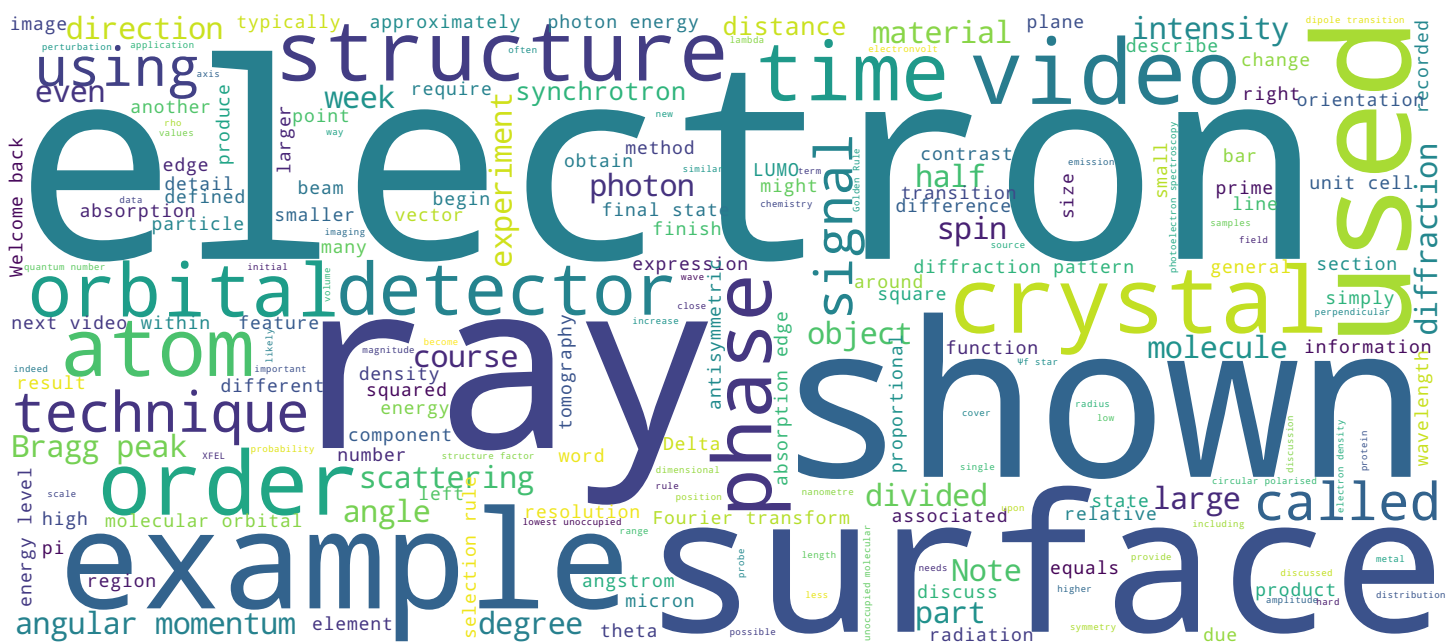


Synchrotrons and x-ray free-electron lasers

Techniques and applications

Prof. Philip Willmott



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Video



Contents and objectives of this video



- Dipole transitions
 - Parity
 - Photons and angular momentum
 - Dipole selection rules
 - HOMOs and LUMOs
- Fermi's golden rule

Welcome back to this course on synchrotrons and XFELs. In this video, we'll consider the role played by the symmetry, or so-called parity of electron orbitals, the conservation of momentum carried by photons, which leads us to dipole transition selection rules and the highest occupied molecular orbitals and lowest unoccupied molecular orbitals. We will finish with a brief overview of the famous Fermi's Golden Rule.

Notes

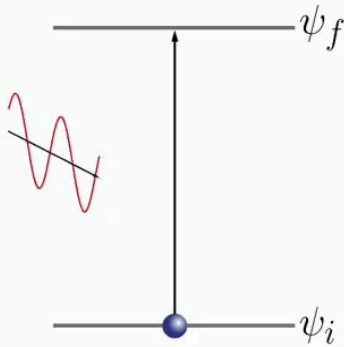
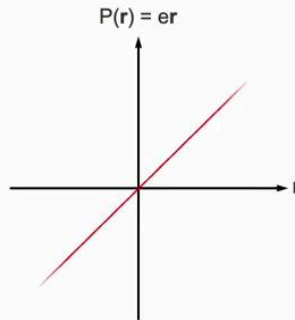
Summary



0m 05s

Electric-dipole transition between quantum states

- Absorption of a photon leads to promotion of an electron from an initial state ψ_i to an excited final state ψ_f
- Electric dipole operator = $e\mathbf{r}$
 - \mathbf{r} is a vector, therefore it is antisymmetric:



$$P_{if} = |\langle \psi_f | e\mathbf{r} | \psi_i \rangle|^2$$

$$P_{if} = \left| \int \psi_f^* e\mathbf{r} \psi_i dV \right|^2$$

- Let's now look at the integrand

$$\psi_f^* e\mathbf{r} \psi_i$$

We now consider the transition of an electron from one quantum state, Ψ_i to another higher energy state, Ψ_f , via the absorption of a photon with an energy, $h\nu$ that corresponds to the energy difference of those two states. We can mathematically describe the transition as being the square of the integral of the matrix element $\Psi_f^* e\mathbf{r} \Psi_i$, where the perturbation that induces the transition from Ψ_i to Ψ_f is the electric dipole operator, $e\mathbf{r}$, originating from this incident electric field of the radiation. Note that \mathbf{r} is a vector, and hence, $e\mathbf{r}$ is antisymmetric. Okay, let's now look more closely at the integrand $\Psi_f^* e\mathbf{r} \Psi_i$. Incidentally, Ψ_f^* means the complex conjugate of Ψ_f .

Notes

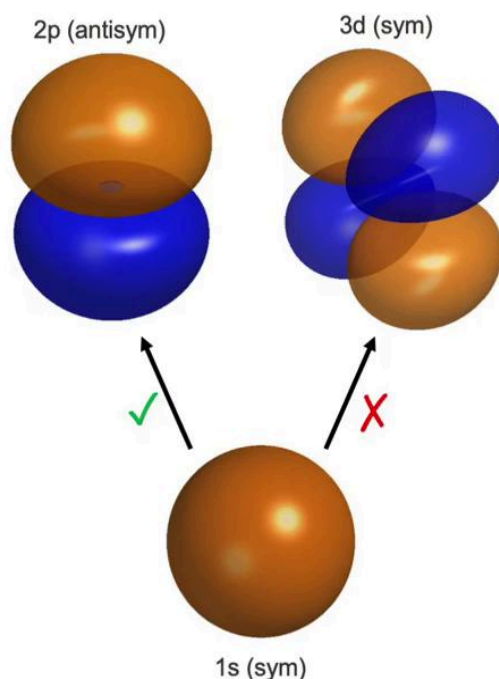
Summary



Symmetry matters

- N.B.
 - $a^*a = s$
 - $s^*s = s$
 - $s^*a = a$
- Integrating over all space
 - Integrand, $\psi_f^* e r \psi_i$, needs to be symmetric for the integral to be nonzero
 - If $\mu = e r$ is antisymmetric [i.e. $\mu(r) = -\mu(-r)$], then

$$\psi_f^* \psi_i$$
 therefore also needs to be antisymmetric
- N.B.
 - / even (s, d, g, ... orbitals) \Rightarrow wavefunction is symmetric
 - / odd (p, f, h, ... orbitals) \Rightarrow wavefunction is antisymmetric



The first thing we should note is that the product of two antisymmetric functions produces a symmetric function, as indeed is the product of two symmetric functions. However, the product of a symmetric with an antisymmetric function is also antisymmetric. If we integrate an antisymmetric function over all space, the result is zero. Therefore, the integrand needs to be symmetric for the integral to be non-zero. Hence, if the perturbation, $e r$, is antisymmetric, we require the product $\Psi_f^* \Psi_i$, also to be antisymmetric. Now, for orbitals with even l , such as the s, or the d, or the g orbitals, the wavefunction is symmetric. Conversely, wavefunctions with odd values for the orbital angular momentum, such as the p and f orbitals, are antisymmetric. From this, we can conclude that a dipole transition can only happen between wave functions of opposite symmetry, also called opposite parity. Symmetric wavefunctions are said to have even parity, antisymmetric ones odd.

Notes

Summary



Photons and angular momentum

- Photons are bosons which have intrinsic integer angular momentum $L = 1$ (in units of \hbar)
- The expectation value L_z defines a specific projection of L along the photon propagation direction k_z that depends on the polarization state of the photon
- RCP
 - Clockwise in direction of propagation
 - $L_z = -1$, antiparallel to propagation
- LCP
 - Anticlockwise in direction of propagation
 - $L_z = +1$, parallel to propagation
- Linearly polarized light
 - Linear combination of LCP and RCP
 - $L_z = 0$



RCP



LCP



LHP

Now let's consider photons and their angular momentum. Photons are bosons. Bosons have intrinsic integer angular momentum in contrast to Fermions, which have half integer angular momentum. Relativity dictates that for a particle moving at the speed of light, such as a photon, this angular momentum can have no component which is perpendicular to the direction of travel and must be exactly in the forwards or backwards direction. In the case of right circular polarised light, convention states that the momentum is anti-parallel to the direction of propagation, and for left circular light, it is parallel. Note that linearly polarised light is simply a linear combination of left circular polarised and right circular polarised radiation in equal measures, and hence, has a total of a zero angular momentum.

Notes

Summary



Selection rules for dipole transitions

- Change in electron spin quantum number $\Delta s = 0$
 - Spin is directional and therefore has odd parity: $s(r) = -s(-r)$
 - Integrand is $\langle s|s \rangle = \text{even}$
 - Spin “flips” ($\frac{1}{2} \rightarrow -\frac{1}{2}$, or $-\frac{1}{2} \rightarrow \frac{1}{2}$) forbidden
- Primary quantum number n
 - Any transition allowed
- Photon has intrinsic angular momentum $L = 1$
 - Absorption or emission must accommodate this in the change in electron orbital angular momentum quantum number l , Δl
 - $\Delta l = \pm 1$
 - e.g. $s \rightarrow p$, $d \rightarrow p$, ...
 - Odd \rightarrow even, or even \rightarrow odd
 - Only between “neighbouring” l -values)
- m_l = projection of l on z -axis: $\Delta m_l = 0, \pm 1$, but not $0 \rightarrow 0$

What selection rules are there for dipole transitions? First, the change in spin quantum number should equal zero. In other words, there should be no spin flip. The reason for this is that spin is directional and therefore has odd parity. The integrand ss must therefore be even, meaning only spin minus a half to a minus a half or plus a half to plus a half. For the primary quantum number n , there are no selection rules. All transitions are allowed. When a photon plunges into an atom and is absorbed, this angular momentum of plus or minus one needs to be accommodated by the system as part of its orbital angular momentum l . Hence, the dipole selection rule for l is Δl is equal to plus or minus one, as we already argued earlier in this video. The projection of l can be zero or plus or minus one, except for l equals zero to l equals zero, as this implies an s to s transition.

Notes

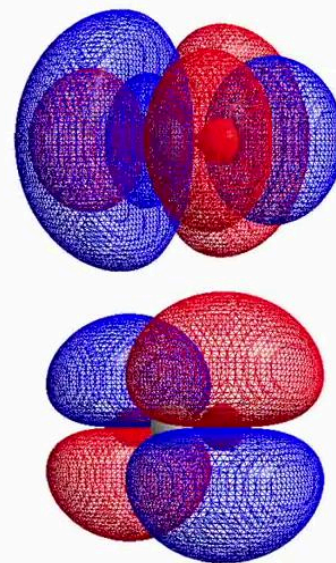
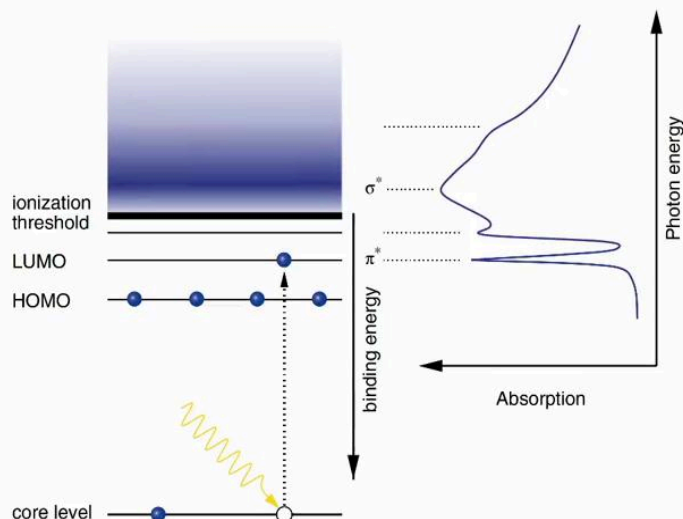
Summary



3m 46s

HOMOs and LUMOs

- Highest occupied molecular orbital
- Lowest unoccupied molecular orbital



HOMO (below) and LUMO (above) of CO₂

https://commons.wikimedia.org/wiki/File:CO2_LUMO.gif
https://commons.wikimedia.org/wiki/File:CO2_HOMO.gif

Highest occupied molecular orbitals and lowest unoccupied molecular orbitals are important concepts in chemistry that are used to describe the electronic structure of molecules. HOMO stands for the highest occupied molecular orbital, which is the energy level of the highest energy electrons in a molecule, while LUMO stands for lowest unoccupied molecular orbital, which is the energy level of the lowest unoccupied energy state in a molecule. HOMOs and LUMOs are useful in understanding the reactivity of molecules as chemical reactions often involve the transfer of electrons between molecules. Molecules with high-energy HOMOs are more likely to act as electron donors, while molecules with low-energy LUMOs are more likely to act as electron acceptors. This is because the energy difference between the HOMO of one molecule and the LUMO of another determines the thermodynamics of the electron transfer. In addition to their importance in understanding chemical reactivity, HOMOs and LUMOs are also used, for example, in the field of organic electronics to describe the energy levels of materials used in electronic devices such as solar cells and organic light-emitting diodes.

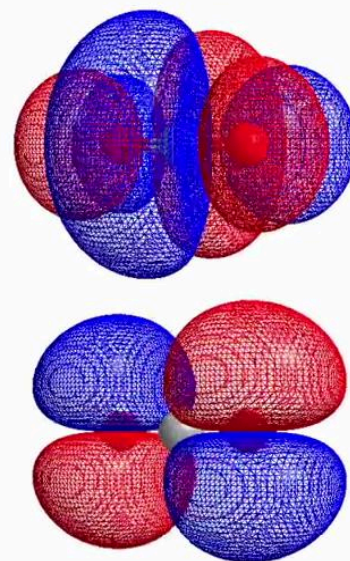
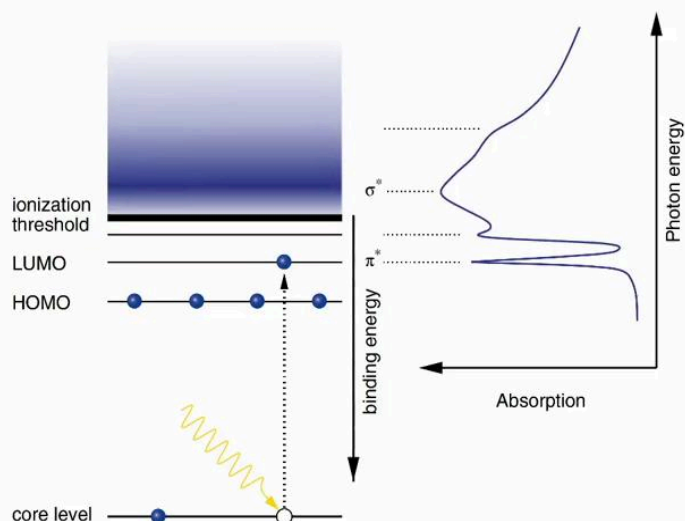
Notes

Summary



HOMOs and LUMOs

- Highest occupied molecular orbital
- Lowest unoccupied molecular orbital



HOMO (below) and LUMO (above) of CO₂

https://commons.wikimedia.org/wiki/File:CO2_LUMO.gif
https://commons.wikimedia.org/wiki/File:CO2_HOMO.gif

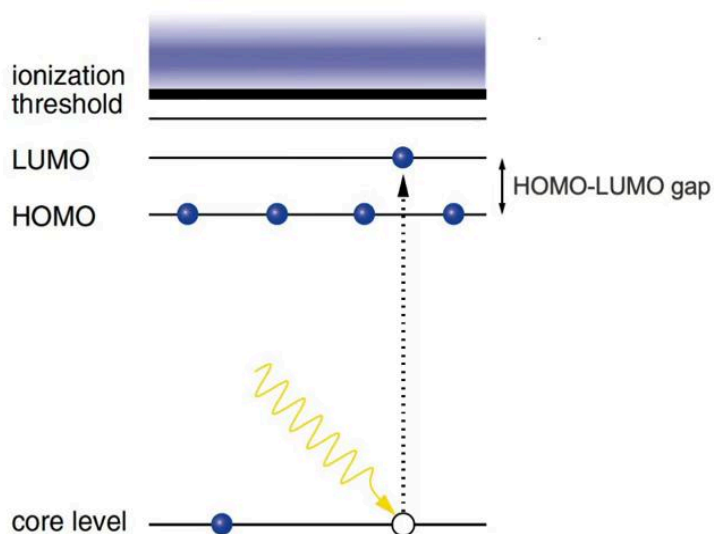
By controlling the energy levels of the HOMO and LUMO, it's possible to design materials with specific photo-electronic properties that are tailored for a particular application. On the right are shown the symmetric HOMO and antisymmetric LUMO of carbon dioxide.

Notes

Summary



HOMOs and LUMOs



- The larger the HOMO-LUMO gap, the more stable is the molecule
 - Typically a few eV
 - In conjugated systems (π -orbitals)
 - HOMO often π bonding orbital
 - LUMO often π^* antibonding orbital
- HOMO

LUMO
- The HOMO level is approximately equivalent to the maximum of the valence band in solid-state chemistry
 - The same analogy can be made between the LUMO level and the conduction band minimum

Just as reactions between high-energy HOMO and low-energy LUMO molecules are favoured, the larger is the HOMO-LUMO gap in a molecule, the more stable it is. In conjugated systems, that is, ones that contain delocalized π orbitals out of the atom-atom plane, such as in benzene, the HOMO is most often a bonding π orbital, while the LUMO is the corresponding π^* anti-bonding orbital. One can think of HOMOs and LUMOs as being equivalent in molecular systems to the valence and conduction bands, respectively, in solid state, condensed matter.

Notes

Summary



6m 35s

Fermi's Golden Rule

- System perturbed

- Perturbation operator H'

- e.g. dipole transition by photon absorption

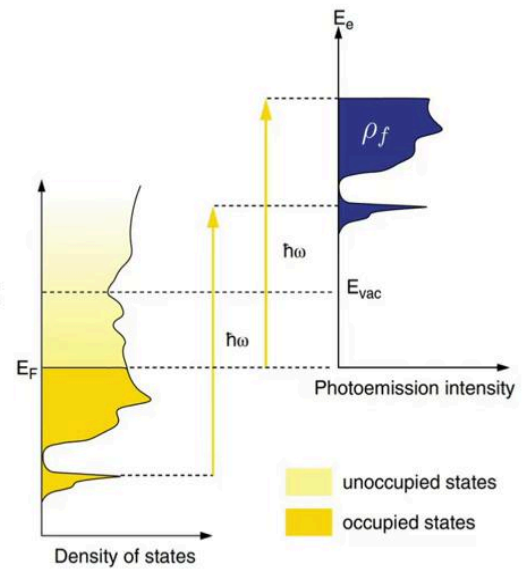
$$H' = e\mathbf{E}_0 \cdot \mathbf{r} e^{\pm i\mathbf{k} \cdot \mathbf{r}}$$

- From initial state ψ_i to continuum of states ψ_f

- e.g., free electrons from photoemission
 - e.g., molecule excited to higher electronic, vibrational ("rovibronic"), rotational state

- Transition rate:

$$P_{if} = \frac{2\pi}{\hbar} \underbrace{|\langle \psi_f | H' | \psi_i \rangle|^2}_{\text{Coupling strength}} \underbrace{\rho_f}_{\text{Density of final states}}$$



Fermi's Golden Rule is a fundamental concept in quantum mechanics that provides a way to calculate the probability of a quantum system undergoing a transition from one state to another due to an applied perturbation or interaction H' . The rule states that the transition rate or probability per unit time of a quantum system going from an initial state i to a final state f due to a weak perturbation is proportional to the square of the matrix element of the perturbation between the initial and final states, multiplied by the density of states of the final state. Mathematically, the golden rule can be expressed as $P_{if} = \frac{2\pi}{\hbar} |\langle \psi_f | H' | \psi_i \rangle|^2 \rho_f$, where P_{if} is the transition rate, \hbar is the reduced Planck constant, H' is the perturbation Hamiltonian, and i and f are the initial and final states, and ρ_f is the density of states of the final state. This rule is widely used in quantum mechanics to study a variety of phenomena, among which, and most importantly for this course, is the emission and absorption of photons.

Notes

Summary



In the next video...



In the next video, we will consider photoemission via the photoelectric effect, the work function, particle-wave duality, and a short recap of photoabsorption edges, first discussed in part one of this course.

Notes

Summary



8m 36s