites are labelled by i and j, the crystal momentum by k and spin by σ. Further, c_ν^+ (c_ν) creates (destroys) an electron in state ν, and $n_\nu \equiv c_\nu^+ c_\nu$ counts them. t_{ij} is the hopping (or 'transfer') integral between sites i and j, and U is the Coulomb energy between two electrons occupying the same site. The corresponding one-electron Green's function is

$$G_{k\sigma}(\omega) = [\omega - \epsilon_k - \Sigma_{k\sigma}(\omega)]^{-1} .$$

Despite the apparent simplicity of the Hubbard model, the exact solution is unknown (except in one dimension) and the self-energy Σ must be approximated. At the lowest level, there is the normal mean-field (i.e. HF) approximation, where Σ is taken to be static, i.e. independent of frequency ω. It is given by $\Sigma_{k\sigma} = U\langle n_{k-\sigma}\rangle$, where the occupation numbers $\langle n_{k-\sigma}\rangle$ must be calculated self-consistently. When the lowest energy solution corresponds to a different occupation between spin-up and spin-down bands $\langle n_{k\uparrow}\rangle \neq \langle n_{k\downarrow}\rangle$, the band energies $E_{k\sigma} = \epsilon_k + U\langle n_{k-\sigma}\rangle$ become exchange split, and the ground state is ferromagnetic. HF and LDA are such static mean-field theories and can account for certain static exchange effects, such as ferromagnetism. But they lack all dynamic correlation, which is crucial for the metal–insulator transition and

for various phenomena seen in photoemission spectra, such as band narrowing and satellite structures.

Dynamic correlation effects can, to some extend, be described by the *dynamical mean-field theory* (DMFT) [27], where the self-energy is taken to be frequency dependent but local, i.e. momentum independent, $\Sigma_{k\sigma}(\omega) \rightarrow \Sigma_{\sigma}(\omega)$. We note that self-energies from static mean-field theory (such as LDA) and dynamical mean-field theory can be, and often are, combined. Although the total self-energy is then both momentum and frequency dependent, it is still an approximation.

The basic idea of DMFT is to map the Hubbard model with correlation ($U \neq 0$) on all lattice sites onto the Anderson model, which describes one correlated atom (the 'impurity') coupled to an effective bath of band states. In the Anderson model, we have $U \neq 0$ only at the impurity site ($i = 0$), and as a consequence, the self-energy is a frequency dependent, but local, quantity $\Sigma_{ij}(\omega) = \Sigma_0(\omega)\delta_{i0}\delta_{ij}$. In DMFT, this local self-energy is taken as the self-energy of the lattice problem (Hubbard model). The mapping, i.e. the definition of the effective bath, must be done in a self-consistent manner such that the on-site matrix elements of the lattice model Green's function $G_{ii}(\omega)$ coincide with those of the impurity model [27]. While the Anderson impurity model is simpler than the Hubbard model, it is nonetheless a complex many-body problem. Implementations of DMFT mostly differ in the approximations used for solving the impurity problem.

DMFT has been applied to photoemission spectroscopy of correlated systems [28] and results in improved spectra compared to independent particle approximation (HF or LDA). In transition metal systems, for example, photoemission spectra calculated in DMFT can account for finite temperature effects, correlation-driven band narrowing and satellite peaks [29].

3.8 Conclusions

In this chapter, I have tried to give a brief introduction to the theory of X-ray absorption and photoemission spectroscopy. Along the way, it appeared useful to present succinctly the principles of several computational methods of electronic structure that are used in spectroscopic calculations. Given the vast nature of the subject, this account is necessarily very incomplete. But I hope that the reader got an idea of the physics underlying the different theoretical methods and that it aroused his/her curiosity to dwell deeper into the subject by reading some of the cited literature.

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