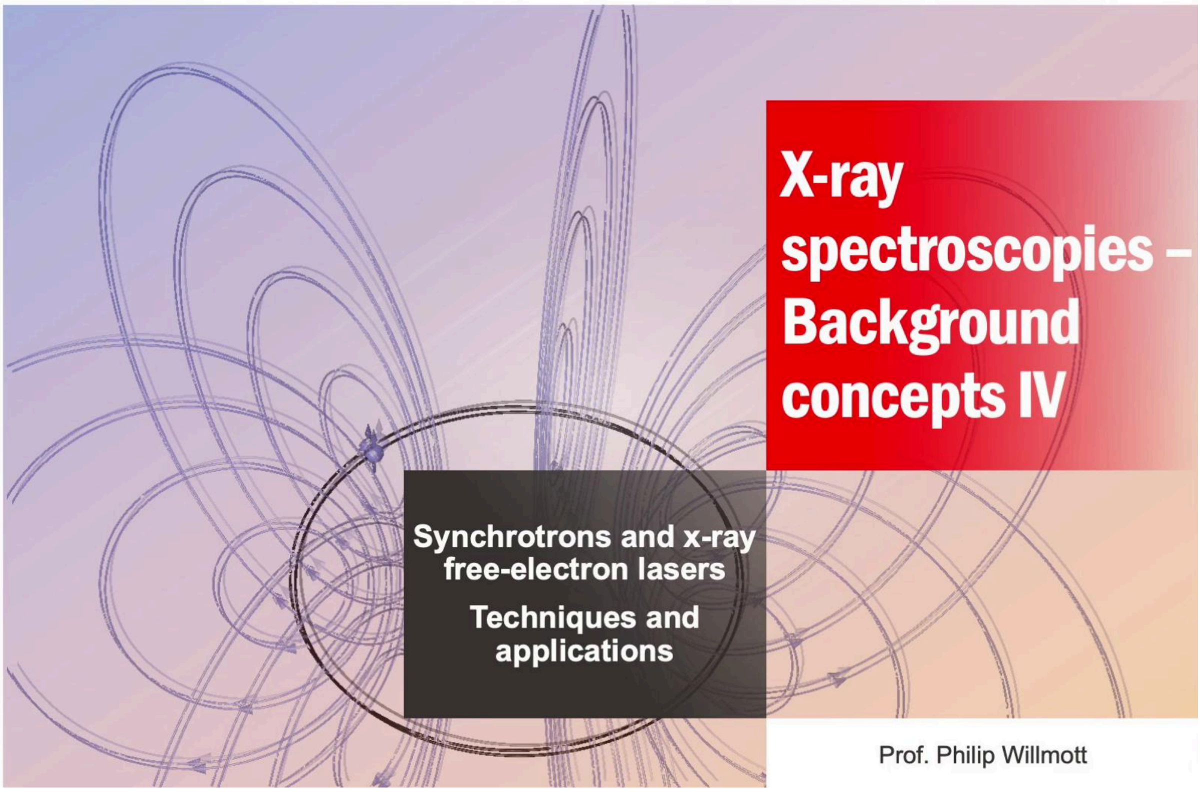
EPFL



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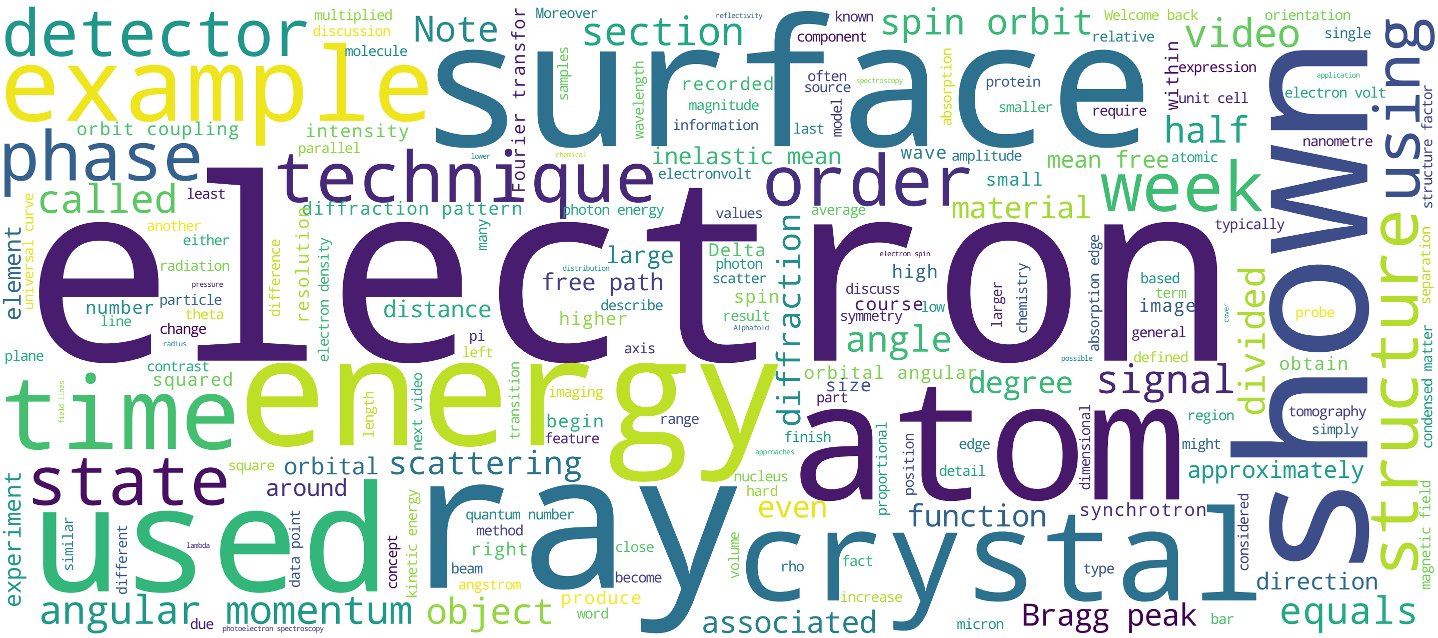

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diffraction pattern
photon energy

Search MOOC

Video

EPFL

Contents and objectives of this video

- Inelastic mean free path
- Universal curve
- Electron angular momentum and spin
- Spin-orbit coupling
- s- and p-polarizations

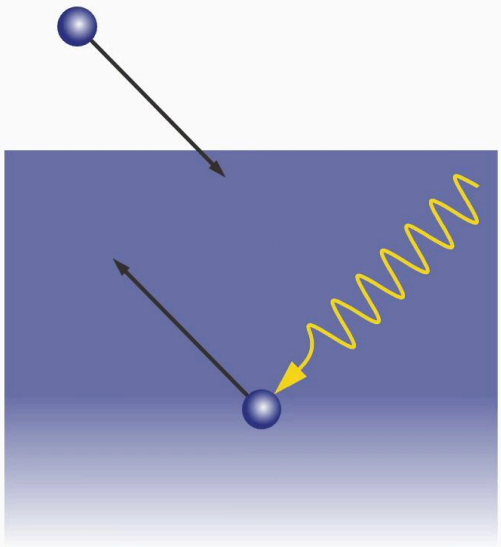
Welcome back to the last of this first section of week three, in which we have been concentrating on concepts in optical and X-ray spectroscopies that we will utilise in the remainder of both this week and in week four. We begin with a discussion of the inelastic mean free path of electrons in condensed matter and why the so-called universal curve is indeed universal. We then proceed to consider different types of angular momentum of electrons and spin-orbit coupling. We finished this section with a brief description of s and p polarised radiation.

Notes

Summary

0m 05s

The inelastic mean free path



- IMFP indicates how far on average an electron travels in condensed matter before losing energy
  - Follows Lambert-Beer law:

$$I = I_0\, e^{-z/\lambda_{\mathrm{IMFP}}}$$

- Primary mechanisms for energy loss
  - Plasmon excitation dominates between $\mathcal{E}_e$ = 20 and 1000 eV
  - Also electron-hole pair formation and vibrational (phonon) excitation
- Depends strongly on $\mathcal{E}_e$
- Only weak dependence on material the electron travels through

The inelastic mean free path describes how far on average an electron will travel through condensed matter before losing energy through inelastic scattering of one sort or another, whether that be from an external origin or via production of a photo electron within the sample. This is of course, a stochastic process and follows the Lambert Beer law of exponential decay, namely that the intensity of a mono energetic beam of electrons with an initial intensity intensity I_0 will on average have been attenuated by 1 over e or approximately to 37% of I_0 after travelling a distance equal to the inelastic mean free path for that energy. The primary mechanism for energy loss between approximately 20 and 1000 electron volts electron kinetic energy is plasmon excitation that is the excitation of concerted, coherent oscillations of an ensemble of electrons. Above this, electron hole formation and phonon excitation begin to dominate. Although the inelastic mean free path depends strongly on the electrons kinetic energy its dependent on the type of matter the electrons are travelling through is fairly weak.

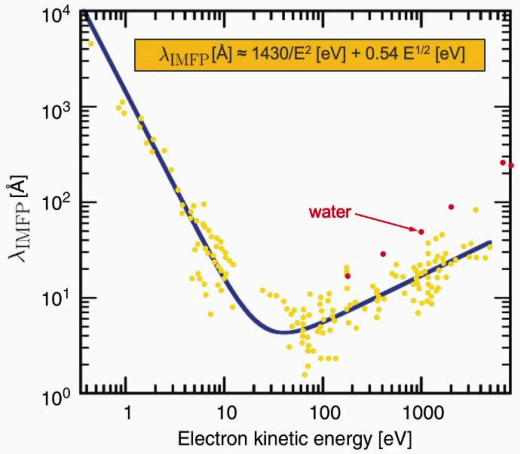
Notes

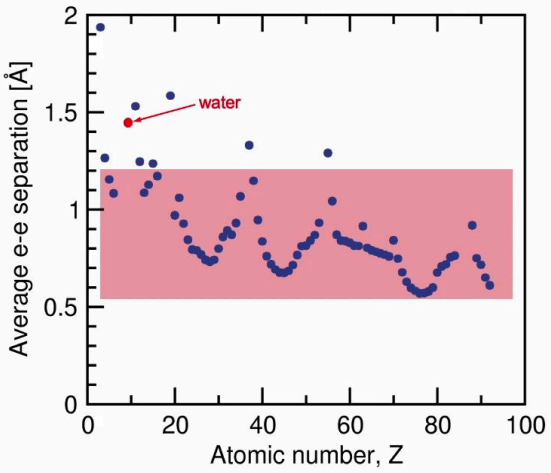
Summary

0m 41s

The universal curve

- Only weak dependence on material the electron travels through… why??
  - Plasmon excitation proportional to average distance between electrons
  - ⇒ proportional to $(1/\rho_e)^{1/3}$, (ρ_e = the electron density in condensed matter





The universal curve is shown bottom left, collated from experimentally determined data points, gleaned from many different materials. The inelastic mean free path can be determined using the expression 1,430 divided by E squared in electronvolts plus 0.54 multiplied by E to the half also in electronvolts. Despite the fact that the data points originate from many different material types, their scatter is fairly modest. The question is why. The reason is that plasmon excitation is directly proportional to the average distance between electrons. On the right is a plot of the electron density as a function of Z, the atomic number, for those elements that are either solid or liquid at room temperature and pressure. The electron separation is thus proportional to the inverse cube root of the electron density shown here. I also highlight the separation for water. Not an element, but given Z is equal to 8 plus 1 plus 1 is equal to 10. One sees that for the large majority of data points, the scatter is less than around plus or minus 30%. On the logarithmic scale, normally used for the ordinate axis of the universal curve, this scatter is indeed modest.

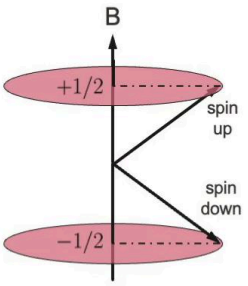
Notes

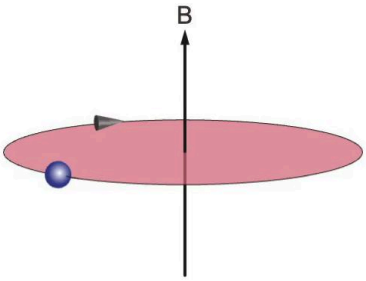
Summary

2m 06s

Electrons' angular momentum and spin

- Electrons are fermions with intrinsic half-integral spin
- Electron spin: intrinsic magnetic moment of an electron with quantum number $s = 1/2$
- Magnitude of spin = $[s(s+1)]^{1/2}\hbar = \sqrt{3/4}\,\hbar$
- Orientation of spin relative to a magnetic field $m_s = \pm 1/2$
  - "Spin up": $m_s = +1/2$
  - "Spin down": $m_s = -1/2$
- Electrons with non-spherically symmetric wavefunctions (i.e., not s-orbitals, $l \geq 1$) have orbital angular momentum
  - Magnitude of angular momentum $L = \sqrt{l(l+1)}\,\hbar$
  - Associated orbital current and therefore magnetic moment
  - Magnetic moment $\mu = \dfrac{-e}{2m_e}L$





What momentum do electrons exhibit? Electrons are fermions defined as having half integer spin. In the case of electrons, this is given by the spin quantum number s is equal to a half. The magnitude of the spin is given by s multiplied by s plus 1 to the half multiplied by h bar, which is equal to root three quarters h bar. Fermions can't exhibit an identical set of quantum numbers. They follow Pauli's exclusion principle. The orientation of the spin vector relative to a magnetic field is either plus a half or minus a half, corresponding to spin up or spin down, respectively. Importantly for those electron orbitals with non spherically symmetric wavefunctions, in other words, for all wavefunctions except s orbitals, the electron will also have an orbital angular momentum given by the square root of l, l plus one, multiplied by h bar. This is associated with the classical orbital current and therefore produces a magnetic field with a magnetic momentum mu is equal to minus e L upon 2me.

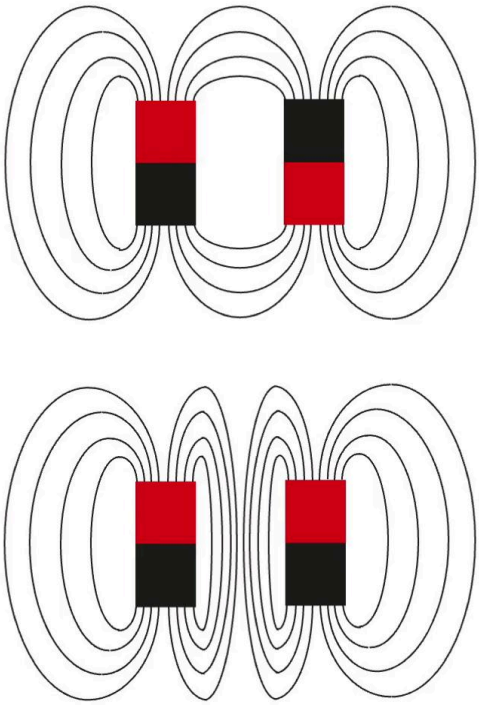
Notes

Summary

3m 32s

Spin-orbit coupling

- Classical approach (didactic, but not fully correct: electron spin has no classical analogue)
  - Electron orbits around nucleus
  - Consider from frame of reference of electron ⇒ nucleus seeming to orbit electron
  - Creation of B-field due to circulating charge ≡ current *i*
  - Does not apply for s-states which have no angular momentum (i.e. no orbit)
  - Consider also “intrinsic” magnetic moment of the electron: the **spin**
  - Like two bar magnets interacting, there is a favourable and less favourable configuration between the orbital- and spin-magnetic moments



Spin-orbit coupling is a fundamental interaction in quantum mechanics that describes the magnetic coupling between an electron spin s and its orbital motion l around the nucleus of an atom or molecule. Spin-orbit coupling results in the lifting of degeneracy or a splitting of atomic energy levels with the same primary quantum number n and orbital angular momentum quantum number l. This splitting is known as fine structure. This phenomenon has important implications for many areas of physics and chemistry. It's responsible for the magnetic properties of materials, the behaviour of atoms in strong magnetic fields, and importantly here, the spectroscopic properties of atoms and molecules. In addition to its fundamental importance, spin-orbit coupling is also of practical significance in areas such as spintronics where it can be used to control the flow of spin currents and quantum computing, where it can be used to implement spin qubits. The explanation given here is based on classical mechanics and is not really fully correct as quantum spin doesn't have a classical analogue. Nonetheless, it does provide important insights. The electrons classically orbit the nucleus.

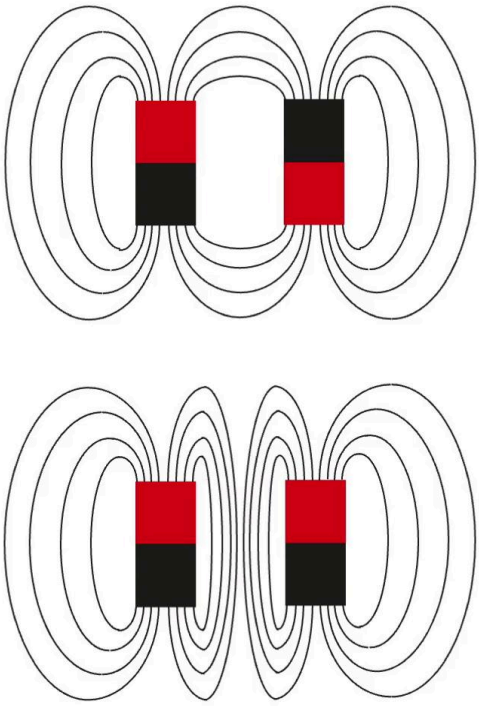
Notes

Summary

4m 47s

Spin-orbit coupling

- Classical approach (didactic, but not fully correct: electron spin has no classical analogue)
  - Electron orbits around nucleus
  - Consider from frame of reference of electron ⇒ nucleus seeming to orbit electron
  - Creation of B-field due to circulating charge ≡ current *i*
  - Does not apply for s-states which have no angular momentum (i.e. no orbit)
  - Consider also “intrinsic” magnetic moment of the electron: the **spin**
  - Like two bar magnets interacting, there is a favourable and less favourable configuration between the orbital- and spin-magnetic moments



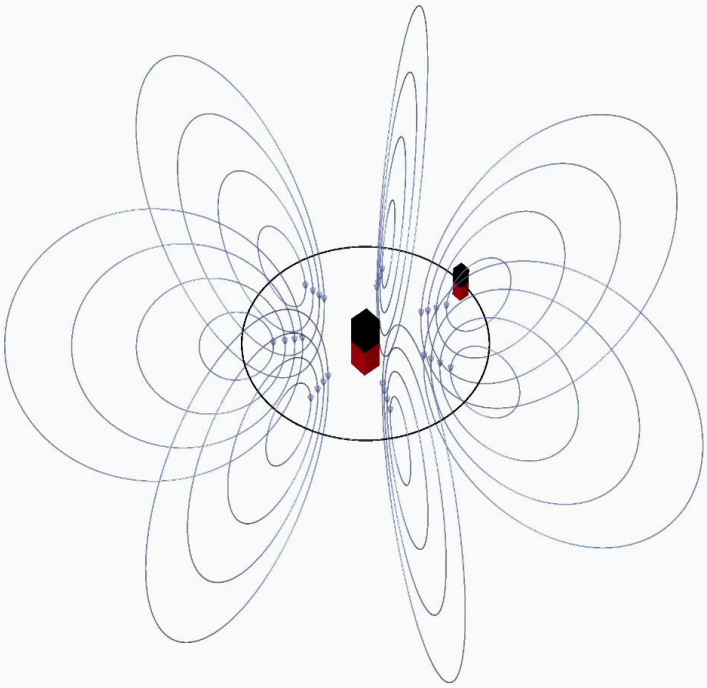
We now consider this situation from the perspective of the electron in a similar manner that we observe the sun orbit around the earth on a daily basis. A magnetic field is generated as a consequence of the circulating charge equivalent to a current i. Note that this does not apply to s orbitals which have no orbital angular momentum. But the electron does have its own intrinsic magnetic moment given by its spin. Just like two bar magnets, there is a favourable and a less favourable orientation between the spin and orbital angular momentum axes. Opposite antiparallel orientation is lower in energy than the parallel orientation, as there is a lower density of stray field lines in the former, thus costing less energy.

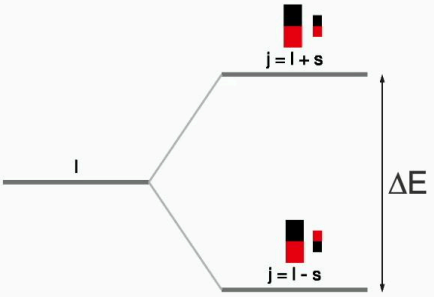
Notes

Summary

6m 07s

Spin-orbit coupling





This is shown in this cartoon. We begin by remembering that we swap the frame of reference between the electron and nucleus. Then let the electron orbit the nucleus. We have a magnet in the centre representing the magnetic field generated by the orbital current. Moreover, we can add a magnet associated with the electron spin which we show initially in the antiparallel orientation, which generates an eigenstate with a lower energy relative to the energy of the state, ignoring any spin-orbit coupling. The total angular momentum is j equals l minus s. If the electron spin is parallel to l, the total angular momentum is j is equal to l plus s, and the corresponding eigenstate is higher. The energy difference is Delta E. The sum of the energy shifts Delta E spin-orbit for each spin state.

Notes

Summary

6m 58s

Spin-orbit coupling

$$\Delta E_{\mathrm{SO}}\,[\mathrm{eV}] = 3.624\times10^{-4}\,Z^4\,\frac{j(j+1)-l(l+1)-s(s+1)}{n^3\;l(l+1/2)(l+1)}$$

$$(j = l \pm s)$$

- Shift relative to unperturbed state ignoring SO-interactions
- e.g. cobalt (Z = 27)
  - $2p_{3/2}$ and $2p_{1/2}$ fine structure levels
  - j = 3/2 (higher energy level) and j =1/2 (lower-energy level)
  - Predicts $\Delta E = \Delta E_{SO}(j = 3/2) - \Delta E_{SO}(j = 1/2) = 24$ eV
  - Reality: $\Delta E = 16$ eV
  - Model assumes hydrogenlike atom (only one electron)
    - Other electrons interact to further perturb energy

In the one electron approximation, that is where the electron with both spin and angular orbital momentum doesn't interact with any other electrons within the atom. The shift in energy of the state with spin-orbit coupling compared to that in which it is ignored, is given by the equation shown here. There are a number of physical constants highlighted here in red which we combine to obtain the expression shown here. Note that for a given prime quantum number n and element, the only variables are j, l and s. Moreover, for a given l and s, the only difference between the spin-orbit states is j which can assume the values of j is equal to l minus s or j is equal to l plus s. Let's consider the case of cobalt with an atomic number 27. The two p states have j equals 1 minus one half and j equals 1 plus a half. Our above equation predicts that an energy split of 24 electron volts should occur.

Notes

Summary

7m 57s

Spin-orbit coupling

$$\Delta E_{\mathrm{SO}}\,[\mathrm{eV}] = 3.624\times10^{-4}\,Z^4\,\frac{j(j+1)-l(l+1)-s(s+1)}{n^3\;l(l+1/2)(l+1)}$$

$$(j = l \pm s)$$

- Shift relative to unperturbed state ignoring SO-interactions
- e.g. cobalt (Z = 27)
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  - Reality: $\Delta E = 16$ eV
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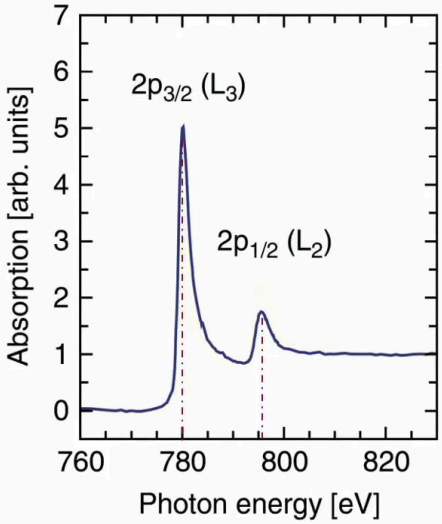


In reality, the energy difference is 16 electron volts which we can attribute to the simplification of the model that we assumed there is no interaction with any of the other electrons.

Notes

Summary

9m 11s

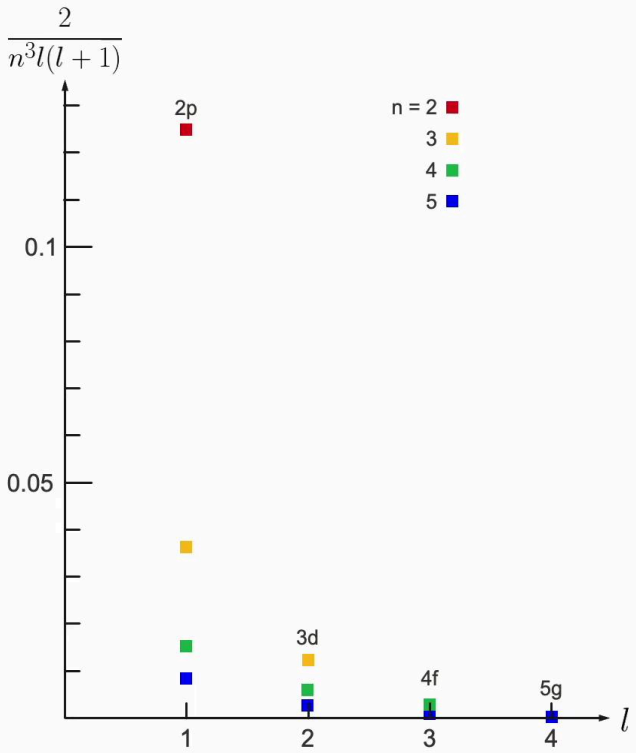
Spin-orbit coupling

- Assume s = ½
- For l ≥ 1

$$\Delta E = \Delta E_{SO}(j = l+1/2) - \Delta E_{SO}(j = l-1/2)$$
$$= \frac{3.624 \times 10^{-4} Z^4}{n^3} \frac{2}{l(l+1)}$$

- ΔE
  - Increases with Z^4
  - Decreases as $1/n^3$
  - Decreases as $1/l(l+1)$

} 2p splitting strongest!



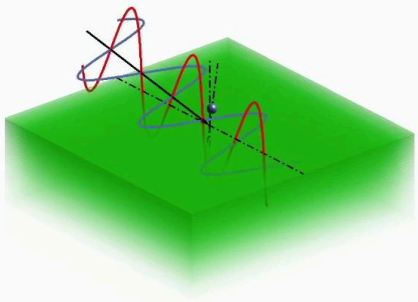
Our equation can be further simplified for a given l and s equals a half to Delta E is equal to 3.624 times 10 to the minus 4 Z to the 4th divided by n cubed and to 2 l l plus one. It should be thus apparent that the larger splitting is for the smallest n and l values that can exhibit orbital angular momentum. This is for l equals one the p state and n equals 2. We see on the right how the term 2 divided by n cubed l l plus 1 changes with l and n. As we will see in techniques such as photoelectron emission microscopy or PEEM, it is the 2p three halves and 2p half spin-orbit split states that are most commonly used to distinguish between and provide contrast for magnetic domains.

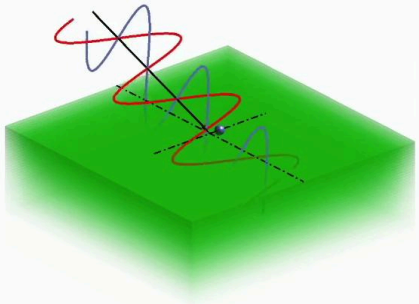
Notes

Summary

9m 24s

s- and p-polarizations





- Orientation of the electric field of the incident radiation w.r.t. a plane, normally a surface
- s-polarized light (from the German “senkrecht”, meaning perpendicular)
  - For a plane, can only approach true perpendicularity
- p-polarized light (from the German “parallel”, meaning, er, parallel)
  - Radiation can be fully p-polarized

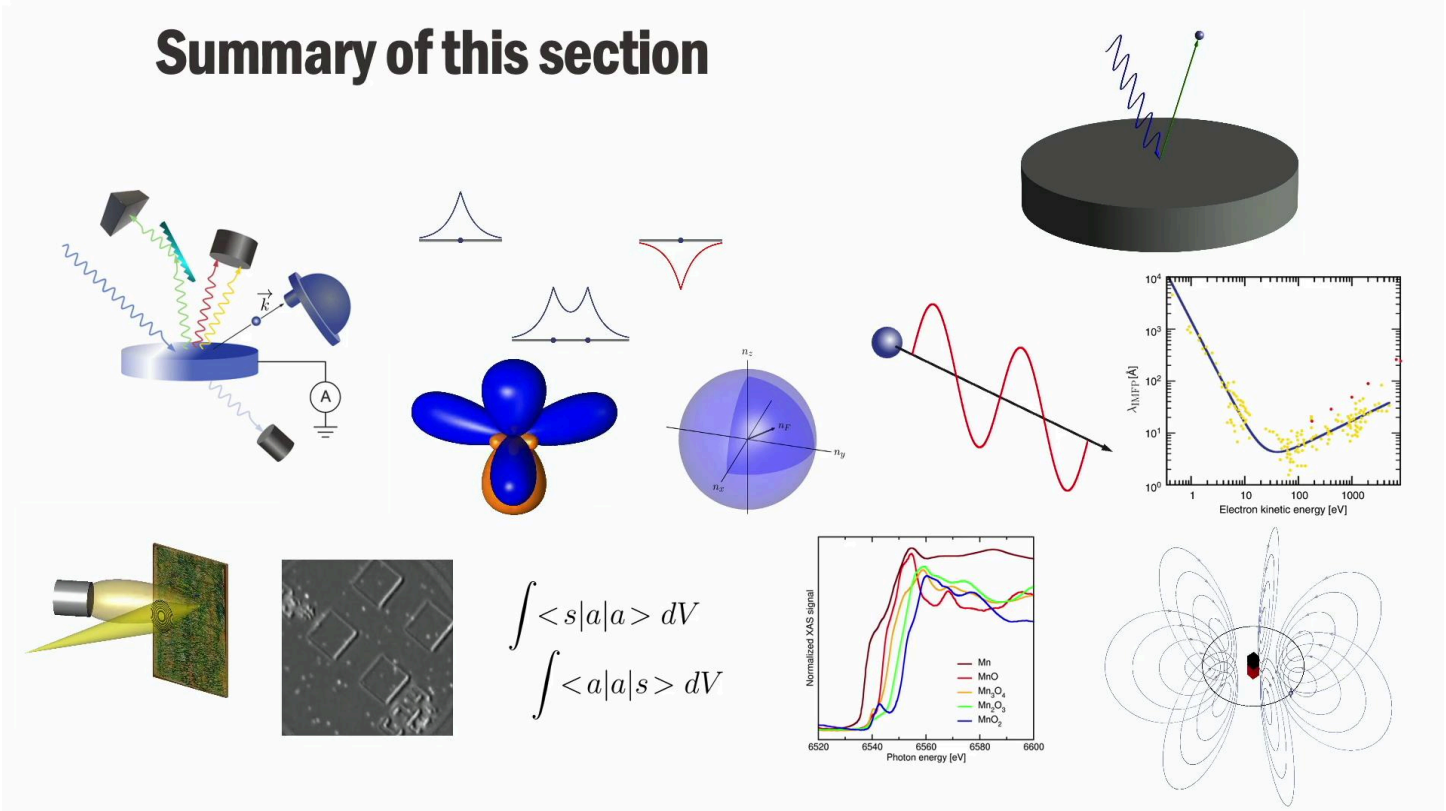
We finish this section by describing the two commonly used orientations of linearly polarised radiation relative to some geometric plane normally the surface of a sample. S polarised light from the German word senkrecht meaning perpendicular is one in which the electric field lines are nearly perpendicular to the surface. As there must be at least a grazing incidence angle, this is only approximately true. P-polarised light, is that in which the electric field lines are parallel to the sample surface.

Notes

Summary

10m 32s

Summary of this section



Summarising this section, we began with a brief overview of what probes and approaches are used in X-ray spectroscopies. Distinguishing between microspectroscopies and spectromicroscopies. We considered what will happen when electrons associated with two isolated atoms approach one another, to produce bonding and antibonding orbitals, and how atomic orbitals can combine to produce new geometries in hybridised orbitals. We then looked at band structure in condensed matter, which led us to the concept of the Fermi energy. The transition from one state to another via dipole perturbation was shown to be only allowed if the symmetry or parity of the orbitals were opposite. That is, even with odd and vice versa. We then looked at the photoelectric effect and the concept of the de Broglie wavelength in describing particles with mass as waves. Finally, we finished with the discussion of the inelastic mean free path and the universal curve, the impact of the local environment on the binding energy of electrons and the coupling between spin and orbital angular momentum of electrons.

Notes

Summary

11m 09s

In the next section...

In the next section, we cover absorption spectroscopies and the various techniques that are based on photoabsorption, including XANES, STXM, PEEM, and EXAFS.

Notes

Summary

12m 23s