"Complementi di Fisica" Lectures 20-22

Livio Lanceri
Università di Trieste

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In these lectures

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    - hydrogen atom
    - angular momentum and spin
    - identical particles: bosons and fermions
    - Pauli exclusion principle for fermions
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    - Periodic table of the elements
    - "nearly-free electron gas" in a crystal: filling of available states
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  - Griffiths
  - Bernstein
  - Taylor-Zafiratos-Dubson

Some QM results

(3-d) Hydrogen atom
angular momentum, spin

Systems with many particles:
fermions and Pauli principle

(These subjects are discussed in more detail in the textbooks (Bernstein, Griffiths, …))

Hydrogen atom

- "simple": time-independent Schrödinger equation for the electron:
  - central "Coulomb" potential $V(r) = q^2/(4\pi\varepsilon_0 r)$
  - spherical coordinates (r, θ, ϕ)
  - Separation of variables (3)
  - 3 integer quantum numbers identify each solution
    $\psi_{n,l,m}(r, \theta, \phi) = R_{nl}(r)\, Y_l^m(\theta, \phi)$

$n = 1, 2, 3 \cdots$	. . . principal quantum number	Energy (= Bohr !)
$l = 0, 1, 2, \cdots n-1$	. . . azimuthal quantum number	Angular momentum
$m = -l$ to l	. . . magnetic orbital quantum number	

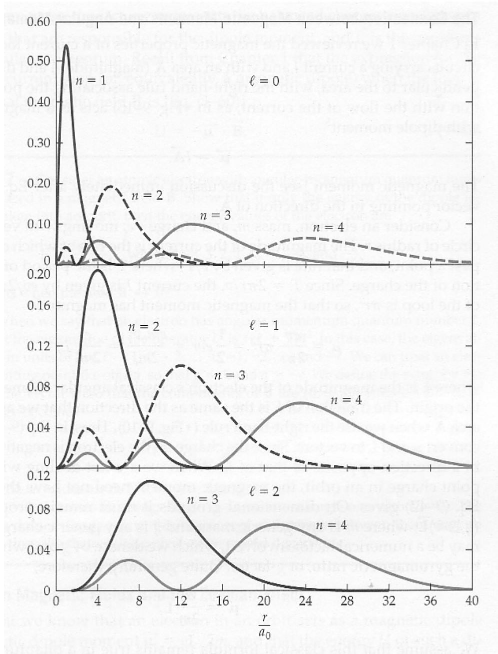
$$\hat{H}\psi_{nlm} = E_n\psi_{nlm} \qquad \hat{L}^2\psi_{nlm} = \hbar^2 l(l+1)\psi_{nlm} \qquad \hat{L}_z\psi_{nlm} = \hbar m\psi_{nlm}$$

Radial pdf

Radial probability distribution function

$$r^2\left[R_{nl}(r)\right]^2$$

Peaks occur at Bohr orbits radii

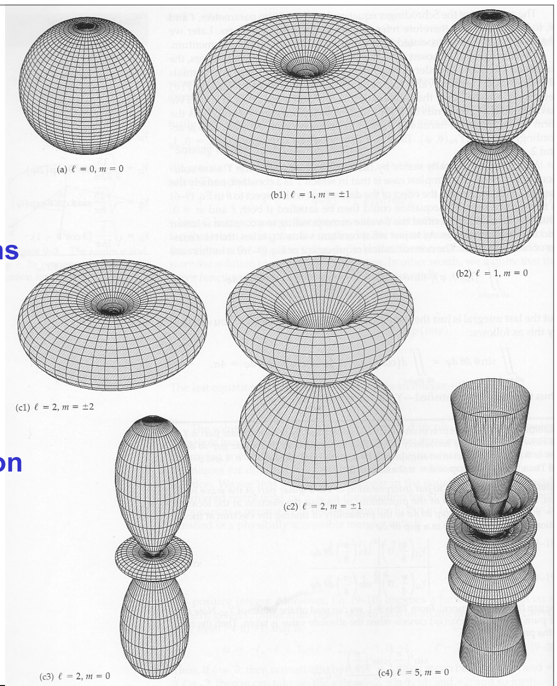


Spherical harmonics

Angular Probability distribution functions

$$\left|Y_{lm}\right|^2$$

Probability of finding the electron In the solid angle (sinθ dθ dφ)



Angular momentum

- **Also angular momentum is quantized !**
  - **One can only measure simultaneously the magnitude square and one component (the components don't commute !)**
  - **Cartesian and spherical coordinates:**

$$\vec{L} \equiv \vec{r} \times \vec{p} \qquad \hat{L}_x = y\hat{p}_z - z\hat{p}_y \quad \hat{L}_y = z\hat{p}_x - x\hat{p}_z \quad \hat{L}_z = x\hat{p}_y - y\hat{p}_x$$

$$\hat{L}^2 \equiv \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2 = -\hbar^2\left(\frac{\partial^2}{\partial\theta^2} + \cot\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)$$

$$\hat{L}_z = -i\hbar\frac{\partial}{\partial\phi}$$

  - **Eigenvalues and eigenfunctions: spherical harmonics are eigenfunctions of the angular momentum operators**

$$\hat{L}^2 Y_{lm}(\theta,\phi) = \hbar^2 l(l+1) Y_{lm}(\theta,\phi) \qquad l = 1, 2, 3, \ldots$$

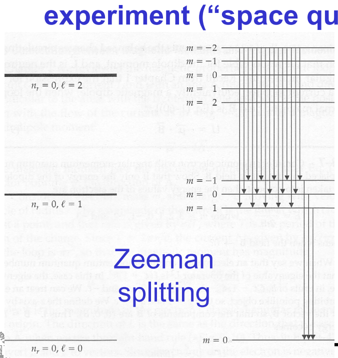
$$\hat{L}_z Y_{lm}(\theta,\phi) = \hbar m Y_{lm}(\theta,\phi) \qquad -l \le m \text{ integer} \le +l$$

Magnetic effects

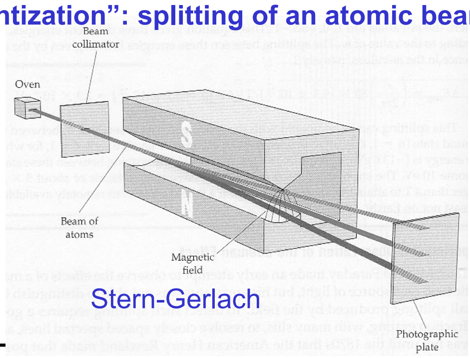
- **On dimensional grounds, for a charged particle with angular momentum we expect a magnetic moment and a contribution to potential energy when interacting with an external B field:**

$$\vec{\mu} = g\frac{q}{2m}\vec{L} \qquad U = -\vec{\mu}\cdot\vec{B}$$

"Zeeman effect" (splitting of degenerate levels) and Stern-Gerlach experiment ("space quantization": splitting of an atomic beam)



Zeeman splitting



Stern-Gerlach

Spin

- **Elementary particles carry also an "intrinsic" angular momentum ("spin" S) besides the "orbital" angular momentum (L)**
  - **The eigenstates are not the spherical harmonics: not functions of *θ*, *ϕ* at all!**
  - **The quantum numbers *s*, *m* can be half-integer**
  - **The magnitude *s* is specific and fixed for each elementary particle, and is called "spin"**
  - **Electrons have spin s = ½, with two possible eigenstates: "up" and "down"**

$$\hat{S}^2|sm\rangle = \hbar^2 s(s+1)|sm\rangle \qquad s = 0, \frac{1}{2}, 1, \frac{3}{2}, \ldots; \quad m = -s, -s+1, \ldots, s$$

$$\hat{S}_z|sm\rangle = \hbar m|sm\rangle$$

electrons: eigenstates and eigenvalues:

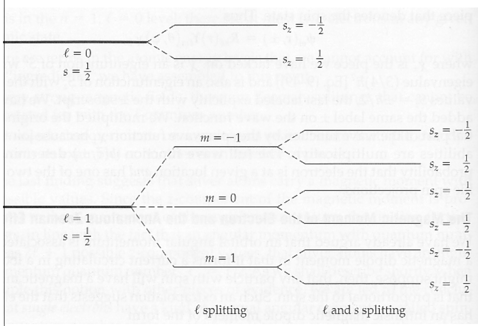
$$s = 1/2 \qquad \chi_+ = \left|\frac{1}{2}\frac{1}{2}\right\rangle = \begin{pmatrix}1\\0\end{pmatrix}, \quad \text{eigenvalue} \quad +\frac{\hbar}{2}$$

$$\chi_- = \left|\frac{1}{2}\left(-\frac{1}{2}\right)\right\rangle = \begin{pmatrix}0\\1\end{pmatrix}, \quad \text{eigenvalue} \quad -\frac{\hbar}{2}$$

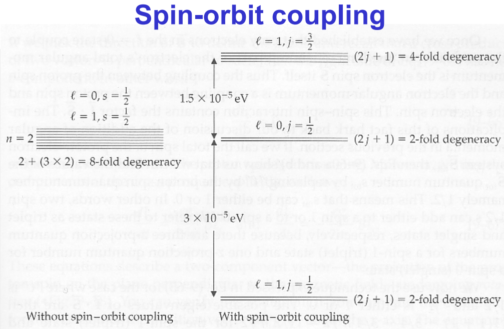
Spin: observable effects

- **For example:**
  - **"Anomalous Zeeman effect": further level splitting in strong B fields**
  - **"Fine Structure" level splitting due to "spin-orbit coupling"**

Anomalous Zeeman effect



Spin-orbit coupling



This is not the end…

- **Hydrogen has been a very interesting laboratory:**
  - **Orders of magnitude of different effects, treated as "perturbations", in terms of the a-dimensional "fine structure constant" α, expressing the strength of the electromagnetic coupling:**

$$\alpha \equiv \frac{e^2}{4\pi\varepsilon_0 \hbar c} \cong \frac{1}{137.036}$$

Table 6.1: Hierarchy of corrections to the Bohr energies of hydrogen.

Bohr energies:	of order	$\alpha^2 mc^2$	
Fine structure:	of order	$\alpha^4 mc^2$	← **Relativity, spin-orbit**
Lamb shift:	of order	$\alpha^5 mc^2$	← **Coulomb field quantization**
Hyperfine splitting:	of order	$(m/m_p)\alpha^4 mc^2$	← **Electron-proton magnetic moments**

Many-particle systems (just a hint…)

Identical particles

Bosons and fermions

Pauli Principle

Periodic table

Identical particles

- **Many-particle systems? Let's start with two:**
  - **Wave function, probability distribution, hamiltonian; S.equation**

$$\Psi(\vec{r}_1,\vec{r}_2,t) \qquad \left|\Psi(\vec{r}_1,\vec{r}_2,t)\right|^2 d\vec{r}_1 d\vec{r}_2$$

$$i\hbar\frac{\partial\Psi}{\partial t}=\hat{H}\Psi \qquad \hat{H}=-\frac{\hbar^2}{2m_1}\nabla_1^2-\frac{\hbar^2}{2m_2}\nabla_2^2+V(\vec{r}_1,\vec{r}_2,t)$$

  - **For time-independent potentials: time-indep. S.eq. and stationary states**

$$\Psi(\vec{r}_1,\vec{r}_2,t)=\psi(\vec{r}_1,\vec{r}_2)e^{-iEt/\hbar}$$

$$-\frac{\hbar^2}{2m_1}\nabla_1^2\psi-\frac{\hbar^2}{2m_2}\nabla_2^2\psi+V(\vec{r}_1,\vec{r}_2)\psi=E\psi$$

Bosons and fermions

- **For distinguishable particles (for instance, an electron and a positron):**
  - **particle 1 is in the (one-particle) state $\psi_a(r_1)$**
  - **particle 2 in state $\psi_b(r_2)$**

$$\psi(\vec{r}_1,\vec{r}_2,t)=\psi_a(\vec{r}_1)\psi_b(\vec{r}_2)$$

- **But: identical particles (for instance, two electrons) are truly indistinguishable in quantum mechanics:**
  - **There are two possible ways to construct the wave-function:**

+ "symmetric": bosons

$$\psi_\pm(\vec{r}_1,\vec{r}_2)=A\left[\psi_a(\vec{r}_1)\psi_b(\vec{r}_2)\pm\psi_b(\vec{r}_1)\psi_a(\vec{r}_2)\right]$$

- "anti-symmetric": fermions

  - **All particles with integer spin are bosons**
  - **All particles with half-integer spin are fermions**

Fermions and Pauli principle

- Connection between spin and "statistics" (or wave-function exchange symmetry)
  - can be proven in relativistic QM
  - must be taken as an axiom in non-relativistic QM
- Pauli exclusion principle:
  - Two fermions (anti-symmetric w.f.) cannot occupy the same state! Indeed:

$$\psi_a = \psi_b \quad \Rightarrow \quad \psi_-(\vec{r}_1,\vec{r}_2) = A\left[\psi_a(\vec{r}_1)\psi_a(\vec{r}_2) - \psi_a(\vec{r}_1)\psi_a(\vec{r}_2)\right] = 0$$

- It can be shown that:
  - The exchange operator P is a "compatible observable" commuting with H ⇒ one can find solutions that are either symmetric or antisymmetric
  - For identical particles, the wave function is required to be symmetric (for bosons) or anti-symmetric (for fermions)

Pauli Principle: consequences for electrons

- For electrons the total wave-function (including spin) must be anti-symmetric, and they cannot occupy the same state (two per level allowed, with opposite spin.
- The anti-symmetry requirement allows some wave-function configurations, prohibits others: equivalent to an "exchange force"
- Filling of available levels by electrons in a box (neglecting interactions among electrons!): Fermi level= highest energy level occupied at T = 0K (see exercises)
- "degeneracy pressure": even neglecting electric interactions between electrons, the Pauli principle implies that "the closest that two electrons can get to each other is roughly a half of the DeBroglie wavelength corresponding to the Fermi energy" (see exercises)

Pauli principle: Periodic table of elements

- **Multi-electron atoms are treated by approximate methods:**
  - **wave functions are modified (and called "orbitals"), but:**
  - **they are labeled by the same quantum numbers n, l, m, and:**
  - **Orbitals are filled by electrons following the Pauli exclusion principle: two electrons cannot have the same quantum numbers (state)**

Table A.3 Energy States and the Electronic Configuration in Elements 1 – 14. Atoms are assumed to be in the ground state.

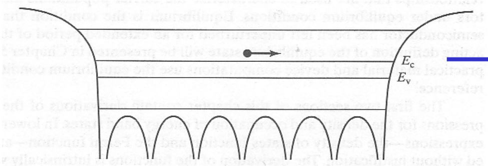
Quantum Numbers	n	1	1	2	2	2	2	2	2	2	2	3	3	3	3	3	3	3	3
	l	0	0	0	0	1	1	1	1	1	1	0	0	1	1	1	1	1	1
	m	0	0	0	0	-1	-1	0	0	1	1	0	0	-1	-1	0	0	1	1
	s	$\frac{1}{2}$	$-\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$
	State	1*s*	1*s*	2*s*	2*s*	2*p*	2*p*	2*p*	2*p*	2*p*	2*p*	3*s*	3*s*	3*p*	3*p*	3*p*	3*p*	3*p*	3*p*

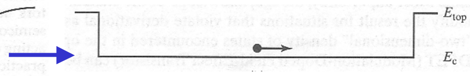
Periodic table of the elements

Atomic Number	*Element*	*Filled States* 1*s*	1*s*	2*s*	2*s*	2*p*	2*p*	2*p*	2*p*	2*p*	2*p*	3*s*	3*s*	3*p*	3*p*	*Electronic Configuration*
1	H	↑														$1s$
2	He	↑	↓													$1s^2$
3	Li	↑	↓	↑												$1s^22s$
4	Be	↑	↓	↑	↓											$1s^22s^2$
5	B	↑	↓	↑	↓	↑										$1s^22s^22p$
6	C	↑	↓	↑	↓	↑	↓									$1s^22s^22p^2$
7	N	↑	↓	↑	↓	↑	↓	↑								$1s^22s^22p^3$
8	O	↑	↓	↑	↓	↑	↓	↑	↓							$1s^22s^22p^4$
9	F	↑	↓	↑	↓	↑	↓	↑	↓	↑						$1s^22s^22p^5$
10	Ne	↑	↓	↑	↓	↑	↓	↑	↓	↑	↓					$1s^22s^22p^6$
11	Na	↑	↓	↑	↓	↑	↓	↑	↓	↑	↓	↑				$1s^22s^22p^63s$
12	Mg	↑	↓	↑	↓	↑	↓	↑	↓	↑	↓	↑	↓			$1s^22s^22p^63s^2$
13	Al	↑	↓	↑	↓	↑	↓	↑	↓	↑	↓	↑	↓	↑		$1s^22s^22p^63s^23p$
14	Si	↑	↓	↑	↓	↑	↓	↑	↓	↑	↓	↑	↓	↑	↓	$1s^22s^22p^63s^23p^2$

Electrons in a solid …

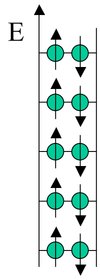
- Individual electrons





"Equivalent" problem: electrons in a box

- Interactions among electrons can be neglected to 1st approx.
  - "screening" by ions (L.Landau: "nearly-free electrons")



- Pauli exclusion principle
  - Obeyed by electrons filling up the available states
- Fermi-Dirac probability distribution
  - Occupation probability for the available states

Lecture 20-22 - summary

- Some results from Quantum Mechanics
  - hydrogen atom from Schrodinger equation
  - angular momentum and spin
  - identical particles: bosons and fermions
  - Pauli exclusion principle for fermions
- Some consequences
  - Periodic table of the elements
  - "nearly-free electron gas" in a crystal: filling of available states