

Chapter 1

Atomic structure and interaction with the electromagnetic field

1.1 LS-coupling

The electronic structure of an atom is determined by the Coulomb interaction between the electrons and the nucleus, as well as between different electrons which is commonly called electron correlation. In the non-relativistic limit, the Hamiltonian H for an atom with N electrons is given in atomic units by

$$H = \sum_{i=1}^N \left(-\frac{1}{2} \nabla_i^2 - \frac{Z}{r_i} \right) + \sum_{i<j=1}^N \frac{1}{r_{ij}}, \quad (1.1)$$

where r_i denotes the relative coordinate of the electron i with respect to the nucleus and $r_{ij} = |r_i - r_j|$. By approximating the Coulomb interaction between the electrons with a mean effective spherical potential $V(r)$, equation (1.1) can be written as

$$H = H_c + H_1 \quad (1.2)$$

with

$$H_c = \sum_{i=1}^N \left(-\frac{1}{2} \nabla_i^2 - \frac{Z}{r_i} \right) + V(r_i) \quad (1.3)$$

and

$$H_1 = \sum_{i<j=1}^N \frac{1}{r_{ij}} - V(r_i). \quad (1.4)$$

H_1 represents the difference between the actual and the averaged Coulomb interactions of the electrons, and contains electron correlation effects. The term H_1 is normally small compared to the terms Z/r_i and $1/r_{ij}$ and can, therefore, be regarded as a perturbation. Due to strong electron-electron correlation in doubly excited two-electron systems, like helium, the Hamiltonian in Eq. (1.2) cannot simply be solved with the perturbation

method. However, the mixing of two-electron hydrogenic configurations due to the interaction term $1/r_{ij}$ can be described well by group-theoretical techniques [23] but not by independent electron picture, resulting in new approximated quantum numbers to characterize the doubly excited states instead of the orbital angular momentum quantum numbers in two-electron systems.

In the relativistic case, other interactions have to be added, of which the spin-orbit interaction represents the largest contribution, which is given by

$$H_2 = \sum_i \xi(r_i) l_i \cdot s_i, \quad (1.5)$$

where $\xi(r_i) = \frac{1}{2r_i} \frac{dV(r_i)}{dr_i}$. l_i and s_i are the orbital angular momentum and spin angular momentum of electron i , respectively. If $H_1 \gg H_2$, the dominating Coulomb interaction preserves the spin and the orbital angular momentum and the vector sums of the individual angular momenta

$$L = \sum l_i \quad \text{and} \quad S = \sum s_i. \quad (1.6)$$

From these, one obtains the total angular momentum J from the coupling

$$J = L + S. \quad (1.7)$$

This is called *LS-coupling*. The opposite case, $H_1 \ll H_2$, is called *jj-coupling* and requires that

$$j_i = l_i + s_i \quad \text{and} \quad J = \sum j_i. \quad (1.8)$$

The case that both perturbations, H_1 and H_2 , are of the same order of magnitude is difficult to handle because both terms must then be treated on the same footing. This situation is called *intermediate coupling*. As a rough rule, one can use *LS-coupling* for the outer shells in low- Z elements, and *jj-coupling* for inner shells in high- Z elements. For other cases, *intermediate coupling* is often required.

From these considerations, *LS-coupling* is expected for He, however, for the special case of doubly excited resonances of helium very close to the $\text{He}^+(N = 2)$ ionization threshold, recent experimental [41] and theoretical results [42] have confirmed that the spin-orbit interaction significantly contributes to the total energy of the atom, and results in a breakdown of *LS-coupling*. Since this particular energy region is not of interest in the present work, the discussions on experimental results and theoretical calculations is based on *LS-coupling* throughout this dissertation.

1.2 Atomic photoionization process

An atom can be ionized by obtaining extra energy from an incoming photon if the extra energy is larger than the negative potential of a bound electron. The single photoionization process of an atom can be expressed by

$$A + h\nu \rightarrow A^+ + e^- . \quad (1.9)$$

This single photoionization process obeys mainly the dipole selection rule for an electronic dipole transition (i.e. a change of the total orbital angular momentum $\Delta L = \pm 1$ and the parity). In the final state, one electron is free and the others remain in a positive ion either in the ground state or in the excited state.

The interaction of a photon with an atom resulting in ionization is usually expressed in terms of a cross section, σ , which is defined as the *transition probability per unit time and per unit target scatterer and per unit flux of incident particles with respect to the atom*. If this photoionization can lead to various channels, i.e. the remaining electrons in the ion could be in various energy levels, we call the cross section specifying to one channel a partial cross section (PCS). In doubly excited helium, PCSs σ_n or σ_{nl} describe satellite cross sections leading to the final states $\text{He}^+(\text{n})$ or $\text{He}^+(\text{nl})$, respectively. A total cross section (TCS), σ_T , can be regarded to be the sum of all PCSs, σ_n or σ_{nl} . The parameter β is related to the scattering angle θ in Eq. (1.22), so that it is called angular distribution parameter (ADP). The ADP together with the TCS and the PCS have become standard quantities in the study of the interactions between photons and atoms. In this section, we shall briefly introduce the derivations of the TCSs, the PCSs, and the ADPs that are employed in this dissertation in order to observe electron correlations and transitions in doubly excited helium.

1.2.1 Interaction of an atom with a photon

For an electron in the electromagnetic field, the mechanical momentum \mathbf{p} has to be replaced by the canonical momentum, which includes the vector potential \mathbf{A} of the field. The scalar potential Φ of the electromagnetic field is also added, giving

$$H = \frac{(\mathbf{p} - e\mathbf{A})^2}{2m_0} + \Phi \quad (1.10)$$

for the Hamiltonian. In Coulomb gauge and space-free electromagnetic field, e.g. in the external field of monochromatized synchrotron radiation, \mathbf{A} and Φ can be chosen

$$\nabla \cdot \mathbf{A} = 0 \quad \text{and} \quad \Phi = 0. \quad (1.11)$$

Under these conditions, the synchrotron radiation field can be described by

$$\mathbf{A}(\omega; \mathbf{r}, t) = A_0 \epsilon \left\{ e^{i(\mathbf{k} \cdot \mathbf{r} - \omega t)} + cc \right\}, \quad (1.12)$$

where ϵ is the polarization vector, A_0 the field intensity, and cc the complex conjugate; \mathbf{k} , \mathbf{r} , ω , and t have their normal meanings. One can regard the interaction with the radiation field as an additional potential energy term, which perturbs the atom with the vector potential \mathbf{A} alone.

The time-dependent Schrödinger equation in an electromagnetic field then reads

$$i\hbar \frac{\partial \Psi}{\partial t} = \left[\frac{(\mathbf{p} - e\mathbf{A})^2}{2m_0} + V(r) \right] \Psi, \quad (1.13)$$

where $\mathbf{p} = -i\hbar\nabla$ and $V(r)$ is the Coulomb potential. With the conditions given in Eq. (1.11), this results in

$$(\mathbf{p} - e\mathbf{A})^2 \Psi = (p^2 - 2e\mathbf{A} \cdot \mathbf{p} + e^2 A^2) \Psi. \quad (1.14)$$

One can therefore write the Schrödinger equation (Eq. (1.13)) as

$$i\hbar \frac{\partial \Psi}{\partial t} = \left[H_{atom} + \frac{ie\hbar}{m_0} \mathbf{A} \cdot \nabla + \frac{e^2}{2m_0} A^2 \right]. \quad (1.15)$$

From the full Hamiltonian given in Eq. (1.15) with three terms, only one term, namely $\mathbf{A} \cdot \nabla$, is responsible for the photon-atom interaction. For a weak vector potential A , it can be treated as a perturbation. On the same footing, the contribution of term A^2 can also be neglected. Employing time-dependent perturbation theory and Fermi's golden rule for the transition rate w from an initial atomic state $|i\rangle$ to a final atomic state $|f\rangle$, one obtains

$$w = \frac{2\pi}{\hbar} |\langle f | H_{int} | i \rangle|^2 \delta(\text{energy conservation}), \quad (1.16)$$

with the time-independent interaction

$$H_{int} = \frac{e\hbar}{2m_0} A_0 e^{i\mathbf{k}\cdot\mathbf{r}} \boldsymbol{\epsilon} \cdot \nabla. \quad (1.17)$$

1.2.2 Dipole transition approximation

The transition matrix between the initial state $|i\rangle$ and the final state $|f\rangle$ can be written according to Eqs. (1.16) and (1.17) as

$$D_{if} \propto \langle f | e^{i\mathbf{k}\cdot\mathbf{r}} \boldsymbol{\epsilon} \cdot \nabla | i \rangle. \quad (1.18)$$

In many cases of practical interest this matrix can be simplified by expanding the exponential function $e^{i\mathbf{k}\cdot\mathbf{r}}$ as

$$e^{i\mathbf{k}\cdot\mathbf{r}} = 1 + (i\mathbf{k} \cdot \mathbf{r}) + \frac{1}{2!} (\mathbf{k} \cdot \mathbf{r})^2 + \dots \quad (1.19)$$

Normally in the low-photon-energy region, the $\mathbf{k} \cdot \mathbf{r}$ term in the expression given in (1.19) is three orders of magnitude smaller than unity. If one just includes the first term, unity, in this expansion, it is known as the *electric dipole approximation*. The electric quadrupole transitions or magnetic dipole transitions described by the second term of Eq. (1.19) are weaker by a factor α^2 for low energies (< 1000 eV), and under these conditions, electric dipole approximation works well. Here, α is the fine structure constant. As the photon energy increases, the electric quadrupole transition strength being proportional to $\omega^4 \alpha^2$, increases dramatically in comparison to the electric dipole transition strength being proportional to ω^2 and magnetic dipole transition being proportional to $\omega^2 \alpha^2$ (for details, see Ref. [43]). Therefore, for doubly excited resonances of helium, which all

have excitation energies below 79 eV, the electric dipole approximation can be employed safely throughout this dissertation. Since the magnetic dipole term is at least a factor α^2 smaller than the electric dipole term, it can be neglected even in the low-energy region.

If one uses linearly polarized light in dipole approximation, the dipole transition matrix D_{if} in Eq. (1.18) can be written as $\langle f | \nabla | i \rangle$, which is called the *velocity form*. With the help of the general commutation relation

$$\frac{d\mathbf{r}}{dt} = \frac{\partial \mathbf{r}}{\partial t} + \frac{i}{\hbar}[H, \mathbf{r}] = \frac{i}{\hbar}[H, \mathbf{r}] \quad (1.20)$$

and $\mathbf{p} = i\hbar\nabla = m_0 d\mathbf{r}/dt$, one finds

$$\langle f | \nabla | i \rangle = m_0(E_f - E_i) \langle f | \mathbf{r} | i \rangle = m_0\omega \langle f | \mathbf{r} | i \rangle, \quad (1.21)$$

which is called the *length form* of the dipole matrix. These forms of the dipole matrix are completely equivalent only for exact initial- and final-state wavefunctions since the relations $H|x\rangle = E_x|x\rangle$, with $x = i$ and f , are used in Eq. (1.21). Therefore, the differences of the matrix elements in these two forms are often used to check the quality of the target wavefunctions used in calculations. In Part III of this dissertation, our calculations employing R-matrix method will be presented in both forms, velocity form and length form.

1.2.3 Cross sections and angular distribution parameters

For photoelectrons ejected from atoms by linearly polarized radiation, the differential cross sections (DCS) can be written, in the electric dipole approximation, as [44, 45, 46]

$$\frac{d\sigma_{nl}}{d\Omega} = \frac{\sigma_{nl}}{4\pi} \left[1 + \beta_{nl} \left(\frac{3\cos^2\theta - 1}{2} \right) \right], \quad (1.22)$$

where n and l are, respectively, the principal and the orbital angular momentum quantum numbers of the residual ion, θ is the angle between the momentum of the photoelectron and the polarization vector of the photon with both directions being in the plane perpendicular to the light propagation direction, which is called *dipole plane*. The PCS σ_{nl} , which leads to the final state $|nl\rangle$ of the ion, can be written as

$$\sigma_{nl} = \frac{1}{3(2L_i + 1)} \sum_{l', L_f} |M(nll'L_f)|^2. \quad (1.23)$$

The ADPs β_{nl} can be described by [45, 46]

$$\begin{aligned} \beta_{nl} = & \frac{5}{\sigma_{nl}(2L_i + 1)} (-1)^{L_i l} \sum_{l'_1, L_f^1} \sum_{l'_2, L_f^2} \left[(2l'_1 + 1)(2l'_2 + 1)(2L_f^1 + 1)(2L_f^2 + 1) \right]^{1/2} \\ & \times \begin{pmatrix} 1 & 1 & 2 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l'_1 & l'_2 & 2 \\ 0 & 0 & 0 \end{pmatrix} \left\{ \begin{matrix} 1 & 1 & 2 \\ L_f^1 & L_f^2 & L_i \end{matrix} \right\} \left\{ \begin{matrix} l'_1 & l'_2 & 2 \\ L_f^1 & L_f^2 & l \end{matrix} \right\} \\ & \times M(nll'_1 L_f^1) M(nll'_2 L_f^2)^*. \end{aligned} \quad (1.24)$$

L_i and L_f are the orbital angular momenta of initial and final states, respectively, and l' is the orbital angular momentum of the photoelectron. $M(nll'L_f)$ is the transition amplitude in the electric dipole approximation and includes the Coulomb phase shift factor. From the experimental side, equations (1.23) and (1.24) for the PCSs, σ , and the ADPs, β , are too complicated to be employed for profile analysis of the spectra. Therefore, these expressions have to be parametrized, which will be presented in detail in Sect. 3.1 together with the parametrization of the resonances in the TCSs, σ_T .

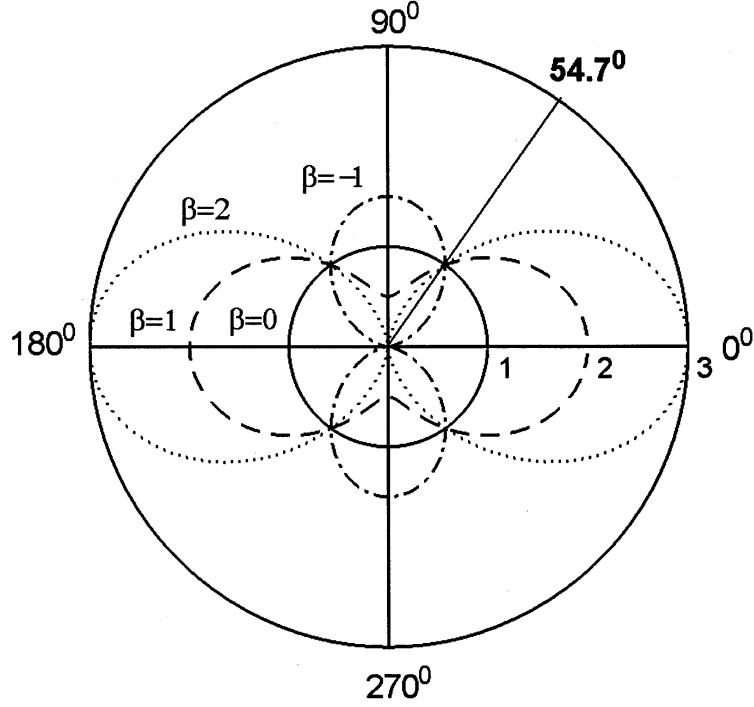


Figure 1.1: Polar plot of the angular distributions of photoelectrons for the four values $\beta = -1, 0, 1,$ and 2 .

From Eq. (1.22), one can derive that the β_{ns} is equal to 2 in LS-coupling. In addition, the requirement that the DCSs in Eq. (1.22) cannot be negative results implies that the values of the ADPs β are restricted by the inequality

$$-1 \leq \beta \leq 2. \quad (1.25)$$

The angular distributions of photoelectrons for the four values $\beta = -1, 0, 1,$ and 2 are plotted in Fig. 1.1. The PCS can be measured directly by mounting the detector at the magic angle, $\theta \approx 54.7$, since under this condition the second term in Eq. (1.22) becomes equal to zero. From Fig. 1.1, one can also see that the photoelectron intensity at the magic angle is independent of the β values. Due to the two unknown parameters σ_{nl} and β_{nl} in Eq. (1.22) at least two detectors have to be mounted at different angles in order to obtain the ADPs from the experiment. A larger number of detectors can, however, provide more precise values for β . Later in this dissertation, two photographs of the experimental set-up allowing the use of up to 12 TOF spectrometers are shown, which was used in the ADP measurements of this dissertation.

In theory, the n -specific ADP β_n are related to the nl -specific β_{nl} by

$$\beta_n = \frac{-8\pi A_n^2}{\sigma_n} = \frac{-8\pi \sum_l A_{nl}^2}{\sigma_n} = \frac{-8\pi \sum_l \frac{A_{nl}^2}{\sigma_{nl}} \cdot \sigma_{nl}}{\sigma_n} = \frac{\sum_l \beta_{nl} \sigma_{nl}}{\sum_l \sigma_{nl}}, \quad (1.26)$$

where A^2 , referred to A_2 in Ref. [46], is proportional to the real part of the transition amplitude, $\text{Re}M(nll'_1 L_f^1)M(nll'_2 L_f^2)^*$. Note that, experimentally, the terms $\sum_l \beta_{nl} \sigma_{nl}$ and $\sum_l \sigma_{nl}$ are averaged over the energies; therefore, in order to compare with experimental data, the calculated β_n should be obtained by the convoluted terms $\sum_l \beta_{nl} \sigma_{nl}$ and $\sum_l \sigma_{nl}$, and not by a convolution of their fraction; this fact was relevant for the present theoretical work which will be presented in part III.