Double Excitations in Helium Atoms and Lithium Compounds

MARCUS AGÅKER
Dissertation presented at Uppsala University to be publicly examined in Polhelmsalen, Ångströmlaboratoriet, Uppsala, Friday, May 26, 2006 at 10:15 for the degree of Doctor of Philosophy. The examination will be conducted in English.

Abstract

This thesis addresses the investigation of doubly excited 2l’nl states in helium atoms and double core excitations in solid lithium compounds.

Measurements on He are made in field free environments and under the influence of electric and magnetic fields, using synchrotron based inelastic photon scattering. Cross sections for scattering to singly excited final states are directly determined and compared to theoretical results and are found to be in excellent agreement. Radiative and spin-orbit effects are quantified and are shown to play an important role in the overall characterization of highly excited He states below the N = 2 threshold. A dramatic electric field dependence is also observed in the fluorescence yield already for relatively weak fields. This signal increase, induced by electric as well as magnetic fields, is interpreted in terms of mixing with states of higher fluorescence branching ratios.

Double core excitations at the lithium site in solid lithium compounds are investigated using resonant inelastic x-ray scattering (RIXS). The lithium halides LiF, LiCl, LiBr and Lil are studied as well as the molecular compounds LiO, LiCO, and LiBF4. States with one, as well as both, of the excited electrons localized at the site of the bare lithium nucleus are identified, and transitions which involve additional band excitations are observed. A strong influence of the chemical surrounding is found, and it is discussed in terms of the ionic character of the chemical bond.

Keywords: Soft X-ray emission, resonant inelastic X-ray scattering, double excitations, lithium halide, helium

Marcus Agäker, Department of Physics, Atomic and molecular physics, Box 530, Uppsala University, SE-75121 Uppsala, Sweden

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ISSN 1651-6214
ISBN 91-554-6572-2
urn:nbn:se:uu:diva-6889 (http://urn.kb.se/resolve?urn=urn:nbn:se:uu:diva-6889)
“... after 5 years of studies, taking 40p of courses, supervising 16 classes of 428 students in the course lab, 94 days as beamline manager at MAX-lab, 271 days of traveling, of which 250 days at synchrotrons divided on 30 occasions, with 3768 hours of beamtime, producing 2695 X-ray absorption spectra and 1311 soft X-ray emission spectra, I am finally done.”
List of papers

This thesis is based on a collection of articles listed below. Each paper will be referred to in the text by its Roman numeral.


VII. **Double Core Excitations in Lithium Halides**, M. Agåker and J.-E. Rubensson, in manuscript

VIII. **Double Excitations at the Lithium Site in Solid Li Compounds**, M. Agåker and J.-E. Rubensson, in manuscript

IX. **Multi-Center Resonant Inelastic Soft X-ray Scattering in LiI?**, M. Agåker and J.-E. Rubensson, in manuscript

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The following articles have been omitted from the thesis. They were omitted either due to the character of the material, or due to the limited extent of my contribution.


Comments on my participation
Experimental studies performed at synchrotron facilities are always an effort of many people, which is often reflected by the lengthy author lists. My contribution to the papers has been on the experimental side for all papers and the analysis and writing for some. Paper I is based upon results from experiments performed at BESSY-II in Berlin, Germany. Here I was only present during one of the two beamtimes. I took part in the onsite preparations of the experiment and for the actual recording of data, but I was not involved in the writing. Papers II-IV contain results from measurements performed at the synchrotron facility ELETTRA in Trieste, Italy. For these measurements I was responsible for designing two of the three experimental set-ups used, as well as partaking in the general preparations. I also participated in the measurements at the synchrotron for all three papers and was partially involved in the analysis and discussion of the data, others made the final analysis and the writing up of the papers. Papers V to IX contain experiments conducted at MAX-Lab in Lund, Sweden. These experiments are the ones in which I have been most active. I designed the experimental set-up, made the preparations for the measurements and carried out the experiment. I also developed the experimental methods needed to avoid problems associated with measurements on sensitive samples and on states with a low yield. This later part of the work included the developments of sample preparation procedures, calibrating and optimizing refocusing optics, development of “slitless” measuring methods as well as the writing of a computer program for measuring that can handle the control of undulator, monochromator and manipulator simultaneously or independently as well as data collection. I have also done the analysis of the experimental data, identified many states not known earlier and demonstrated their participation in various physical processes. The writing of the papers has been done in close collaboration with Professor J.-E. Rubensson.
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Abbreviations

BCC  Body Centered Cubic
CB   Conduction Band
CI   Configuration Interaction
DOS  Density of States
DSBE Doubly Excited Symmetry Basis
eV   electron volts
FBR  Fluorescence Branching Ratio
FCC  Face Centered Cubic
FS   Final State
FY   Fluorescence Yield
g   Gerade
GS   Ground State
IS   Intermediate State
LCAO Linear Combinations of Atomic Orbitals
LS   Russell-Saunders
MCP  MultiChannel Plate
MO   Molecular Orbital
o   Odd
PFY  Partial Fluorescence Yield
RIXS Resonant Inelastic X-ray Scattering
(R)XES Resonant XES
SC   Simple Cubic
SO   Shake Off
SXA  Soft X-ray Absorption
SXE  Soft X-Ray Emission
TS1  Two Step One
TS2  Two Step Two
u   Ungerade
VB   Valence Band
XAS  X-ray Absorption Spectroscopy
XES  X-ray Emission Spectroscopy
Introduction

The investigation of the electronic structure of atoms and molecules has been the subject of continuous research efforts during the last 100 years. Parallel to the experimental discoveries, theoretical models, describing the observed phenomena as well as predicting new ones, not yet observed, has evolved. The theories about the dynamics of the electrons and their correlations are still being developed, particularly in order to give insight to states of exotic atoms. From Bohr’s atomic model in 1913 to the more advanced quantum mechanical models developed during the 30’s until today, the search for a better model is still a highly active field of research. Even though we are still using quantum mechanics as a general tool the internal models and concepts in this field are continuously developing. To further enhance our understanding and improve the models we are looking for more and more exotic systems where we can study the most extreme behaviors and test our current understanding, be it more complex systems, strange combinations of atoms or strange and unusual states in atoms and molecules.

One such state is the hollow atom. In a hollow state one entire sub shell of an atom or ion has been emptied of its content of electrons. This is not a natural state for the electronic configuration (on earth) and can only be induced artificially and with low probability compared to the alternative of single electron ionization. By studying these states we can learn about the electron-electron interaction in the atoms since the electrons in this case are correlating strongly with each other. Hollow states have traditionally been studied in free atoms and ions using a range of different excitation methods, electron discharges, photon induced excitations and ionic recombination. Here the atoms are free of influences from the surroundings and there are no spatial limitations to the kind of states produced, giving a very fundamental picture of the internal electron-electron correlation. Investigations of these states have historically been restricted because of experimental limitations. Intensities, both in target-beams, excitation-beams and in the signal detection, have been too low to make extensive measurements of these systems. Since the introduction of the third generation synchrotron sources, sufficient photon excitation intensity is now available as well as selective excitations through energy tuning, and the efficiency of the detector systems have been improved with the introduction of electronic measurement systems, making it possible to study these states in a methodical way.
Background

Author’s Introduction
In this chapter I have chosen to review some basic concepts of quantum mechanics and radiation generation. I am by no means a theoretician and the following description is not a complete derivation of the formulas (for a complete derivation see [B1-B8]) describing observed phenomena in experimental physics, nor is it intended to be so. It is meant to be a background to the experimental part and in some parts a motivation to why we do the experiments that we do.

The first part of this chapter contains a short history of the early developments of quantum mechanics. After that there are some basic descriptions of the concepts in quantum mechanics describing the state of particles and their interaction with photons. Some of these descriptions are very basic while others are more advanced. Several of the presented models describe the same phenomenon in different ways. Depending on what one wants to describe one can choose a model of sufficient complexity for the task. Since this work spans over a large part of atomic, molecular and solid state physics, utilizing parts of them all, it becomes a rather large section.

The second part concerns the generation of synchrotron radiation which has been the workhorse in the experimental studies presented here. In this section general principles are explained as well as specific methods of producing high intensity monochromatic radiation.

The third and last part concerns the conceptual picture we work with when interpreting and discussing our results. This part is perhaps not so much theory as a “handwaving” interpretation of theory. It obviously has its flaws since it is a simplified picture of the theoretical models but it is useful when thinking about possible processes to explain observed features.

Short history
Until the beginning of the 20th century, classical mechanics had been enough to explain most observations made in experimental physics. Newton mechanics explained the movements of bodies, both terrestrial and celestial. Maxwell’s equations explained the electric and magnetic fields, as well as ordinary optics. There were theories about electricity and how to manipulate it. Chemists had characterized the different elements (known at the time) and
organized them according to their properties into the periodic table. But there were a few observations that could not be explained in these classical models. For example, such phenomena as black body radiation, the photoelectric effect, and the dark lines observed in the sun spectrum. A new theory was needed in order to explain these observations, and the answer was quantization. In 1900 M. Planck [1-4] explained the black body radiation by introducing the quantization of energy for a harmonic oscillator. The oscillator could not have any energy but was limited to discrete, quantized energies or frequencies:

\[ E_n = n\hbar \nu \quad n = 0, 1, 2, \ldots \]

Here \( n \) is an integer and \( \nu \) the frequency of the oscillator. The proportionality constant \( \hbar \) is Planck’s constant. The photoelectric effect was explained by A. Einstein [5-7] in 1905 as a result of an adaptation of M. Planks hypothesis of quantized energies into the absorption and emission of radiation particles, photons, of an energy corresponding to the difference between two discrete energies of the harmonic oscillator. These photons also had the remarkable property that they could behave both as particles and as waves. The observation of emission and absorption lines for different atomic species also led N. Bohr to present his atomic model [8-10] in 1913 which could explain the spectrum of atomic hydrogen. Since hydrogen is present in the outer regions of the sun the dark lines in the sun spectrum could be identified as absorption in hydrogen atoms. N. Bohr proposed that the atom consists of a nucleus around which an electron is circling. The electron could however only circulate on certain specific orbits corresponding to discrete energy levels. This model is a development of E. Rutherford’s model of the constitution of the atom [11] and an adaptation to the idea of quantization. Bohr also postulated that an electron in an orbit does not radiate as a normal charged accelerated particle would (a circular orbit implies acceleration), he called these orbits stationary states. A transition between two levels in the atom would require/release an energy quantum equal to the difference between the two orbital levels and this energy would be absorbed / released in the form of a photon so that:

\[ \hbar \nu = E_b - E_a \]

\( E_a \) is the energy of the first state and \( E_b \) is the energy of the second state, \( \nu \) is the frequency of the radiation and \( \hbar \) is Planck’s constant. The Bohr atomic model is however only a combination of classical mechanics and the idea of quantization. Even though it can predict the energy levels of a one-electron atom it is not entirely satisfying, since it can’t provide a method for calculat-
ing the rates of transitions and it can’t be generalized to two or more electrons. The model had to evolve to provide more answers.

In 1923 L. de Broglie [12-17] suggested that not only photons could exhibit both a wave and particle nature. He suggested that this applies to all particles such that the wavelength, \( \lambda \), is proportional to the inverse of the momentum, \( p \).

\[
\lambda = \frac{h}{p}
\]

All this contributed to the postulation of quantum mechanics. In 1925-26 matrix mechanics was presented by W. Heisenberg, M. Born and P. Jordan [18-20] and in 1926 E. Schrödinger [21-23] presented his wave mechanics which was inspired by L. de Broglie’s matter waves. These two theories are equivalent, as Schrödinger proved in 1926 [24]. Today they form the basics of quantum mechanics. In 1929 P. A. M Dirac presented a general formalized formulation of quantum mechanics [25-27] where he introduced the mathematical concepts of group theory. The fundamental equation in quantum mechanics is the time independent Schrödinger equation and the concept of the wave function:

\[
\hat{H}\Psi = E\Psi
\]

\( \hat{H} \) is an operator, called Hamiltonian, that will extract information from the wave function \( \Psi \), in the form of the eigenvalues \( E \). The wave function \( \Psi \) contains all information about the observables of a system. The equation is unchanged and it is the expression of \( \hat{H} \) and the methods of solving the Schrödinger equation and finding \( \Psi \) and \( E \) that are evolving to accommodate more complex systems and phenomena in modern quantum mechanics. [B1, s 1-39]

Quantum mechanics

Electronic states

The fundamental assumption of (non relativistic) quantum mechanics is that all observable quantities of a particle can be described by a single function, a wave function. By applying an operator to this wave function any particular observable can be obtained from the function, such as energy, momentum, position etc.
Quantum mechanics is built around the Schrödinger wave equation [B1, s 82]:

\[ \dot{\Psi}(\vec{r}, t) = i\hbar \frac{\nabla^2 \Psi(\vec{r}, t)}{2m} - \frac{\hbar^2}{2m} \nabla^2 \Psi(\vec{r}, t) = \frac{i\hbar}{\partial t} \Psi(\vec{r}, t) \]

Assuming that the wave equation can be written as a separable time independent part and a time dependent part the wave function can be expressed as a product of the two such that:

\[ \Psi(\vec{r}, t) = \Psi(\vec{r})\Phi(t) \]

Using this form of the wave function the wave equation reduces to a time independent and a time dependent Schrödinger wave equation.

\[ -\frac{\hbar^2}{2m} \nabla^2 \Psi(\vec{r}) + V(\vec{r})\Psi(\vec{r}) = E\Psi(\vec{r}) \]

\[ i\hbar \frac{\partial}{\partial t} \Phi(t) = E\Phi(t) \]

The time independent wave equation can then be written as:

\[ \hat{H}\Psi = E\Psi \]

This is an eigenvalue equation, where \( \hat{H} \) is an operator called the Hamiltonian and \( \Psi \) is the wave function describing the state of the system. \( E \) is the eigenvalue of the function to the Hamiltonian operator. [B1, s 99-100]

*When describing quantum mechanical states in formula it is usually done with the wave function notation or through Dirac bracket notation. Dirac bracket notation is related to the wave function by the symbol \( \langle \Psi_2 \mid \Psi_1 \rangle \) defined as:

\[ \langle \Psi_2 \mid \Psi_1 \rangle = \int \Psi_2^* (\vec{r}) \Psi_1 (\vec{r}) d\vec{r} \]

This symbol \( \langle \Psi_2 \mid \Psi_1 \rangle \) consists of two parts \( \langle \Psi_2 \rangle \) and \( \mid \Psi_1 \rangle \) which are known as bra and ket respectively. \( \Psi_1 \) and \( \Psi_2 \) are two square integrable functions. [B1, s 193]
Independent particle model

In its simplest form the atom consists of a positive nucleus (proton) to which a negative charge is bound (electron). In this case the description of the system becomes a two body problem. If it is assumed that the mass of the nucleus is much larger than that of the bound electron, so that the nucleus can be considered as stationary, only the motion of the electron has to be considered. In the independent particle model each electron’s interaction with the nucleus is treated independently. The electron is assumed to move in an average field of the other electrons but does not interact directly with them. In the one electron atom the Hamiltonian becomes:

\[ \hat{H} = -\frac{\hbar^2}{2m} \nabla^2 - \frac{Ze^2}{4\pi\varepsilon_0 r} \]

The Hamiltonian, \( \hat{H} \), is an energy operator and the eigenvalues to this operator are the energies of the wave function. \( Ze \) is the nuclear charge (\( Z \) is the number of protons in the nucleus), \( e \) is the electronic charge, \( m \) is the reduced mass, \( \varepsilon_0 \) is the permittivity of vacuum and \( r \) is the position vector of the electron.

The square of the wave function can be viewed as a position probability density, \( P(\vec{r}, t) \), that gives the probability of finding the particle in a certain volume element when integrated over said volume. The generalized solution to the Schrödinger equation for the system corresponding to a specific energy (\( E \)), has the property of being time independent since the position probability density is:

\[ P(\vec{r}, t) = \Psi^*(\vec{r}, t)\Psi(\vec{r}, t) = \Psi^*(\vec{r})\Psi(\vec{r})e^{-\frac{L(E-E')}{\hbar}} = \Psi^*(\vec{r})\Psi(\vec{r}) = |\Psi(\vec{r})|^2 \]

These states, \( \Psi(\vec{r}) \), are called stationary states. The solution to the Schrödinger wave equation can be seen as a standing wave where the intensity oscillates in time but does not change in space and the wave functions form probability distributions representing the probability of finding the electron in a specific location. [B1, s 99-102]

For the one electron system the wave function can be expressed as a product of radial functions (\( R_{nl} \)) and spherical harmonics (\( Y_{lm} \)) such that:

\[ \Psi(\vec{r}) = R_{nl}(r)Y_{lm}(\theta, \phi) \]

Each electronic state is represented by three quantum numbers, generally integers. Here \( r, \phi \) and \( \varphi \) are spherical coordinates and \( n, l \) and \( m_l \) are quan-
tum numbers defining the physical state of the electron. The quantum number \( n \) is the principal quantum number, which is related to the radial position of the electron. The quantum number \( l \) is the angular momentum quantum number and reflects the electron’s orbital momentum. The quantum number \( m_l \) represents the angular momentum projection along the \( z \)-axis which is correlated to the vertical motion of the electron. There is also another quantum number associated with the electronic system which is usually mentioned, \( m_s \), which is the electron spin projection which is related to the electron’s magnetic moment, but this part has not been included above as it generally does not influence the physical extension of the wave function. It does however become necessary to include when discussing the occupancy of a certain orbitals or when magnetic interactions has to be considered. The parts of the wave function, which are not needed or influenced by the current treatment of the state can be neglected and are usually set to one in the theoretical treatment. Therefore spin will be ignored until later. For one electron systems, with the above mentioned wave function and Hamiltonian, the eigenvalues \( E \) become:

\[
E_n = -\frac{m e^4 Z^2}{8e_0 \hbar^2 n^2}
\]

As can be seen from the inclusion of the principal quantum number \( n \), the energy levels are discrete and separated due to the radial position of the electron. The principal quantum number \( n \) can take any integer number \( 1, 2, 3..., \infty \). The angular momentum \( l \) can take the values \( 0, 1, 2... n-1 \). These are in turn degenerate with respect to \( m_l \) which can take the values \( l, l-1, l-2 ... -l \) This gives each state a unique set of quantum numbers. These sets are usually grouped into what is called shells and orbitals. Shells are dependent on the principal quantum number \( n \) and are named \( K, L, M, N... \) while orbitals are called \( s, p, d... \) regarding to the \( l \) quantum number of \( 0,1,2,... \). Each of these are then divided on \( m_l \) so that there are one \( s \) orbital, three \( p \) orbitals and five \( d \) orbitals etc. Each orbital can contain two electrons with different spin according to Pauli’s exclusion principle [28].

In the independent particle model, where each electron only interacts with the nucleus and the presence of other electrons are treated as an average-field perturbation, the wave function can be expanded to include many-electron systems by the use of perturbation theory. The exact method of doing this is not within the scope of this text, but the wave functions will be of the type:

\[
\Psi_{12...}(\vec{r},t) = \Psi_1(\vec{r}_1,t)\Psi_2(\vec{r}_2,t)...
\]
\( \Psi_n(\vec{r},t) \) represents the state wave function of the \( n^{th} \) electron so that the total wave function consists of an antisymmetric product of single electron wave functions, where each electron is described by its own set of quantum numbers, \( n, l, m_l, \) and \( m_s. \)

When there is more than one electron in the system the quantum numbers are coupled to represent the total state of the atom in a term symbol. There are several ways to couple the quantum numbers depending on the different interaction strengths.

The most common couplings in atomic physics is \( LS \) (Russell-Saunders) coupling (weak spin-orbit interaction), and \( jj \)-coupling (strong spin-orbit interaction). In \( LS \) coupling the angular momentum \( L \) and spin \( S \) is defined as the vector-sum of the contributing electron’s angular momentum \( l_n \) and spin \( s_n \) (only electrons outside closed shells contribute):

\[
L = l_1 + l_2, l_1 + l_2 - 1, ... |l_1 - l_2|
\]

\[
S = s_1 + s_2, s_1 + s_2 - 1, ... |s_1 - s_2|
\]

If there are more than two electrons that need to be coupled, the vector addition is repeated for each extra electron brought in so that \( l_1 \) and \( l_2 \) is coupled to \( l_{12} \); then \( l_{12} \) is coupled to \( l_3 \) forming \( l_{123} \) etc, the same is done for the spin quantum numbers. Once all electrons are coupled into a total \( L \) and \( S \), these two are coupled to a total angular momentum quantum number \( J \).

\[
J = L + S, L + S - 1, ... |L - S|
\]

This is normally represented in a term symbol \( ^{2S+1}L_J \). There are selection rules governing the coupling to eliminate equivalent electrons, i.e. electrons that would have the same quantum numbers, limiting the number of allowed terms. \( LS \) coupling is mostly used when treating light atoms where the electrostatic interaction between the electrons is larger than the spin-orbit interaction.

If the spin-orbit interaction is not weak compared to the electrostatic interaction between the electrons, as in heavy atoms, \( jj \)-coupling is used. In \( jj \)-coupling each electrons \( l_n \) and \( s_n \) is coupled to an electronic \( j_n \) through vector addition and then all electronic \( j_n \)'s are coupled to a total \( J \).

[\[B2, s 69-72\]}

In some cases an outer valence electron or excited electron outside a nearly filled shell will experience different interaction strengths compared to the core electrons. In this case something called pair coupling is used. There are two limiting cases of this type of coupling called \( JK \) and \( LK \) coupling. Pair coupling is applied mainly when the excited electron has large angular
momentum, as the electron does not penetrate the core in this case, and hence experiences only a small spin-dependent Coulomb interaction.

The most common limiting type of pair coupling is $JK$ coupling, also known as $JL$ coupling [29]. In this case the outer electron’s spin-orbit interaction is greater than the electrostatic interaction between the electrons. The core electrons outside the closed shells are coupled in the normal way in to a $L'$, $S'$ and $J'$ for the atomic core. Then the outer electron’s angular momentum $l_{\text{out}}$ is coupled to the atomic core’s total angular momentum $J'$ with vector addition. This results in a new quantum number $K$:

$$K = J' + l_{\text{out}}, J' + l_{\text{out}} - 1, \ldots, |J' - l_{\text{out}|}$$

The total angular momentum of the system is then determined by coupling the outer electron’s spin to the $K$ quantum number through vector addition.

$$J = K \pm s_{\text{out}}$$

The term symbol is $J'[K]_J$.

The other limiting form of pair coupling is $LK$ coupling [30]. Here (two–electron configurations) the direct Coulomb interaction is greater than the spin-orbit interaction of either electron and the spin-orbit interaction of the inner electron is the second most important factor. First the two electron’s angular momenta, $L'$ and $l_{\text{out}}$, are coupled to a total $L$. $L$ is then coupled to the inner electron’s spin, $S'$, in $K$. $K$ and the outer electron’s spin, $s_{\text{out}}$, is then coupled to the total angular moment $J$.

$$L = L' + l_{\text{out}}, L' + l_{\text{out}} - 1, \ldots, |L' - l_{\text{out}}|$$

$$K = L \pm S'$$

$$J = K \pm s_{\text{out}}$$

The standard term notation in this case is $L[K]_J$.

[B3, s 128-130]

In a doubly excited state where one electron stays close to the nucleus, while the other might be excited to high orbitals far from the nucleus, pair coupling might be used since the electrons are located at different distances from the nucleus and thus experience different interaction strengths.
Configuration interaction

The states described so far have been described in the independent particle model, i.e. the wave function is composed of single electron wave functions individually modified with perturbation theory to accommodate the other electrons screening of the nucleus and the electron-electron interaction. This holds for single electron excitations where only one electron moves at a time. When discussing double excitations, the independent particle model is no longer valid [31, 32, 33] and the introduction of Configuration Interaction (CI) is needed. This states that the actual stationary states may be represented as a superposition of states of different configurations, which are “mixed” by the interaction between the electrons, but not just as a superposition but with interference between the configuration channels as well.

When the energy introduced to a system is larger than the binding energy of the loosest bound electron in the atom, this electron can be removed from the system creating an ion and a free electron, which is referred to as continuum states or a continuum channel. The energy introduced to the system might also excite a deeper bound electron to a discrete empty state below the ionization threshold within the continuum of the weaker bound electron if the energy is large enough. If the system contains two or more electrons the energy introduced to the system can also be shared among the electrons in such a way that the system is excited to a discrete energy level creating a multiply excited state. Since these discrete states exist parallel with the continuum states the two channels interact with each other and the CI give rise to a phenomenon called autoionization where the excited state “relaxes” into the continuum state instead of going back to the ground state. The exact coincidence in energy between the discrete state and the continuum state makes normal perturbation theory inadequate to handle these kinds of states. Rice [34] developed a basic theory of treating stationary states with configuration mixing under conditions of autoionization.

There is also configuration interaction between nearly degenerate stationary states, i.e. different electronic configurations with almost the same energy. Rydberg states in He [35] is such an example. The states converging to the \( N = 2 \) ionization threshold should consist of two series according to the classic independent particle model, the \( 2snp \) and \( 2pns \) series with about equal strength. This is however not observed in experiments. The \( 2snp \) and \( 2pns \) levels are nearly degenerate in He so the electron-electron interaction will, if sufficiently strong, remove the degeneracy and replace the independent electron wave functions \( \psi(2snp) \) and \( \psi(2pns) \) with new configuration interaction (CI) wave functions:
The + and – (quantum number) signs correspond to the radial motions of the two electrons. The quantity |r₁-r₂|, where r₁ and r₂ are the two electron distances to the nucleus is small for the + states as the two electrons move in step with each other and it is large for the – states as they are moving out of step with each other. The description of the He Rydberg series below the N = 2 threshold has since the original paper been expanded with the 2pnd series corresponding to the quantum number 0. For these series the 2snp+2pns series has a much larger oscillator strength and autoionization width than the 2snp-2pns and 2pnd series and hence only one series was seen in the initial experiments.

DESB

The CI description with quantum numbers ± and 0 is only concerned with radial correlation and works well below the N = 2 threshold. At higher thresholds, for example the N = 4 threshold, the series, 4snp, 4pns, 4dnp, 4dnf, 4fnd and 4fng have a strong Columbic interaction resulting in configuration-mixed series. These are not only radially correlated but angular correlation also has to be accounted for. To describe the total correlation a Doubly Excited Symmetry Basis (DESB) was introduced by D. R. Herrick et al. represented by two new correlation quantum numbers K and T [36, 37]. The DESB wave functions are described by the quantum numbers \{N, n, L, S, \pi, K, T\}. The configuration mixing is in this case given by:

\[
\Psi(2n \pm) = \frac{\psi(2snp) \pm \psi(2pns)}{\sqrt{2}}
\]

\[
\Psi(2n \mp) = \frac{\psi(2snp) \mp \psi(2pns)}{\sqrt{2}}
\]

\[
N is the principal quantum number of the inner electron and \(n N = 1, 2, 3 \ldots \) and \(n = N, N+1, N+2 \ldots \). L is the total angular momentum quantum number of the system and S is the total spin, \(\pi\) is the parity of the state, i.e. the inversion symmetry of the wave function (whether it changes sign under the transformation \(\vec{r} \rightarrow -\vec{r}\)). \(D^{KTL\pi}_{Ni,ni}\) are vector coupling coefficients that are dependent on the new quantum numbers K and T. T needs only to be specified for states with \(L \geq 2\) and \(N > 2\). Single excitations are characterized by \(K = T = 0\). For the He double excitation case below the N = 2 threshold the DESB states are a mixture of hydrogenic configurations so that:
The DESB give fairly good agreement with experiments and give predictions of selection rules.

**Hyperspherical base functions**

The DESB set of functions is equivalent to approximate CI functions where only the intrashell correlations are included and hence lack enough of the radial correlation [38-40] outside the shell. To correct this and take larger intershell correlation into account C.D. Lin expanded D. R. Herrick’s set of quantum numbers to include a radial correlation quantum number $A$. In this definition of the angular correlation quantum numbers, $K$ and $T$ are separated from the DESB functions and only describe angular correlation but are otherwise the same. $A$ can take the values $+1$, $-1$ and $0$, similar to the $\alpha$ and $\beta$ series of U. Fano. One important consequence of this system is that channels having the same $(K,T)A$ but different $L$, $S$ and $S$ have isomorphic correlation patterns. In C.D. Lin’s system the wave functions are quasiseparable hyperspherical functions such that:

$$\Psi = F^\mu_n(R) \Phi_{\mu}(R; \Omega)$$

The channel index $\mu = (N, (K,T)A, L, S, \pi)$ represents a channel or Rydberg series and $\Phi_{\mu}(R; \Omega)$ is the channel function. $F^\mu_n(R)$ is a radial function obtained from the channel potential $U(R)$. The channel function contains all the information about electron correlations of states within the channel. $K$ is proportional to the projection of the radial direction of one of the electrons on to the direction of the other. $T$ describes the relative orientation between the orbitals of the two electrons. If the two electron orbitals are in the same plane, $T = 0$. The angular correlation pattern is independent of $R$ in this description. The $A$ quantum number is associated with the radial function’s nodal pattern where $A = +$ is antinodal and $A = -$ is nodal. $A = 0$ exhibits similarities to singly excited states in radial correlation. There are well-defined procedures for calculating these functions [41] but they will not be discussed here.

By use of these quantum numbers it is possible to label all states observed in $He$. For the three series below the $N = 2$ threshold in $He$ the hyperspheri-
cal \((K,T)^n_{N}2^{S+1}L^z\) labels would be \((0,1)^1P^o\) for \(2snp+2pns\), \((1,0)^1P^o\) for \(2snp-2pns\) and \((-1,0)^1P^o\) for \(2pnd\).

**Molecular orbitals**

To describe the properties of solids the first thing to consider is the formation of molecules. Here, two free atoms with their corresponding atomic wave functions are joined together to form a molecule. There are several ways to describe the formation of molecules. Two of the most common are valence bond theory (VB) and molecular orbital theory (MO).

**Valence bond theory**

In valence bond theory it can be assumed that following applies for the formation of \(H_2\). When the two hydrogen atoms are at a great distance from each other the system can be described by the separate atomic wave functions:

\[
\Psi = \psi_A(\vec{r}_1)\psi_B(\vec{r}_2)
\]

A represents one hydrogen atom and B the other one, while the index 1 and 2 refers to the two electrons on the two respective atoms, \(\vec{r}_i\) is the position vector of the respective electron. As the two atoms are brought closer to each other it is no longer possible to say which electron is on which atom and the wave function has to be expressed as a linear combination of the two possibilities such that:

\[
\Psi = \psi_A(\vec{r}_1)\psi_B(\vec{r}_2) \pm \psi_A(\vec{r}_2)\psi_B(\vec{r}_1)
\]

This expression forms two possible molecular orbitals, one for the + sign and one for the – sign. For \(H_2\) it turns out that the + sign represents the lowest energy as this corresponds to a gathering of charge in-between the two nuclei attracting them towards the centre forming a molecule if the two hydrogen atoms are brought together. In molecular theory spin becomes important as an orbital can be filled by two electrons with different spin, up and down, according to the Pauli principle. An atom with an outer valence occupancy of \(2s^22p\) can be “promoted” to \(2s2p,2p,2p\) to create more unpaired valence electrons and hence be able to bond to more atoms if this in the end lowers the total energy of the system. In this case the orbitals are also hybridized to create equal bonds to the other atoms, for example four bonds such that:
In this case the bond of a hydrogen 1s ($\psi_{1s}$) orbital to an atom $X$ with the valence occupancy 2s2p is would be:

$$
\psi_{x, H_{2}} = N_{1} \left( h_{1} (\vec{r}_{1}) \psi_{1s} (\vec{r}_{2}) + h_{1} (\vec{r}_{2}) \psi_{1s} (\vec{r}_{1}) \right)
$$

$N_{1}$ is a normalization factor. The different hybridized orbitals are identical but with different spatial orientations, so in this case four such bonds could be made creating a $XH_{4}$ molecule. There are other ways to make hybridized orbitals other than this depending on the occupancy and character of the valence orbitals.

[B4, s 388-394]

**Molecular Orbital theory**

In molecular orbital theory the electrons are not seen as being part of a particular bond but are seen as spreading out over the whole molecule. MO theory has been more developed than VB theory and is more generally used. Here molecular orbitals are created as Linear Combinations of Atomic Orbitals (LCAO). Such orbitals are called LCAO-MO. In the hydrogen case of $H_{2}$ the one electron orbital would be:

$$
\psi_{\pm} = \frac{N}{2} \left( \psi_{A} \pm \psi_{B} \right)
$$

where $N$ is a normalization factor. From this model, bonding and antibonding orbitals can be derived, as the square of the wave function is the electron probability density:

$$
\psi_{+}^{2} = N^{2} \left( \psi_{A}^{2} + \psi_{B}^{2} + 2 \psi_{A} \psi_{B} \right)
$$

$$
\psi_{-}^{2} = N^{2} \left( \psi_{A}^{2} + \psi_{B}^{2} - 2 \psi_{A} \psi_{B} \right)
$$

$\psi_{A}^{2}$ is the probability density for the electron to be on $A$ and $\psi_{B}^{2}$ is the probability density to be on $B$ and $2 \psi_{A} \psi_{B}$ is an extra contribution due to interference between the two wave functions. Here the $+$ becomes bonding and the $-$ antibonding.
When two $H$ atoms combine to a $H_2$ molecule two orbitals are formed, one with a lower energy than the original atomic orbitals and one with higher energy. These will be bonding (1$\sigma$) and antibonding (2$\sigma^*$) respectively.

The molecular orbitals are usually classified according to their projections as viewed along the molecular axis. Two $s$ orbitals combine to a $\sigma$ molecular orbital as this looks like an $s$ orbital when viewed along the molecular axis. Atomic $p$ orbitals can combine to either form $\sigma$ or $\pi$ orbitals, two $p$ orbitals oriented along the molecular axis will form a $\sigma$ orbital while two $p$ orbitals oriented perpendicular to the molecular axis will form a $\pi$ molecular orbital. There are also other characteristics to the formed molecular orbitals such as parity which depends on the inversion symmetry of the molecular orbital. If it is unchanged by the transformation $x \rightarrow -x$, where $x$ is any Cartesian room coordinate, it is said to be “gerade” (g) and if the function changes sign then it is “ungerade” (u). This symmetry applies only to molecules with an inversion center.

If the system contains several atoms of the same or different species the total wave function is a weighted sum over all available atomic valence orbitals. The molecular orbital can then be described in its general form.

$$\Psi = \sum_i c_i \psi_i$$

The difference between diatomic orbitals, such as in the $H_2$ molecule, and polyatomic orbitals is the greater range of possible shapes in the later. Diatomic molecules are by necessity linear but a triatomic molecule may be linear or angular with a characteristic bond angle.

[B4, s 394-410]

Calculations of molecular orbitals are generally done by systematically trying different atomic configurations and positions for the wave function, and then the energy eigenvalues are compared to determine the lowest possible energy and hence the corresponding configuration.
Fig. 2  Picture of the formation of $\sigma$ and $\pi$ orbitals from $s$ and $p$ atomic orbitals. The symmetry axis determines if the combination of $p$ orbitals become $\sigma$ or $\pi$ orbitals.

Initial values for these calculations are usually obtained from experiments if the calculations are not done in first principle. There are different schemes for the calculation and formation of molecular orbitals in different standard geometries, described in their own separate theories but that is beyond the scope of this text.

**Solid state bands**

As the molecules become larger the different orbitals will start forming bands consisting of closely spaced energy levels corresponding to the different orbitals. This can be illustrated by considering a homoatomic linear solid formed by successively adding one atom after another.

In the first step where the atom is alone the molecular energy/orbital is the same as in the atom. As another atom is added two orbitals are formed, one bonding and one antibonding as shown above. The energy levels corresponding to this are two levels with the bonding orbital below the atomic level and the antibonding level above the atomic level. As a third atom is added a third orbital/level is added that may be neither bonding nor antibonding. As further atoms are added the levels split again, into two bonding and two antibonding orbitals. By continuing in this way until an infinite number of atoms are present, a band that looks continuous is formed. The bottom of the band is bonding while the top is antibonding. Depending on the orbitals from which the band is created the bands can have $s$, $p$, $d$ ... character. If one of the constituting atoms is subjected to a disturbance localized levels will once again form at this site separating them from the rest of the band. These states are called excitons. [B4, s 418-419]
Fig. 3 In the first stage (a) where the solid consist of a single atom the atomic (left) and molecular energy levels are the same. As another atom (b) is introduced the energy levels split in the molecular orbitals. As successively more atoms are brought in (c, d) the energy levels start to split into more and more finely separated energy levels until they form a continuous band (e).

Depending on the number of electrons in the orbitals the material will be a conductor, semiconductor or an insulator. If $N$ atoms with one valence orbital each form a band it will contain $2N$ independent orbitals in the band since each valence orbital can contain two electrons with different spin according to Pauli. If a band is half filled, i.e. $N$ electrons (one from each atom) in a band, at temperature $T = 0$ the material is said to be a conductor. If $2N$ electrons (two electrons per atom) are present at $T = 0$ the material is an insulator at $T = 0$ but if electrons can be moved by thermal excitations to an empty band formed by other unoccupied valence orbitals the material becomes a semiconductor. The distance between two bands is called a band gap. If thermal energies are smaller than the band gap the material will remain an insulator even at higher temperatures. So far this discussion has been concerned with bands formed in one direction. Solids are generally three dimensional structures with a certain periodicity, there are also materials that behave as if they were of a lesser dimensionality. [B4, s 420-421]
Crystal lattice

A solid is a crystal structure where atoms and molecules are arranged periodically in space. An ideal crystal for example is a repetition of identical substructures which may contain many atoms or molecules. The structure of all crystals can be described by a lattice, with a group of atoms/molecules attached at each lattice point. These subgroups are called the basis and they are identical in composition, arrangement and orientation.

As the crystal is an infinite repetition of similar basis sets, cells are used to represent the material and its properties so that a repetition of the cell will fill the space of the crystal. There are many ways of choosing such cells but the smallest possible cell is called a primitive cell and contains exactly one lattice point. The parallelepiped in Fig. 4, defined by the primitive axes $a_1$, $a_2$ and $a_3$ is called a primitive cell. [B5, s 3-7]

Fig. 4  The axis $a_1$, $a_2$ and $a_3$ are called primitive axis and define the coordinate system in the crystal lattice. They also form a primitive cell.

It is not always preferable to work with primitive cells as other configurations are more convenient. Cells are generally characterized by the length of their sides and the angle between them.

In three dimensions there are 14 different lattice types, the general lattice is called triclinic, where all parameters are different (side lengths and angles) and then there are 13 special lattices where one or more parameters are the same.
Fig. 5  The simple cubic (SC) lattice contains one lattice point per cell and is the only one that coincides with the primitive cell, BCC has two points per cell and FCC has four points per cell.

These are grouped into six subgroups: Monoclinic (2 lattices), Orthorombic (4 lattices), Tetragonal (2 lattices), Cubic (3 lattices), Trigonal (1 lattice) and Hexagonal (1 lattice). The cubic lattice, where all sides are equal and all angles are $90^\circ$ have three subgroups, Simple Cubic (SC), Body-Centered Cubic (BCC) or Face-Centered Cubic (FCC) lattices. The SC contains one lattice point per cell and is the only one that coincides with the primitive cell, BCC has two points per cell and FCC has four points per cell. [B5, s 8-12]

Reciprocal lattice

Since crystals are periodic structures it is useful to have something called a reciprocal lattice when performing calculations in solids, i.e. a mathematical construct that utilizes the periodicity of the crystal structure to make some calculations easier (Fourier analysis). This reciprocal space was first derived to explain Bragg reflection of photons, neutrons and electrons from crystals. It is assumed that beams are reflected specularly from parallel planes of atoms, where each plane only reflects a small amount of the intensity. In this way interference between wave fronts in different directions will occur, similar to a grating. There is positive interference when the path distance from two planes differ with an integer number $n$ of wavelengths $\lambda$. This is described by the Bragg law.

$$2d \sin \theta = n\lambda$$

where $d$ is the distance between two planes and $\theta$ is the angle from the plane. The Bragg law is a consequence of the periodicity of the crystal lattice. To describe the properties of a material the electronic distribution in the crystal has to be determined. Since the crystal is a periodic lattice of identical base
sets the number density of electrons in the crystal $n(\vec{r})$ is a periodic function such that the number density is invariant under a crystal translation $\vec{T}$:

$$n(\vec{r} + \vec{T}) = n(\vec{r})$$

$$\vec{T} = u_1\vec{a}_1 + u_2\vec{a}_2 + u_3\vec{a}_3$$

where $u_1$, $u_2$ and $u_3$ are integers and the $\vec{a}_1$, $\vec{a}_2$ and $\vec{a}_3$ are the primitive vectors of the crystal lattice. Using the primitive vectors of the crystal lattice a set of primitive reciprocal lattice vectors $\vec{b}_1$, $\vec{b}_2$ and $\vec{b}_3$ can be defined as:

$$\vec{b}_1 = 2\pi \frac{\vec{a}_2 \times \vec{a}_3}{\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3}$$

$$\vec{b}_2 = 2\pi \frac{\vec{a}_3 \times \vec{a}_1}{\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3}$$

$$\vec{b}_3 = 2\pi \frac{\vec{a}_1 \times \vec{a}_2}{\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3}$$

A point in reciprocal lattice space is described by a reciprocal lattice vector, $G = v_1\vec{b}_1 + v_2\vec{b}_2 + v_3\vec{b}_3$ where $v_1$, $v_2$ and $v_3$ are integers. This is a situation that lends itself well to Fourier analysis. By expanding the electron number density in Fourier space it is found that the number density can be expressed as:

$$n(\vec{r}) = \sum_G n_G e^{i\vec{G} \cdot \vec{r}}$$

Here $n_G$ is a set of Fourier coefficients that determines the X-ray scattering amplitude. Every crystal structure has two lattices associated with it, the crystal lattice and the reciprocal lattice.

[B5, s 29-34]

**Free electron model**

In a simple conductor the behavior of the conduction electrons can be approximated by the free electron model. Here the electron is described as a plane wave that is periodic in $x$, $y$, and $z$ with the period $L$ equal to the edge of an imaginary cube containing the electrons.
\[ \Psi_i(\vec{r}) = e^{i\vec{k} \cdot \vec{r}} \]

Provided that the components of the \( \vec{k} \) satisfy

\[ k_i = 0; \pm \frac{2\pi}{L}; \pm \frac{4\pi}{L}; \ldots \]

The wavevector \( \vec{k} \) of a free electron is related to the momentum of the electron through \( m\vec{v} = \hbar \vec{k} \) (\( m \) is the mass of the electron and \( \vec{v} \) is the velocity, \( \hbar \) is Planck’s constant divided by \( 2\pi \)). From this it can be shown that the energy of the state with the wavevector \( \vec{k} \) is:

\[ \epsilon_k = \frac{\hbar^2}{2m} |\vec{k}|^2 \]

The ground state of a system of \( N \) free electrons can be represented as points inside a sphere in \( \vec{k} \) space defined by \( \vec{k}_N \). The energy at the surface of the sphere is called the Fermi energy.

\[ \epsilon_F = \frac{\hbar^2}{2m} \left( \frac{3\pi^2 N}{V} \right)^{\frac{2}{3}} \]

\( N/V \) is the concentration of electrons. From this expression the number of states per unit energy range \( D(\epsilon) \), called the Density of States (DOS) can be defined as.

\[ D(\epsilon) \equiv \frac{dN}{d\epsilon} = \frac{V}{2\pi^2} \left( \frac{2m}{\hbar^2} \right)^{\frac{3}{2}} \left( \frac{\hbar^2}{2m} \right)^{\frac{1}{2}} \epsilon^{\frac{3}{2}} \approx \frac{3N}{2\epsilon} \]

From this relation the properties of heat capacity, thermal conductivity, magnetic susceptibility and electrodynamics of metals can be derived. But the free electron model fails to describe the difference between metals, semimetals, semiconductors and insulators. [B5, s 146-151]

**Nearly free electron model**

The failure of the free electron model to describe insulator and semiconductors is a result of the fact that it can not separate the electrons into bands. To do this the periodic lattice has to be incorporated into the free electron model.
which is done in the nearly free electron model. The Bragg condition for diffraction of a wave with wavevector $k$ becomes in one dimension

$$k = \pm \frac{n\pi}{a}$$

where $a$ is the lattice constant and $n$ is an integer.

The first reflection is at $\pm \frac{\pi}{a}$. At these points the electronic wave function is no longer a wave traveling in one direction but a combination of equal parts in either direction. The time independent state is represented by standing waves.

$$\Psi(+) = e^{\frac{i\pi x}{a}} + e^{-\frac{i\pi x}{a}}$$
$$\Psi(-) = e^{\frac{i\pi x}{a}} - e^{-\frac{i\pi x}{a}}$$

The $\Psi(\pm)$ waves collect electrons at different regions and hence they have different values of their potential energy. This is the reason for the band gap. The charge density is:

$$\rho(+) = |\Psi(+)|^2 \propto \cos^2\left(\frac{\pi x}{a}\right)$$

This piles up negative charge centered at $x = 0, a, 2a \ldots$ where the potential energy is lowest since this is where the positive nuclei are. On the other hand

$$\rho(-) = |\Psi(-)|^2 \propto \sin^2\left(\frac{\pi x}{a}\right)$$

Which concentrates electrons away from $x = 0, a, 2a \ldots$ giving a higher potential energy, placing the electrons far from the nuclei, in-between the base pairs.
Fig. 6  (a) The band in the free electron model, here the band is continuous. (b) The band structure in the nearly free electron model. Here the band has separated into two bands separated by a band gap due to the standing waves of $\Psi(+)$ and $\Psi(-)$ at $\pm \pi/a$.

The free wave is found in between the $\Psi(+)\text{ and }\Psi(-)$ waves. The band gap $E_g$ is the difference between the energies of the $\Psi(+)\text{ and }\Psi(-)$ waves. [B5, s 176-180]

For the general case where the potential energy of an electron can be described by $U(\vec{r})$ in a periodic lattice such that $U(\vec{r}) = U(\vec{r} + \vec{T})$ where $\vec{T}$ is a crystal lattice translation. The potential can be Fourier expanded in the reciprocal lattice vectors $\vec{G}$:

$$U(\vec{r}) = \sum_{\vec{G}} U_0 e^{i\vec{G} \cdot \vec{r}}$$

In the one electron approximation the Schrödinger wave equation becomes:

$$\left( \frac{1}{2m} \frac{\partial^2}{\partial \vec{r}^2} + \sum_{\vec{G}} U_0 e^{i\vec{G} \cdot \vec{r}} \right) \Psi(\vec{r}) = \varepsilon \Psi(\vec{r})$$

F. Bloch proved that the solutions to the Schrödinger equation for a periodic potential also can be expanded in a Fourier series over the reciprocal lattice vectors $\vec{G}$ and that it must be of the special form:

$$\Psi(\vec{r}) = u_{k}(\vec{r}) e^{i\vec{k} \cdot \vec{r}}$$

where $u_{k}(\vec{r})$ has the period of the crystal lattice.

$$u(\vec{r}) \equiv \sum_{\vec{G}} C(\vec{k} - \vec{G}) e^{-i\vec{G} \cdot \vec{r}}$$
Bloch functions are a sum of traveling waves organized into localized wave packets that represent electrons that propagate freely through the potential field of the crystal. Because $\psi_k(\mathbf{r})$ is a Fourier series over the reciprocal lattice vectors it is invariant under crystal lattice translation $\mathbf{T}$ which means that a solution in a limited volume of the lattice is a general solution for the whole lattice. When making band calculations a limited space of the crystal lattice is used, some time called a super cell in which the calculations are performed. The result is then assigned to be applicable in the whole crystal. There are different ways, covered in other texts, to make such band calculations but these will not be discussed here.

[B5, s 179-180, 183-185]

Interaction of radiation with matter

When an energetic particle interacts with the target atom the interaction can be of some different types. The most common is the single interaction event where the projectile interacts once with the target, transferring energy and is then either annihilated or moves on. The projectile can also cause the system to go into a multi-excited electron configuration. In this case the projectile has to interact with the target in such a way as to excite several electrons through some mechanism.

In the literature several ways to create such multi-excited atoms using different projectiles are mentioned. Energetic charged particles can interact with the target in two ways, single interaction and multi-interaction, to create multi-excited atoms [42]. Photons can only utilize single interaction processes as it is annihilated during the interaction and hence can not take part in multiple interactions.

The simplest way to view the interaction between a charged particle and the target is as a collision where energy is transferred in an inelastic scattering event. Interactions resulting in multi electron excitations can then be viewed as a two step interaction where the projectile interacts with the electrons in the target individually, first interacting with one electron, transferring energy and then interacting with the next etc, successively transferring energy to the electrons, exciting/ionizing them. This is referred to as a two step two (TS2) interaction. Another way to create multi excited atoms is if the projectile strongly interacts with one electron and transfers energy to this one. Then a secondary interaction between the excited electron and the remaining electrons causes the other electrons to be excited. This secondary interaction can be of two types, two step one (TS1) and shake off (SO). TS1 is an interaction similar to a collision; the fast outgoing electron then interacts with another electron in an inelastic scattering event, which excites/releases the second electron. SO is a process where the sudden removal
of the first electron leaves the system in an unstable configuration. When the
system reconfigures to the final state another electron is excited or ejected.

Both charged particles and photons interact with the target through elec-
tromagnetic fields but since photons are not allowed to interact with more
than one electron before being annihilated, the first, TS2, process is not ap-
plicable in photoexcitation of multiple electrons. This leaves TS1 and SO to
create multi-excited species with photons. Double ionization with photons
high above the ionization threshold is generally attributed to the SO process
where the first electron is suddenly removed and the second is released dur-
ing the final state rearrangement of the remaining ion. The process for dou-
ble excitations and ionizations close to the threshold is understood in the
context of electron correlation. There is no general description of how this
correlation takes place; but it can be described in CI, DESB, hyperspherical
functions or any other appropriate method of calculation.

To describe a transition from one stationary state to another stationary
state in quantum mechanics, the Hamiltonian is modified with an extra inter-
action part, so that:

$$\hat{H} = \hat{H}_0 + \hat{H}_{\text{int}}$$

$\hat{H}_0$ is the stationary state Hamiltonian and $\hat{H}_{\text{int}}$ is the operator performing the
interaction. The actual description of this interaction part can be done in
several ways depending on what approximations are made.

**Dipole approximation**

In first order perturbation theory the photon field is treated as a continuous
variable were the photon field behaves classically while the atom is treated
quantum mechanically. In the dipole approximation it is assumed that radia-
tion is uniform over the whole atom so that higher order terms can be ne-
glected, which makes the electric field vector $\vec{E}$ independent of position.
This approximation is reasonable for soft X-rays since the wavelength of the
radiation is usually much larger (but not always) than atomic distances (~Å)
in the atomic range. In radiative transitions of first order the dipole operator
is used in $\hat{H}_{\text{int}}$:

$$\hat{H}_{\text{int}} = -\vec{\varepsilon} \cdot \vec{D}$$

This is just the first term in an expansion of the electromagnetic operator but
it generally holds for the normal electronic transitions. In this case the one
electron Hamiltonian becomes:
The dipole operator $\vec{D} = -e\vec{r}$ is the electric dipole moment of the system where $e$ is the electronic charge and $\vec{r}$ is the position vector of the electron. $\hat{\varepsilon}$ is the polarization vector of the incoming radiation, which is independent of position in the dipole approximation.

A system in a well defined bound stationary state $a$, at time zero can be described by $\Psi_a$. The radiation field of an incoming photon is represented by the dipole operator $\hat{D}$. The absorption from the state $a$ to a state $b$, described by $\Psi_b$, is then described by the transition matrix element between the ground state $\Psi_a$ and the excited state $\Psi_b$ using the dipole operator. The transition element $D_{ba}$ is defined as:

$$D_{ba} = \langle \Psi_b | \hat{D} | \Psi_a \rangle = -e \int \Psi_b^*(\vec{r}) \hat{\varepsilon} \psi_a(\vec{r}) d\vec{r}$$

The square of $D_{ba}$ is proportional to the probability $P_{ba}$ of transition from state $\Psi_a$ to state $\Psi_b$ such that:

$$P_{ba} \propto |\hat{\varepsilon} \cdot D_{ba}|^2$$

From the probability expressions, transition rates, cross-sections etc can be obtained. Some transition matrix elements do however become zero as there is no overlap between initial state and final state wave function with the dipole operator. This leads to the formulation of selection rules for optical transitions between different states.

*For example, the principal quantum number $n$ can change with any integer. The angular momentum quantum number can however only change by plus minus one. The angular momentum projection, $m_l$ can only change by plus minus one or not at all. Spin does not change in a radiative transition.*

In first approximation the absorption rate between the ground state $\Psi_a$ and the excited state $\Psi_b$ can be shown to be:

$$W_{ba} = \frac{\pi I(\omega_{ba})}{\hbar^2 ce_0} |\hat{\varepsilon} \cdot D_{ba}|^2$$

$I(\omega_{ba})$ is the intensity of the photon field per unit angular frequency range, $e_0$ is the permittivity of vacuum and $c$ is the speed of light. In a similar way it
can be shown that an excited state $\Psi_b$ can be stimulated to return to ground state $\Psi_a$ by an external field so that a stimulated emission rate is obtained.

$$W_{ab} = \frac{\pi I(\omega_{ba})}{\hbar c e_0} |\hat{\epsilon} \cdot D_{ab}|^2$$

(stimulated emission)

There is however a third kind of transition observed in nature which is the transition from an excited state $\Psi_b$ to the ground state $\Psi_a$ without the influence of an external filed. This is called spontaneous emission. The rate for this can not be obtained directly in this approximation (the radiation field must be quantized) but by considering statistical conditions it can be shown to be:

$$W_{ab} = \frac{\omega_{ba}^3}{\pi \hbar c e_0} |\hat{\epsilon} \cdot D_{ba}|^2$$

(spontaneous emission)

Another useful quantity in atomic and molecular physics is the cross-section or transition probability per unit atom which is the rate of absorption of energy per atom divided by the intensity of the incoming radiation times the energy of the radiation.

$$\sigma_{ba} = \frac{\hbar \omega_{ba} W_{ba}}{I(\omega_{ba})}$$

For a full derivation see [B1, s 493-501].

**Quantized fields**

The first order approximation applies to non-resonant absorption and emission. When getting close to resonances and absorption thresholds, the absorption and emission of a photon can no longer be seen as a two step process but has to be viewed as a one step process. To derive an expression for this scattering the photon field can not be viewed as a continuous variable where the addition or subtraction of a photon is negligible. This situation has to be treated in a fully quantized manner where also the photon field is quantized and represented in the state wave function. In this representation the dipole operator becomes a part of a larger operator that handles both the transitions in the atom as well as the creation and annihilation of photons. In this representation the interaction Hamiltonian becomes:
\[ \hat{H}_{\text{int}} = \sum_i \left[ -\frac{e}{2mc} (\hat{p}_i \cdot A(\vec{r}_i, t) + A(\vec{r}_i, t) \cdot \hat{p}_i) + \frac{e^2}{2mc^2} A(\vec{r}_i, t) \cdot A(\vec{r}_i, t) \right] \]

\[ A(\vec{x}, t) = \frac{1}{\sqrt{V}} \sum_k \sum_{\alpha} c \sqrt{\frac{\hbar}{2\omega}} \left[ a_{k,\alpha}(0) e^{i \vec{k} \cdot \vec{x} - i\omega t} + a_{k,\alpha}^+(0) e^{-i \vec{k} \cdot \vec{x} + i\omega t} \right] \]

where \( a_{k,\alpha} = a_{k,\alpha}(0) e^{-i\omega t} \) and \( a_{k,\alpha}^+ = a_{k,\alpha}^+(0) e^{i\omega t} \) are annihilation and creation operators, decreasing or increasing the number of photons with one. \( V \) is a normalization volume and \( \vec{k}, \hat{\epsilon}^{(\alpha)} \) and \( \omega \) are the momentum vector, polarization and angular frequency of the photon respectively. \( \hat{p}_i \) is a differential operator. \( \hat{A}(\vec{x}, t) \) is called the quantized field operator where \( \vec{x} \) and \( t \) are parameters on which the field operator depends. \( \vec{x} \) and \( t \) are however not the space-time coordinates of the photon. The summation is over the electrons that take part in the interaction.

The interaction Hamiltonian is made up of two parts, one linear \((A \cdot \hat{p})\) and one quadratic \((A \cdot A)\) term. In the case of absorption / emission, the photon number change only with one and it is only the \((A \cdot \hat{p})\) terms that are applied since the \((A \cdot A)\) term will either change the photon number by two or not at all. Transition matrix elements can be defined in a similar way as in the semi-classical case

\[
D_{ab} = \langle \Psi_b; n_{k,\alpha} - 1 | \hat{H}_{\text{int}} | \Psi_a; n_{k,\alpha} \rangle =
\]

\[
= \langle \Psi_b; n_{k,\alpha} - 1 | -\sum_i \frac{e}{2mc} (\hat{p}_i \cdot A(\vec{r}_i, t) + A(\vec{r}_i, t) \cdot \hat{p}_i) | \Psi_a; n_{k,\alpha} \rangle \quad \text{(absorption)}
\]

\[
= -\frac{e}{m} \sqrt{\frac{\hbar}{2\omega V}} \sum_i \langle \Psi_b | e^{-i\vec{k} \cdot \vec{r}_i} \hat{p}_i \hat{\epsilon}^{(\alpha)} | \Psi_a \rangle e^{-i\omega t}
\]

\[
D_{ab} = \langle \Psi_b; n_{k,\alpha} + 1 | \hat{H}_{\text{int}} | \Psi_a; n_{k,\alpha} \rangle =
\]

\[
= \langle \Psi_b; n_{k,\alpha} + 1 | -\sum_i \frac{e}{2mc} (\hat{p}_i \cdot A(\vec{r}_i, t) + A(\vec{r}_i, t) \cdot \hat{p}_i) | \Psi_a; n_{k,\alpha} \rangle \quad \text{(emission)}
\]

\[
= -\frac{e}{m} \sqrt{\frac{\hbar}{2\omega V}} \sum_i \langle \Psi_b | e^{-i\vec{k} \cdot \vec{r}_i} \hat{p}_i \hat{\epsilon}^{(\alpha)} | \Psi_a \rangle e^{i\omega t}
\]

Here stimulated and spontaneous emission is contained within the same expression as is seen from the \( \sqrt{\frac{(n_{k,\alpha} + 1)\hbar}{2\omega V}} \) term which will be separated from.
zero even if the number of photons in the external field \( n_{k_0} \) is zero. \( A(\vec{r}, t) \)

is assumed to act on a photon state at \( \vec{r}_i \), where \( \vec{r}_i \) is the coordinate of the \( i \)th electron.

When applying field theory to the scattering of photons by atomic electrons the incoming and outgoing photons are represented by states, \( \left( \vec{k}', \hat{\epsilon}^{(a')} \right) \) and \( \left( \vec{k}, \hat{\epsilon}^{(a)} \right) \) respectively. Since the field operator \( A \) changes the number of photons by one the \( \hat{p}_A \) term does not contribute to the scattering of photons in first order. The \( (A \cdot A) \) term does however contain parts that give non-vanishing contributions, i.e. terms containing one annihilation and one creation operator each provided that they agree with the photon states given. The transition matrix element for photon scattering in first order then becomes

\[
\langle b | \hat{H}_\text{int} | a \rangle = \langle b | \left( \hat{k}', \hat{\epsilon}^{(a')} \right) \left| A(\vec{r}, t) \right| \left( \vec{k}, \hat{\epsilon}^{(a)} \right) | a \rangle
= \frac{e^2}{2mc^2} \frac{1}{2V\sqrt{\omega \alpha \omega'}} 2\hat{\epsilon}^{(a)} \hat{\epsilon}^{(a')} e^{-(\omega - \alpha)t} \langle b | \Psi_a \rangle
\]

The \( (A \cdot \hat{p}) \) term in the interaction Hamiltonian does not contribute to the photon scattering in first order but it does in second as an \( (A \cdot \hat{p}) \) term taken twice is on the same order as the \( (A \cdot A) \) term and hence a double \( (A \cdot \hat{p}) \) term has to be treated simultaneously with the \( (A \cdot A) \) term in second order calculations. Feynman diagrams show how this is possible.

![Feynman Diagrams](image)

Fig. 7  The first part (a) represents the double \( (A \cdot A) \) term where the absorption and emission is seen as a direct scattering, the second part (b) shows a double \( (A \cdot \hat{p}) \) term where first there is absorption and then emission of a photon, the third part (c) shows the double \( (A \cdot \hat{p}) \) term where first there is emission and then absorption of a photon.
Using the results from where absorption and emission are treated separately and taken consecutively, this second order interaction can be accounted for. The combination of the first and second order transition probabilities then leads to the Kramers-Heisenberg [43] scattering formula where the differential cross-section is described as follows:

\[
\frac{d\sigma}{d\Omega} = r_0^2 \left( \frac{\omega'}{\omega} \right) \left| \langle \Psi_a | \Psi_b \rangle \hat{\varepsilon}^{(a)} \cdot \hat{\varepsilon}^{(a')} \right|^2
\]

\[
- \frac{1}{m} \sum_i \left( \frac{\langle \Psi_b | \hat{p} \cdot \hat{\varepsilon}^{(a')} | \Psi_i \rangle \langle \Psi_i | \hat{p} \cdot \hat{\varepsilon}^{(a)} | \Psi_a \rangle}{E_i - E_a - \hbar \omega} \right)^2
\]

where \( E_i \) and \( E_a \) are the energies of the intermediate and ground state respectively, \( \hbar \omega \) and \( \hbar \omega' \) is the energy of the incoming and outgoing photons. \( r_0 \) stands for the classical radius of the electron. This formula can be applied for example when discussing Rayleigh scattering i.e. elastic scattering of light, Thomson scattering i.e. where the photon energies are much larger than the atomic binding energies and Raman scattering i.e. where outgoing photon energy is less than the incoming photon energy (if the target is in its ground state). This formula does however become inadequate close to resonances where \( E_i - E_a \) is close to the photon energy \( \hbar \omega \). The problem with this formula is that it assumes that the intermediate state is a stationary state with an infinite long life time. By introducing a dampening into the equations due to spontaneous emission, which was left out before, the following modified Kramers-Heisenberg formula can be reached:

\[
\frac{d\sigma}{d\Omega} = r_0^2 \left( \frac{\omega'}{\omega} \right) \left| \langle \Psi_a | \Psi_b \rangle \hat{\varepsilon}^{(a)} \cdot \hat{\varepsilon}^{(a')} \right|^2
\]

\[
- \frac{1}{m} \sum_i \left( \frac{\langle \Psi_b | \hat{p} \cdot \hat{\varepsilon}^{(a')} | \Psi_i \rangle \langle \Psi_i | \hat{p} \cdot \hat{\varepsilon}^{(a)} | \Psi_a \rangle}{E_i - E_a - \hbar \omega - \frac{i\Gamma_1}{2}} \right)^2
\]

\[
+ \frac{\langle \Psi_b | \hat{p} \cdot \hat{\varepsilon}^{(a')} | \Psi_i \rangle \langle \Psi_i | \hat{p} \cdot \hat{\varepsilon}^{(a)} | \Psi_a \rangle}{E_i - E_a + \hbar \omega'} \right)^2
\]
Here $\Gamma_i$ is the mean life time of the intermediate state. Ignoring the non-resonant terms in this expression it can be shown that it is simply the probability of absorbing a photon of energy $\hbar\omega$ multiplied with the probability of emitting a photon of energy $\hbar\omega'$ divided by the flux density.  
[B6, s 29-57].

**Transitions and CI**

In the description of states in doubly excited atoms CI was introduced [33] as a way to explain the behavior of the multi-excited states since the independent particle model could not handle these states. When discussing transitions to CI mixed states interference effects become apparent. In the case of CI between a continuum and discrete states, the transition matrix element for exciting the CI state $\Psi_E$ from the ground state $\Psi_a$ by the operator $\hat{T}$ (which can be any interaction operator) can be shown to be:

$$D_{Ea} = \langle \Psi_E | \hat{T} | \Psi_a \rangle = \frac{1}{\pi V_{Ea}^*} \langle \Phi | \hat{T} | \Psi_a \rangle \sin \Delta - \langle \Psi_E | \hat{T} | \Psi_a \rangle \cos \Delta$$

where

$$\Phi = \varphi + P \int \frac{V_{Ea} \psi_{E'}}{E - E'} \partial E'$$

$\Delta$ is a phase shift due to the configuration interaction between the discrete state and the continuum. $|V_{Ea}|^2$ is an index of the configuration interaction strength and has the dimension of energy. P stands for “principal part of”. The first term corresponds to transitions to the discrete state $\Phi$ modified by an admixture of states of the continuum (a modified state $\Phi$). The second term treats transitions to the unperturbed continuum states $\psi_{E'}$. The transition rate from the state $\Psi_a$ to state $\Psi_E$ is proportional to the square of the matrix element $D_{Ea}$. The fact that the transition matrix can be expressed as a sum of terms leads to interference effects in the transition probability due to the cross term.

$$W_{Ea} \propto |D_{Ea}|^2 = \left| \langle \Psi_E | \hat{T} | \Psi_a \rangle \right|^2$$

The transition probability to the unperturbed continuum can be represented by a single family of curves known as Fano profiles:
\[ y(\varepsilon) = \frac{|\langle \Psi_E | \hat{T} | \Psi_d \rangle|^2}{|\langle \Psi_E | \hat{T} | \Psi_d \rangle|^2} = \frac{(q + \varepsilon)^2}{1 + \varepsilon^2} \]

where \( \varepsilon \) and \( q \) are defined by:

\[ \varepsilon = \frac{E - E_g - F(E)}{\pi |V_E|^2} \]
\[ q = \frac{\langle \Phi | \hat{T} | \Psi_d \rangle}{\pi V_E * \langle \Psi_E | \hat{T} | \Psi_d \rangle} \]

Fittings of curves of this type to actual measured data yield information about the configuration interaction strength, the shift of the discrete level and the ratio between the excitations to the continuum state and the discrete state. A full description of this treatment is given in [33, 44] but will not be discussed further here.

**Synchrotron radiation**

When studying material properties it is not possible just to observe the system in its ground state. The system has to be disturbed to yield any information. One way of disturbing the system is by adding energy in the form of a photon and monitoring the reaction to this energy input.

The atomic binding energies lie far above the energies of ordinary light except for the outermost valence orbitals. To study deeper bound electrons more energetic photons are needed, i.e. X-rays. In the early 20th century X-ray photons were generated primarily with anode based radiation sources. Here the internal transitions following energetic impacts in atoms were used. These sources produce X-rays of a limited range corresponding to the characteristics of the anode material used. As particle accelerators were introduced in nuclear science as colliding apparatus, a phenomenon called synchrotron radiation was discovered. This manifests as an energy loss of the particle beam as it circles around the storage ring due to the emission of radiation. Synchrotron radiation is produced by charged particles moving at relativistic velocities undergoing an accelerated motion.
Fig. 8  A synchrotron consists of several parts. An accelerator is used to inject the storage ring with electrons. At some synchrotrons a booster is used to increase the energy of the electron beam even more before transferring it to the storage ring. The storage ring of a 3rd generation synchrotron facility consists of a number of straight sections connected through bending magnets. In one of these a cavity is place that replaces the lost energy of the beam in each revolution. In the other straight sections insertion devices are placed that generate most of the used radiation.

At first, synchrotron radiation users were parasitic users on the nuclear colliding rings (first generation), then dedicated synchrotron rings were built specifically for atomic research (second generation), and finally rings were built with insertion devices, magnetic structures specifically designed to increase the photon yield (third generation). Synchrotron radiation is due to the fact that a charged particle, undergoing an accelerated motion will emit electromagnetic radiation, the radiated power per unit area is proportional to the square of the acceleration.

Fig. 9  The emitted radiation lobes of an accelerated charged particle is perpendicular to the direction of acceleration forming a torus around the acceleration axis.
This is the same principle as electrons moving in an antenna emitting radio waves.

In storage rings relativistic charged particles are kept in a circular orbit which is an accelerated motion. An accelerated charged particle radiates as described by:

$$|\vec{S}| = \frac{\mu_0 Q^2 \dot{v}^2 \sin^2 \theta}{16\pi^2 c_0 r^2}$$

where $\mu_0$ is the permeability, $Q$ is the charge of the particle, $\dot{v}$ is the time derivative of the velocity i.e. the acceleration and $c_0$ is the speed of light. $\theta$ and $r$ are defined by Fig. 9. This applies to velocities where $v << c_0$, $\vec{S}$ is the Poynting vector i.e.

$$\vec{S} = \vec{E} \times \vec{H} = c_0 \varepsilon_0 \vec{E} \times \vec{B}$$

where $\vec{E}$ is the electric field and $\vec{H}$ is the magnetic field of the emitted radiation. $Q$ is the charge of the particle, $\varepsilon_0$ is the permittivity of vacuum. If the particle is moving with a relativistic speed ($v \approx c_0$), the radiation lobes has to be transformed from the rest frame of the particle into the laboratory frame using relativistic velocity addition. [B7, s 231]

When talking about relativistic phenomena there are two parameters, $\beta$ and $\gamma$, that are used, defined as:

$$\beta \equiv \frac{v}{c}$$

$$\gamma \equiv \frac{1}{\sqrt{1 - \frac{v^2}{c^2}}}$$

where $v$ is the velocity of the particle and $c_0$ is the velocity of light. The following formula applies to the relativistic addition of velocities.

$$u_x = \frac{u'_x + v}{1 + u'_x v / c_0^2}$$
\[ u_y = \frac{1}{\gamma \left(1 + \frac{u'_x v}{c_0^2}\right)} \]

where \( u'_x \) and \( u'_y \) is the velocity components of a particle (emitted photon) in the given coordinate system (rest frame of the electron) and \( v \) is the velocity of this coordinate system (i.e. the electron) relative to the laboratory frame in the x direction. \( u_x \) and \( u_y \) is the particle (photon) velocity components in the laboratory frame after transformation. In the rest frame of the electron, i.e. the frame moving with the electron, the emitted radiation is in two lobes in the horizontal direction forming a torus perpendicular to the acceleration, if the acceleration of the electron is in the vertical direction. [B7, s 149]

Fig. 10 The radiation lobes emitted by a charged particle in its rest frame (left) and in the laboratory frame (middle). There are 5° between each point in the rest frame, i.e. 72 points. Acceleration is in the vertical direction. The movement of the electron’s rest frame is to the right. In the middle panel the radiation lobes are shown for a \( \gamma \) of 10 and 100 where most of the emitted radiation to the left has been transformed into the right hand side. In reality \( \gamma \) is several thousands where all points outside the axis in the reference frame would be on the right hand side axis in the laboratory frame as seen in the panel on the right.

When the radiation lobes are (Lorentz) transformed into the laboratory system, i.e. the reference frame through which the electron moves, most of the radiation emitted outside the direction of motion has been shifted into the forward direction (Fig. 10, middle and right panel). As the velocity of the particle is increased (\( v \approx 0.9999995c_0 \) at \( \gamma \approx 3000 \)) this shift will be even more pronounced and any radiation emitted at any angle from the direction of motion (\( u'_x > -c_0 \)) will be shifted to the forward direction (although with a small angular spread). Only radiation emitted directly in the opposite direc-
tion of motion \((u' x = -c_0)\) will not be shifted to the forward direction, i.e. the point on the left side in Fig. 10 right panel.

Bending magnets

In a synchrotron, electrons (or positrons) are used to produce synchrotron radiation. The charged particles are kept in orbit with the help of bending magnets and focusing magnets. Whenever the electron orbit is bent in the magnetic fields the electrons are subjected to a central acceleration and radiate in the forward direction, tangential to the orbit according to the Lorentz transformation. This was the type of synchrotron radiation used in first and second generation rings. In the bending magnets the radiation cone sweeps by a small opening in the magnet. The time it takes for the radiation cone to sweep over this opening is very short due to the very high velocity of the electrons which gives a wide energy spectrum according to Heisenberg’s uncertainty principle.

Fig. 11  To keep the electrons in a closed orbit, bending magnets are used. As the electron beam is bent in the magnetic field of the magnets, synchrotron radiation is produced and the “search light” of X-rays are emitted tangential to the electron beam orbit. A small hole in the magnet lets the radiation into the beamline. The short time it takes for the radiation cone to sweep by the opening broadens the spectrum according to Heisenberg’s uncertainty principle.

The duration time of the radiation pulse seen through the hole in the bending magnet is proportional to the difference in the time it takes for the electrons to travel the path covering the opening \(\tau_1\) (the arc-length of the orbit divided by the speed of the electrons) and the time it takes for the photons to reach the opening \(\tau_2\) (the radiation path divided by the speed of light).
There is the radius of the path, and \(\theta\) is the angle segment of the path seen through the hole in the bending magnet, see Fig. 11. \(v\) is the speed of the electron and \(c_0\) is the speed of light. Heisenberg’s uncertainty principle states that:

\[\Delta E \Delta T \geq \frac{\hbar}{2}\]

The uncertainty in energy is related to the duration of the pulse, so the shorter the pulse is the larger the energy spread is. The radius \(R\) of the path is related to the magnetic flux density \(B_0\) in the bending magnets according to:

\[evB_0 = \frac{\gamma m_0 v^2}{R}\]

Here \(e\), \(v\) and \(m_0\) refers to the charge, velocity and rest mass of the electron. When combining the Heisenberg uncertainty formula with the duration of the pulse and the radius of the path expressed in \(B_0\), the uncertainty in the energy is given as a function of the magnetic flux density and \(\gamma\).

\[\Delta E \geq \frac{2\hbar}{m_0} B_0 \gamma^2\]

A more rigorous solution of Maxwell’s equations for a relativistic electron in a uniform magnetic field gives the critical energy, where there are equal amounts of radiated power in higher energy photons as in lower energy photons.

\[E_c = \frac{3e\hbar}{2m_0} B_0 \gamma^2\]

Also see [B8, s 126-134]
Fig. 12  (a) As the electrons pass in front of the opening in the banding magnet they emit radiation proportional to the acceleration. The radiation cone has an angular spread of $1/\gamma$.
(b) The intensity profile from a bending magnet is a broad band emission covering a wide range of energies up to hard X-rays.

The critical energy is a useful parameter for characterizing synchrotron facilities. Typically $B_0 = 1$ T in a bending magnet and $\gamma \approx 3000$ which give energies up to the hard X-ray region (2080 eV) and a critical energy of 1560 eV. The natural width of the emitted radiation cone is $1/\gamma \approx 0.3$ mrad.

Insertion devices
Between the bending magnets, in the straight sections of a third generation ring, radiation producing magnetic structures can be inserted called insertion devices. There are two such devices in general use, the undulator and the wiggler, both working on the same principle but with different parameters and hence different characteristics.

Fig. 13  The magnetic structure in an undulator or wiggler consists of a number of permanent magnets with alternating directions. The distance between two magnets of the same direction is called the undulator period $\lambda_u$. 
The undulator produces narrow energy peaks of high spectral brightness in the fundamental and low harmonics while the wiggler produces broad energy peaks of higher harmonics that merge to a semi-continuous spectrum with a high power output but with a smaller spectral brightness than the undulator.

The undulator/wiggler consists of a magnetic structure with alternating magnet poles that makes the electron beam wiggle as it passes through the structure. The wiggles are made perpendicular to the magnetic field between the poles, causing the electrons to radiate into a narrow forward cone. The periodic motion of the electron orbit causes the beam to radiate as a dipole with the frequency of the motion instead of a broad spectrum as in the bending magnet. In the rest frame of the electron the magnetic structure is Lorentz contracted. This gives a new periodicity to the magnetic structure \( \lambda' \) and hence to the emitted radiation.

\[
\lambda' = \frac{\lambda_o}{\gamma}
\]

\( \lambda_o \) is the period of the magnetic structure in the lab. As the beam undulates it radiates as a dipole with the frequency \( f' \):

\[
f' = \frac{c_0}{\lambda'}
\]

\( c_0 \) is the speed of light. When viewing the radiation in the laboratory frame the Doppler shift increases the observed frequency even more. The Doppler shift is however dependent on the relative velocity and therefore dependent on the observation angle \( \theta \) relative to the motion giving an additional energy spread in the radiation cone. Considering a small radiation cone close to the axis of the magnetic structure and velocities of the electron beam close to the speed of light we have, \( \theta \approx 0 \) and \( \beta \approx 1 \) which gives, \( \cos \theta \approx 1 - \frac{\theta^2}{2} \) and \( 1 - \beta \approx \frac{1}{2\gamma^2} \). The relativistic Doppler shift then becomes:

\[
f = \frac{f'}{\gamma(1 - \beta \cos \theta)} \approx \frac{\gamma c}{\lambda_o} \frac{1}{\gamma \left(1 - \beta \left(1 - \frac{\theta^2}{2}\right)\right)} \approx \left[ \beta \approx 1, \ 1 - \beta \approx \frac{1}{2\gamma^2} \right] \approx \frac{c_0}{\lambda_o} \frac{2\gamma^2}{1 + \gamma^2 \theta^2}
\]
From this formula an expression for the wavelength as a function of the undulator period $\lambda_u$, the relativistic factor $\gamma$ and observation angle $\theta$ can be derived.

$$\lambda = \frac{\lambda_u}{2\gamma^2 \left(1 + \gamma^2 \theta^2\right)}$$

This equation only applies to first order and gives the wavelength of what is called the fundamental, a more thorough investigation of the electron motion shows that the electron velocity along the axis of the magnetic structure will vary as the electron beam makes its excursions in the wiggles as $\gamma$ (i.e. the velocity of the electrons) is constant (unless the energy loss is substantial) in magnitude but changes direction during the motion. In the electron rest frame moving with the average axial speed of the electron this variation in speed along the axis will cause the electrons to wiggle also in the transverse direction to the acceleration. These transverse wiggles make the $\gamma$ value appear less than it is along the direction of the magnetic structure so that the effective axial $\gamma^*$ becomes.

$$\gamma^* = \gamma \frac{\sqrt{1 + \frac{K^2}{2}}}{\gamma}$$

$$K = \frac{eB_0\lambda_u}{2\gamma m_0 c_0}$$

Here $e$ is the electronic charge, $B_0$ is the magnetic flux density, $\lambda_u$ is the period of the magnetic structure in the lab, $m_0$ is the rest mass of the electron and $c_0$ is the speed of light. Using this effective axial $\gamma^*$ in the expression for the generated wavelength, a modification to the expression for the wavelength is obtained; the result is called the undulator equation:

$$\lambda = \frac{\lambda_u}{2\gamma^*^2 \left(1 + \gamma^*^2 \theta^2\right)} = \frac{\lambda_u}{2\gamma^2 \left(1 + \frac{K^2}{2} + \gamma^2 \theta^2\right)}$$

$K$ is called the magnetic deflection parameter. The wave length generated by the magnetic structure is determined by $\frac{\lambda_u}{2\gamma^2}$ and sets the general energy
region. \( \frac{K^2}{2} \) is the magnetic tuning which can be used to shift the energy by changing the magnetic flux density \( B_0 \). Depending on the values of these parameters the generated radiation will be either classified as undulator radiation or wiggler radiation.

The transverse movement not only gives rise to a lowering of the axial \( \gamma \); and hence lowering the wavelength of the fundamental, it also introduces higher harmonics to the motion which in turn generate radiation of higher harmonics i.e. radiation generated at higher orders due to the more complex orbits (they contain more frequency components). The transverse wiggles will cause the electrons to radiate perpendicular to the axis of the magnetic structure. When the radiation lobe of this radiation is transformed to the laboratory frame it will form a hollow cone around the radiation from the fundamental motion. This off axis radiation is called the second harmonic. The amplitude of the harmonics scale with \( K^n \) where \( n=1,2,3,\ldots \) is the number of the harmonic. It can be shown that it is only the odd harmonics 1,3,5... that give intensity on axis at moderate \( n \) while the even harmonics give intensity of axis. At very high harmonics the even harmonics will also give intensity on axis. The wavelength of the \( n^{th} \) harmonics is the \( n^{th} \) fraction of the fundamental wavelength, \( \lambda/n \). Harmonics are usually used to increase the energy range of an undulator and are fundamental in the generation of wiggler radiation. [B8, s 135-147]

**Undulator**

In an undulator the \( K \) value is equal to or less than one. The electron excursions are harmonic, with maximum excursion \( K/\gamma \). For an undulator these excursions are within the natural radiation cone \( 1/\gamma \). This leads to interference effects that are manifested in cone narrowing and in some cases partial coherence. A closer inspection of the emission profile in the undulator show that most of the emitted radiation is confined to a central radiation cone

\[
\theta_{cen} \approx \frac{1}{\gamma \sqrt{N}}
\]

This is much smaller than the natural width of the radiation cone. The spectral narrowness of the emission cone leads to higher spectral brightness. The spectral width of the undulator fundamental is of the order of \( \Delta\lambda/\lambda \approx 1/N \). Undulators normally operate in the fundamental frequency or wavelength as given by the undulator equation. Higher harmonics are used to increase the range of the undulator, but as the intensity of the harmonics scales with \( K^n \) intensity rapidly disappears at higher harmonics as \( K<1 \). [B8, s 125]
Fig. 14  (a) The small excursions of the electron beam in an undulator cause the electron beam to radiate mainly in the fundamental and low harmonics. Interference effects in the beam cause the radiation cone to be far more narrow than the natural radiation cone $1/\gamma$ and hence the undulator has a high spectral brightness. (b) Intensity is found mainly in the first harmonic. Higher harmonics are used to increase the energy range but as intensity scales with $K^n$ it rapidly decreases for higher $n$. There is no radiation produced in-between the harmonics making it necessary to tune the undulator, i.e. move the harmonic peak to the desired energy.

For a facility with $\gamma = 3000$ an undulator with a magnetic field of 0.2 T and a period $\lambda_u$ of 5.0 cm and 89 periods give the first harmonic energy at $\sim 310$ eV. Tuning the undulator from 0.05 T to 0.5 T gives an energy range from 430 eV to 120 eV.

**Wiggler**

In a wiggler the $K$ value is much greater than one. In principle a wiggler works in a similar way as the undulator but in a wiggler the wiggles are larger than the natural radiation width due to the higher $K$ value, i.e. higher magnetic fields. Since the beam excursions are outside the natural radiation cone there are no interference effects and the cone narrowing and high spectral brightness observed for the undulator is lost. The increase in magnetic field strength also leads to an increase of harmonic motions of the electrons which in turn leads to higher harmonic generation. Since the intensity of the harmonics scale with $K^n$ the intensity of the higher harmonics increase ($K >> 1$) shifting the radiated power to shorter wavelengths. The large excursions of the beam at very large $K$ values cause the harmonics to become broader in wavelength, from values of $\Delta\lambda/\lambda \approx 1/N$ to values dominated by $\gamma^2 \theta^2$ and the radiation cone will take on the dimensions of $\theta \approx K/\gamma$. At very high harmonic numbers the intensity of the harmonics start to overlap, and the intensity distribution approaches a continuum, which resembles the bending magnet profile but has a $2N$ increase in power output and a shift to harder X-rays.
Spectral merging takes place for a finite acceptance angle $\theta$ when

$$n \geq \frac{1}{\gamma \sqrt{2} \theta^2}.$$ 

Wigglers do not generally have the ability to tune the emission peak as they are designed to work in the high harmonic region at a specific energy where the emission profile is continuous over a large range.

In a similar way to the critical energy in a bending magnet, a critical harmonic number can be derived to characterize the wiggler for which equal part intensity is in lower harmonics as are in higher harmonics.

$$n_c = \frac{3K}{4} \left( 1 + \frac{K^2}{2} \right)$$

Depending on the acceptance angle spectral merging can be ensured well below the critical harmonic number.

[B8, s 125, 177-184]

For a facility with $\gamma = 3000$ a wiggler with a magnetic field of 2.5 T and a period $\lambda_u$ of 20 cm and 19 periods corresponds to a $K$ value of 47. Using an acceptance angle of 1 mrad this give spectral merging for $n > 11000$ while the critical harmonic number is 38200 giving a critical energy of $\sim$3.9 keV.
Concepts of Soft X-ray spectroscopy

When an atom interacts with a radiation field and absorbs energy, there is an electronic rearrangement to accommodate the increase in energy compared to the initial ground state ($GS$) configuration. The system goes into an excited state or intermediate state ($IS$). However, the system is not stable with this much energy and decays to a final state ($FS$) with less energy releasing some of the absorbed energy. In a solid, there are also transitions between different bands and between core levels and bands. This allows the system to be studied. By measuring the decay products, information about the $GS$, $IS$ and $FS$ can be obtained. When discussing these processes in a system, several ways are used to represent the transitions between $GS$, $IS$ and $FS$.

Transitions can be represented in transition diagrams by electrons moving between orbitals, horizontal lines, or continuum states, boxes. Each line can contain two electrons and the vertical separation between two lines corresponds to the absorbed or emitted energy.

Fig. 16 (a) Transitions can be represented by “hopping” electrons where the horizontal lines represent electronic local orbitals/states and the box represents continuum states or delocalized orbitals. Each orbital energy is for the respective electron.
(b) Band transitions are represented by vertical arrows where an electron with a certain $k$ value goes from an occupied band to an empty band, crossing the band gap. Solid lines represent bands and their energy dispersion for different $k$ values.
(c) Transitions between states or configurations where the total energy of the state is given rather than specific electronic orbitals or bands. Horizontal lines represent local states and boxes represent delocalized continuum states or bands.
Round “balls” represent the electron occupancy in the different orbitals, electrons can also be represented by vertical arrows either pointing up or down, indicating spin. Holes in the orbitals left by an electron are represented by empty circles.

Band structures are represented by band maps, where the energy of the band is plotted against the k vector of the electrons. There might be several symmetry points in such maps representing the different directions in reciprocal lattice space. Normally the photon for a band transitions does not have a large k vector compared to the k vector of the electrons. Therefore an electron that is excited from one k state will retain this k after the excitation. This is represented with a vertical arrow from a core level to the band. In the soft X-ray region this is not entirely true and the photon impulse starts to make a difference so that there is a slight offset in k in some transitions and in others it becomes very important. Band transitions are represented by a vertical arrow between bands in the band map if the photon k is small. Since there are a number of symmetry directions in a crystal, and not all of them have many band states the band edges can be somewhat indistinct as more and more states in different directions become available with increasing excitation energy. Transitions can also be represented in a total energy picture where the total energy of the state is shown. In this case no individual electrons are shown but the lines represent localized states and boxes continuum/band states. Transitions between states are shown with arrows.

If the energy of the incoming photon is sufficiently high the excited system may relax by the emission of an electron that takes away any excess energy as kinetic energy (part of the absorbed energy will be needed to release the electron) which can be measured, as well as the direction of motion yielding information about the binding energy and momentum of the electron. The excited system may also relax through the emission of a photon that can be measured, yielding information of internal energies and symmetries. There is always a competition between these two channels where both are possible and in this work only photons have been analyzed.

There are also other relaxation channels that are non-radiative such as internal relaxation via vibrations and charge transfer. These energies are however small compared to core level energies and are usually only visible as extra structures accompanying the electronic transitions or broadenings of these levels. As each species of atom have their own unique set of electronic energy levels, these can be used to identify or study specific atomic species and their chemical surrounding in a multi atomic specimen.
Fig. 17  (a) Excitation from ground state to an intermediate state (IS). The atom is left with a core hole and an excited electron. (b) Auger decay, where one electron fills the core hole while another electron is released. (c) Radiative decay where the core hole is filled by an electron and excess energy is released with a photon.

There are three basic ways to do spectroscopy with x-ray photons. X-ray absorption spectroscopy (XAS), X-ray emission spectroscopy (XES) and resonant inelastic X-ray scattering (RIXS). Then there are a multitude of special techniques where these basic principles are used in combination with other techniques to study specific things.

X-ray absorption
In X-ray absorption the absorption cross-sections are measured as a function of the incoming photon energy. If the incoming photon energy matches a transition from an occupied state to an empty state, a resonance in the absorption intensities will be observed. If the energy of the incoming photon is much higher than that required to excite to an empty local state the absorption may lead to ionization of the atom. Hence X-ray absorption maps the empty density of states in the system as well as ionization thresholds.
X-ray emission

In XES the emitted radiation from a decay of an excited state is analyzed in its spectral components. The excitation energy is normally above the ionization limit for the core level from which the electron is excited. The excited state can then decay by filling the core hole with an electron from a higher state under the emission of a photon. The photon energy represents the energy difference between the core level and the level from which the electron came. This emitted energy is generally independent of the energy of the exciting radiation. In this way the occupied states can be investigated. In resonant XES ((R)XES) the excitation energy corresponds to an empty level in the atom. The relaxation however still occurs by filling the core hole with an electron from another orbital but now the emission may be influenced by the presence of the core-excited electron.
Resonant Inelastic X-ray Scattering

When the energy is tuned just below or on a localized state a resonant phenomenon can occur in the X-ray emission where the emission energy is following the excitation energy at a constant energy loss. In this case the intermediate state lifetime is too short for the state to delocalize prior to the decay to the final state. This cannot be viewed as a two-step process where excitation and decay are separate steps but it is rather a one-step process where excitation and decay can’t be separated. This is referred to as resonant inelastic X-ray scattering (RIXS). In principle all photon scattering events are RIXS, described by the Kramer-Heisenberg scattering formula (the second term), but historically photon experiments have been divided on absorption (XAS) and emission (XES) and a two-step description where possible, leaving RIXS to represent states where the two-step approach is not entirely applicable.

In RIXS the emitted radiation is analyzed as in the XES case but it is done at several different excitation energies covering the resonance. The process can then be seen as a scattering event where the incoming light loses energy due to final state excitations such as vibrations and electron transfer. The energy loss can also correspond to an excitation of a low energy state such as transition within the valence band.

Fig. 19 (a) X-ray emission from a resonantly excited state.
(b) X-ray emission from a state excited high above the ionization threshold.
(c) A fictive XES spectra excited resonantly and high above threshold. The profiles might differ somewhat as the spectator electron can influence the profile.
Fig. 20  (a) The ground state before scattering. (b) The resonant inelastic scattering process, excitation and emission occur in a one step process. As the excitation energy is swept over the resonance the emitted photon energies follow the excitation energy dispersion. (c) Fictive RIXS spectra as the excitation energy is swept over the resonance. The emission energy follows the excitation energy. The difference between the excitation energy and the emission energy is the final state energy relative to the ground state. As the excitation energy is varied different emission profiles might result as the final states are populated differently.

The emitted radiation is (generally) of lower energies than the incoming radiation but follows the energy dispersion of the excitation radiation. This lost energy, corresponding to the final state energy relative to the ground state, can be calculated as the difference between incoming energy and outgoing energy. In this way the final states can be investigated. This scattering process can then be seen as an excitation to the final state just as if one had the energy of the difference in an ordinary XAS process. The selection rules are however different in this case and other symmetries are reached giving complementary information to XAS measurements.

Angular dependence
In free atoms the polarized light of the incoming light excites orbitals according to the state of the polarization. When the decay occurs the radiation will be emitted in different directions depending on the symmetries of the orbitals.
In the case of horizontally polarized light the angular dependence can be described by the differential cross section of photon scattering into the solid angle, \(d\Omega\), assuming 100% linear polarization:

\[
\frac{d\sigma}{d\Omega} = \frac{\sigma}{4\pi} \left(1 + \frac{\beta}{2}(3\cos^2 \theta - 1)\right)
\]

where \(\sigma\) is the total scattering cross section, \(\theta\) is the angle between the polarization of the incoming photon and the direction of the outgoing photon.

For a two electron system excited below the \(N = 2\) threshold i.e. doubly excited \(He\), the excitations are to \(^1P_1\) states that decay to \(^1S_0\) and \(^1D_2\) final states assuming \(LS\) coupling. Here \(\beta = -1\) and \(\beta = -0.1\) for \(^1S_0\) and \(^1D_2\) final states, respectively. Thus, measuring in the horizontal direction (\(\theta = 0\)) the spectrum isolates contributions from \(^1D\) final states, \((\sigma_{S}^{\text{horizontal}} \approx 0\) and \(\sigma_{D}^{\text{horizontal}} \approx 0.9 \cdot \frac{\sigma}{4\pi} \Delta\Omega\)), whereas in the vertical direction (\(\theta = 90^\circ\)) both \(^1S\) \((\sigma_{S}^{\text{vertical}} \approx 1.5 \cdot \frac{\sigma}{4\pi} \Delta\Omega\)) and \(^1D\) \((\sigma_{D}^{\text{vertical}} \approx 1.05 \cdot \frac{\sigma}{4\pi} \Delta\Omega\)) contribute to the spectrum. By measuring angular resolved spectra the symmetries of the final states can be derived by comparing measurements in the plane of polarization and perpendicular to the plane of polarization [45]. This applies to free atoms. When discussing molecules and solids the strict rules might be relaxed through solid state interactions. The degree to which the rules apply give an indication of how atomic the character of the state is.
Experimental

Author’s Introduction
This chapter concerns the experimental facilities that I have worked with and the instruments used. Many of the instruments and setups are specific for the respective beamlines as the instruments are custom made to fit the requirements of the beamline. There are however some general traits and similarities between the different experimental equipments and this part is dedicated to viewing the general principles rather than being an accurate description of each instrument used. At the end there is a section which describes the different beamlines used and the respective experimental set up. Apart from the I511-3 beamline at MAX-Lab I have had no part in maintaining and operating the beamlines and the equipment described here even if I have designed some of the setups used at these beamlines.

Beam lines
A synchrotron radiation facility is a storage ring where bunches of electrons are orbiting in a vacuum pipe at relativistic velocities. This is generally a large facility where the storage ring is approximately 30 m to 300 m in diameter.

Fig. 21 The beamline consists of three main parts; the optics which consists of monochromator and refocusing optics, end station where samples and measuring equipment are mounted and control where the recording of data and running of the experiment is done.
To this, office buildings, workshops etc are attached. Along the storage ring focusing magnets and bending magnets keep the electron beam in place. In a third generation source insertion devices such as undulators and wigglers produce the main part of the radiation. The storage ring is enclosed by a radiation protection, usually concrete walls to protect the experimental hall and its users from the produced radiation. From the bending magnet or undulator/wiggler the radiation goes into a pipe known as the beamline front end. This part of the beamline is inside the radiation protection, and is usually not accessible for users. This contains safety valves protecting the ring in case something goes wrong with the vacuum in the beamline. After the front end the beam enters the experimental hall where the rest of the beamline is situated. The beamline consists of three main parts; optics, experiment and control.

Optics

A monochromator focuses the radiation beam with an X-ray mirror and selects the desired energy with a diffracting grating (low-energy beamline) or a diffraction crystal (high-energy beamline). There are several designs utilizing plan, spherical or toroidal gratings and a number of mirrors. Most monochromators have an exit slit which determines the energy resolution of the radiation passed along. The ultimate resolution of the monochromator is determined by the design and the quality of the optical elements. In front of the monochromator (although not on all designs) a set of vertical and horizontal blades are placed to limit the amount of radiation let into the monochromator.

Fig. 22 The monochromator consists of radiation limiting blades, a pre-focusing and collection mirror (M1), a second movable mirror (M2) and a movable diffraction grating (G1). Before the exit slit a third mirror (M3) is placed to collect the outgoing radiation and focus it on the exit slit. The slit determines the angular spread from the grating that is passed along and hence the resolution of the monochromator. After the monochromator refocusing optics (M4 and M5) might be placed to focus the beam onto the sample.
This also limits the effective collection angle from the insertion device narrowing the energy spread. After the radiation passes the monochromator the beam is divergent and depending on distances between monochromator and experiment as well as requirements at the experimental station there may be need for refocusing optics.

The refocusing optics can consist of a number of mirror arrangements and types of mirrors with different shapes and properties. The purpose of the refocusing optics is to collect the radiation into a well-defined spot at the experimental station, utilizing as much of the radiation as possible or irradiating a limited amount of the sample.

**Endstation**

The part of the beamline where the experiment is set up is known as the end station. This can consist of a number of vacuum chambers designed for measurements with mounted detector systems as well as preparation chambers where samples can be prepared and characterized. There may also be storage chambers where sensitive samples can be kept under vacuum when not used in the experiment. These chambers are usually connected with some sort of transfer system so that samples can be moved between different chambers under vacuum.

**Control**

From this part of the beamline insertion devices and monochromators are controlled and data collection is performed. It is either situated at the endstation or in a hutch close by. Data is collected with normal personal computers (PC or Mac). Special Data Acquisition Cards (DAC) inserted into the computers are used to interface with the different measuring equipments. There is also the possibility to use programs for preliminary analysis of results, helping to monitor the overall progress of the experiment.

**Absorption measurements**

To measure true XAS one has to measure the intensity of the radiation that has passed through a sample as a function of the energy of the incoming photons. The transmitted intensity can for example be measured with a photodiode behind the sample. Such measurements are however unusual. In solids this is not even always possible and it is more common to measure the intensity of the decay products of the excited states as a function of the incoming radiation energy, as this is approximately proportional to the absorption cross section. This is usually done as draincurrent or electron- or photon- yield measurements. The energy scale of the XAS measurement is ei-
ther set by the monochromator, if it is well calibrated and the energy resolution is not of uttermost importance, or if energy calibration is needed either a reference sample can be used to calibrate the energy scale or a complementary measurement of known lines can be made with the same or another method.

When measuring drain current, electron- or photon- yield from a solid sample one has to observe that almost all the incoming radiation is absorbed (if it is thick enough which it usually is for soft X-rays) during a certain distance which is dependent on the incoming energy. The ejected particles then have to escape from the sample for a signal to be detected. The depth from which the particles can escape is dependent on the type of particle and the energy. Electrons generally have a much shorter escape depth than photons and hence can only escape if produced close to the surface. Photons on the other hand can escape from much greater depths and are used to probe the bulk. Self absorption can however be a problem with photon yield measurements. Saturation effects can occur if all ejected particles are able to escape. The geometry of the experiment has to be adjusted so that enough particles are able to escape to give sufficient signal intensity, but there has to be a contrast in the signal regarding the absorption length, i.e. the absorption cross section.

Drain currents are measured using a nano-ampere meter connected to the sample through wires. As electrons are ejected from the sample following an excitation and the following Auger decay (one electron is released removing the energy as another electron fills the core hole) of the excited state or the direct ionization of the sample, electrons from the surroundings rush in to neutralize the sample. This current can be measured and it is assumed to reflect the amount of absorbed radiation in the sample as a function of excitation energy. This however only works for conducting samples. The photodiode used in true absorption (other detectors can also be used) works on a similar principle. The surface of the detector is coated with a material that easily ejects electrons after the absorption of a photon and the current to the detector can be measured.

In electron and fluorescence yield the ejected particles (electrons and photons respectively) are measured directly instead. When measuring electron yield there might also be a problem with the charging of the sample. Measurements are usually done either with a multichannel plate (MCP) or a channeltron.

The multichannel plate is a glass plate through which small tubes have been etched creating a honeycomb structure. A voltage is placed over the plate (the field is always directed to accelerate electrons through the plate but the front of the plate is usually negative for photons and positive for electrons) and as an electron or photon hits the surface or inner walls of the tubes electrons are released from the glass. These released electrons are then accelerated by the voltage through the tubes where they bounce off the walls
successively releasing more electrons that are in turn accelerated. This builds up a charge pulse that can be detected with voltage measuring equipment (current measurements can also be done). In this way the number of particles hitting the detector can be counted.

A channeltron is a horn-shaped continuous dynode structure that is coated on the inside with an electron emissive material. A voltage is placed between the mouth (the entrance of the horn) and the collector (end of the horn). Electrons released at the mouth following an electron or photon impact are accelerated down the tube and since it is curved they will hit the walls on their way to the collector releasing more electrons. Measurements of the charge collected at the collector are measured in a similar way as with a multichannel plate. It should be noted that the tubes in the MCP are much smaller (µm scale) than the tube of the channeltron (mm scale). The active area of the MCP is usually larger than the channeltron and the supporting frame is also larger which makes it difficult to come close to the sample in some cases which limits the solid angle of detection. The multichannel plate retains the position information of where on the detector the initial event occurred while this is not the case for the channeltron. This information can be used if the incoming particles have been dispersed in space with regard to their energy or if one which to do element specific microscopy.

**Soft X-ray emission spectrometer**

The spectral decomposition of the emitted energies in XES is made with an X-ray spectrometer, in our case a grazing incidence Rowland spectrometer.

![Fig. 23](image)

Fig. 23  A point source (S) on a circle with radius R has its diffracted lines focused on the same circle by a grating with radius 2R.
Due to the nature of the radiation at these energies all reflections have to be at grazing incidence. In the spectrometer the different energies of the emitted radiation are separated in space with a diffraction grating. The intensities of the lines are then measured with a spatially resolving detector (multichannel plate with a position sensitive anode). The geometry of the spectrometer is based on the Rowland criterion; if a source is placed on a circle with a radius R tangential with a grating with a radius 2R, it will have its diffracted lines focused on the same circle.

The lines can then be recorded by placing a spatially resolving detector tangential to the circle at the appropriate position. The detector image is then processed by a computer to produce a two-dimensional picture of the anode containing the energy resolved spectral image of the emission energies. The resolution of the spectrometer is limited by the source (slit assembly of the spectrometer) since the image of the source at the detector position is overlapping with the energy dispersion of the diffracted lines. There are also other factors that limit the ultimate resolution of the spectrometer such as grating size, radius, groove density and the quality of the grating. If high resolution is needed and the grating parameters are fixed the size of the source must be limited by a slit. This will however reduce the solid angle of detection, severely reducing the count rate in the spectrometer making the measuring process time consuming. An experimental solution to this is to reduce the actual source by the use of refocusing optics prior to the experimental chamber. In this case the beam spot on the sample can be used as the source for the spectrometer optics rather than the slit assembly. This will increase the spectrometer signal without losing too much resolution.

**Energy resolved emission spectra**

The spectrometer is equipped with a spatially resolving MCP which gives a two-dimensional image of the photons hitting the detector. Emission lines are dispersed along the Rowland circle as described above. Perpendicular to this there is no energy dispersion but there is however a slight curve to the observed lines due to the use of spherical gratings in our case. This has to be corrected for when summing the spectral image over the detector surface.

The energy scale of the spectrometer has to be calibrated for each setup of the detector. Therefore is important to have some reference lines to set the energy scale with. This can normally be done with a reference sample containing known species with emission lines in the same energy region as those of interest. Alternatively one can use the elastically scattered excitation radiation from the monochromator. The latter is only applicable at low energies as the reflectivity is rather low at high energies and it is dependent on the calibration of the monochromator.
Partial fluorescence yield

Partial Fluorescence Yield (PFY) is a method for measuring fluorescence yield from a specific state. By monitoring the intensity emitted in a certain energy interval covering the emission from this state as a function of excitation energy, the absorption profile to this state can be recorded. This is useful when looking for a weak signal that otherwise would be drowned by emission from other states in normal fluorescence yield. PFY measurements are done with the X-ray spectrometer, by gating the detector to count only events in a certain region of the detector corresponding to the signal of interest and then recording the count rate as function of excitation energy. This is done using hardware potentiometers on the position analyzer electronics. Both gated and ungated signals can be recorded and compared. Since the solid angle of acceptance defined by the slit assembly restricts the total count rate, and the energy resolution of the spectrometer is not of great importance it is beneficial to run the spectrometer in a slit-less mode when measuring PFY.

Samples

There are two types of samples used in this work. The first is gaseous He contained in a small gas cells. Two pressures ranges were used during the different measurements. When measuring He SXE a closed cell with a gas pressure of ~10 mbar was used. In the FY measurements several types of cells were used but they were all differentially pumped and there were no entrance or exit windows for the synchrotron beam. The pressure was in this case ~10⁻³ mbar

The second type of samples used were solid lithium compounds, lithium fluoride (LiF), lithium chloride (LiCl), lithium bromide (LiBr), lithium iodine (LiI), lithium bortetrafluoride (LiBF₄), lithium oxide (LiO₂) and lithium carbonate (Li₂CO₃). The samples were prepared from commercially available lithium compound crystal grains / powder. These grains / powders were compressed into flat pellets with about 10 mm diameter and 2 mm thickness. The disc was then placed in vacuum mounted to a sample plate with tungsten wires. These samples are very sensitive to radiation damage and to reduce this effects the samples were moved with regular intervals so that the radiation successively hits a new spot on the tablet. The time between movements of the sample was usually 5 to 30 seconds depending on the sample.
Experimental facilities

U125/1 PGM1 at BESSY-II

XES measurements of the doubly excited $He$ states were made at beamline U125/1 PGM1 [46, 47] at BESSY-II, Berlin. This beamline can be equipped with a Rowland grazing incidence spectrometer and the energy range of the undulator, 20-800 eV covers the needs for this experiment (62-66 eV). There is also a refocusing system consisting of two refocusing mirrors, one spherical and one cylindrical. This gives a focus of 30 µm horizontal and 25 µm vertical FWHM at a 100 µm exit slit on the monochromator. The beamline has a variable deflection angle, collimated plane grating monochromator (SX-700 design) giving the needed energy resolution and stability to measure XES on the narrow resonances in He close to the $N = 2$ threshold.

A small closed gas cell with 1000 Å Al windows both for beam entrance and emission were used to contain the $He$ sample. The pressure in the cell was ~10 mbar. The gas pressure in the cell was regulated with a needle valve. The cell was mounted directly in front of the entrance slit to the Rowland grazing incidence spectrometer. The spectrometer was focused on the beam spot using it as source in the optics leaving the slits fully opened. The beam intensity was monitored with a photodiode after the cell enabling true absorption measurements. Electrodes mounted in the cell also provided the opportunity to measure electron/ion yield.

Fig. 25 The $He$ gas-cell is mounted directly in front of the slit assembly of the spectrometer, which is looking in the plane of polarization. A cut out has been made in the cell to show the ray paths from the cell.
Gasphase Beamline 6.2 at ELETTRA

The $^4$He fluorescence experiments under the influence of static magnetic and electric fields as well as in field free environments were carried out at the ARPES end station of the gas-phase beamline [48] at ELETTRA, Trieste. This beamline has a very high resolution monochromator, a Variable Angle Spherical Grating Monochromator (VASGM), with fixed positions of the slits giving a resolution of about 1.5 meV. The energy range, 14 eV to above 1000 eV, of the undulator (U12.5 at exit U6.2) is also suitable for the experiments performed. Most of the intensity is to be found in the first harmonic around 100 eV. The optical design includes a toroidal pre-focusing and two refocusing mirrors (spherical and plane-elliptical) giving a small well defined spot (100µm) at the endstation, which is needed due to the small entrance holes to the gas cell. The beamline also offers a large experimental chamber where custom experimental setups can be mounted. The chamber is also easily removable which gives the opportunity to use custom chambers as well; this was the case for the B-field measurements as magnetic components are not allowed in the ARPES chamber.

Fluorescence yield measurements were made with a MCP and a differentially pumped gas cell. Beam entrance to the gas cell was through small holes in the walls, ~2 mm diameter. Emitted radiation was monitored by one or two MCP’s looking perpendicular to the plane of polarization.

![Fig. 24](image)

Fig. 24  (a) The field free gas cell.
(b) The two part cell with one reference cell without field and one where two electrodes are running along the beam creating a static electric field. Cut outs are made in the setup to show the interior of the gas-cell
(c) The magnetic field gas cell, where two poles are sticking in to the cell in the plane of polarization. Cut outs are made in the setup to show the interior of the gas-cell. This experiment was mounted in a separate chamber to avoid magnetization of the ARPES chamber.
Exit windows of the gas cell were 1000Å thick aluminum filters. The MCP’s were protected against background electrons by an enclosing can and two copper wire meshes at the front kept on negative potential. Several designs of the gas cells were used in the experiments. In the field free experiment a simple rectangular cavity was used with exit windows at opposite sides, Fig.24 (a). In the electric field measurements two flat electrodes were placed parallel to the beam in the horizontal plane (plane of polarization) with a distance of 2.5 mm, and a reference cell was placed prior to the cell containing the electrodes to record reference spectra in a field free environment. Emitted radiation was measured with two MCP’s mounted to record in the vertical direction, two on the field free set up and one on each cell in the setup with electrodes, Fig.24 (b). In the measurements under the influence of a magnetic field only one MCP was used. The cell was modified to allow two magnet poles to enter the cavity with a separation of 2.4 mm. The magnet coils were placed outside vacuum and the fields were conducted to the poles through iron rods, Fig.24 (c). An ion chamber was also used to monitor the production of ions in all three setups, which was later used to calibrate the energy scale of the measurements.

**Beam line I511-3 at Maxlab**

The experiments on lithium halides and lithium compounds were made at the I511-3 beam line at MAX-Lab [49], Lund. This is an undulator beam line with a range of approximately 100-1000 eV. The photon flux at the end-station is approximately $10^{13}$ Ph/s at 140 eV. The monochromator is a modified SX-700 plane grating monochromator with a resolution of \(~0.1\) eV at 140 eV. Exit slits widths between 100 µm and 300 µm were used in the measurements.

![Fig. 26](image)

The lithium sample is mounted on a sample plate that is moved by the manipulator with regular intervals. The beam spot on the sample is used as source in the spectrometer optics. In some measurements the whole set up is rotated so that measurements are made in the vertical direction. In this case a slit was used as source in the spectrometer optics.
The beam is focused to a 20µm horizontal by 50µm vertical spot at the sample position using Kirkpatrick-Baez mounted elliptical refocusing mirrors. The intensity of the incoming beam is monitored with a gold mesh inserted into the beam after refocusing but before the sample. The photocurrent from the mesh is measured with a Keithley nanoamperemeter.

The experimental station consists of three chambers mounted in a row with a linear transfer system. The first chamber is a dedicated analysis chamber with an XES spectrometer [50], fluorescence yield detector and a 6-axis manipulator where three axes are motorized (x, y and z). This is used to reduce the effects of sample damage by moving the sample with regular time intervals. The manipulator has a resolution of 25 µm per step in the scanning direction (vertical). The distance between different scans was set to ~50µm (horizontal). The integrity of the sample was checked so that the emitted intensity at constant excitation energy was constant as the spot was scanned over the sample. The sample was turned so that the surface normal of the sample was about 60 deg from the beam. Generally the acquisition time per spectrum is 30 min. During PFY measurements the sample and monochromator were scanned together with 5-10 seconds per point. Several such spectra were then added for the final PFY spectrum giving an accumulated measuring time of approximately 30-60 seconds per energy point. In some of the measurements the undulator was also scanned together with the monochromator and manipulator.
Results

Author’s Introduction
The result section of this thesis consists of two main parts and two minor parts. The first main part deals with doubly excited states close to the \( N = 2 \) threshold in free helium atoms subjected to different field-environments. This part spans paper I to IV where paper I and II concern measurements on He in a field free environment. Papers III and IV deals with doubly excited states in He under the influence of external electric and magnetic fields respectively.

The second main part is concerned with double excitations at the lithium site investigated in the lithium halide series of LiF, LiCl, LiBr and LiI. This part spans paper V to VII. The text is compiled from all papers rather than an individual abstract of each. This is due to the similarities in these substances and the necessity to compare the results.

The third (first minor) part concerns the application of the method of double excitations at the lithium site to lithium compound materials which is treated in paper VIII.

In the fourth (second minor) part, paper IX, focus is placed on the observation of scattering at the halide site rather than the lithium site in LiI. The results in this part are based on the same data as presented in paper VII.

This is by no means a closed field of investigations and this work is only the beginning, more work is needed to fully understand these states, both theoretical and experimental.

Double excitations in \( \text{He} \)

Field free environment
The helium atom is the prototype two-electron system and is therefore used as a test bench for atomic multi-electron theory. Since the discovery of the doubly excited states in \( \text{He} \) [51,52] the photoabsorption spectrum associated with doubly excited states, has been investigated by R. P. Madden et al.[53], and theoretically described by U. Fano and co-workers [33, 44, 35]. Later the theoretical description has been expanded by C. D. Lin and others [40,
These studies have been a fundamental part in the understanding of the VUV photoabsorption processes.

During recent years it has been realized that detection of uncharged secondary particles such as photons [56, 57, 58, 59] and metastable atoms [57, 60] also can give important information about the absorption process.

The photoionization cross section in He can be described by three non-interacting series of Fano profiles. These series were characterized by J. W. Cooper, U. Fano and F. Prats [35] as the combinations $2snp \pm 2pns$ and $2pmd$ for quantum number $A = \pm 1$ and $A = 0$ respectively, with the important property that the $2snp+2pns$ series has a much larger oscillator strength and autoionization width than the $2snp-2pns$ and $2pmd$ series. Quantitatively the actual mixings and resonance parameters are more complicated [40] and are energy dependent in general [55, 61]. Here a simplified notation for these states are used. The $2snp+2pns$, $2snp-2pns$ and $2pmd$ series are referred to as $n^+$, $n^-$ and $n^0$ where $n$ refers to the outer electron’s principal quantum number in the excited state and the $\pm$ and 0 refers to the quantum number $A$.

Fig. 27  Partial (~38–42 eV) fluorescence yield spectra compared to predictions based on the calculations of Zitnik et al. [62, 45] for $P_v = 0$ (full line) and $P_v = 0.007$ (dotted line), normalized on the 40 resonance, for all resonances except $^1D$, $^6P$, $^7P$, $^7D$ and $^8P$. For these states the lines represent fit results, giving intensities of 0.04, 0.28, 0.44, 0.24 and 0.33 relative to the $^4P$ resonance, respectively.
At excitation energies with small \( n \) values the three Fano series of \( n^+, n^- \) and \( n^0 \) can be represented in the \( LS \) coupling scheme. To characterize the excitation-emission scattering process, i.e. to determine the cross section for inelastic scattering to specific singly excited states both the excitation profile and the emission profiles has to be measured. The strongest transitions have been resolved earlier [59, 62] but most of the information about the decay paths so far comes from measuring secondary decays [59, 62, 63, 64]. In paper I measurements of the excitation profile of the low \( n \) members of the doubly excited helium states below the \( N = 2 \) threshold are investigated, and Soft X-ray Emission (SXE) spectra from these states are also presented.

The intensity \( I(n^a \rightarrow ml) \) for scattering from the ground state to a final \( ml \) state (\( m \) is the outer electron’s principal quantum number), is proportional to the oscillator strength for exciting doubly excited states, \( f_{nm} \), the radiative decay rates \( \Gamma_{n^a \rightarrow ml} \) and the rate for autoionization to the ionic ground state \( \Gamma_{n^a \rightarrow He^+} \). Neglecting radiative transitions between the doubly excited states and interference effects a two step model can be used:

\[
I(n^a \rightarrow ml) \propto f_{n^a} \frac{\Gamma_{n^a \rightarrow ml}^{\Delta \Omega}}{\sum_{ml} \Gamma_{n^a \rightarrow ml} + \Gamma_{n^a \rightarrow He^+}}
\]

Here the \( \Delta \Omega \) superscript indicates that the scattering in the small solid angle is measured in the experiment. Using \( LS \) coupling only \( ^1D_2 \) and \( ^1S_0 \) final states are allowed. With the angular anisotropy in the experimental setup \( md \) \( ^1D_2 \) final states are emphasized.

\[
\Gamma_{n^a \rightarrow ml}^{\Delta \Omega} \propto \left[(0.9 + 0.15P_v) \cdot \Gamma_{n^a \rightarrow ml} + 1.5P_v \cdot \Gamma_{n^a \rightarrow ml}^H \right]
\]

where the vertical fraction \( P_v \) relates the intensity of the incoming radiation polarized in the vertical \( I_{in}^v \) and horizontal \( I_{in}^h \) direction in the expression for the total incoming intensity:

\[
I_{in} = P_v I_{in}^v + (1 - P_v) I_{in}^h
\]

Scattering to \( ms \) final states are however observed in this experimental geometry, indicating that \( P_v \neq 0 \) but no larger than 0.07. Partial Fluorescence Yield (PFY) measurements presented in Fig. 27 are used for normalization of the Soft X-ray emission spectra.
Fig. 28  (a) Experimental $n^0 \rightarrow ml$ scattering spectra for $n = 3-6$, where the intense $n = 3, 4$ scattering is measured with better energy resolution than the other emission spectra. Scattering to $2s$ final states is shown as inserts. The slope in the $4^0 \rightarrow 2s$ spectrum is due to edge effects in the detector. The energy positions of the final states are marked with full and dashed vertical lines for the $md$ and $ms$ series respectively, starting with $m = 3$ around 23 eV, and ending with $m = 6$ just above 24 eV. Curves through the data points for $n = 3-5$ are normalized theoretical predictions. For $6^0 \rightarrow ml$ the line through the data points is a fit assuming only $md$ final states, giving intensities of 0.0014, 0.0041, 0.0111, 0.30 relative to $\sum_{ml} f(4^0 \rightarrow ml)$ for $m = 3, 4, 5, 6$, respectively. There is also obvious intensity for $m > n$ both for $n = 5$ and 6.

(b) Experimental $n^0 \rightarrow ml$ scattering spectra for $n = 3-7$. The curves through the data points for $n = 4-6$ are theoretical predictions. For $3^0 \rightarrow ml$ the lines through the data points is a fit assuming only $md$ final states, giving intensities of 0.15, 0.014, 0.008 relative to $\sum_{ml} f(4^0 \rightarrow ml)$ for $m = 3, 4, 5$. For $7^0 \rightarrow ml$ the fit values are 0.0008, 0.0039, 0.0092, 0.33 for $m = 3, 4, 5, 6$. Unresolved intensity for $m > n$ is obvious for $n = 5-7$.

(c) Experimental $n^+ \rightarrow ml$ scattering spectra from $n = 3-6$. The curves through the data points are theoretical predictions.

The agreement with theoretical predictions is excellent. There are however some significant discrepancies at $3^0$ which is 19% larger and for $4^+$ and $5^+$ which are 15% and 11% weaker respectively than predicted by theory.

SXE spectra excited at the various resonances are shown in Fig. 28 Also here the general agreement between theory and experiments is excellent. There are however some small discrepancies between the measured data and theory. In Fig. 28 experiment gives significantly lower $\frac{\Gamma_{4^+ \rightarrow 4d}}{\Gamma_{4^+ \rightarrow 3d}}$ ratio than
predicted. The relative $\Gamma_{n^a \rightarrow ms}$ are depending on the population of $ms$ final states. The presence of $n^a \rightarrow ms$ intensity is rather well described assuming a $P_v$ of 0.07 (Fig. 28).

Including vertical polarization in the analysis has a large impact on the $n^+$ series for which it improves the agreement between experiment and theory, but the predicted total intensity is still generally lower than the measured intensity.

For final $LS$ coupled states of $^1D_2$ symmetry, both the $n^+ \rightarrow md$ and $n^0 \rightarrow md$ scattering with $n = m$ dominates and $n^+ \rightarrow md$ scattering giving $m = n-1$ are emphasized. Qualitatively this is in agreement with what is found in indirect measurements [59, 62, 63, 64] and in excellent agreement with theory [62, 65, 45]. The appearance of the $2p6d \ ^1D_1$ resonance (Fig. 27) marks the only deviation from $LS$ coupling in this energy range.

When the excitation energy is increased close to the $N = 2$ threshold the fluorescent yield cannot be explained in the normal theory as was shown in an experimental study [56] of the radiative decay of photoexcited He $2l'n'l$ states [57]. Here the authors tried to include radiative effects in a simple model based on a description where the fluorescence rate is independent of $n$ while both the autoionization rate and oscillator strength goes as $n^{-3}$. This simple model shows that fluorescence dominates for low $n$ in the $n^0$ states and $n^-$ series but not in the $n^+$ which is dominated by autoionization.

![Helium fluorescence cross sections](image)

**Fig. 29** Helium fluorescence cross sections: theoretical results are convoluted with a Voigt profile; experimental results are arbitrarily normalized to coincide with JK theory near 65.38 eV. The first peak to the left is the $11^+$. 

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The authors also show that the model does not work close to threshold. It is speculated that the $LS$ coupling scheme breaks down and that the $^1P$ states are split over an intermediate coupling regime into $jj$-coupling.

At higher $n$ the $2pnl \rightarrow 1snl + \gamma$ radiative decay competes with and eventually dominates the $2pnl \rightarrow 1s + e^{-}$ autoionization. The measurements presented in paper II reveal a rich structure in the fluorescence yield close to threshold where the $n^+$ series can be followed up to $n \approx 26$ as seen in Fig. 29. Interspaced between the $n^+$ series states, the experimentally unresolved $(n+1)/n^0$ series can be found. Close to the threshold there is an over all increase of the FY intensity at 65.382 eV followed by a dip in FY intensity at 65.389 eV and even closer to threshold another intensity shoulder is seen in the fluorescence yield at 65.329 eV.

Using the R-matrix multichannel quantum defect theory (MQDT) method with optical potentials and frame transformation the fluorescence yield both for a traditional $LS$ coupling with radiative decay and a $JK$ coupled case containing both radiative and spin orbit effects where forbidden $LS$ states were allowed could be calculate. The trends at low $n$ can be reproduced using the normal $LS$ coupling scheme which gives good results as can be seen from the dashed line in Fig. 29 and which is also in agreement with the observations in paper I. However, close to the threshold this does not comply with the measured spectrum, as was also observed in [56].

To introduce the effect of the $2p \rightarrow 1s$ radiative decay and the $2p_{1/2}-2p_{3/2}$ spin-orbit splitting in the calculations additional potentials are applied that introduces differences in the nodal behavior of the higher-$n$ (more diffuse) orbitals, leading to a breakdown of nonradiative $LS$-coupling descriptions.

At low $n$, where radiative and spin-orbit effects can be neglected and $LS$ coupling applies, there is a threefold degeneracy of the closed channel energies complying with the description of $2snp, 2sns, 2snp$ ($^1P$) and $2pnd$ ($^1D$) description. Allowing for relativistic effects, total spin is not necessarily conserved, and the five $LS$-forbidden, $1sp$, $2snp$, $2sns$, $2pnd$ ($^1P_{1/2}$) and $2pnd$ ($^3P_{1/2}$) channels need to be considered. Since the dominating effect of the spin-orbit operator for higher-$n$ states is a fine-structure splitting of the $2p_{1/2}$ and $2p_{3/2}$ thresholds, this causes the valence $nl$ electron to propagate away from the atom with different wave numbers. Only final momentum $J = 1$ are allowed and a parity $\pi = -1$ (odd) giving the $2l'nl$ $LS$ terms $^1P_{3/2}$, $^3P_{1/2}$, and $^3D_{3/2}$ (the spin-orbit operator mixes only terms with the same total $J$ and $\pi$).

This results in a difference in the wave number between the $LS$ coupled case (no spin-orbit, determined using only the $2p_{1/2}$ threshold energy) and the $JK$ coupled case (using spin-orbit split energy levels), $\Delta\nu = \sqrt{LS} - \sqrt{JK}$. When it is an integer, such as far below threshold, where $\Delta\nu = 0$, or at 65.389 eV, where $\Delta\nu = 1$, there is no departure from $LS$ predictions. At these energies the $2p_{1/2}nl$ outgoing wave acquires an extra half wave as it is propagated away from the atom to its turning point, and another half wave as it is propa-
gated back in, so it is back in phase with the $2p_{3/2} nl$ wave, and there is no destructive interference between the two.

When $\Delta \nu$ is a half integer, on the other hand, such as at 65.382 eV where $\Delta \nu = \frac{1}{2}$, the magnitude of the spin-orbit perturbation is maximum, and the greatest departure from $LS$ coupling predictions is expected. The different outgoing orbitals are $\pi$ radians out of phase once they have propagated out from the atom and back to the matching radius, so maximum destructive interference occurs between the channels.

The $n^+$ series has a small fluorescence branching ratio (FBR) while the $n^-$ and $n^0$ series, which have much smaller ground-state oscillator strength and autoionization rates than the $n^+$ series, has large FBR. The $JK$ mixing causes a redistribution of oscillator strength to states, both $LS$ allowed and forbidden, with larger FBR, increasing the overall fluorescence cross section. So fluorescence flux is increased when $\Delta \nu$ is a half integer and decreased when $\Delta \nu$ is an integer.

Electric fields
The prediction of external electrical field ($\epsilon$ field) effects on the doubly excited states of $He$ is a theoretical challenge because it involves the influence of electron correlation as well as the various decay paths. Work has been done on states below the $N = 2$ threshold using field strengths of 100 kV/cm [66] where Stark shifts and splittings can be readily measured. Theoretical work has also dealt with fields on this scale [67, 68, 69, 70]. In paper III we investigate the effect of weak fields in the order of 0-10 kV/cm.

At $\epsilon = 0$ the same as in paper II applies. The fluorescence yield intensity is enhanced periodically due to the $JK$ coupling close to threshold. As even moderate $\epsilon$ field strengths are applied the return to $LS$ coupling disappears. The additional influence of even weak $\epsilon$ fields destroys the interference between the spin-orbit and Rydberg nodal structures that was responsible for the return to $LS$ coupling. The fields might appear small but at $n = 35$ the influencing potential $V(r) = \epsilon r$ is on the same scale as the energy spacing between Rydberg manifolds, so strong $\epsilon$ field mixing is not surprising in this region.

But even at lower $\epsilon$ fields there are effects at low $n$ values. The FY due to the $(n+1)/n^0$ states quickly disappears as $\epsilon$ is increased above zero and at $\epsilon = 435 \text{ V/cm}$ the $14/13^0$ is unobservable as seen in Fig. 30. In the range of $7<n<15$ the $\epsilon$ field can be tuned to effectively turn the fluorescence on and off. On the other hand the $n^-$ states close to threshold become more prominent with increasing $\epsilon$, getting broader and more intense.
Fig. 30  Experimental and theoretical fluorescence yield spectra close to the $N = 2$ field-modified ionization thresholds (indicated by the arrows), excited at various $\epsilon$ fields. Just below 65.32 eV the $13^+$ state appears in this series having almost constant intensity. Less intense and with decreasing intensity we find the unresolved $(n+1)^-$ and $n^0$ peaks in between the $n^+$ and $(n+1)^+$ states, with the unresolved $14^+/13^0$ just above 65.32 eV.

In paper III R-matrix multichannel quantum defect theory, modified to deal with external field effects using a spherical-to-parabolic frame transformation are used. Here all possible $2l nl L\bar{S}$ terms needs to be consider since the electric field operator $\hat{H}_e = \alpha \cos \theta$ mixes outer-electron states with angular momentum and parity differences $\Delta l, \Delta \pi = \pm 1$. Even though the general behavior is reproduced by theory there is some discrepancy due to pressure effects and not fully converged calculations.
The reason for the decrease in FY in the $n^-$ and $n^0$ series can be attributed to a mixing of $n^-$ and $n^0$ states, which has a relatively low autoionization rate, with dipole-forbidden states with a high autoionization rate which decreases the FY. In the calculations no further effect is observed on the $n^0$ state as the field increase above 450 V/cm. Since the increased field reduces the FBR, the ground state oscillator strength must then increase to give the same intensity to the state. This is attributed to a strong mixing with the $n^+\hspace{0.5em}$.  

The $n^+$ feature is virtually unaffected by the $\varepsilon$ field except for a Stark shift. The observed increase of the $n^+$ feature in Fig. 31 is attributed to the appearance of a dipole-forbidden manifold on the high energy side giving a much broader and taller convoluted feature. These states are attributed to $\varepsilon$ mixing with spin-allowed dipole-forbidden states, sharing only a small frac-
tion of the oscillator strength. However these mixed states have small autoionization rates and therefore large FBR. The result is that the FY of the broad $n^+$ states is essentially unaffected, but the FY of the narrower mixed states becomes comparable in magnitude.

The periodic oscillations seen in Fig. 31 above the ionization threshold are generally expected for excitation spectra of Rydberg atoms in an external field [71]. The periodicity can be used for calibration of the $\varepsilon$ field.

External electric fields have a strong influence on the balance between autoionization and fluorescence where the main effect of the $\varepsilon$ field is to mix the $n^+$ series, which has a small FBR, with other states having larger FBR, thereby increasing the overall FY.

**Magnetic fields**

When applying magnetic fields to the double excitation in He similar results are obtained as for $\varepsilon$ fields since the fluorescence yield spectra close to the $N = 2$ thresholds are determined by a subtle balance between the radiative and autoionizing channels. In paper IV the doubly excited states in He below the $N = 2$ thresholds is investigated under the influence of external magnetic fields ($B$-fields) ranging from 0-1 T. At $B = 0$ T the spectra behaves as presented in paper II and III under field free conditions. The characteristic interference dips, where the coupling returns to $LS$ can be seen where $\Delta\nu$ has integer value (1 and 2 in Fig. 32).

![Intensity vs Photon Energy](image)

Fig. 32  Fluorescence yield spectra of helium in magnetic fields varying up to 1 T. The spectra are normalized by assuming that the FY intensity above the $N = 2$ thresholds is independent of the applied field. Increasing the B consistently increases intensity just below the threshold. Some $n^+$, $n^-$ and $n^0$ states are labeled for orientation. Arrows below the main features indicate $\Delta\nu$ values for the field-free spectrum.
A general enhancement in the FY as a function of increasing magnetic field is observed close to threshold in Fig. 32. A significant increase in the FY is observed for states \( \Delta \nu > 20 \), and especially at the energy position of 65.389 eV (\( \Delta \nu = 1 \)) and 65.393 eV (\( \Delta \nu = 2 \)). At the thresholds the FY enhancement falls off smoothly to zero.

It is just in the region where \( \Delta \nu \) is an integer, i.e. where the system returns to LS coupling, that the most prominent field effects are observed. This implies that the breakdown of LS coupling is essential for the understanding of the B-field induced effects.

The shift of the \( N = 2 \) thresholds due to the Zeeman effect on the ion can be estimated to be of the same magnitude as the energy spacing between the Rydberg levels without fields. The shift is too small to be measured directly but it affects the Rydberg series further down in the spectra. The additional level splitting due to the Zeeman effect corrupts the interference conditions and a return to LS-like excitations can not be expected and the mixing with LS-forbidden states increases the FY.

To describe the magnetic-field effect on the Rydberg electron one must take the diamagnetic term into account as it increasingly mixes the \( L \) as the principal quantum number increases, much in the same way as the \( L \) mixing due to a static \( E \)-field as presented in paper III. The predicted energy spread within an \( n \)-manifold is of similar size as the spread introduced by the threshold displacements.

The biggest magnetic-field influence on the FY is due to mixing with states that have larger FBR than the states that are reached in the field-free case. This is further supported by the observation that the magnetic-field effects vanishes the last few meV before the thresholds. Here the fluorescence branching ratio is already close to unity for all contributing Rydberg states and hence the mixing mechanism cannot lead to further FY enhancement.

A more complete theoretical description, similar to that presented in paper III, has to be employed to fully describe the effects of the B-field on these states. It is however clear that the magnetic field effects on the inner electron as well as on the Rydberg electron must be taken into account.

**He summary**

Photon scattering measurements on doubly excited states below the \( N = 2 \) threshold confirm the LS couplings validity at low \( n \) as well as showing remarkable agreement with theoretical predictions. Close to the \( N = 2 \) threshold LS coupling can however not be used other than at certain points where interference effects make sure that the system behaves as a normal LS coupled system. Instead a JK coupled system has to be applied that mixes LS forbidden states into the normal LS states. These forbidden states have a higher fluorescence branching ratio than the normal LS states which results.
in an FY increase close to threshold, except where the system returns to pure LS coupling. This gives the threshold region a characteristic intensity profile where the FY oscillates between JK and LS coupling. The primary effect of field application to the doubly excited He states close to the threshold is the removal of the interference that returns the system to LS coupling. The external field also introduces mixing between the \( n^+, n^- \) and \( n^0 \) series, as well as a further mixing with dipole forbidden states not included in the JK coupling. The result is a fluorescence yield increase in some cases but also a disappearance of some states from the FY.

Double excitations in Li halides

Doubly excited states in He have been investigated in a field free environment as well as under the influence of electric and magnetic fields in *paper I-IV*. To investigate the influence of a solid state environment on these doubly excited states, a He atom in a bound state can be approximated by a Li ion in an ionic solid. The lithium atom is the prototype three-electron system and as such it can be used in the investigation of highly correlated states and the development of advanced atomic theory.

Hollow states in solids have been studied by impinging highly charged ions on surfaces [72, 73], the neutralization of the ion creates a highly excited atom with empty inner shells. Electronic and radiative decay of these states within the solid is used to monitor the charge states, and thereby to gain information about the neutralization process and the general dynamics as the ion enters the material.

Using selective excitation of multiple electrons with synchrotron radiation enables specific hollow states to be created and studied. This has been a particularly useful method for a detailed characterization of the hollow states and their excitation-decay dynamics [74]. The radiative decay of states with a double core vacancy in the 1s orbital leads to so-called hypersatellites [75] in X-ray emission, and in recent years photoexcitation of hollow states in solids [76, 77] have been presented in the literature. Generally, the cross section shows a smooth monotonic increase from the on-set at threshold, a behavior which has been analyzed in terms of shake-off processes.

In *paper V-VII* hollow or doubly excited core states at the Li site in solid lithium halides are investigated with resonant inelastic X-ray scattering.

When the excitation energy is tuned close to the \( 1s^2 \, ^1S \rightarrow 2s2p \, ^1P \) transition in free \( Li^+ \) at 150.3 eV [78, 79] strong resonances appear in the emission from the lithium halides close to the \( 2p^2 \, ^3P \rightarrow 1s2p \, ^3P \) transition in the free lithium ion at 87.9 eV [80] and the predicted energy of the \( 2s2p \, ^1P \rightarrow 1s2s \, ^1S \) transition, at 89.3 eV [78].
Fig. 33 The scattering maps are compiled from SXE spectra taken at different excitation energies. These have been normalized to the respective partial fluorescence yield as seen in the PFY part of each field, intensity increases to the right. The number of spectra in each map and the excitation energy density varies between the different halides. LiF has 29 different excitation energies, LiCl has 68, LiBr has 52 while LiI only has 21. The LiI SXE spectra have been modified by subtracting a background signal of Si L emission.

These resonances are obviously associated with the creation of double core vacancies at the lithium site in the lithium halide salts. The investigated salts are lithium fluoride (LiF), lithium chloride (LiCl), lithium bromide (LiBr) and lithium iodine (LiI).

Lithium has a fairly low electronegativity while the halides are amongst the most electronegative elements in the periodic system, which creates an ionic crystal with well defined ionic bonds. The lithium atom experiences a quasi-atomic environment where the Li ion is exposed to a crystal field of more or less static electric and magnetic fields generated by the valence electrons. The more ionic the system is the more atomic-like the environment is.

As the lithium ion absorbs energy it can either ionize further or both of the remaining electrons can correlate in absorbing the energy in a doubly excited state.
The doubly excited core state decay by the return of one of the two electrons to the lithium $1s$ orbital, emitting a photon, which can be analyzed and the result plotted as a function of the excitation energy.

The scattering maps in Fig. 33 from LiF, LiCl, LiBr and LiI are equi-intensity contour maps created from the measured soft X-ray emission (SXE) spectra collected at different excitation energies. The excitation energy ($E_1$) is plotted against the vertical axis and the emission energy ($E_2$) is plotted against the horizontal axis. To the right side of each scattering map, the corresponding partial fluorescence yield spectra are shown. The PFY spectra show the integrated intensity, in the emission region marked with vertical bars, as a function of excitation energy. The diagonal line going from $E_1 \approx 150$ eV, $E_2 \approx 75$ eV to $E_1 \approx 170$ eV, $E_2 \approx 85$ eV is elastically scattered radiation in second order of diffraction. As can be seen from the different scattering maps in Fig. 33 the general structure of the maps are the same.
but with some variation. The PFY spectra, shown to the right of each scattering map, are also shown in Fig. 34.

Localized double excitations

In the lithium halides several interesting features are observed. The most prominent is the localized double core excitation resonance where both of the Li ions $1s$ electrons are excited to the $n = 2$ shell where they stay localized at the lithium site as seen in Fig. 33 at $E_1 = 145-150$ eV and $E_2 = 87-89$ eV. In Fig. 34 this localized double excitation is represented by the main intensity feature seen around 145-150 eV. This doubly excited state then decays with the return of one of the electrons to the $1s$ level. The final state can be both a localized excitonic state, similar to the state reached in normal $K$-edge absorption [81, 82], where the excited electron stays in the localized $n = 2$ level or it can be excited to the conduction band in a shake process during the decay. If $GS$ is the ground state, $e_L$ and $e_{CB}$ denote a localized and conduction band electron, respectively; the possible scattering processes can be described as:

$$GS \rightarrow 1s^{-2}e_L^2 \rightarrow 1s^{-1}e_L^1 \quad (\alpha_I)$$

$$\left(GS \rightarrow 1s^{-2}e_L^2 \rightarrow 1s^{-1}e_{CB}\right)$$

This type of scattering ($\alpha_I$) has two core holes and two localized electrons in the intermediate state and one core hole and one local or delocalized electron in the final state.

The $\alpha_I$ resonance is seen in Fig. 33 as a high intensity dispersing feature, i.e. a feature that change emission energy with a change in excitation energy. The energy position of this resonant peak is dependent on the electronegativity of the halogen atom forming a linear relationship, inset Fig. 34.

In Fig. 35 the SXE spectra excited at the dispersive resonance are plotted on the final state scale and compared to the $K$-edge soft X-ray absorption (SXA) measured by Haensel et al. [81, 82]. The different halides behave in similar ways but with some differences. The sharp peak, which coincides with the SXA exciton, represents local final states. LiF has two such peaks in the spectra corresponding to the similar structure in the $K$-edge absorption spectra. The other halides only have one peak but instead it is dispersing slightly towards higher final state energies with excitation energy. The emission peaks are however contained to the SXA exciton peak indicating excitations of higher energy states within the SXA peak.
Fig. 35 Here SXE spectra from LiF, LiCl, LiBr and LiI are shown on the energy loss or final state scale. Together with each set of SXE spectra are the K-edge SXA spectra as measured by Haensel et. al. The bottom of the band is marked with arrows in the respective PFY.

These excitations are of electronic as well as vibronic nature as described in paper VI. There is also a tail on the main peak in LiCl and LiBr that stretches outside the final state exciton and into the conduction band which represents excitation of delocalized final states. The tail gain in relative intensity as the excitation energy is increased, showing an increase in the shake process with an increase in excitation energy.
Delocalized double excitations

There are also delocalized doubly excited states seen in all lithium halides where only one of the excited electrons stay localized at the lithium site while the other goes into the continuum. At excitation energies above ~150-152 eV the emission features appear at constant emission energy as seen in Fig. 33. The still localized electron in the \( n = 2 \) level fills one of the core holes under the emission of a constant energy photon in the decay. Thus, the intermediate states in this type of scattering (\( \beta_1 \)) have two core holes, one localized electron and one electron in the continuum, and the final states have one core hole and one electron in the continuum. The scattering can be described as:

\[
\text{GS} \rightarrow 1s^{-2}e_{cb}^{-1}e_{cb}^{-1} \rightarrow 1s^{-1}e_{cb}^{-1}
\]

(\( \beta_1 \))

The emission profiles of the \( \beta_1 \) scattering is shown in Fig. 36.

---

Fig. 36 The SXE profile of the \( \beta_1 \) scattering from the different lithium halides excited above the localized scattering. For LiF the light colored curve is excited at 154.0 eV while the dark colored curve is excited at 158.2 eV. The 154.0 eV excited curve show the \( \beta_1 \) scattering and the 158.2 eV excited curve show \( \chi_1 \) scattering derived from the presence of \( N = 3 \) electron.
As the continuum electron is excited in the first step it does not influence the emission. The peak shape must then reflect the intermediate state population of the localized electronic levels in the presence of two core holes. The asymmetric peak shape, common for all the halides shows that there are several different such excitonic states. For LiF the $\beta_1$ emission retains the double structure of the $\alpha_1$ scattering while the other halides show a single peak with a large tail towards lower energies. As the excitation energy is increased the $\beta_1$ scattering profile varies in intensity reflecting the DOS in the conduction band (CB) but it does not change shape to any large extent except for LiF. At excitation energies of ~158 eV there is a resonance in the emission from LiF. Here the emission profile changes through the addition of a high energy shoulder, see Fig. 33 and 36. This scattering is referred to as $\chi_1$ and it is associated with local $n = 2,3$ states where the extra high energy feature is attributed to the influence of a local $n = 3$ electron.

**Band interaction**

It is not only the lithium $1s$ electrons that are involved in transitions associated with the lithium double excitations. Another phenomenon is also observed; band transitions, where a valence electron is promoted across the band gap to the conduction band, can be induced in the solid as a result of the double excitation. This induced band transition can occur either in the excitation process or in the decay. These band excitations are associated both with the localized double excitations and the delocalized double excitations. When the band transition occurs in the emission process it is called $\alpha_2$ scattering if it occurs in the decay from a localized double excitation and $\beta_2$ if it occurs in the decay from a half localized state. This is seen as a broad intensity maximum around $E_2 = 70$ eV as seen in Fig. 33. The additional energy loss compared to $\alpha_1 / \beta_1$ scattering is attributed to an additional valence hole and conduction band electron. This has earlier been suggested to explain features in the $K$-edge absorption spectrum, in particular feature $E$ (LiF, LiCl and LiBr). Fig.34 [83]. With $e_{VB}$ and $e_{CB}$ denoting a valence band and conduction band electron, respectively the process can be written:

\[
GS \rightarrow 1s^{-2}e_L^2 \rightarrow 1s^{-1}e_L^{-1}e_{VB}e_{CB}^1 \hspace{1cm} (\alpha_2)
\]
\[
GS \rightarrow 1s^{-2}e_L^1e_{CB}^1 \rightarrow 1s^{-1}e_{VB}^{-1}e_{CB}^2 \hspace{1cm} (\beta_2)
\]

At 156-158 eV excitation energy a feature appear in LiCl, LiBr and LiI ($E_2 \approx 87$ eV) that is shifted to lower energies compared to the $\beta_1$ emission. This is due to a scattering process in which three electrons are excited by the photon in the first step; the two lithium $1s$ electrons are excited to localized states,
and simultaneously a band electron is promoted across the band gap. In the second step, a photon is emitted as one of the localized electrons returns to the $1s$ orbital. A large part of the $\sim -2\ eV$ emission energy shift of this ($\gamma_1$) feature, relative to the $\beta_1$ feature can be understood as a Coulomb shift due to the local spectator electron. The scattering process can be described as:

$$GS \rightarrow 1s^{-2}e_L^1e_{VB}^1 e_{CB}= 1s^{-1}e_L^1e_{VB}^1 e_{CB} \quad (\gamma_1)$$

$$\left( GS \rightarrow 1s^{-2}e_L^2 e_{CB}\rightarrow 1s^{-1} e_{CB}^2 \right)$$

The decay is similar to that observed in the $\alpha_1$ scattering but in the presence of a valence hole and a conduction band electron. The emission profile of the $\gamma_1$ scattering is very similar to the $\alpha_1$ scattering profile as described in paper VI.

With the assignment $GS \rightarrow 1s^{-2}e_L^2 \rightarrow 1s^{-1}e_L^1e_{VB}e_{CB}$ ($\alpha_2$) and $GS \rightarrow 1s^{-2}e_L^1e_{VB} e_{CB} \rightarrow 1s^{-1}e_L^1e_{VB}e_{CB}$ ($\gamma_1$) the two scattering channels have the same final states, also when maintaining the one-electron picture.
The large energy difference between the intermediate state resonances makes it difficult to observe any interference effects and it makes it feasible to rely on the two-step approximation. Hence, the principal difference between the two processes is that the band excitation occurs in the first step ($\gamma$) or the second step ($\alpha_2$) of the scattering process.

The SXE spectra in Fig. 37 are shown on an energy-loss scale together with the PFY spectra where the spectra are offset with the energies corresponding to the $GS \rightarrow 1s^{-1} \epsilon_i^1$ excitation and the $GS \rightarrow 1s^{-2} \epsilon_i^2$ excitation, respectively. The agreement of the peak position for the $\gamma$ excitation and the $\alpha_2$ emission peak is excellent as well as the agreement with the documented band gaps in the respective halide [81]. From this it can be concluded that it is foremost the exciton states, A ($LiCl$ and $LiBr$) and B ($LiF$ and $LiI$) in the $K$-edge SXA ($\alpha_2$) and $\alpha_4$ ($LiCl$, $LiBr$ and $LiI$) in the PFY ($\gamma$), that interact with the band, inducing a band transition.

Calculations for $LiCl$

Fig. 38  The crystal structure of $LiCl$ is a FCC lattice. The model consists of a $2 \times 2 \times 2$ super cell with 32 lithium atoms and 32 chlorine atoms. The numbers indicate the inequivalent sites of $Li$ (light/pink) and $Cl$ (dark/grey) atoms. The center dark (small/dark/blue) $Li$ atom is treated as an impurity when the $1s$ electrons are removed.
In an attempt to investigate the observed features theoretically we have performed band calculations for LiCl as presented in paper VI. The model system consists of 32 chlorine atoms at 4 inequivalent sites, and 32 lithium atoms at 6 different sites distributed in an FCC crystal.

The unit cell volume was relaxed with an *ab initio* plane wave program (VASP), [84], and the full-potential linearized augmented plane wave method (FP-LAPW) [85] was used to compute density of states (DOS) and X-ray absorption near edge spectra (XANES). An APW+local orbital [86] basis set was used with additional local s-orbital for all the Li and Cl atoms.

To account for the effect of single (1s^1 2s^1) and double (1s^0 2s^1) core holes on the electronic band states, the excited Li atom was formally treated as an impurity in a LiCl supercell of dimension 2×2×2, a background charge was used in order to keep the system neutral.

From the calculations, Fig.39, it is seen that the ground state chlorine and lithium states with s-character appear to be well localized. The top of the valence band, near to the Fermi level, is mainly formed by chlorine p-states with some admixture of Li s- and p-orbitals. The bottom of the conduction band consists of a mixture of empty Li and Cl states of both s- and p-character. The bonding type between Li and Cl is ionic, where the Li atoms give fractions of electrons to the surrounding chlorine atoms.

![Fig. 39](image)

*Fig. 39  The ground state density of states projected on the s, p and d symmetry for the different Li and Cl sites.*
When removing a 1s electron (Fig. 40) from the central Li atom forming a 1s$^1$ 2s$^1$ configuration the VB states of Li$_i$ and Cl$_i$ move downward in energy. Furthermore, Li$_i$ and Cl$_i$ show a strong mixing of their s- and p-states, indicating a high level of hybridization between the two atoms. Such an electronic s,p-hybridization brings a certain amount of covalent character into the LiCl system. In a qualitative way one can say that the Pauling’s electronegative value of the Li$_i$ atom becomes as high as that of neighbors Cl$_i$ atoms so that the two species tend to share electrons and to form directional bonds. The bottom of the CB is also dominated by localized empty s- and p-states of Li$_i$ and Cl$_i$ that have moved downward in energy with respect to the GS case in order to screen the strong 1s-hole potential.

For the case of a 1s$^0$ 2s$^1$ configuration (Fig. 41) the VB is dominated by the strong hybridization between the s- and p-states of Li$_i$ and Cl$_2$, while the bottom of the CB shows localized empty s- and p-states. The band widths of the occupied Li$_i$ and Cl$_i$ s- and p-states increase considerably for the double core-hole system pointing to a larger hybridization between the central lithium atom and neighboring chlorine atoms. The removal of two s-electrons from the Li core generates a charged pseudo-atom that turns out to be more electronegative than the surrounding chlorines. Therefore, the type of Li-Cl
bonding around the excited Li site becomes stabilized when the s- and p-electrons are shared in between the two atomic sites instead of accounting for an effective charge transfer. The system gets a more covalent character.

Fig. 41  The density of states projected on s, p and d symmetry in the presence of two core holes for the different Li and Cl sites.

Angular resolved measurements for LiCl

To separate the different symmetries in the final states experimentally, measured spectra with the spectrometer in the vertical and horizontal directions are compared. In the atomic picture under LS coupling, spectra measured in the plane of polarization contains contributions from $^1D$ final states while spectra measured perpendicular to the plane of polarization contain contributions from both $^1S$ and $^1D$ final states.

In the angular resolved PFY spectra, Fig.42 (bottom field), there is a pronounced angular dependence. The sharp $\alpha A$ resonance is more dominating relative to other structures in the vertical direction than in the horizontal. An interpretation in terms of the expected angular dependence in a free ion suggests that the sharp $\alpha A$ resonance must be associated more with sp –like excitations then pd –like excitations, whereas the $\alpha A'''$, $\alpha A''$, $\alpha A'$ resonances have larger pd weight.
The SXA measured by Haensel et. al can be fairly well explained by the DOS in the presence of one core hole ($1s^1 2s^1$) projected on the symmetries of $s$, $p$ and $d$. The structure of the PFY can not be explained by the simple DOS in the presence of two core holes ($1s^0 2s^1$) but a convolution of the empty and filled DOS give fairly good agreement. The PFY measured in vertical and horizontal direction shows a remarkable angular anisotropy, the filled spectrum shows the difference between the two.

The predictions of the unoccupied DOS calculated in the presence of one core hole (Fig. 40, lower panel, right side), projected on the $Li$ site and angular momentum symmetries $s$, $p$ and $d$ are compared to the strongest features in the SXA spectrum in fig. 42 top panel.

The local $p$ DOS predicted by the supercell band calculation give a fairly good representation of the spectrum. Since the DOS calculated in the presence of two core holes (Fig. 41 bottom panel right side) fail to explain the observed features in the PFY, in the same way as can be done with the SXA (top panel Fig. 42), a simple model is used, based on the super cell calculations. It is assumed that one of the excited electrons is found in the occupied DOS (Fig. 41 bottom panel left side) in the presence of two core holes, and the other in the unoccupied DOS (Fig. 41 bottom panel right side); therefore the experimental spectra in Fig. 42 (bottom) is compared to a convolution of the occupied and unoccupied DOS in the presence of two core holes.
Fig. 43  SXE spectra measured in vertical and horizontal direction are shown in line spectra, the difference spectra is shown in filled form. Vertical and difference spectra has been smoothed for clarity in right panel. The $K$-edge SXA is shown at the top left for reference.

In this convolution it is required that primary energy is divided between the two electrons so that the sum always agrees with the incoming energy. The agreement between the predictions of this crude model and the experimental data is remarkable even though the model is not expected to be accurate.

The angular resolved SXE spectra, excited on the $\alpha$ resonance, presented in Fig. 43 (left) imply that $s$, $p$, and $d$ symmetries are represented in the whole range where the SXA spectrum has its principal intensity. This contradicts the fact that the calculations predict isolated sharp localized $s$, $p$, and
final states at different energies, Fig. 42 (top). The discrepancy is partly
due to excitonic effects, which are not fully described by the theory. The
observations strongly suggest that vibronic coupling breaks the symmetry,
thereby relaxing the dipole selection rules [87, 88], and hence affecting the
angular dependence, this phenomenon is well-known in gas-phase scattering
[89, 90].

Phonon coupling also introduces shifts and broadening of the spectral fea-
tures. The fact that narrow states are identified when dipole allowed s-
symmetry is emphasized shows that vibronic coupling is particularly weak in
the transitions corresponding to the \( \alpha_i \) spectral feature. The identification of
d symmetry is less certain, however, because it is based on the relatively
small angular anisotropy, which could also be attributed to solid state effects.
In the horizontal geometry in which s-symmetry is forbidden, the intensity is
smeread out over a larger energy region, suggesting that vibronic coupling is
stronger, and thus that symmetry breaking may be important for populating
these states.

In Fig. 43 (right) the SXE spectra excited above the localized \( \alpha \) resonance
are shown. Here the \( \beta_i \) emission shows a distinct double structure in the
vertical direction while the profile in the horizontal is a broad asymmetric
feature. At the \( \gamma \) resonance excitation energy (158.5 eV) the \( \gamma_i \) emission is
seen on the low energy side of the \( \beta_i \) emission. The similarities to the \( \alpha_i \)
emission profile, fig.43 (left) is obvious, reflecting the similarities in the core
state. At all excitation energies the relative \( \gamma_i \) intensity is smaller when meas-
uring in the vertical direction in which \( \beta_i \) becomes totally dominating at 162
eV excitation energy and above.

Pursuing the atomic angular selectivity model this implies that \( \beta_i \) scatter-
ing emphasizes final states of s symmetry to a much higher degree than \( \gamma_i \)
scattering. For the \( \beta_i \) process it is conceivable that the local partial DOS in
the continuum for final states preferentially is of s character, thus leading to
the angular anisotropy.

The final states of the \( \gamma_i \) scattering are more complex and therefore the
anisotropy is more difficult to explain. A dominating isotropic contribution
due to complete loss of angular momentum symmetry information is totally
in line with the observation that \( \gamma_i \) intensity effectively vanishes as a result of
the subtraction procedure.

Li summary

The doubly excited states observed in RIXS at the lithium site in the lithium
halide series show a remarkable complexity even though only \( 2l'2l' \)-like
states are populated, in LiF \( 2l'3l \) like states can also be excited but it still
only covers \( n = 2, 3 \) compared to the \( 2l'nl \) states in He which spans a much
greater range of \( n \).

\( 99 \)
Several doubly excited states are observed from pure localized double excitations to delocalized states as well as induced band transitions in conjunction with the double excitations. This plethora of states gives rich information about the chemical surroundings of the Li atom. Chemical shifts in both the PFY spectra and in the SXE spectra reflect the influence of the halogen atoms on the lithium site. The interaction with the band, and the presence or absence of such states, gives information about the interaction between the lithium atom and halogens. Also the semi atomic behavior reflects the strong ionic environment and the subtle differences in the profiles tell about population probabilities in the different cases.

An accurate theoretical description of the localized doubly excited states in the lithium halides is however beyond the scope of this thesis, and the hope is that this investigation will stimulate theoretical activity. The challenge is to properly account for the quasi-atomic correlation between the two excited electrons, and simultaneously take the solid state effects into account.

Double excitations in molecular Li compounds

Fig. 44  The scattering map from LiF, LiBF₄, Li₂O and Li₂CO₃. The PFY shown to the right of each map represents the integrated intensity between the vertical bars in the respective scattering map, 85.2 to 95.2 eV for LiBF₄, 85.2 to 95.2 eV for Li₂O and 85.6 to 95.8 eV for Li₂CO₃.
In paper V-VII it was shown that the doubly excited \textit{Li} states in the lithium halides have semi-atomic properties and that there is a strong interaction with the surrounding halogen atoms. Induced valence to conduction band transitions are also observed in all of the investigated compounds.

The main resonances are also subject to chemical shifts, making the double excitations directly useful in chemical analysis. Using the doubly excited states it is possible to investigate the local environment of the \textit{Li} in different materials and at different stages in processes of technical or pharmaceutical relevance. In paper VIII a series of lithium compounds, \textit{Li$_2$O}, \textit{Li$_2$CO$_3$} and \textit{LiBF$_4$} are investigated.

Fig. 44 shows the scattering maps of the measured soft X-ray emission spectra, similar to those presented in Fig. 33, for \textit{LiF} (included as a reference), \textit{LiBF$_4$}, \textit{Li$_2$O} and \textit{Li$_2$CO$_3$} in the excitation region of 140 eV to 170 eV. The PFY is plotted to the right of each map.

![Scattering maps of X-ray emission spectra](image)

**Fig. 45** PFY measures the integrated intensity over the double excitation as a function of excitation energy.

From the scattering maps several common features are seen in the profiles. All lithium compounds show a resonant emission feature around $E_1 = 145-150$ eV and $E_2 = 85-90$ eV. The emission is dispersing with excitation energy indicating a scattering event where the same final state is reached. For \textit{Li$_2$O} and \textit{Li$_2$CO$_3$} the dispersion is not as distinct as in \textit{LiF} and \textit{LiBF$_4$} and the resonant behavior is almost lacking. From these maps $\alpha_1$, $\alpha_2$, $\beta_1$ and $\beta_2$ scattering can be readily identified. \textit{LiBF$_4$} is very similar to \textit{LiF} which is not surprising.
since the local electronic structure at the Li site is similar in the two compounds. There is a small broadening of the $\beta_1$ channel in the map at $E_1 > 165$ eV which could be associated with $\gamma_1$ like scattering.

The appearance of $\chi_1$ intensity suggests that the bonding in LiBF$_4$ is sufficiently ionic for $n = 3$ derived states to influence the spectra.

The Li$_2$O and Li$_2$CO$_3$ behavior at $E_1 \approx 150$ eV is more of an edge jump at threshold to almost constant intensity. The dispersive behavior of the SXE peak is very similar to what is expected when emission ‘turns on’ as the excitation energy is tuned across the region of a continuum threshold [91, 92] without local resonances. This strongly suggests that localization is less important in these compounds than for the more ionic compounds studied so far. There are no signs of any direct $\gamma_1$ scattering in Li$_2$O and Li$_2$CO$_3$ which can be explained by the lack of a localized double excitation to induce $\gamma_1$ scattering. The non-dispersing features can however be assigned to $\beta_1$ scattering. The $\alpha_\alpha/\beta_\beta$ scattering is very strong in Li$_2$O and Li$_2$CO$_3$ compared to the $\alpha_\alpha/\beta_1$ scattering. This clearly indicates that the coupling to the valence electrons is stronger in these compounds.

Fig. 45 shows the PFY measured for the compounds. The obvious resemblance in shape between LiF and LiBF$_4$ is apparent as well as the resemblance between Li$_2$O and Li$_2$CO$_3$. There is also some resemblance between the LiBF$_4$ and Li$_2$O and Li$_2$CO$_3$ if the area between the $\alpha$ peak and the $\chi$ peak in Li$F$ is filled up with $\beta$ excitations. There is a clear chemical shift of the onset of the double excitations between the Li-$F$ and Li-$O$ compounds. There is also a small shift within the Li-$F$ compounds depending on the presence of boron and within the Li-$O$ compounds depending on the presence of carbon. It is apparent that similar states as are seen in the lithium halides are found also in other lithium compounds and that the resonances reflect the lithium atoms chemical surroundings.

In conclusion it has been shown that these states can be used to monitor the lithium atoms/ions chemical surroundings and give information about the system. It is yet to be established exactly how this information is to be used in the characterization of Li materials.

McRIXS

In the data set pertaining to the double excitations in the lithium halides other dispersing features were also observed that are not directly related to the lithium site. These features increase in intensity close to excitation energies corresponding to the Li double core excitation which suggests a correlation between the double excitations in Li and the population of these states.

Core orbitals are localized to a single atomic site and in compounds they are only slightly influenced by the surrounding influence of the other atoms. Observations which seem to indicate electronic transitions between core
levels at different sites have therefore always attracted attention in the community of X-ray spectroscopists [93, 94]. They challenge both spectroscopic common sense, and theoretical descriptions of X-ray spectra in which the so-called one-centre approximation [95] is still the conventional starting point [96].

The scattering map of LiI (Fig. 33) shows a sharp double resonance dispersing from $E_1 = 140$, $E_2 = 85$ eV to $E_1 = 155$, $E_2 = 100$ eV. In fig. 46 the LiI scattering map has been plotted against the final state energy scale. At the top two SXE spectra are shown and to the right of the scattering map the PFY is shown together with PFY’s constructed for the two SXE peaks on the final state scale.

Fig. 45 Two-dimensional scattering map of LiI, with colour coded intensity as a function of excitation and final state energy. Two scattering spectra, taken at 147 eV and 153.5 eV are shown on top, indicating structures associated with I 4d and Li 1s vacancies are found. Partial fluorescence yield spectra are shown in the right panel. PFY is the photon yield in the 83-92 eV emission energy region, directly as measured, and the other spectra are constructed from the scattering map, with PFY I 5/2 and 3/2 corresponding to the (as indicated in the Fig) 52.3-53.3 eV and 53.9-55 eV final state energy intervals, respectively, and the PFY Li corresponding to the 84-89.7 eV emission energy interval. For all these spectra a background determined from the spectrum excited at 137 eV, far below the relevant resonances has been subtracted.
The scattering map of LiI (Fig. 46) shows a sharp resonance corresponding to final states around 60 eV, when the excitation energy is tuned to 146 eV. This resonance is the localized Li 1s double excitations, populating single Li 1s core hole states. The dispersing line starting around 148 eV excitation energy and 60 eV emission energy is the delocalized $E_1$ emission.

The additional feature with two rather sharp structures with maxima at 53.0 eV and 54.7 eV energy loss are associated with scattering to states with $I 4d$ vacancies. The energy difference, 1.7 eV, is very close to the spin-orbit splitting between $j = 5/2$ and $j = 3/2$ coupled pure $I 4d$ hole states. The spectral structures are similar to features in the near-edge $I 4d$ absorption spectrum of $KI$ and other ionic iodine compounds [82], which have been assigned to excitations of electrons from the $I 4d$ level to the conduction band.

The excitation energies in the scattering map, Fig. 46 are in the excitation energy continua of the ‘$I 4p$’ states [97, 98, 99]. In the configuration interaction description the $4p^{-1}$ configuration strongly mixes with the $4d^{-2}4f$ configuration, resulting in a multitude of broad continuum states, spread out over around 50 eV, from the first threshold which we estimate to be around 125 eV in LiI. Energetically, these states could all contribute to the RIXS process. Designating these states $|4p^{-1}e_{CB} + 4d^{-2}4f_{CB}⟩$, the principal RIXS mechanism for population of final $4d$ holes can be described by the following excitation-emission path:

$$GS \rightarrow |4p^{-1}e_{CB} + 4d^{-2}4f_{CB}⟩ \rightarrow 4d^{-1}e_{CB}$$

From the scattering map and the PFY the scattering process populating final states with an iodine core vacancy seems correlated with the population of lithium core vacancies. At excitation energies below the edge for population of $Li$ final states there is little population of $I 4d$ final states but the $I 4d$ population increases where the $Li 1s$ population has the main resonance and above the $Li$ ionization thresholds they both have a rather excitation-energy independent cross section (Fig. 46). This observation strongly suggests a cross section interdependence which requires interaction between core levels on both the lithium and iodine sites.

In paper V and VI it has been shown that a double core vacancy on the lithium site in LiCl strongly polarizes the bond, so that it gets substantial covalent character. The iodine ion in LiI has a large dipole polarizability [99], and the orbitals will strongly relax to screen a Li double excitation. As the electrons in the $I n = 4$ shell show strong collective behaviour, any relaxation is associated with virtual dipole excitations. It is conceivable that a multi-center coupling could be understood in terms of such excitations.
Final remarks

It has been shown that local double core excitations both in He and Li can be studied using inelastic soft X-ray scattering. The doubly excited states are highly correlated and hence the theoretical description of them must be adapted to fully describe their behaviour, which in some cases has been done successful as shown, while more work is needed in others.

The doubly excited states are also very sensitive to the influence of external fields which make them useful in the characterization of the local environment. For He the theoretical description of static electric fields is fairly well developed while the description of the magnetic field influence needs some more work. The challenge in the case of double excitations in solid lithium compounds is to properly account for the quasi-atomic correlation between the two excited electrons, and simultaneously take the solid state effects into account.

It is a complementary work between experimentalists and theoreticians that drives the development of our understanding of the world around us forward. This work has shown that phenomena observed in experiments can be used to develop the theoretical descriptions as well as leaving a challenge for future experimentalist and theoreticians.

Here I will leave for others to continue the investigation of doubly excited core states.
Acknowledgements

The production of such a work as this is not an effort solely by one person. Not only are the experiments by necessity an effort of many people but the education needed to perform the experiments and take part of the results, both data treatment and evaluation, is something that has to be acquired by the interaction with colleagues.

I therefore would like to start my acknowledgements with Prof. Jan-Erik Rubensson, my supervisor for his contributions both in educating me on concepts in physics and for his help in the writing of papers. He was the first person to take me in as an undergraduate student, provided me with some interesting things to do during summers instead of working as a gardener, sales attendant or not at all. He introduced me to the world of synchrotrons, doubly excited states and much more. Later he supervised my masters thesis and also provided me with a project for my PhD study within the Grad-U program. I also have to thank Joseph Nordgren for his support as the head of the research group and for excellent explanations of the principles of synchrotron based soft X-ray spectroscopy.

The actual know how of synchrotron based experiments were learned from Conny Såthe and Magnus Ström in the beginning of my education during our work at ELETTRA and later by Thorsten Schmitt, Andreas Augustsson and Tanel Käämbre during the commissioning of beamline 1511-3 at MAX-lab. I also have to thank Chris Glover and Dennis Nordlund who were working on our sister branch 1511-1 at MAX-lab during my first years for their help in explaining the life at synchrotrons. The people at the Gas Phase beamline at ELETTRA also has to be mentioned, Stefano Stranges, Robert Richter and Michele Alagia. Their help during 24h beamtimes has been invaluable. I will also mention Lidia Gridivneva who worked as post doc on 1511-3 and Elisabeth (Lizzy) Sörgaard who replaced Chris as beamline postoc at 1511-1 for their help at MAX-lab as well as the other staff who willingly helped with broken waterlines, power supplies, pumps, computers etc.

Carl-Johan (Calle) Englund also has to receive my most sincere thanks for his help during the design of my experiments and trials to work with CAD programs, and producing drawings, as well as with the interaction with the workshop and different suppliers of hardware. In this section I would also like to thank Johan Gräsjö for his help with making lithium slat/compound tablets without which most of the experiments would not have been possible.
Performing experiments are not always a funny business as one tends to work 14 to 16 ours a day for one or two or even three weeks at a time. Some of these shifts I have done alone and some I have been accompanied by others, some already mentioned and some who needs to be mentioned. Here I have to thank Johan Söderström for his support during measurements both at Maxlab and at Elettra, as well as for our discussions before going abroad. During my time at Fysikum I have at times shared a room with some people, Limin Qian, Håkan Holmark and Joakim Andersson. The latter has to be thanked for his support during the writing of this thesis, both in the discussion of how to write, and the reading of this text and not least the nice lunches at Brasserie Blå without which I would have perished. I also have to acknowledge the rest of the people that I have worked with in the soft X-ray group, Lars Werme, Kevin Smith, Laurent Duda, Sergei Butorin, Martin Magnuson, Kristina Kashnina, Johan Forsberg, Anders Olsson, Egil Andersson and Anders Modin.

During my time as a PhD student I have not only worked with my research but I have also been teaching in the course-lab and I would like to thank Lars-Åke Näslund and Stefan Eriksson for their help in introducing me to the art of teaching. During my time in the course-lab I also worked with Petros Souvatzis, Emma Kristensen, Katharina Nilsson, Andreas Kissavos and Thorsten Schmitt.

Finally I would like to acknowledge Fanny Larsson, Prof. Leif Karlsson, and Prof. Joseph Nordgren for their input on the text as well as Prof. Jan-Erik Rubensson.
Våra modeller för att beskriva verkligheten omkring oss har alltid varit beroende av våra observationer. Det är däremot inte alltid som vi har förstått vad det är vi sett och många av de modeller som använts har byッツ ut mot nya förbättrade varianter under årens lopp. Detta gäller inte minst atom- och molekylfysiken, eftersom det här rör sig om partiklar som inte kan ses med blotta ögat.

I början av 1900-talet visade det sig att det fanns fenomen som man inte kunde förklara inom ramarna för de klassiska modellerna. Lösningen visade sig vara introduktionen av kvantisering av energier vilket i slutändan ledde fram till formuleringen av kvantmekaniken. Till en början studerade man enkla system som väte vilket består av en kärna och en elektron som binds samman av de två partiklarnas olika laddning. I takt med att man började förstå hur man skulle använda denna nya formulering av fysiken utvecklades modellen och man kunde börja studera mer avancerade system. För att testa de modeller som används och se hur allmängiltiga de är behöver man applicera dem på system som går utöver den normala beskrivningen då det gäller växelverkan mellan elektronerna.

Ett sådant system är "ihåliga atomer", det vill säga atomer där ett helt skal tömts på dess innehåll av elektroner. I dessa system samverkar elektronerna väldigt starkt vilket gör att vi kan undersöka hur väl modellens beskrivning av interaktionen mellan elektroner i atomer stämmer med verkligheten.

Denna avhandling behandlar två sådana system av ihåliga atomer, dubbelexciterat helium under inverkan av olika yttre fält samt dubbelexciterade lithiumjoner i solida material. Dessa system har studerats med fotonspridning. De ihåliga atomerna skapas genom att de två 1s-elektronerna i helium respektive lithium absorberar en foton och delar på energin genom elektronkorrelation så att båda elektronerna stannar i atomen, i stället för att den joniseras. Det dubbelexciterade tillståndet sönderfaller sedan genom att en av elektronerna återgår till 1s nivån under utsändandet av en ny foton. Genom att mäta intensiteten av utsända fotoner (absorption) som en funktion av energin på de inkommande fotornas kan man bestämma excitationsenergin, och även till viss del bestämma sannolikheten att excitera de olika dubbelexciterade nivåerna. Man kan också analysera de utsända fotonernas energi (emission) med hjälp av en gitterspektrometer och på så sätt få information om sluttillstånden efter spridningen.

Om man applicerar ett extern elektriskt fält kommer man att störa denna interferenseffekt, även om fältet är väldigt litet. Dessutom kommer fler icke tillåtna tillstånd att blandas in i LS tillstånden och de "relativistiska" tillstånden. Dessa "nya" tillstånd har även de en högre sannolikhet att sönderfalla via utsändandet av en fotom, vilket leder till att man observerar en förstärkning i signalen även långt ifrån tröskeln.

Samma sak händer om man istället applicerar ett extern magnetfält. Även i detta fall kommer man att störa det interferensfenomen som gör att man återgår till LS-koppling, och inblandningen av icke tillåtna tillstånd gör att intensiteten går upp. Effekterna av magnetfältet är dock mer begränsade till området nära tröskeln än vad effekterna av de elektriska fälten är.

För att kunna studera dubbelexciterade tillstånd i fasta material kan man använda litium bundet i en jonisk kristall. Om bindningarna är tillräckligt joniska kommer litiumatomen att reduceras till en litiumjon med bara två elektroner som då påminner mycket om heliumatomens konfiguration. Inverkan av de omgivande atomernas fält på de dubbelexciterade tillstånden kan då studeras. Då det gäller dubbelexcitationer i litiumjoner i fasta material är det inte alls självlklart att det går att observera några sådana tillstånd. Det begränsade utrymmet i ett fast material samt bindningen till omgivande atomer kan mycket väl förhindra dubbelexcitationer i kärnnivån.

I den fösta delen av litiumexperimenten undersöks dubbelexcitationer i LiF, LiCl, LiBr och LiI. Halogenerna är mycket elektronegativa i jämförelse med litium vilket får till följd att då litium binds till dessa i en kristall kommer litiumatomens valenselektron att helt övergå till halogenatomen vilket lämnar litiumatomen i ett joniserat tillstånd.
Ett flertal olika dubbelexciterade tillstånd i litiumatomen har observerats. Det finns två typer av primära dubbelexciterade tillstånd i litium, ett lokalt och ett icke-lokalt tillstånd. I det lokala tillståndet har de två 1s-elektronerna exciteras till n = 2 nivån vilket lämnar 1s skalet tomt. En av de två exciterade elektronerna faller sedan tillbaka till 1s nivån under utsändandet av en foton. Sluttillståndet blir då liknande det som hade nätts om bara en elektron hade exciterats. I det icke-lokala tillståndet stannar en elektron lokalt i litiumatomen medan den andra delokaliseras till ledningsbandet. Den elektron som stannat lokalt återvänder sedan till 1s nivån under utsändandet av en foton. Utöver dessa två typer av dubbelexcitationer har inducerade bandexcitationer, där en valenselektron går från valensbandet till ledningsbandet samtidigt som de två 1s-elektronerna exciteras eller en av dem dexciterar, observerats.

Mätningar har också gjorts på molekyllära litiummaterial. I dessa kan man finna liknande tillstånd som observerats i de joniska litiummaterialen. Vissa av tillstånden kan observeras i alla litiummaterial som undersöks medan andra bara kan ses i vissa material. Till exempel kan man inte se några bandexcitationer tillsammans med dubbelexcitationen i de molekyllära materialen. Däremot kan man se sädana övergångar associerade med sönderfallet av de dubbelexciterade tillstånden. Dessutom varierar energipositionen för excitation och emission beroende på den kemiska omgivningen vilket gör att man kan använda tillstånden för att analysera olika material. Då litium användes både inom läkemedelsbranschen och i litiumjonbatterier finns det goda möjligheter att applicera dessa dubbelexciterade tillstånd i en analysprocess med praktisk tillämpning.

Utöver dubbelexcitationer i litiumatomen har vi observerat att vissa tillstånd även exciteras på de intilliggande atomerna och att dessa excitationer är kopplade till vad som händer i litium atomen. Detta är ett fenomen som är välkänt att förklara teoretiskt då man i teorierna anser att "kärntillstånd" är lokalt begränsade till en atom och att dessa inte interagerar med omgivningen. I LiI ser man två emissionstoppar som motsvarar ett sluttillstånd där en 4d elektron har exciterats till ledningsbandet uppdelat på J = 3/2 och J = 5/2. Spridningen går via en blandning av enkeljonisation och dubbelexcitationer i jodatomen. Det exciterade tillståndet kan då beskrivas med hjälp av konfigurationsinteraktion där jod 4p² -2feCB tillstånd blandas med 4p²eCB tillstånd. Intensiteten i denna spridningskanal förefaller bero på förekomsten av dubbelexciterade tillstånd i litiumatomen. Vid excitations energier under litium dubbelexcitationsresonansen är det förhållande vis svag intensitet i de två jodtopparna. Då excitations energin överstiger litium dubbelexcitationsenergin ökar intensiteten i jodkanalen. Det kan förklaras med att jods elektroner i n = 4 skalet är väldigt starkt korrelerade och att dubbelexcitationen i litiumatomen polariserar bindningen mellan jodatomen och litiumatomen, vilket ökar chansen för excitationer i jodatomen. Detta motsvarar en oelastisk flerkärnespridning.
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