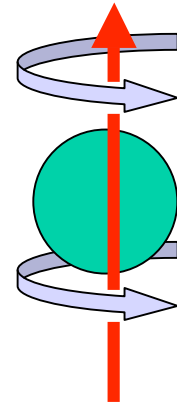


Spin of the electron

We learned that angular momentum is quantized in integer numbers l , such that the eigenvalues of L^2 are:

$$l(l + 1)\hbar^2$$

This is valid for the *orbital* angular momentum, associated in classical physics to the motion of the particle. In Quantum Mechanics there is another kind of angular momentum, which is “intrinsic” to a particle (it is there whether it moves or not) and has the same magnitude for a given kind of particle. It is as though the particle were “spinning”, that’s why this non-classical property is called “SPIN”



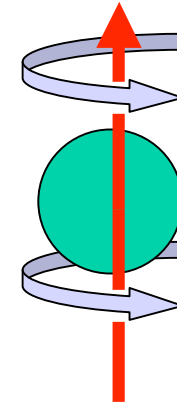
Spin of the electron

Spin can not only take integer, but also *half-integer* values, i.e.

$s=1/2, 1, 3/2, 2, 5/2, \dots$ and the possible eigenvalues of its square, S^2 are:

$$s(s + 1)\hbar^2$$

For electrons, $s=1/2$ (electrons are fermions)



We know that given l , then the possible eigenvalues of L_z are:

$$m\hbar, m = -l, -(l - 1), \dots, (l - 1), l$$

The same holds for spin, so for $s=1/2$ the eigenvalues of s_z are:

$$\sigma\hbar, \sigma = \pm\frac{1}{2}$$

Spin of the electron

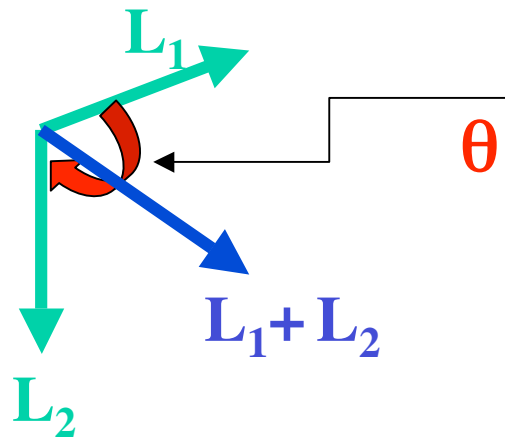
So, the degeneracy of the H atom levels is doubled, because each state can be occupied by an electron with spin up ($\sigma=+1/2$) or spin down ($\sigma=-1/2$).

Addition of angular momenta

If I have two momenta L_1 and L_2 (e.g, momenta of 2 different particles, angular momentum and spin of same particle, etc.) and they have magnitudes:

$$l_1(l_1 + 1)\hbar^2, l_2(l_2 + 1)\hbar^2$$

Classically, the sum of the two, $|L_1 + L_2|$ can take a continuous range of values depending on the angle θ between them.



Quantum Mechanics: the eigenvalues of $(L_1 + L_2)^2$ obtainable from l_1, l_2 are:

$$l_{sum}(l_{sum} + 1)\hbar^2$$

with the possible values of l_{sum} :

$$l_{sum} = |l_1 - l_2|, |l_1 - l_2 + 1|, \dots, |l_1 + l_2|$$

The spin-orbit interaction

Every energy level of the H atom is characterized by the quantum numbers n, l, m . The angular (L) and spin (S) angular momenta add up to form the total angular momentum $J=L+S$. For a level with a given l , this gives two values, $j=l+1/2$, $j=l-1/2$. For example, the 2p level has $l=1$, so there is a 2p with $j=3/2$, and a 2p with $j=1/2$, denoted by $2p_{1/2}$ and $2p_{3/2}$.

There is a relativistic effect known as **“spin-orbit” interaction**, which is proportional to:

$$H_{so} = \frac{e\hbar}{2mc} \vec{S} \cdot (\vec{\nabla}V \times \vec{p})$$

where V is the potential felt by the electron. For a central potential, $V(r)$,

$$\vec{\nabla}V(r) = \frac{dV}{dr} \frac{\vec{r}}{r}$$

So the above expression reduces to:

$$\hat{H}_{so} = \frac{e\hbar}{2mc} \frac{1}{r} \frac{dV}{dr} \vec{L} \cdot \vec{S}$$

The scalar product of L and S, in an eigenstate of J^2 , L^2 , S^2 can be written:

$$\frac{j(j+1) - l(l+1) - s(s+1)}{2}$$

The spin-orbit interaction shall therefore produce a splitting of the levels with same l,s but different j. This is not so relevant in hydrogen, but it is in other atoms: the more so the heavier they are, because the factor $(1/r)(dV/dr)$ is largest near the nucleus of a large-Z atom.

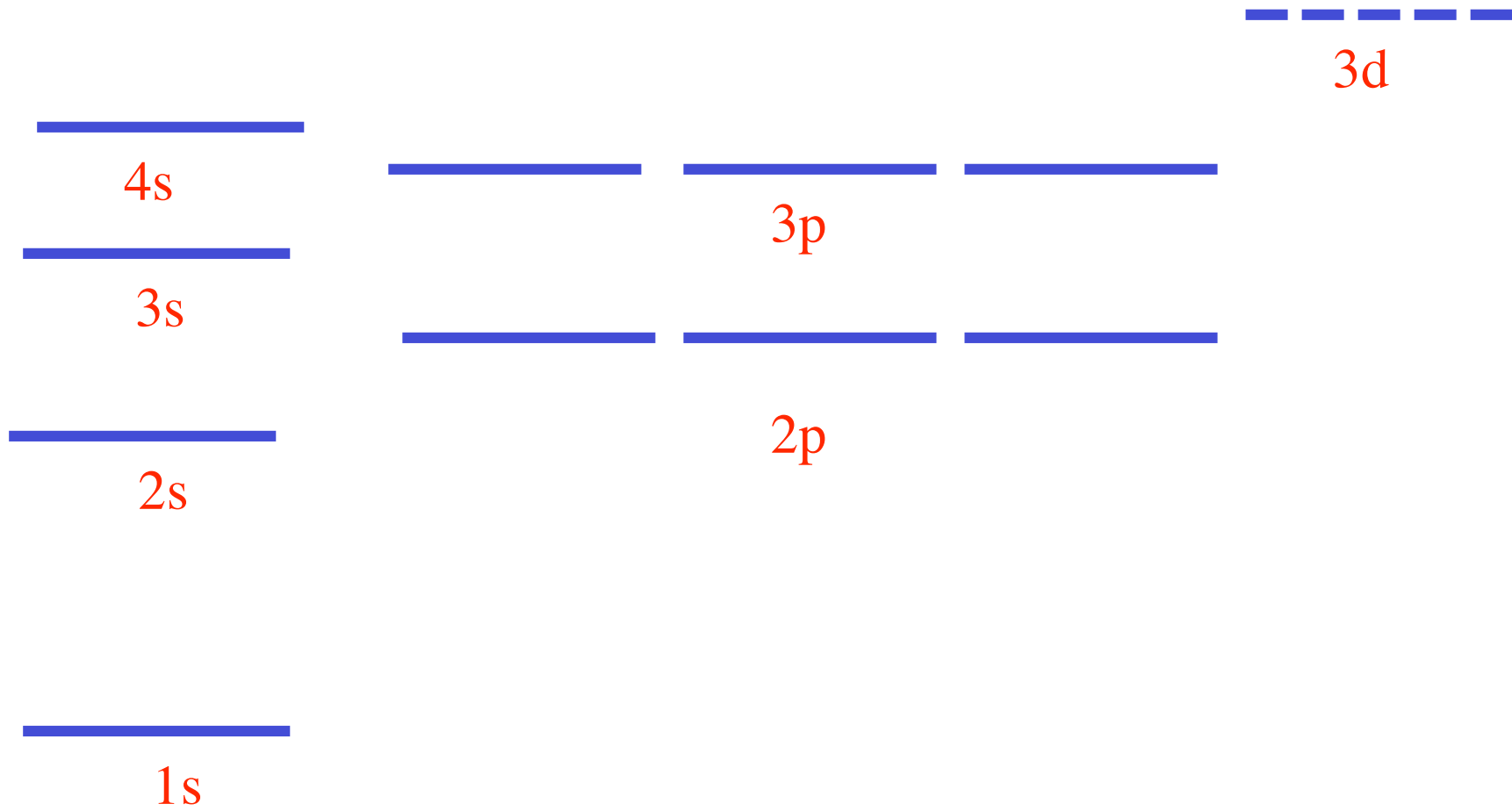
From Hydrogen to Many - Electron Atoms

Many-body problems (many means > 2) are essentially impossible to solve exactly in QM.

For atoms with $Z > 1$, a good approximate start is the central field approximation, which allows to describe, if not really calculate, the possible states.

According to this approach, every electron moves in a central potential, $V(r)$, which is however not Coulombic, because it is caused by the nucleus but also by the other electrons, which provide some “screening”.

We can classify the solutions in this potential like in the H atoms, but with a very important difference: levels with same n , but different l are no longer degenerate.



Pauli exclusion principle

Electrons are **fermions** (they have half-integer spin) and **only one electron** can occupy a fully-defined quantum state.

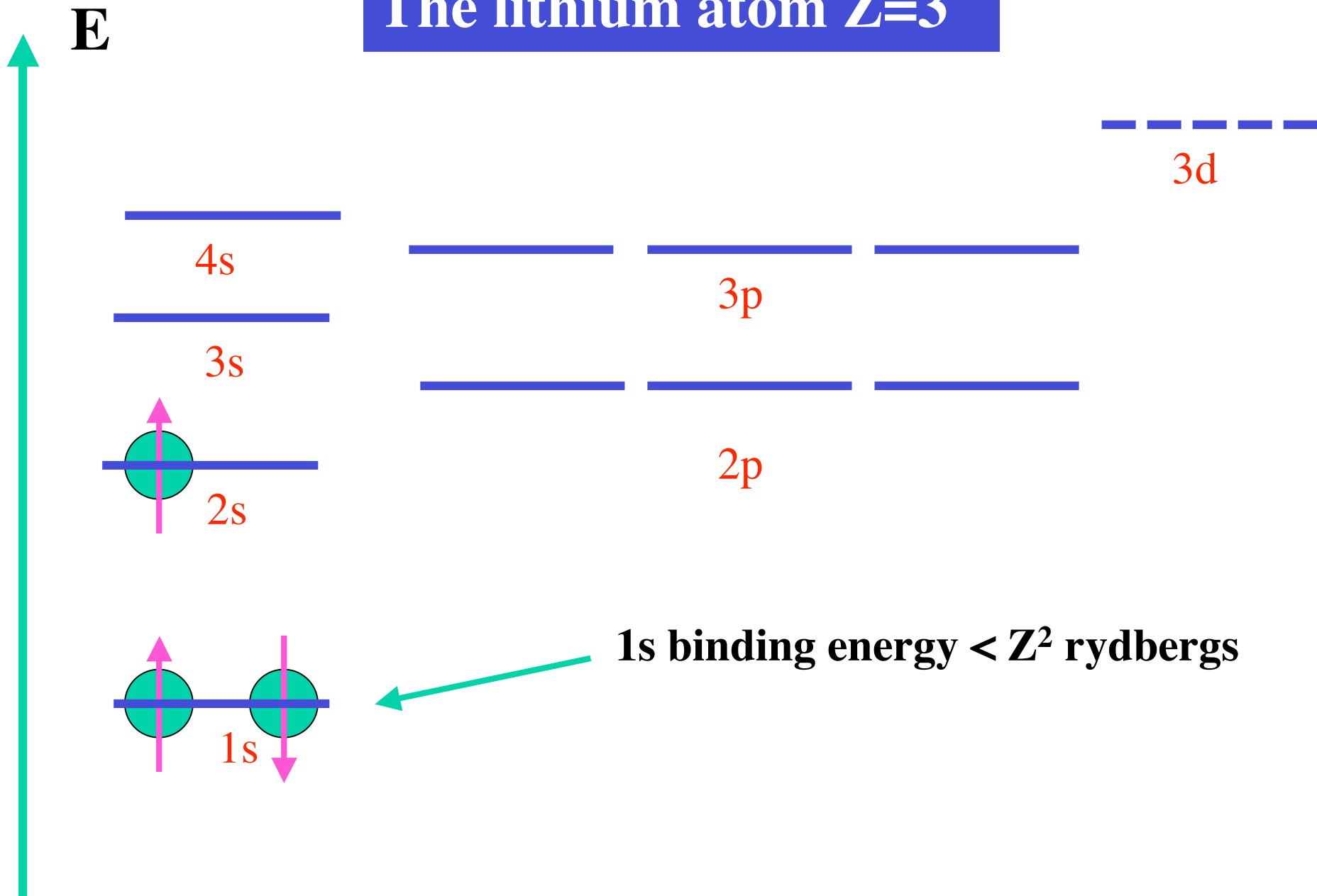
Therefore on each atomic level, we can put **at most one electron with spin up and one with spin down**

A more general formulation for the wavefunction of N electrons (fermions):

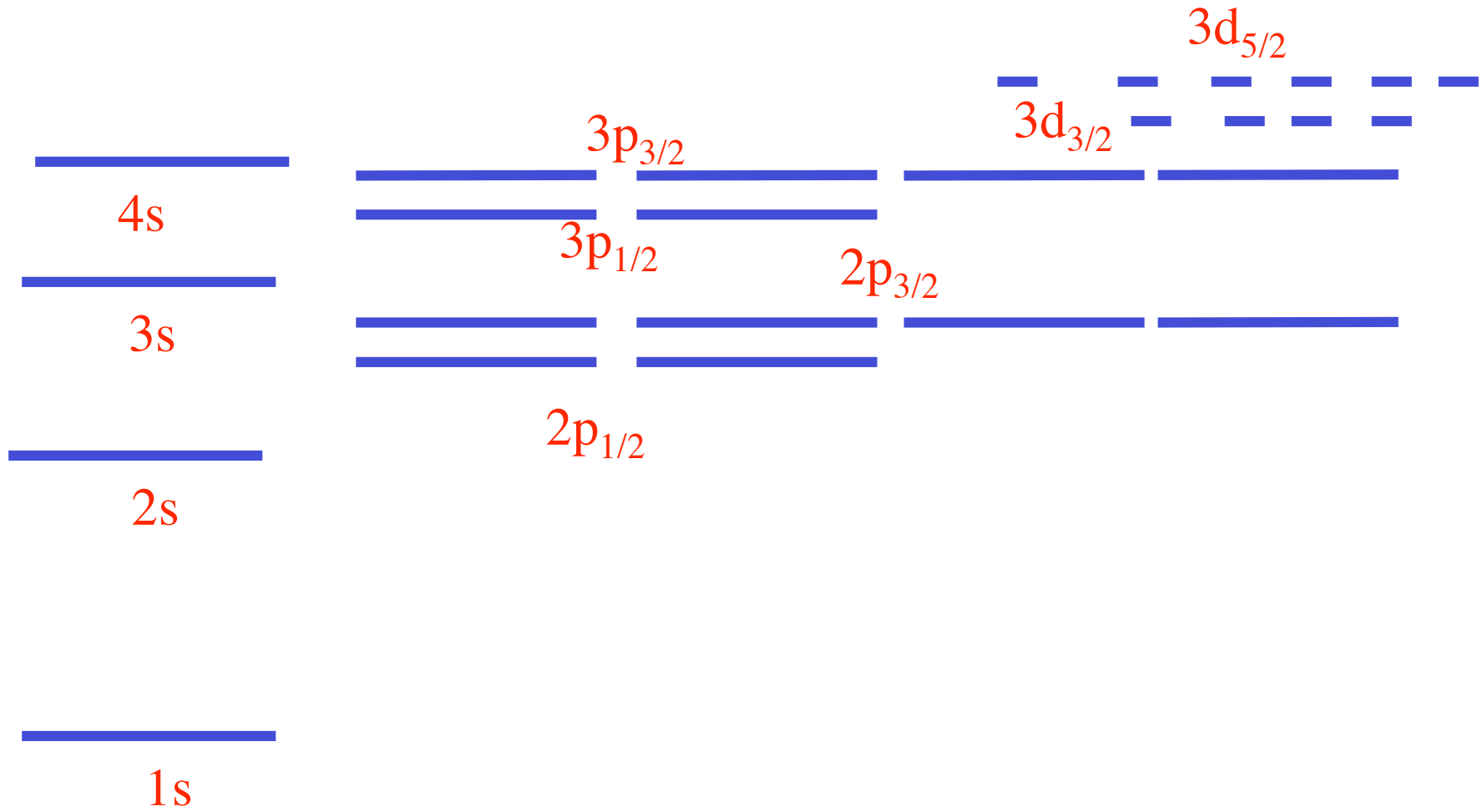
$$\Psi(\vec{r}_1, \dots, \vec{r}_i, \dots, \vec{r}_j, \dots, \vec{r}_N) = -\Psi(\vec{r}_1, \dots, \vec{r}_j, \dots, \vec{r}_i, \dots, \vec{r}_N)$$

Antisymmetry

The lithium atom $Z=3$



With spin-orbit splitting



For atoms with larger Z , there are degenerate one-electron levels that can be occupied in more than one way.

HUND'S RULES:

Start from one-electron levels without spin-orbit and start filling the lowest levels with two electrons (spin up and down).

When you get to the first “incomplete shell”:

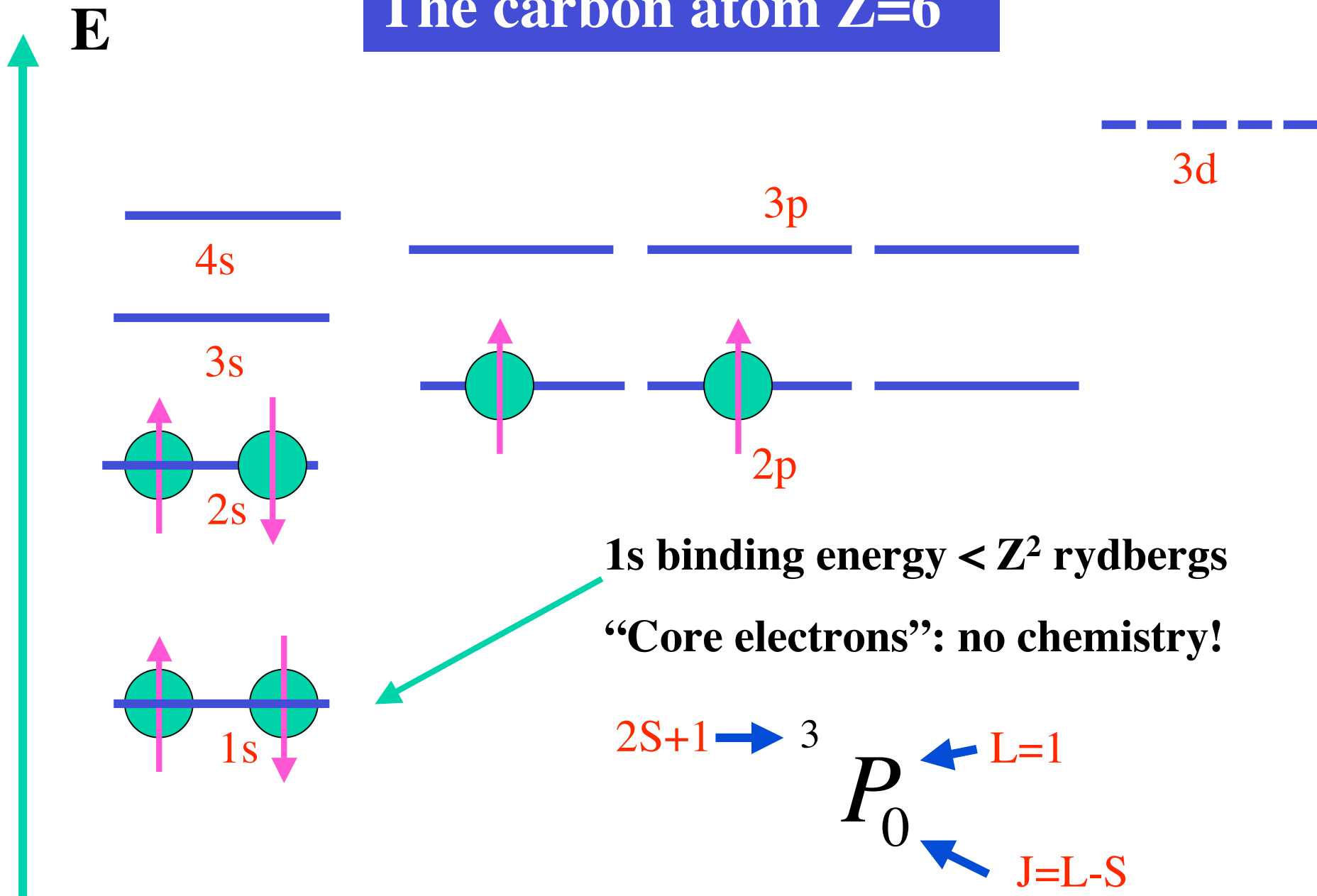
Rule # 1. *Maximise S*

Rule # 2. *Maximise L for that value of S*

Rule # 3. *Spin-orbit: $J = L - S$ for less than half filled shells*

$J = L + S$ for more than half filled shells

The carbon atom $Z=6$



Mn IV 104 Lines of Data Found (page 1 of 10)

Configuration Term J Level Leading percentages
(cm-1)

3d4	a 5D		
	0	0.0	5D_J
	1	99.0	
	2	286.8	
	3	552.2	
	4	885.8	
3d4	a 3P		
	0	20 654.2	3P_J
	1	21 278.8	
	2	22 324.7	
3d4	a 3H		
	4	21 280.7	${}^3H_j; (L = 5)$
	5	21 474.8	
	6	21 679.3	
3d4	a 3F		
	2	22 791.0	${}^3F_j; (L = 3)$
	3	22 862.3	
	4	22 959.1	

Interaction of Electromagnetic Radiation with Matter

1. Perturbation Theory

2. Description of the Interaction

3. Absorption and Emission of Photons

4. Scattering of Radiation

Perturbation Theory

Consider a physical system described by the Hamiltonian:

$$\hat{H} = \hat{H}_0 + \eta \hat{H}'$$

Assume that we know how to solve for the eigenvalues and the eigenfunctions of \hat{H}_0 . If η becomes sufficiently small, it is reasonable to look for an expression of the eigenvalues and eigenfunctions of \hat{H} as a power series of η . This approach is called “**perturbation theory**”

Perturbation Theory (cont.)

We are interested in time-dependent perturbations:

$$\hat{H} = \hat{H}_0 + \eta \hat{H}'(t)$$

and, in particular, in the case of periodic perturbations, when $\hat{H}'(t)$ takes the form:

$$\hat{H}'(t) = \hat{H}'(0)(e^{i\omega t} + e^{-i\omega t})$$

Examples: the electric field of an EM wave of frequency ω
the disturbance in the distance and in the interaction of atoms by an ultrasonic wave

Perturbation Theory (cont.)

The perturbation can induce *transitions* between stationary states of H_0 , which differ in energy by $\pm \hbar\omega$

Assume the system is initially in the ground state Ψ_0 . The number of transition per unit time dN/dt is given, to the lowest order of perturbation, by Fermi's "golden rule":

$$\frac{dN}{dt} = \frac{2\pi}{\hbar} \sum_f \left| \langle \Psi_0 | \hat{H}'(0) | \Psi_f \rangle \right|^2 \delta(E_f - E_0 \pm \hbar\omega)$$

Sum over possible final states

Matrix element of H' (η suppressed)

δ function of energy conservation. "+" for emission, "-" for absorption

STRATEGY

- 1. Write Hamiltonian describing the electrons in the system in presence of external EM fields**
- 2. Identify terms contributing to absorption, emission, scattering, etc.**
- 3 Develop perturbation theory for transition probabilities, etc.**

Consider a set of electrons moving in the field of the nuclei, $V_N(\mathbf{r}_i)$ and interacting with one another via a Coulomb potential $V_c(|\mathbf{r}_i - \mathbf{r}_j|)$, described by the Hamiltonian:

$$\hat{H} = \sum_{ji} \frac{\vec{p}_i^2}{2m} + V_N(\vec{r}_i) + V_c(|\vec{r}_i - \vec{r}_j|)$$

Simplify this many-body by somehow making an average potential for each electron:

$$\hat{H} = \sum_i \frac{\vec{p}_i^2}{2m} + V(\vec{r}_i)$$

Forget spin, spin-orbit for the moment

$$\mathbf{B} = \nabla \times \mathbf{A}$$

$$\mathbf{E} = -\nabla\Phi - (1/c)\frac{\partial\mathbf{A}}{\partial t},$$

Fields \mathbf{E} , \mathbf{B} from potentials A , F

where the vector $\nabla = \left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z}\right)$.

To describe electromagnetic waves, we can choose a gauge where the scalar potential $F=0$, and the vector potential is:

$$\vec{A}(\vec{r}, t) = \sum_{\vec{k}, \lambda} \left(\frac{he^2}{\Omega\omega_k}\right)^{1/2} [\vec{e}_\lambda a(\vec{k}, \lambda) e^{i(\vec{k} \cdot \vec{r} - \omega_k t)} + c.c.]$$

Normal.
Box Volume

Polarization
vector $\lambda = 1, 2$

$\omega_k = ck$

General recipe (from classical physics) to
introduce interaction of electrons with field $\mathbf{A}(\mathbf{r},t)$:
 $\Rightarrow \mathbf{p} - (e/c)\mathbf{A}$

$$\hat{H} = \sum_i \frac{1}{2m} (\vec{p}_i - \frac{e}{c} \vec{A}(\vec{r}_i, t))^2 + V(\vec{r}_i) =$$

$$\sum_i \frac{1}{2m} \vec{p}_i^2 + V(\vec{r}_i) + \frac{e^2}{2mc^2} A^2(\vec{r}_i, t) - \left(\frac{e}{mc}\right) \vec{A}(\vec{r}_i, t) \cdot \vec{p}_i$$

H_0
 H'_1
 H'_2

Pure electronic

Electron-radiation
interaction

“Golden Rule” for H'_2 : Absorption and Emission

Number of transitions per unit time:

$$\frac{dN}{dt} = \frac{2\pi}{\hbar} \sum_f \left| \langle \Psi_0 | \hat{H}'_2(0) | \Psi_f \rangle \right|^2 \delta(E_f - E_0 \pm \hbar\omega)$$

$$\hat{H}'_2(0) = \left(\frac{e}{mc} \right) \sum_i \vec{A}(\vec{r}_i) \cdot \vec{p}_i$$

$$\vec{A}(\vec{r}_i) \approx \text{Re} \sum_{\vec{k}, \lambda} a(\vec{k}, \lambda) \vec{e}_\lambda e^{i\vec{k} \cdot \vec{r}_i}$$

Take one particular \vec{k}, λ (monochr., collimated, polarized wave), and try to calculate matrix element

Multipolar Expansion of H'_2

The relevant matrix element is

$$\langle \Psi_0 | \hat{H}'_2(0) | \Psi_f \rangle \approx \left(\frac{e}{mc} \right) \langle \Psi_0 | a \vec{e}_\lambda \cdot \vec{p}_i e^{i\vec{k} \cdot \vec{r}_i} + c.c. | \Psi_f \rangle$$

In almost all of the interesting cases, one can expand:

$$e^{i\vec{k} \cdot \vec{r}_i} = 1 + i\vec{k} \cdot \vec{r}_i + \dots$$

And the expansion is converging rapidly, i.e. each term is much larger than the next.

Reason : $k=2\pi/\lambda$ (wavelength), and wavelength \gg atomic dimension (in the visible $\lambda \sim 400-700$ nm, atoms ~ 0.1 nm)

Multipolar Expansion of H'2 (cont)

More precisely consider the matrix element:

$$\begin{aligned} \langle \Psi_0 | a \vec{e}_\lambda \cdot \vec{p}_1 e^{i\vec{k} \cdot \vec{r}_1} | \Psi_f \rangle = \\ \int d^3 r_1 d^3 r_2 \dots d^3 r_N \Psi_0^*(\vec{r}_1 \vec{r}_2 \dots \vec{r}_N) a \vec{e}_\lambda \cdot \vec{p}_1 e^{i\vec{k} \cdot \vec{r}_1} \Psi_f(\vec{r}_1 \vec{r}_2 \dots \vec{r}_N) \approx \\ a \int d^3 r_1 \psi_0^*(\vec{r}_1) \vec{e}_\lambda \cdot \vec{p}_1 e^{i\vec{k} \cdot \vec{r}_1} \psi_v(\vec{r}_1) \end{aligned}$$

In the last step we took a one-electron approximation, in which one electron “jumps” from ψ_0 to ψ_v , and all others “look”.

The last integral receives a contribution from the region where ψ_0 and ψ_v are nonvanishing; The size of this region is that of the wavefunction of the most tightly bound level ψ_0 .

Multipolar Expansion of H'_2 (cont)

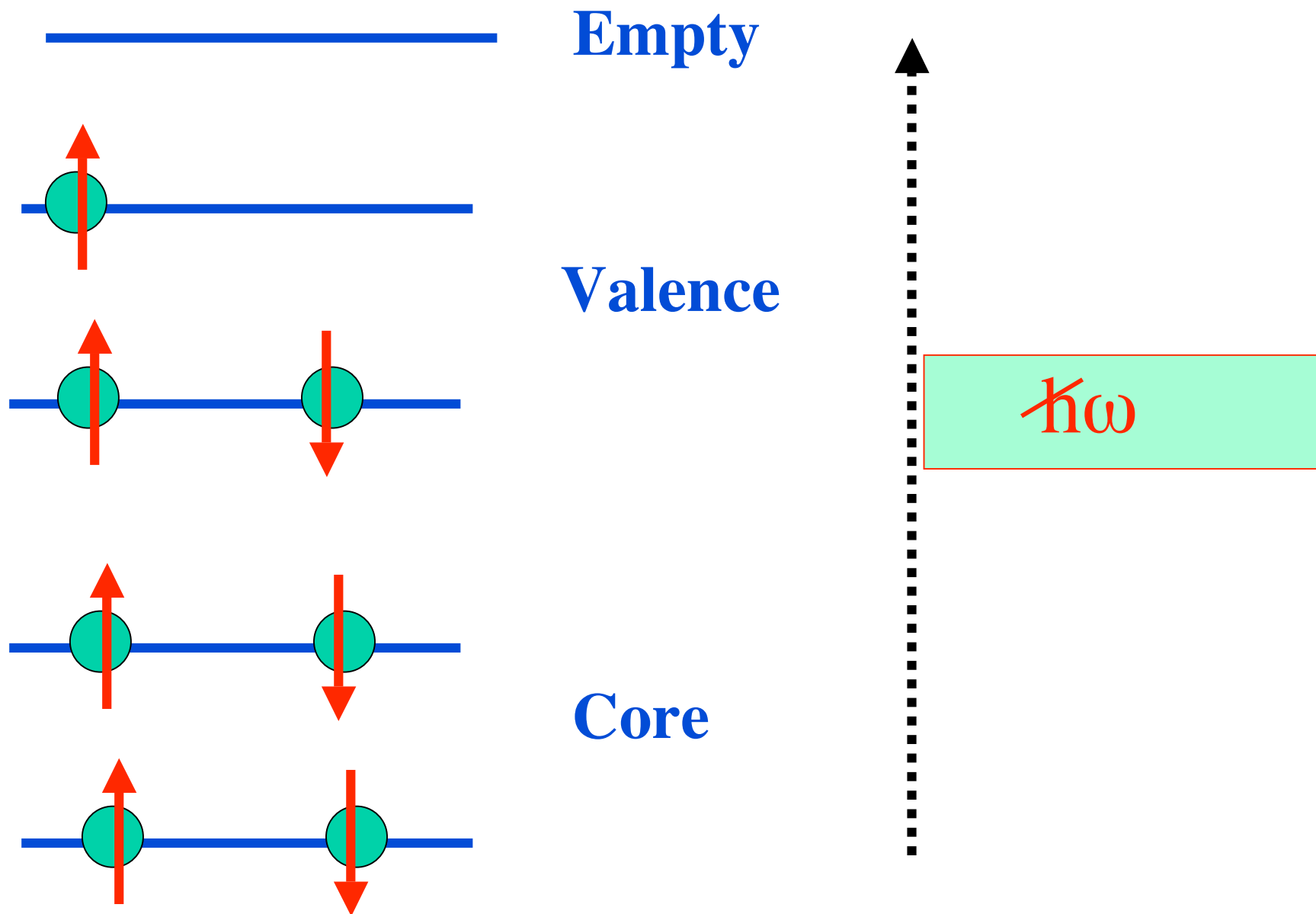
There is a relationship between the photon energy, which is of the same order as the binding energy E_B of ψ_0 , and the size of the wavefunction r_0 :

$$\hbar\omega \approx E_B \approx \frac{\hbar^2}{2mr_0^2}$$

and therefore:

$$kr_0 = \frac{\omega}{c}r_0 \approx \frac{\hbar}{2mcr_0} = \sqrt{\frac{1}{2mc^2} \frac{\hbar^2}{2mr_0^2}} \approx \sqrt{\frac{E_B}{2mc^2}}$$

Therefore since mc^2 , the rest energy of the electron, equals $5.11 \cdot 10^5$ eV, this means that even for x-ray transitions from core levels as deep as 50 keV, the exponential can be safely expanded.



Therefore, in calculating matrix elements for absorption or emission, it is a good approximation to replace the exponential with the first term, 1. This is called “the dipole approximation”. The remaining terms can be neglected, unless the first matrix element vanishes.

Under which circumstances the matrix element

$$\langle \Psi_0 | a \vec{e}_\lambda \cdot \vec{p}_1 | \Psi_f \rangle \approx a \int d^3 r_1 \psi_0^*(\vec{r}_1) \vec{e}_\lambda \cdot \vec{p}_1 e^{i\vec{k} \cdot \vec{r}_1} \psi_v(\vec{r}_1)$$

vanishes or not, is established by the “**dipole selection rules**”. The most important one says that it vanishes for the one-electron wavefunctions ψ_0 and ψ_v , if, for their l quantum numbers :

$$l_0 \neq l_v \pm 1$$

If on the other hand,

$$l_0 = l_v \pm 1$$

the matrix element can still vanish for some photon polarization and some values of the quantum number m_0 and m_v . For example, if $m_0 = m_v$, and the photon is linearly polarised along the z axis, then it does not vanish, while it does for polarization along x or y .

The proof of these selection rules is based on symmetry arguments (group theory)

Golden Rule for H'_1 : Elastic Scattering of X-rays

Let us now consider the other term of H' :

$$\hat{H}'_1 = \frac{e^2}{2mc^2} A^2(\vec{r}_i, t)$$

The square of the EM field implies that there are terms in which the \mathbf{k}, λ mode (with frequency $\omega = c|\mathbf{k}|$) is mixed with a different mode \mathbf{k}', λ' , with frequency ω' . The Fourier expansion of A^2 contains therefore terms with frequency $\psi = \omega + \omega'$, and terms with frequency $\omega - \omega'$. We want to explore the latter case when $\omega = \omega'$. In this case the δ -function that conserves energy forces to consider initial and final states with no difference in energy: this is elastic photon scattering

The “Golden Rule” expression is:

$$\frac{dN}{dt} = \frac{2\pi}{\hbar} \sum_f \left| \langle \Psi_0 | \hat{H}'_1(0) | \Psi_f \rangle \right|^2 \delta(E_f - E_0)$$

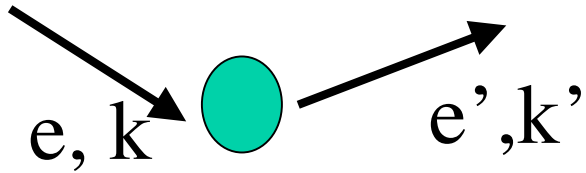
$$\hat{H}'_1(0) = \left(\frac{e^2}{mc^2} \right) \sum_i \vec{A}^2(\vec{r}_i) \cdot$$

$$\vec{A}^2(\vec{r}_i) \approx \sum_{\vec{k}, \lambda} a(\vec{k}, \lambda) \vec{e}_\lambda e^{i\vec{k} \cdot \vec{r}_i} \sum_{\vec{k}', \lambda'} a^*(\vec{k}', \lambda') \vec{e}_{\lambda'}^* e^{-i\vec{k}' \cdot \vec{r}_i} + \dots$$

where the missing terms at the end are those obtained by taking the complex conjugate of either or both factors.

Assume the ground state Ψ_0 is non-degenerate (the only possible Ψ_f is Ψ_0).

Elastic Scattering Processes



This photon present
in the initial state

$$|i\rangle = |0; \dots, (\mathbf{e}_\lambda, \mathbf{k}), \dots\rangle;$$

$$|f\rangle = |0; \dots, (\mathbf{e}'_{\lambda'}, \mathbf{k}'), \dots\rangle$$

Electronic
ground state

This photon present
in the final state

The important piece of the matrix element, for a given k, k' pair is:

$$\langle \Psi_0 | \hat{H}_1(0) | \Psi_0 \rangle \approx \frac{e^2}{mc^2} (e_\lambda \cdot e'^*_{\lambda'}) \sum_i \langle \Psi_0 | e^{i(\vec{k} - \vec{k}') \cdot \vec{r}_i} | \Psi_0 \rangle =$$

$$\frac{e^2}{mc^2} (e_\lambda \cdot e'^*_{\lambda'}) \sum_i \int |\Psi_0(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)|^2 e^{i(\vec{k} - \vec{k}') \cdot \vec{r}_i} d^3 r_1 d^3 r_2 \dots d^3 r_N$$

Using antisymmetry:

$$\langle \Psi_0 | \hat{H}_1(0) | \Psi_0 \rangle \approx$$

$$\frac{e^2}{mc^2} (e_\lambda \cdot e'^*_{\lambda'})^2 N \int |\Psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)|^2 e^{i(\vec{k} - \vec{k}') \cdot \vec{r}} d^3 r d^3 r_2 \dots d^3 r_N$$

Definition of electron density:

$$\rho(\vec{r}) = N \int |\Psi(\vec{r}, \vec{r}_2, \dots, \vec{r}_N)|^2 d^3\vec{r}_2 \dots d^3\vec{r}_N$$

Can rewrite matrix element in terms of *Fourier transform* of the electron density:

$$\langle \Psi_0 | \hat{H}_1(0) | \Psi_0 \rangle \approx \frac{e^2}{mc^2} (e_\lambda \cdot e_{\lambda'}^*) \tilde{\rho}(\vec{q})$$

where: $\vec{q} \equiv \vec{k} - \vec{k}'$

Thompson scattering

$$\frac{dN_{k, \lambda \rightarrow k', \lambda'}}{dt} \approx |(e_\lambda \cdot e_{\lambda'}^*)|^2 |\tilde{\rho}(\vec{q})|^2$$

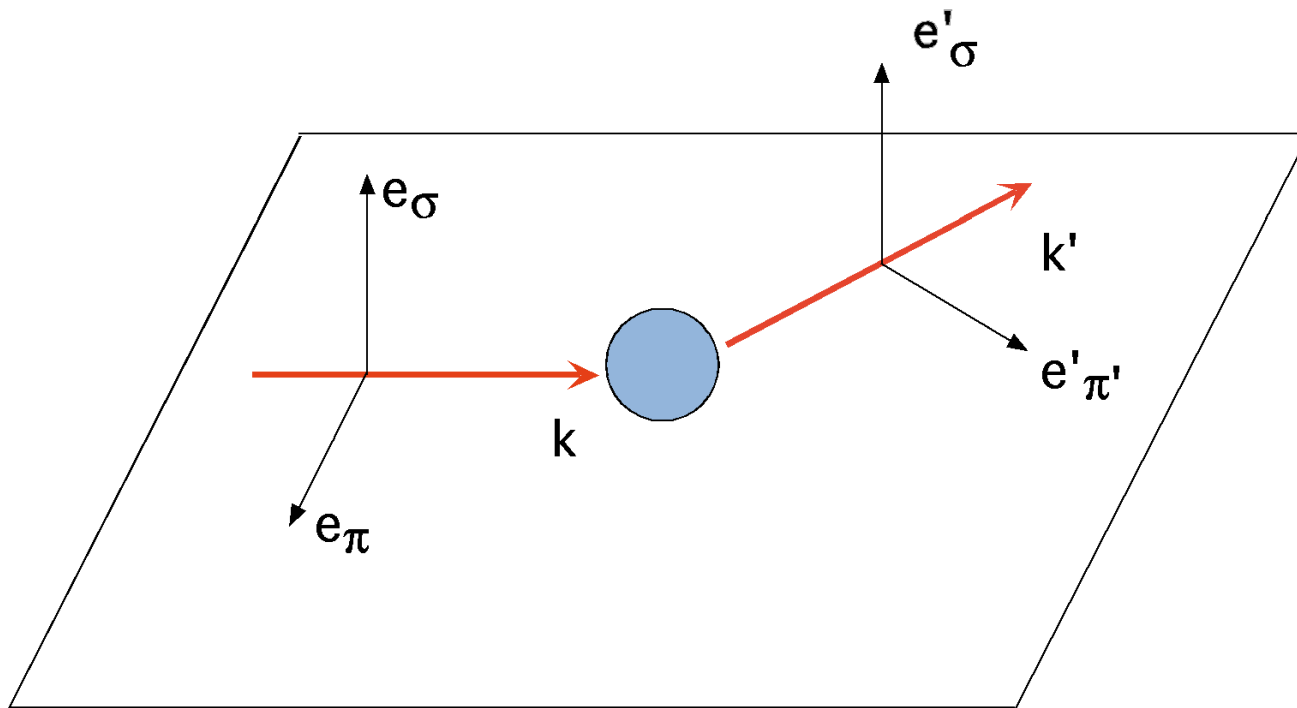


Fig. 1a

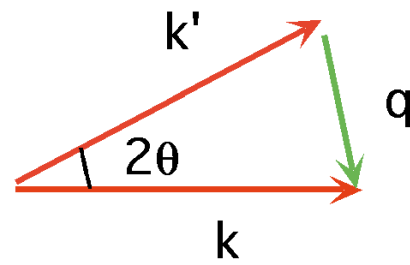


Fig. 1b