

# AMO-1: Table of Contents

## Fall 2004, C. D. Lin

Textbook used: (BJ) B. H. Bransden and C. J. Joachain, " Physics of Atoms and Molecules", 2nd edition, 2003.

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## Chapter 1. The preliminary

### 1.1. Atomic units— $\hbar = m = e = 1$ (a.u.) (The units in the electron's world.)

Length=  $a_0$ = Bohr radius= $0.528 \times 10^{-8}$  cm

Velocity=  $v_0$ =electron velocity in 1<sup>st</sup> Bohr orbit=  $\alpha c=2.18 \times 10^8$  cm/s

Energy= twice of ionization potential of H=27.21 eV (called Hartree by chemists)

Time=  $a_0/v_0 = 2.42 \times 10^{-17}$  sec= 24.2 as (1fs= 41 a.u)

units of frequency= $v_0/a_0 = 4.13 \times 10^{16}$  sec<sup>-1</sup>

Electric field= $e/a_0^2 = 5.14 \times 10^9$  V/cm

#### Other units:

One atomic unit of magnetic field is defined for a Bohr magneton in a B field which has the energy of 13.6 eV. Or  $\mu_B B = 13.6 \text{ eV}$  where  $\mu_B = e\hbar / 2mc = 5.788 \times 10^{-5} \text{ eV / Tesla}$

Thus 1 a.u. of magnetic field =  $2.35 \times 10^5$  Tesla

Laser intensity=  $\frac{1}{2} \epsilon_0 c E^2 = 3.51 \times 10^{16} \text{ W/cm}^2$  for peak E field at 1 a.u.

**Exercise 1:** Confirm the atomic units of B and Laser intensity are indeed given by the values shown above.

**Exercise 2:** Calculate the electron's and the proton's kinetic energy if each of their velocity is given by one atomic unit.

For a complete list of fundamental physical constants and other useful data, see

<http://physics.nist.gov/cuu/Constants/index.html>

### 1.2. Energy conversion factors

1 eV = 8065.54  $\text{cm}^{-1}$

1 a.u = 27.211396 eV = 219 474.63 05  $\text{cm}^{-1}$  = 2 Ry

1 Ry = 13.6057 eV

1 degree kelvin= 0.0862 meV (energy units for cold atoms)  
= 0.695  $\text{cm}^{-1}$

1 Kcal/mol= 0.0434 eV = 43.4 meV (energy units used by chemists)

1 GHz  $\rightarrow$   $6.6 \times 10^{-7}$  eV (energy units by laser physicists)

(be careful here-- GHz is the frequency f, to get the energy you need the conversion  $\omega = 2\pi f$  to get it right. Thus  $2\pi \times 4.13 \times 10^{16} \text{ Hz} \rightarrow 27.21 \text{ eV}$ )

### 1.3 Frequently used constants

Speed of light in vacuum  $c = 2.997 924 580 \times 10^8$  m/s (exact-by definition)

Planck's constant,  $h = 6.6260755 \times 10^{-34}$  J-s =  $4.136 \times 10^{-15}$  eV-s

electron charge  $q = 1.60217733 \times 10^{-19}$  coulomb

Avogadro number=  $6.022 \times 10^{23}$  /mole

Boltzmann's constant  $k = 1.380658 \times 10^{-23}$  J/K =  $8.617 \times 10^{-5}$  eV/K

### 1.4. Short-hand notations.

$10^9$ =giga,  $10^{12}$ =tera;  $10^{15}$ =peta;  $10^{18}$ =exa;  $10^{21}$ =zetta;  $10^{24}$ =yocto

$10^{-9}$ =nano  $10^{-12}$ =pico;  $10^{-15}$ =femto;  $10^{-18}$ =atto;  $10^{-21}$ =zepto;  $10^{-24}$ =yotta

### 1.5. Notable wavelengths, frequencies and energies

photon wavelength to ionize H:  $911 \text{ \AA}$

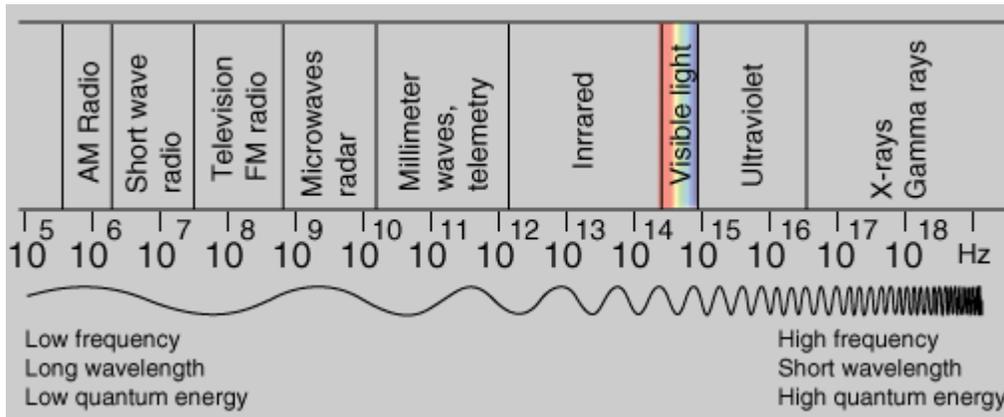
Lyman- $\alpha$  of H:  $1216 \text{ \AA} \rightarrow 10.2 \text{ eV}$

or  $1 \text{ nm} \rightarrow 1.24 \text{ keV}$

**Exercise 3:** Look for the energy separation of the hyperfine structure of the ground state of atomic hydrogen and show that its wavelength is  $21 \text{ cm}$ .

**Exercise 4:** confirm that  $1$  atomic unit in wavelength is  $45.6 \text{ nm}$ . For Ti-Sapphire laser of wavelength  $800 \text{ nm}$ , calculate its mean photon energy in eV's, its wavelength and frequency in atomic units, its period in fs and its frequency in Hertz.

### 1.6. The Electromagnetic Spectrum



## Chapter 2. Quick Summary of BJ- chapter1

You need to know:

- **Black-body radiation:** Planck distribution eq. (1.28), (1.31)
- **Compton effect:** an increase of x-ray wavelength after scattered off an atom  
The shift depends on the scattered angle of the x-ray, see (1.54)  
It is due to the scattering of x-ray photon by the "free" outer electrons  
Scattering by the inner electron is essentially "elastic"
- **Bohr atom:** Rydberg formula, Lyman series, Balmer series, Paschen series  
Need to know the basic assumptions of the classical Bohr model
- **de Broglie's relation between momentum and wavelength**  
All "particles" have wave nature  $\rightarrow$  diffraction effect  
**Diffraction**  $\rightarrow$  wavelength about the size of the slit  
enhanced by periodic structure-- as from a crystal lattice

#### Recent progress:

1. "double-slit experiment" for single electron diffraction, see BJ p.53
2. electrons diffracted by light: Kapitza-Dirac effect.  
Use two counter propagating lasers to create standing waves which can act like grating, see <http://physicsweb.org/article/news/5/9/5/1>
3. Diffraction by  $C_{60}$  (1999): see <http://physicsweb.org/article/news/3/10/12/1>
4. Diffraction has been used to identify the existence of  $He_2$  dimer.

**Exercise 5.** You can learn a lot about hydrogen atom using Bohr model. Go over the derivation and use atomic units. Now remember to use reduced mass to go from two-body system to one-body problem. Let the total energy of the ground state of H is -13.6 eV.

(1) What is the energy difference between the ground state of H and of D, in meV.

(2) Consider a muonic hydrogen, i.e., replace the electron by a negatively charged muon which has mass 206 in atomic units. What is the binding energy of the ground state of such a system. What is the velocity (in atomic units) and the radius of the muon with respect to the proton in the ground state? What is the wavelength for the  $n=2 \rightarrow 1$  transition?

**Exercise 6.** BJ problem 1.8 (If part a is too hard, you can skip it)

**Exercise 7.** BJ problem 1.9 (note that this method is used to obtain high energy gamma ray photons)

### Historical Experiments

#### 1. EM waves as particles

1900 Planck law-- energy of EM waves quantized (hypothesis)

1905 Einstein-- Photoelectric effect (use Planck law--indirect)

1923 Compton effect

#### 2. Atomic structure

1906-13 Rutherford experiment

1913 Bohr Model

1914 Franck and Hertz experiment

1922 Stern-Gerlach experiment

#### 3. Particles as waves

1924 de Broglie hypothesis

1926 Schrodinger theory

1927 Davisson and Germer experiment-- diffraction by electrons

double slit + diffraction experiments

## lecturenotes-3

A few remarks on Chapter 2 of BJ

#### 1. Relation between time-dependent and time independent Schrodinger equation

$$H\Psi(x,t) = i\hbar \frac{\partial}{\partial t} \Psi(x,t)$$

For isolated system, E is constant, thus write  $\Psi(x,t) = \phi(x) \exp(-iEt/\hbar)$

And then you have the time-independent Schrodinger equation

$$H\phi(x) = E\phi(x)$$

#### 2. Coordinate space vs momentum space wave functions

Related by the Fourier transform, thus the uncertainty relation

$$\Delta x \Delta p \geq \hbar \quad \text{or} \quad \Delta E \Delta t \geq \hbar$$

#### 3. Time variation of expectation values—to relate to classical physics

$$\langle A \rangle = \int \Psi^* A \Psi d\tau$$

$$\frac{d}{dt} \langle A \rangle = \left\langle \frac{\partial A}{\partial t} \right\rangle + \frac{1}{i\hbar} \langle [A, H] \rangle$$

This can be used to prove the Ehrenfest theorem

$$\langle \vec{p} \rangle = m \langle \frac{d\vec{r}}{dt} \rangle \quad \text{and} \quad \frac{d}{dt} \langle \vec{p} \rangle = - \langle \nabla V \rangle$$

4. Complete set of basis functions

Let  $\{\phi_n(x)\}$  form a complete set of eigensolutions of some Hermitian operator

It is possible to expand the wavefunction in terms of the complete set

$$\Psi(x,t) = \sum_n c_n(t) \phi_n(x)$$

This is called eigenfunction expansion, or close coupling method.

The closure relation follows:

$$\sum_n \phi_n(x') \phi_n(x) = \delta(x'-x)$$

$$\text{Well-known relation: } \sum_{\ell m} Y_{\ell m}^*(\Omega') Y_{\ell m}(\Omega) = \delta(\Omega' - \Omega) = \frac{\delta(\theta' - \theta) \delta(\phi' - \phi)}{\sin \theta}$$

5. Orbital Angular momentum

Know about  $L^2, L_z, L_+, L_-$ .

Need to have visual pictures of the spherical harmonics

To review spherical harmonics, see

<http://mathworld.wolfram.com/SphericalHarmonic.html>

Spherical harmonics in real form—has direction—good for chemical bonds

$$Y_{\ell, \cos} = \frac{1}{\sqrt{2}} (Y_{\ell m} + Y_{\ell m}^*)$$

$m > 0$

$$Y_{\ell, \sin} = \frac{1}{\sqrt{2}} (Y_{\ell m} - Y_{\ell m}^*)$$

6. Rigid rotor

$$H = \frac{L^2}{2I} \quad \text{thus the eigenstates are just } Y_{\ell m}$$

7. Electron spin

Spinors, Pauli matrices

8. Total angular momentum

$$\vec{J} = \vec{L} + \vec{S}$$

9. Central forces

$$\Psi(\vec{r}) = R(r) Y_{\ell m}(\theta, \phi)$$

$$\text{Parity } \pi = \pm 1 = (-1)^\ell$$

$$\text{For free particle } R(r) = j_\ell(kr)$$

Expansion of a plane wave

$$e^{i\vec{k} \cdot \vec{r}} = \sum (2\ell + 1) j_\ell(kr) P_\ell(\cos \theta)$$

Additional useful equations: BJ A4.24—A4.27

10. Many-body systems

Not identical particles—product functions if non-interacting

Identical particles -- need to satisfy Fermi or Bose statistics

-- always go to the center-of-mass frame to remove the global cm motion

11. Perturbation theory

Time-independent—first and 2<sup>nd</sup> order theory

Degenerate perturbation theory

Time-dependent --- perturbation theory (will go over the Fermi Golden Rule)

---- two-state or three-state approximation (strongly coupled)

12. Variational Method

Exercise 8. BJ 2.8

Exercise 9. BJ 2.11

Exercise 10: BJ 2.18

lecturenotes-4.

A few key remarks on Section 2.8 of BJ-- Time-dependent perturbation Theory

The starting Hamiltonian is time-dependent,

$$H(t) = H_0 + \lambda H'(t)$$

We need to assume that the eigensolutions of  $H_0$  are already known and that the initially the system is in the eigenstate  $|a\rangle$  of  $H_0$ .

Two cases:

(i) **final state is discrete**

Then assume the probabilities for transitions to other states are small, then transition probability to  $|b\rangle$  is given by

$$P_{ba}(t) = \frac{1}{\hbar^2} \left| \int_0^t H'_{ba}(t') e^{i\omega_{ba}t'} dt' \right|^2$$

Note: the exponential factor involving  $\omega_{ba} t$ , thus the integral will be small if the energy difference (inelasticity) is large.

(ii) **final state is in the continuum-- density of state  $\rho(E)$**

Fermi Golden rule for transition rate:

$$W_{ba} = \frac{dP_{ba}}{dt} = \frac{2\pi}{\hbar} |H'_{ba}|^2 \rho(E)$$

**Important case: Periodic Perturbation (eg in an EM field)**

Assuming a periodic perturbation with frequency  $\omega$  (not so with short pulse lasers)

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

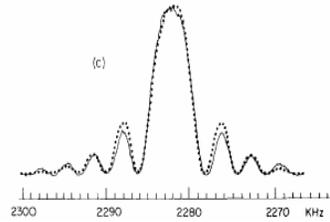
The absorption probability is then given by

$$P_{ba}(t) = \frac{2}{\hbar^2} |A_{ba}^+|^2 F(t, \omega_{ba} - \omega)$$

$$\text{where } F(t, \omega) = \frac{1 - \cos \omega t}{\omega^2}$$

In real experiment in general, the  $\omega$ -dependence is not seen since the interaction must be averaged over some distributions of frequencies  $g(\omega)$ .

However, using molecular beam resonant exp, the dependence on  $\omega$  has been observed, see JCP 57, 2277(1972) for HCN molecules shown right. The dotted curve is the function  $F(t, \omega)$  and the dots are exp.



### Two-level atoms in a periodic field---very important

Two concepts: detuning  $\Delta = \omega - \omega_{ba}$

$$\text{Rabi flopping frequency: } \omega_R = [\Delta^2 + 4 \frac{|A_{ba}^+|^2}{\hbar^2}]^{1/2}$$

The probability will oscillates with frequency  $\omega_R$ .

**Exercise 11.** In this exercise we want to derive eq. (2.380) and (2.381) of BJ.

Start from the first-order coupled eqs. (2.377a,b), reduced them to two uncoupled second-order ordinary differential equations. Then solve each second-order differential equation analytically.

## Hydrogen Atom

### 1. Model-1: spinless and Coulomb force only

In this approximation, the electron and the proton are taken as point particles interacting with a Coulomb force.

#### 1.1. Quantum numbers and wavefunctions

The Schrodinger equation is separable in spherical coordinates

$$E_n = -\frac{13.6}{n^2} (eV) \quad \Psi(\vec{r}) = R_{nl}(r)Y_{lm}(\theta, \varphi)$$

Three quantum numbers n,l,m to specify a state. You are expected to have a mental picture of the radial and angular wavefunctions. Energy independent of  $\ell$  implies additional symmetry—Runge-Lenz vector is a constant of motion for a pure Coulomb potential.

#### 1.2. Scaling for excited states (Rydberg states)

Energy  $E_n = -13.6/n^2$  eV, radius goes like  $n^2$ , velocity like  $1/n$ ; period like  $n^3$ .

The radiative lifetime of 2p state is 1.6 ns. For 25p, it is about 25  $\mu s$ . The other non-dipole states have much longer lifetimes.

#### 1.3. Scaling with mass and charge

- For hydrogenlike systems, the energy scales with the reduced mass, ie, proportional to the reduced mass. Thus for positronium its energy is half that of H for the states with identical n,l,m.
- The radius is inversely proportional to the reduced mass. The velocity is independent of the reduced mass.
- Energy scales with  $Z^2$ , radius with  $1/Z$ , velocity scales with  $Z$ .

#### 1.4. Some remarks on the properties of the radial wavefunctions

Often times you need to know the behavior of the wavefunction in small  $r$  or at large  $r$ . Recall that the radial wavefunction

$$R_{n\ell}(r) = N_{n\ell} r^\ell e^{-r/n} L_{n-\ell-1}(r)$$

where  $N$  is a normalization constant and  $L_{n-\ell-1}$  is a Laguerre polynomial of order  $(n-\ell-1)$ , thus with  $(n-\ell-1)$  radial nodes. To first order the normalization constant  $N$  goes like  $1/n^{3/2}$ . Thus at small  $r$ , the density of Rydberg states for a fixed  $\ell$  goes like  $1/n^3$ . In the perturbation regime, the excitation cross sections from a tightly bound initial state to the Rydberg states thus go like  $1/n^3$ . This is the rule of thumb for making simple estimates in scattering problems.

### 1.5. Separable in Parabolic coordinates (see BJ section 3.5 also)

In parabolic coordinates, the solutions are given in the form of  $f(\xi)g(\eta)e^{im\phi}$  and the states are labelled by  $n_1, n_2$ , and  $m$  where  $n_1 + n_2 + |m| + 1 = n$ , and  $n$  is the principal quantum number as in the spherical coordinates.

The eigenstates in parabolic coordinates are often called Stark states. They are also the eigenstates for a hydrogen atom in a weak electric field. In fact, the Stark states can be obtained from the degenerate perturbation theory for a given  $n$  by diagonalizing the electric field potential (the dipole field) within the subspace of  $n$  for each value of  $m$ .

The Stark states are eigenstates of  $H, L_z$  and  $A_z$  where  $\mathbf{A}$  is the Runge-Lenz vector for the Coulomb potential. In contrast the familiar wavefunctions in spherical coordinates are eigenstates of  $H, L^2$  and  $L_z$ .

(you can review Runge-Lenz vector in Schiff, p234-8.)

(More details, see the attached file: Hydrogen-ParabolicCoord.doc)

The Stark states and spherical states are related by a unitary transformation. Stark state  $|nn_1n_2m\rangle$  can be expanded in terms of spherical states  $|nlm\rangle$  as follows:

$$|nn_1n_2m\rangle = \sum_l |nlm\rangle \langle nlm | nn_1n_2m\rangle$$

where the transformation coefficient is given in terms of Wigner 3j-symbols as

$$\langle nn_1n_2m | nlm\rangle = (-1)^{(1-n+m+n_1-n_2)/2+l} \sqrt{2l+1} \begin{pmatrix} \frac{n-1}{2} & \frac{n-1}{2} & l \\ m+n_1-n_2 & m-n_1+n_2 & -m \end{pmatrix}$$

The Equations are taken from T. Gallagher "Rydberg atoms", p.76.

A convenient ref is: K. Molmer and K. Taulbjerg, J. Phys. B. Atom. Mol. Opt. Phys. **21** (28 May 1988) 1739-1749

- Problem 12:** (1) Write down explicitly the wavefunctions of the three Stark states in terms of linear combination of hydrogenic wavefunctions in spherical coordinates using the formula above for  $m=0$  and  $n=2$ .
- (ii) Plot the charge density in polar coordinates for each Stark state.
- (iii) Prove that each Stark state is not an eigenstate of  $L^2$ , thus parity is not a good quantum number for each Stark state.
-

(iii) Calculate the diagonal and off-diagonal matrix elements of the two Stark states. Show that the off-diagonal term is zero. This shows that Stark states are eigenstates for a hydrogen atom in a static electric field. Use z-axis to be in the direction of the electric field.

(If you are good at using computers, do this problem for  $m=0$  and  $n=5$ , and give a good writeup. I like someone to show the density plots of the five Stark states.)

### 1.6. Circular states; elliptical states

For a Rydberg state with  $\ell = n - 1$  and  $m = \pm \ell$ , it is called a circular state. An electron in a circular state has little probability of penetrating near the nucleus.

One can form elliptical states which are the closest analog of classical ellipses that can be formed from quantum states. These states form the minimum wavepacket and in fact each is a stationary state, see Gay et al, Phys. Rev. A39, 6587 (1989). One can prepare a Rydberg atom in such an elliptical state and study the collision of atoms or ions with such “classical ellipse”, see Lundsgaard et al, J. Phys. B27, L611(1994).

An elliptical state can be expressed in terms of spherical states as

$$|n, e\rangle = \sum_{\ell m} c_{n\ell m}(e) |n\ell m\rangle$$

where  $e$  is the eccentricity of the classical ellipse, and

$$c_{n\ell m}(e) = (-1)^{(\ell+m)/2} \frac{2^{n-\ell-1} (n-1)!}{[(\ell-m)/2]!(\ell+m)/2)!} \left( \frac{(\ell+m)!(\ell-m)!(2\ell+1)}{(n-\ell-1)!(n+\ell)!} \right)^{1/2}$$

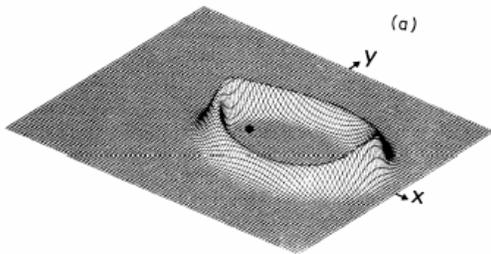
$$x \left( \sin \frac{\alpha}{2} \right)^{n-m-1} \left( \cos \frac{\alpha}{2} \right)^{n+m+1}$$

where  $e = \sin \alpha$  is the eccentricity of the ellipse. For such an elliptic state, one can show that

$$\langle L_y \rangle = 0, \langle L_x \rangle = 0, \langle A_y \rangle = 0, \langle A_z \rangle = 0 \text{ and}$$

$$\langle L_z \rangle = \pm(n-1)\sqrt{1-e^2} \text{ and } \langle A_x \rangle = (n-1)e$$

The paper by Gay et al quoted above has examples of such ellipses. Below is an example of an elliptic state with  $n=50$  and  $e=0.6$  from that paper.



### 1.7. Hydrogen wavefunction in momentum space

One can obtain the hydrogenic wavefunction in momentum space from Fourier transformation of the hydrogenic coordinate space wavefunction.

One can also rewrite the Schrodinger equation in momentum space directly and then solve the resulting equation. This latter method is more general.

This part of the lecture is adopted from BJ--Appendix 5. Here are just a few key remarks.

(i) The momentum space satisfies an integral eq. (A5.13). The potential becomes a kernel of the integral equation.

(ii) For spherical potential, the momentum space wavefunction is separable,

$$\phi(\vec{p}) = F_{E\ell}(p)Y_{\ell m}(\theta_p, \phi_p)$$

An integral equation can be written down for  $F_{E\ell}$ , see eq. (A5.33). For hydrogen atom, analytical solution for the bound momentum space wavefunction can be obtained in terms of Gegenbauer functions. The full solution is given by (A.5.34).

The momentum space wavefunctions for  $n=1-3$  are given in (A. 5. 37). For 1s, it varies like  $1/(1+p^2)^2$ , and drops like  $p^{-4}$  for large  $p$ . For  $n=2$ , if  $\ell = 0$ , it drops like  $1/p^4$ , and if  $\ell = 1$ , it drops like  $1/p^5$ . This just shows that larger  $\ell$  means the wavefunction is less penetrating and thus tends to have less larger momentum.

### note-7-dirac-lamb

## 2. Hydrogen Atom--Dirac Theory

### 2.1. Dirac Theory of atomic hydrogen

The best way to introduce electron spin and the relativistic effect of atomic hydrogen is to start with the Dirac theory. I will follow Appendix 7 of B-J. (written notes added)

### 2.2. Pauli approximation

In the Pauli approximation, the Hamiltonian takes the form

$$H_{Pauli} = H_0 + H_{LS} + H_{rel} + H_{Darwin}$$

Their expressions can be found in standard textbooks.

### 2.3. Speaking of quantum numbers:

Including spin, each electron has 4 degrees of freedom -- a spin function, or spinor in general, has to be added to the spatial wavefunction. The total angular momentum for each electron is  $\vec{j} = \vec{\ell} + \vec{s}$  and eigenstates are now given by  $n, \ell, j, m_j$ .

You need to know some angular momentum algebra, Clebsch-Gordon coefficients or the 3-j symbols.

- Exercise 13: Write down the  $2p_{1/2}$  and  $2p_{3/2}$  wavefunctions of H in the Pauli approximation explicitly. Use  $\alpha$  and  $\beta$  to represent the spin-up and spin-down wavefunctions and  $R_{21}(r)$  to represent the 2p radial wavefunction.

The spin-orbit interaction is due to the interaction between the magnetic dipole (from the electron's spin) with the magnetic field generated by the electric field from the nucleus in the moving frame of the electron. Note that this effect has to be treated by relativistic mechanics--recall the discussion in Jackson's book (in the chapter that deals with relativistic kinematics.)

Exercise 14. The  $n=2$  states of atomic hydrogen are degenerate. Look it up and sketch the energy levels at the following successive approximations:  
 (a) including spin-orbit interaction; (b) according to Dirac theory; (c) including QED effect; (d) including hyperfine interaction from the nucleus. State clearly the good quantum numbers at each

level of approximation and the degrees of degeneracy. For actual splittings you may want to consult BJ or some books.

### 3. Lamb shift

According to QED, there are additional corrections generally called Lamb shift. This Lamb shift removes the degeneracy between say  $2s_{1/2}$  and  $2p_{1/2}$  states. The Lamb shift is the result of quantizing the electromagnetic field, including major contribution from the self-energy and the vacuum polarization. QED effect should be included in the high-precision spectroscopy. In that case the volume effect from the nucleus has to be included as well.

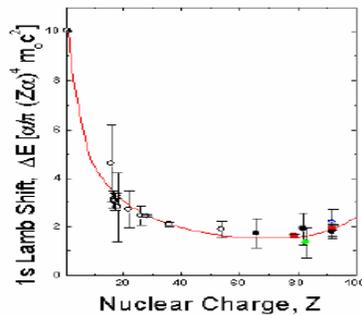
The small terms considered above are important for high precision spectroscopy, but not essential in collisions with electrons or ions.

The Lamb shift has to be calculated using QED. Experimentally the energy splitting of  $2s_{1/2}$  and  $2p_{1/2}$  has been measured by Lamb and Retherford in 1947 to be 1057.846 MHz. From QED calculation, the Lamb shift comes from three major terms: -27 MHz from vacuum polarization, 1017 MHz from electron mass renormalization and 68 MHz from anomalous magnetic moment of the electron.

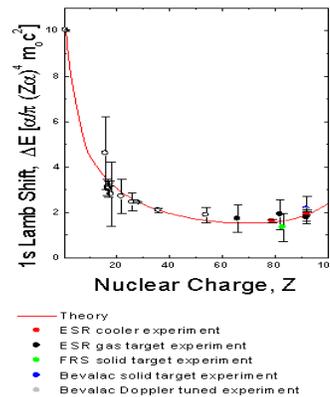
#### Lamb shift For High-Z one-electron ions

One of the most sensitive experimental approaches for the investigation of the effects of quantum electrodynamics in strong Coulomb fields is a precise determination of the [ground state energies in high-Z one-electron systems](#). Similar investigations for low-Z ions are primarily sensitive to the lowest-order self-energy corrections. The study of the higher-order [self-energy and vacuum polarization contributions](#), however, requires the heaviest ions available. Here, the goal of the experiments is to probe [higher-order QED contributions](#) which correspond to Feynman diagrams such as the two-photon exchange diagrams. For the case of uranium, where the total 1s Lamb shift contributes 464 eV to the total ground state binding energy of 131.816 keV, a stringent test of QED requires an absolute experimental accuracy of about  $\pm 1$  eV which represents the accuracy theoreticians claim presently. For such studies the ESR storage ring provides favorable experimental conditions. This has been demonstrated within the [first series of experiments](#) performed at the ESR gas jet target as well as at the electron cooler device. For the case of the 1s-Lamb shift in hydrogen-like uranium, the [achieved accuracy of  \$\pm 13\$  eV](#) is already a substantial improvement by almost one order of magnitude compared to a former experiment conducted at the BEVALAC accelerator.

SUMMARY OF 1s LAMB SHIFT



SUMMARY OF 1s LAMB SHIFT



## note-8-hyperfine structure

### Hyperfine structures

—due to the interaction of the electrons with the nucleus

Hyperfine structures can be probed with microwaves or radio waves, and they play important roles in the current studies involving cold atoms.

The key physics:

1. Finite mass—*isotope shifts*—due to different reduced mass
2. existence of magnetic dipole moment of the nucleus—*hyperfine splitting*
3. Volume effect—due to the fact that nucleus occupies finite volume. Deviation of the potential from point charge inside the nucleus
4. Nonspherical nucleus: hyperfine due to quadrupole moment of the nucleus (nonspherical nucleus)

Nucleus is considered to be made of nucleons. Since each nucleon has spin  $\frac{1}{2}$ , the nucleus can have integer or half-integer spin quantum numbers  $I$ , depending on even or odd numbers of nucleons. Each nucleus has a magnetic dipole moment given by

$\vec{\mu}_N = g_I \mu_n \vec{I} / \hbar$  where  $g_I$  is the “Lande g-factor” and  $\mu_n$  is the nuclear magneton. The latter is  $\mu_B / 1836.15$  as compared to the Bohr magneton. The Lande g-factor for proton is 5.59 and -3.8 for neutron. For deuteron it is 0.857. For other nucleus one has to look up in nuclear physics data tables.

#### Hyperfine structure due to the magnetic dipole moment of the nucleus.

Origin: From the orbiting electron which produces a magnetic field at the nucleus, thus

introducing  $\vec{L} \cdot \vec{I}$  term.

From the magnetic dipole moment of the electron’s spin, thus has

$\vec{S} \cdot \vec{I}$  term.

The calculation of the interaction Hamiltonian can be expressed as

For  $r \neq 0$

$$H'(\text{magnetic - dipole}) = \frac{\mu_0}{4\pi} \frac{2}{\hbar^2} g_I \mu_B \mu_n \frac{1}{r^3} [\vec{L} \cdot \vec{I} - \vec{S} \cdot \vec{I} + 3 \frac{(\vec{S} \cdot \vec{r})(\vec{I} \cdot \vec{r})}{r^2}]$$

and for  $r=0$

$$H'(\text{Fermi - contact}) = \frac{\mu_0}{4\pi} \frac{2}{\hbar^2} g_I \mu_B \mu_n \frac{8\pi}{3} \delta(r) \vec{S} \cdot \vec{I}$$

Note that the second term, known as the Fermi contact term, does not vanish only for an s-electron.

The angular momentum of the atom  $\vec{F} = \vec{J} + \vec{I}$ . For hydrogen atom, such a hyperfine eigenstate can be expressed as  $|\ell s j I F\rangle$  and the energy of each state can be calculated using the first order perturbation theory. The final result for the hyperfine interaction has the form

$$\Delta E = (C/2)[F(F+1) - I(I+1) - j(j+1)] \quad [5.65]$$

where the coefficient has been worked out in B-J, see eq. [5.70] and [5.78]. The final expression for the hyperfine splitting due to the existence of magnetic dipole moment of the nucleus is given by [5.79].

Note that due to [5.65] the energy splitting between the successive hyperfine levels of  $F$  and  $(F-1)$  is  $CF$ , i.e., the splitting increases with  $F$ .

The hyperfine splitting can be measured using microwave spectroscopy. From such measurements the nuclear Lande g-factor can be determined. From the number of hyperfine levels the nuclear spin can be determined.

The hyperfine splitting between F=0 and F=1 in atomic hydrogen is 1420 MHz, or about 21 cm. It is one of the most important line in radio astronomy.

The precise separation is 1420.405751 7667 (10) MHz

#### Electric quadrupole hyperfine structure

If the nucleus is not spherically symmetric, then it possesses a nuclear quadrupole moment Q. In quantum mechanics, the quadrupole moment of a nucleus is defined as the expectation value of  $Q_{zz}$  operator for the nuclear wavefunction  $|IM_I\rangle$  for  $M_I=I$ . The interaction energy is proportional to a

quadrupole coupling constant  $B=Q\langle\frac{\partial^2 V}{\partial z^2}\rangle$  where  $\langle\frac{\partial^2 V}{\partial z^2}\rangle = -\langle jj|\frac{3z^2-r^2}{r^5}|jj\rangle$  is the

average gradient of the electric field produced by the electron at the nucleus. The final expression for the quadrupole hyperfine structure is given by [5.90]. Note that the energy separation due to the quadrupole hyperfine interaction deviates from the simple proportionality as seen for the magnetic dipole case.

#### All about the 21 cm line:

From <http://encyclopedia.thefreedictionary.com/21%20cm%20line>

In [physics](#) and [astronomy](#), the **21 cm line** is the name for a highly [forbidden emission line](#) of [hydrogen](#). This emission line is often observed by radio astronomers to study both our own Galaxy and external galaxies.

#### History

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During the 1930s, it was noticed that there was a radio 'hiss' that varied on a daily cycle and appeared to be extraterrestrial in origin. After initial suggestions that this was due to the [Sun](#), it was observed that the radio waves seemed to be coming from the centre of [the Galaxy](#). These discoveries were published in 1940 and were seen by Professor [J.H. Oort](#) who knew that significant advances could be made in astronomy if there were [emission lines](#) in the radio part of the spectrum. He referred this to [Dr Hendrik van de Hulst](#) who, in 1944, discovered that [neutral hydrogen](#) could produce radiation at a [frequency](#) of 1420.4058 [MHz](#) due to two closely spaced energy levels in the [ground state](#) of the [hydrogen atom](#).

The 21cm line (1420.40058 MHz) was first observed in 1951 by Ewen and [Purcell](#) who were closely followed by Muller and Oort and Christiansen and Hindman. After 1952 the first maps of the neutral hydrogen in the Galaxy were made and revealed, for the first time, the spiral structure of the [Milky Way](#).

#### **note-9-alkaliatom**

Alkali Atoms--

ref: Laser Cooling and Trapping by H. Metcalf and P. Van der Straten, Springer 1999

ISBN: 0-387-98747-9 (cited as Metcalf)

#### 1. Rydberg formula and quantum defect

For an atom in the highly excited state or the valence and excited states of an alkali atom, the outermost electron is far away from the core electrons. The outer electron can be considered to be moving in an

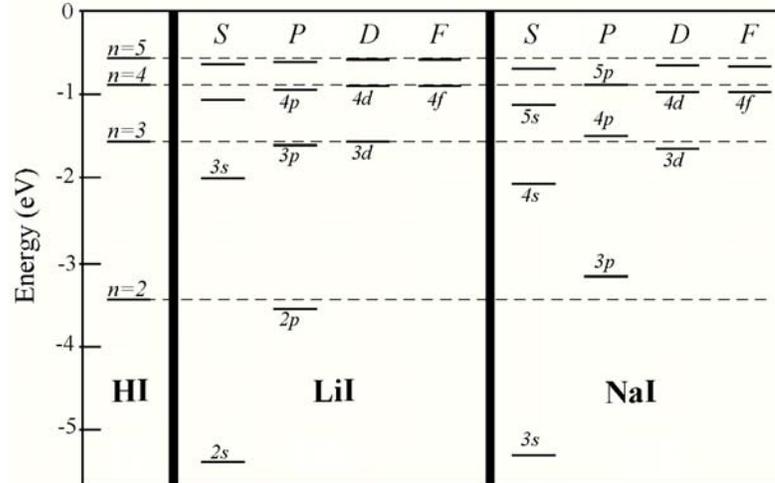
effective potential  $V(r) = -\frac{1}{r} + V_s(r)$  where the latter is a short-range potential. The energy levels can

thus be expressed as  $E_{n\ell} = -\frac{1}{2(n-\mu_\ell)^2}$  where  $\mu_\ell$  is the quantum defect and it is nearly independent

of the energy for the higher excited states. This is the Rydberg formula. The figure below shows the energy

levels of H, Li and Na. Note that the quantum defect decreases to nearly zero for higher  $\ell$ . The quantum defect near the threshold is related to the phase shift by  $\delta_\ell = \pi\mu_\ell$ . (The proof is in Friedrich, p123).

To account for the effect of the polarization of the core, the short range potential  $V_s(r)$  has the asymptotic form  $V_s(r) \rightarrow -\frac{\alpha_d}{2r^4}$  where  $\alpha_d$  is the dipole polarizability.



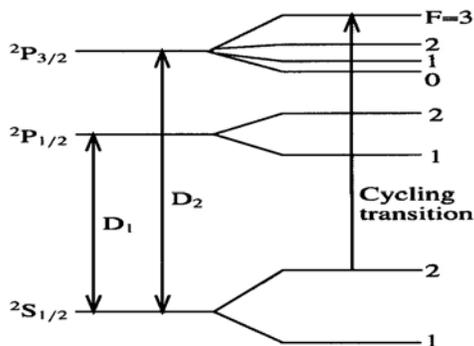
Here is the quantum defect for the alkali atoms:

$\ell$	Li	Na	K	Rb	Cs
s	0.40	1.35	2.19	3.13	4.06
p	0.04	0.85	1.71	2.66	3.59
d	0.00	0.01	0.25	1.34	2.46
f	0.00	0.00	0.00	0.01	0.02

## 2. Fine and Hyperfine structure

The ground state and the first excited states of the alkali atoms are used these days in laser cooling and trapping. The 3s and 3p states of Na are indicated in Fig.1 showing the fine and hyperfine structures, and the D<sub>1</sub> and D<sub>2</sub> lines of Na and the transition between the two hyperfine states for laser cooling.

Fig1. 3s and 3p levels of Na for laser cooling.



For the hyperfine structures, the shift is given by

$$\Delta E_{\text{hfs}} = \frac{1}{2} \hbar A K + \hbar B \frac{3/2 K(K+1) - 2I(I+1)J(J+1)}{2I(2I-1)2J(J-1)},$$

in terms of the so-called A and B coefficients where  $K=F(F+1)-I(I+1)-J(J+1)$  for A and B that are adjusted to experimental data.

A good review article for hyperfine structure of alkali atoms is given by E. Arimondo\*, M. Inguscio, and P. Violino, Rev. Mod. Phys. 49, 31 (1977).

## note-10

### Helium and helium-like ions

The helium atom is the simplest three-body system that we can think of. First we will look at the structure of helium atom, from the familiar ground state and singly excited states, then doubly excited states. There are many new concepts when we deal with identical particles. The concept of multi-channel phenomena also will enter.

#### 1. The Schrodinger equation--nonrelativistic theory

The nonrelativistic Hamiltonian for the helium atom in the center-of-mass frame is

$$H = -\frac{\hbar^2}{2\mu} \nabla_1^2 - \frac{\hbar^2}{2\mu} \nabla_2^2 - \frac{\hbar^2}{M} \vec{\nabla}_1 \cdot \vec{\nabla}_2 - \frac{Ze^2}{r_1} - \frac{Ze^2}{r_2} + \frac{e^2}{r_{12}} \quad (1)$$

where  $r_i$  is the distance of electron  $i$  from the nucleus, the reduced mass has been used. Note that the

term  $-\frac{\hbar^2}{M} \vec{\nabla}_1 \cdot \vec{\nabla}_2$  is called the **mass polarization** term. It is the result of not using the **Jacobi coordinates**. This term vanishes when  $M$  is taken to be infinity. In actual calculation, this term is always treated as a perturbation.

The simplest approximation is to solve the eigenstates of

$$H\Psi = \left\{ -\frac{\hbar^2}{2\mu} \nabla_1^2 - \frac{\hbar^2}{2\mu} \nabla_2^2 - \frac{Ze^2}{r_1} - \frac{Ze^2}{r_2} + \frac{e^2}{r_{12}} \right\} \Psi(\vec{r}_1, \vec{r}_2) = E\Psi(\vec{r}_1, \vec{r}_2) \quad (2)$$

#### 1.2. The spatial symmetry

Equation (2) is symmetric under exchange of 1 and 2, thus the solution

$$\Psi(2,1) = \pm \Psi(1,2), \quad (3)$$

i.e., the wavefunction is symmetric or antisymmetric under particle exchange.

#### 1.3. Spin symmetry

The two spins can add up to singlet  $S=0$  or triplet  $S=1$ . The former is antisymmetric and the latter is symmetric under 1 and 2 exchange. Since electrons are fermions the total wavefunctions should be antisymmetric.

#### 1.4. Shell model and Level scheme

For the Hamiltonian (2), the good quantum numbers are L, S and parity, in addition to the total energy. If the relativistic effect and the spin interactions are considered then L and S are not good quantum numbers separately, but J and parity are good quantum numbers.

Eq. (2) is not separable due to the electron-electron interaction term. The simplest approximation in solving (2) is to treat  $H' = \frac{e^2}{r_{12}}$  as the perturbation, then

$$H_0 \Psi_0 = \left\{ -\frac{\hbar^2}{2\mu} \nabla_1^2 - \frac{\hbar^2}{2\mu} \nabla_2^2 - \frac{Ze^2}{r_1} - \frac{Ze^2}{r_2} \right\} \Psi_0(\vec{r}_1, \vec{r}_2) = E \Psi_0(\vec{r}_1, \vec{r}_2) \quad (4)$$

is separable and the solutions are just products of hydrogenic solutions (shown in class). Within this approximation, the quantum numbers are  $n_1, \ell_1, n_2, \ell_2, L, M_L, S, M_S$ , i.e., we have eight quantum numbers to describe a two-electron state. Note that the parity is well-defined since it is given by  $\pi = (-1)^{\ell_1 + \ell_2}$ .

The good quantum numbers for H are  $L, S, M_L$  and  $M_S$ . The rest are good quantum numbers for  $H_0$  but not H. They are used to define the **configurations**. Thus we use 1s2s, 1s2p, 2p3d, etc to define a configuration, each coupled to give well-defined  $^{2S+1}L^\pi$ .

**Exercise 17.** This exercise will guide you through the construction of the two-electron wavefunctions of a helium atom in the nonrelativistic approximation.

- (a) Assume that the electron-electron interaction can be neglected, construct explicitly the wavefunctions of the two electrons that can be labelled as 1s2p  $^1P$  and 1s2p  $^3P$ . Consider the case that  $M_L=0$  and  $M_S=0$ . You will write the wavefunctions as the product of the spin function and the spatial wavefunction. Show that the wavefunctions you have constructed are eigenstates of  $\ell_1^2, \ell_2^2, L^2, S^2$ . Show that under exchange of electron 1 and electron 2, the total wavefunction indeed is antisymmetric. What is the parity of each state? Find the eigenvalues of  $L^2, S^2$ , and the energy of each state.
- (b) Construct the same wavefunctions using the Slater determinants. Prove that the resulting wavefunctions are identical to the one derived from (a).
- 

## 1.5 Calculation of wavefunctions and energies

1.5.1. First-order perturbation theory allows you to calculate the correction in energy from  $H'$ . This is in the standard textbook.

Discuss the essential approach, the angular part and then the exchange energy.  
Discuss the angular momentum algebra.

1.5.2. Variational principles: in textbooks, for ground state of each symmetry. The **Hylleraas wavefunctions** use the coordinates

$$s=(r_1+r_2), t=(r_1-r_2) \text{ and } u=r_{12} \quad (5)$$

- (i) Choose the variational form

$$\Psi = \exp(-\alpha s) \quad (6)$$

The effective charge  $\alpha = Z - \frac{5}{16}$  is obtained variationally. Within this approximation the

$H'$  has no bound state.

**Exercise 18.** Use eq. (6) and the variationally obtained effective charge, calculate the total energy of the two-electron Hamiltonian. Compare this energy with the ground state of the one-electron Hamiltonian, i.e., after one electron has been removed. The difference of these two energies gives the binding energy. Do the calculation for He and H. Compare your answers to the experimental data.

- (ii) For H, a three-parameter variational wavefunction of the form

$$\Psi = [\exp(-ar_1 - br_2) + \exp(-ar_2 - br_1)](1 + cr_{12})$$

yields  $a=1.075, b=0.478, c=0.312$  and the binding energy of 0.705 eV, which is to be compared to experimental value of 0.75 eV. Without the c-term, the binding energy thus obtained is 0.368 eV. This shows that the importance of "angular correlation", as represented by the term in  $r_{12}$ .

(iii) A general Hylleraas method is to expand the wavefunction in the form

$$\Psi = e^{-\alpha(r_1+r_2)} \sum c_{\ell,m,n} (r_1 + r_2)^\ell (r_1 - r_2)^m r_{12}^n$$

Very accurate energies can be obtained in this way.

(iv) Another method is to use Fock expansion using hyperspherical coordinates

$$R = \sqrt{r_1^2 + r_2^2} \quad \text{and} \quad \alpha = \tan^{-1}(r_2/r_1)$$

This is called Fock expansion.

### 1.5.3. Shell model or Hartree-Fock approximation:

A better approximation to  $H_0$  is to include some part of  $e^2/r_{12}$  into  $H_0$ . To maintain separability, one can define another  $H_0$  as

$$H_0 = -\frac{\hbar^2}{2\mu} \nabla_1^2 - \frac{\hbar^2}{2\mu} \nabla_2^2 + V(r_1) + V(r_2) \quad (5)$$

The difference of this  $H_0$  from  $H$  in (2) is the perturbation. The  $V$  is chosen as a central potential so that the configurations can still be defined. A variational approach where  $\Phi_0(\vec{r}_1, \vec{r}_2)$  is taken as the products of basis functions from each electron (with proper symmetry) results in the Hartree-Fock approximation. In this case the resulting  $V(r)$  is not a local potential, but rather contains an exchange potential.

Eigenfunction expansion method or configuration interaction method. The eigenstates of  $H_0$  form a complete set, thus in principle one can get the eigensolutions of  $H$  by expanding it in terms of

$$\Psi(\vec{r}_1, \vec{r}_2) = \sum_{\alpha} c_{\alpha} \Phi_{\alpha}(\vec{r}_1, \vec{r}_2) \quad (6)$$

Here  $\alpha$  spans the complete set of  $n_1, \ell_1, n_2, \ell_2$  for a given  $L, M_L, S, M_S$ . This is usually called **configuration interaction (CI)** method. The expansion (5) in general is seriously truncated and only configurations that have energies nearby to the state of interest are included in (6).

The level scheme: The helium spectra can be separated into singlet states (para-helium) and triplet states (ortho-helium). They do not mix in general since they are not connected by the E1 radiative transitions. If there is only one electron is in the excited state, with the designation such as 1s2s, 1s3d, then we have the singly excited states. For the outer electron to become free, it takes 24.56 eV. This is the first ionization energy for He.

## 2. Spin-orbit interactions and coupling schemes

### 2.1. Angular momentum coupling schemes

$$\text{LS coupling} \quad \vec{J} = (\vec{\ell}_1 + \vec{\ell}_2) + (\vec{s}_1 + \vec{s}_2) = \vec{L} + \vec{S}$$

$$\text{jj-coupling} \quad \vec{J} = (\vec{\ell}_1 + \vec{s}_1) + (\vec{\ell}_2 + \vec{s}_2) = \vec{j}_1 + \vec{j}_2$$

The LS coupling scheme is the better approximation for low-Z atom and JJ scheme is better for heavy elements. Note that only  $J$  and  $M_J$  are good quantum numbers for a two-electron atom in addition to the eigen-energy. The admixture of LS or JJ components is called intermediate coupling in general.

The above two coupling schemes work better for valence orbitals and low-lying excited states. For Rydberg states where the outer electron is farther away from the inner electron, a better coupling scheme is

$\vec{J} = (\vec{\ell}_1 + \vec{s}_1) + \vec{\ell}_2 + \vec{s}_2$  where the inner electron's J couples to the orbital angular momentum and then to the spin of the outer electron. The approximate coupling scheme depends on the relative energies of the various interactions.

### 2.2. The relativistic theory for Helium atom.

There is no closed-form Dirac theory for two-electron or many-electron atoms. Usually the relativistic Dirac theory for many electron atoms or molecules take the form of the Breit equation (Bethe-Salpeter, pp170, called B-S). The two-electron Hamiltonian is

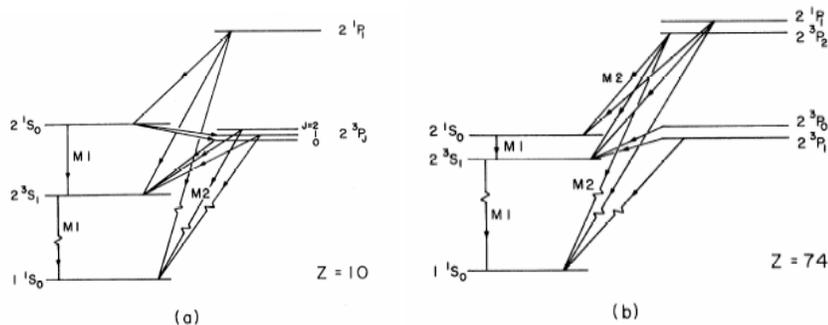
$$H = H_1 + H_2 + 1/r_{12}$$

where  $H_1$  and  $H_2$  are the Dirac Hamiltonian for the one-electron system. The spin-interaction part between the two electrons has addition term, but has to be calculated by perturbation theory. This additional term is called **Breit interaction**

$$H'_2 = \frac{e^2}{2 r_{12}} (\vec{\alpha}_1 \cdot \vec{\alpha}_2 + \frac{(\vec{\alpha}_1 \cdot \vec{r}_{12})(\vec{\alpha}_2 \cdot \vec{r}_{12})}{r_{12}^2})$$

Similar to the Pauli approximation for atomic hydrogen, one can also write down the helium Hamiltonian using the Pauli approximation. There are six different terms in this case (see Bethe and Salpeter, p181). Since there are so many terms one may as well start with the Dirac version of the Hamiltonian outlined above. On the other hand, the Pauli form is more transparent in terms of the "physical terms". Consult with (39.14) on p. 181 of B-S, one can find effects due to the retardation of the EM field produced by the other electron, the spin-orbit, spin-spin, spin-other-orbit interactions.

### 2.3. The fine structure of 1s2l states from low-Z to high-Z elements



The fine structure of He-like ions for low-Z ( $Z=10$ ) and high-Z ( $Z=74$ ) evolving from the LS coupling scheme to JJ-coupling scheme. [CDL-PRA15, 154 (1977)].

### 2.4. an example from modern measurement [PRL 82, 1112 (1999)]

#### Measurement of the Helium $2^3P_0-2^3P_1$ Fine Structure Interval

We report the most accurate measurement of the helium fine structure splitting. The  $2^3P_0-2^3P_1$  energy splitting is  $29\,616\,949.7 \pm 2.0$  kHz. Laser saturation spectroscopy, heterodyne pure frequency determination, and fluorescence detection were combined in a novel experimental approach. The

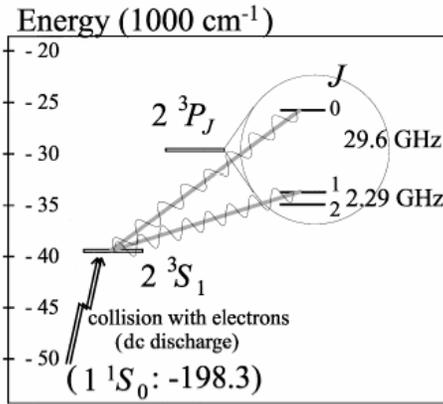


TABLE II. Comparison of this work with previous measurements and the theoretical prediction.

	$\nu_{01}$ value (kHz)	Difference (kHz)
This work	29 616 949.7(2.0)	...
Shiner <i>et al.</i> [7]	29 616 962(3)	-12(3)
Hughes <i>et al.</i> [11]	29 616 844(21)	+106(21)
Theory [18]	29 616 974(10)	-24(10)

note-11-helium-2

### 3. Autoionizing states and nonradiative transitions

#### 3.1. Quick review of continuum states or unbound states

For **short-range potential** at large  $r$  where the potential is zero, the two independent solutions of the radial Schrodinger equation are  $j_\ell(kr)$  and  $n_\ell(kr)$ . For large  $kr$ , these two functions approach

$\sin(kr - \frac{\ell\pi}{2})$  and  $\cos(kr - \frac{\ell\pi}{2})$ , respectively. The general solution in the outside region is given by

$$\Phi(r) = A_\ell j_\ell(kr) + B_\ell n_\ell(kr) \rightarrow C_\ell \sin(kr - \frac{\ell\pi}{2} + \delta_\ell)$$

for the large  $r$  where  $C_\ell$  is the normalization and  $\delta_\ell$  is the phase shift.

For **Coulomb potential**, there are also two independent solutions in the region where only Coulomb potential is present. The two solutions are regular and irregular Coulomb functions

$$F_\ell(\eta, kr) \rightarrow \sin(kr - \eta \ln 2kr - \frac{\ell\pi}{2} + \sigma_\ell)$$

$$G_\ell(\eta, kr) \rightarrow \cos(kr - \eta \ln 2kr - \frac{\ell\pi}{2} + \sigma_\ell)$$

for large  $r$ . Here  $\eta = -Z/k$  (in atomic units) is the Coulomb parameter and

$\sigma_\ell = \arg[\Gamma(\ell + 1 + i\eta)]$  is the Coulomb phase shift. Thus the continuum wavefunction in a Coulomb field in the asymptotic region has the general form

$$\Phi(r) = A_\ell F_\ell(\eta, kr) + B_\ell G_\ell(\eta, kr) \rightarrow C_\ell \sin(kr - \eta \ln 2kr - \frac{\ell\pi}{2} + \sigma_\ell + \delta_\ell)$$

#### 3.2. Normalization of continuum wavefunctions (from QMII homework)

Assume that the radial wave function  $R(r)=u(r)/r$ , the normalization for the bound state wave function is well understood. In this exercise we will walk through the procedure to normalize the continuum wavefunctions. In the asymptotic region, the continuum wave function can be written as

$$R_k(r) = u_k(r)/r \rightarrow \frac{A}{r} \sin(kr - \ell\pi/2 + \delta) \quad \text{as } r \rightarrow \infty \quad (1)$$

if we have a short range potential. If there is a Coulomb potential at large distance then you need to add a logarithmic term in the phase plus a Coulomb phase.

We say that the continuum wave function  $R_k$  is **normalized per unit momentum k** if

$$\int_0^\infty u_k(r)u_{k'}(r)dr = \delta(k - k') \quad (2)$$

Similarly we say that the continuum wave function  $R_E$  is **normalized per unit energy** if

$$\int_0^\infty u_E(r)u_{E'}(r)dr = \delta(E - E') \quad (3)$$

We want to derive what A should be if the wave functions are normalized to either scheme.

The expression (2) is equivalent to

$$\int_0^\infty u_k(r)dr \int_{k-\Delta}^{k+\Delta} u_{k'}(r)dk' = 1 \quad (4)$$

We will use (4) to find out what A should be in (1).

Start with the Schrodinger equation for  $u_k$  and  $u_{k'}$  and *do integration by parts* to construct expression like (4) except by setting the upper limit in r to a large number a. You can then use (1) for the u's at r=a. You will need the integral

$$\int_0^\infty \frac{\sin x}{x} dx = \frac{\pi}{2}$$

which you can prove by using contour integration. From this procedure prove that

$$A = \sqrt{\frac{2}{\pi}}$$

if the wave function is normalized in the k-scale and

$$A = \sqrt{\frac{2}{\pi k \hbar}}$$

if the wave function is normalized per unit energy as in equation (3).

Note that different normalization will give you different expressions for the density of states. If the wave function is normalized per unit energy, then the density of states  $\rho(E) = 1$ . If the wave function is normalized per unit in k-space, then the density of state  $\rho_k(E) = dn/dk = \frac{dn}{dE} \frac{dE}{dk} = \hbar k$ .

Note that according to Fermi Golden rule (later) the transition rate is proportional to  $|\langle 0 | T | f_T \rangle|^2 \rho_T(E)$  where f is the final state continuum wave function, 0 stands for the initial state and T is some transition operator. Clearly this exercise shows that the transition rate does not depend on how you normalize the continuum wave function.

### 3.3. Phase shift in scattering theory

For a repulsive potential, the wavefunction is pushed away from the origin in comparison with field free wavefunction at the same energy, thus the phase shift is negative. For an attractive potential, the phase shift would be positive. However, the phase shift is defined between  $-\pi$  and  $\pi$  so it is not possible to get the absolute phase shift unless you calculate (or count) the phase shift from very high energies where the phase shift is expected to approach zero.

For collisions at very low energies (for short-range potential), only the s-wave scattering is important. Here the important concept is the **scattering length**, defined by taking the limit  $-\frac{\tan \delta}{k}$  in the limit of k goes to zero. Thus if the scattering length is positive it is equivalent to scattering from a hard sphere, or by a repulsive force. For negative scattering length it is equivalent to scattering from an attractive force. We will touch upon this subject in the future.

One can show that the derivative of phase shift with respect to energy is a measure of the time-delay for a wavepacket (You can prove it by examining the time dependence of a wavepacket.). Resonance is a phenomenon where the time-delay is large. Near a resonance one can express the phase shift as

$$\tan \delta_\ell = -\frac{\Gamma/2}{E - E_R}$$

where  $E_R$  is the resonant energy,  $\Gamma$  is the resonance width. Note that according to this expression the phase shift changes by  $\pi$  across the resonance. The partial wave cross section and the energy derivative of phase shift both have the Lorentzian, or Breit-Wigner form

$$\frac{d\delta}{dE} = \frac{\Gamma/2}{(E - E_R)^2 + (\Gamma/2)^2}$$

### 3.4. Potential resonance or shape resonance

For a potential like

$$V(r) = -V_0 e^{-r/\beta^2} + \frac{\ell(\ell+1)}{2\mu r^2}$$

there is a potential barrier at larger r. Clearly when the scattering energy is near the top of the barrier there is a chance that the inner potential well can support a bound state, but the tunneling to the outer region results in a resonance. This type of resonance comes from the “shape” of potential, and is called shape resonance, or potential resonance.

4. Feshbach Resonances (eqs. in this note require mathtype fonts)

For a two-channel problem where the first channel is open and the second channel is closed. With respect to the second channel, a bound state in channel 2 can decay to channel 1. Follow the derivation of Friedrich' Chapter 1.4, we consider

$$\left\{ \left( -\frac{\hbar^2}{2\mu} \frac{d^2}{dr^2} + V_1(r) \right) \phi_1(r) + V_{12}(r) \phi_2(r) = E \phi_1(r) \right. \quad (1)$$

$$\left. \left( -\frac{\hbar^2}{2\mu} \frac{d^2}{dr^2} + V_2(r) \right) \phi_2(r) + V_{21}(r) \phi_1(r) = E \phi_2(r) \right. \quad (2)$$

$$V_{12}(r) = V_{21}(r)$$

The Schrödinger Eq. is Hermitian

$$\text{Let } \left( -\frac{\hbar^2}{2\mu} \frac{d^2}{dr^2} + V_2(r) \right) \phi_0(r) = E_0 \phi_0(r) \quad (3)$$

where  $\phi_0(r)$  is a bound state of channel 2. Near the resonance  $E_0$ , we assume

$$\phi_2(r) = A \phi_0(r) \quad (4)$$

Then the coupled equations become

$$\left\{ \begin{aligned} \left( E + \frac{\hbar^2}{2\mu} \frac{d^2}{dr^2} - V_1(r) \right) \phi_1(r) &= A V_{12}(r) \phi_0(r) & (5) \\ A(E - E_0) \phi_0(r) &= V_{21}(r) \phi_1(r) & (6) \end{aligned} \right.$$

Define the Green function

$$\left( E + \frac{\hbar^2}{2\mu} \frac{d^2}{dr^2} - V_1(r) \right) G(r, r') = \delta(r - r') \quad (7)$$

Thus

$$\begin{aligned} \phi_1(r) &= \phi_{\text{reg}} + A \int G(r, r') V_{12}(r') \phi_0(r') dr' \\ &\quad \uparrow \\ &\quad \text{homogeneous solution} \\ &\quad \rightarrow N \sin(kr + \delta_{\text{bg}}) \\ &\quad \uparrow \text{normalization} \quad \downarrow \\ &\quad \text{background phase shift (without} \\ &\quad \text{the presence of channel 2)} \end{aligned} \quad (9)$$

Put (8) into (6) and take the dot product with  $\langle \phi_0 |$ , then

$$A = \frac{\langle \phi_0 | V_{12} | \phi_{\text{reg}} \rangle}{E - E_0 - \langle \phi_0 | V_{21} G V_{12} | \phi_0 \rangle} \quad (10)$$

The Green function can be constructed using regular and irregular solutions of the homogenous Eq.

$$G(r, r') = -\pi \begin{cases} \phi_{\text{reg}}(r) \phi_{\text{irr}}(r') & r < r' \\ \phi_{\text{reg}}(r') \phi_{\text{irr}}(r) & r > r' \end{cases} \quad (11)$$

↑  
need to work out

where  $\phi_{\text{irr}}(r) \xrightarrow{r \rightarrow \infty} N \cos(kr + \delta_{\text{bg}})$

From (8), for  $r \rightarrow \infty$ , we can use the lower expression in (11) for  $G(r, r')$ , then

$$\phi_1(r) = \phi_{\text{reg}} + \tan \delta \phi_{\text{irr}}(r) \quad (12)$$

$$\tan \delta = -\pi \frac{\langle \phi_0 | V_{21} | \phi_{\text{reg}} \rangle^2}{E - E_0 - \langle \phi_0 | V_{21} G V_{12} | \phi_0 \rangle} \quad (13)$$

The asymptotic form of (12) is proportional to

$$\phi_1(r) \xrightarrow{r \rightarrow \infty} \sin(kr + \delta_{\text{bg}} + \delta) \quad (14)$$

Put Eq.(13) in the form

$$\tan \delta = -\frac{\Gamma/2}{E - E_R} \quad (15)$$

Key results

[ energy shift	(16)
$E_R = E_0 + D = E_0 + \langle f_0   V_{21} G V_{12}   f_2 \rangle$	
$G = 2p \langle f_0   V_{21}   f_{\text{reg}} \rangle^2$	(17)
- width	

Equation (12) in the asymptotic region is not normalized. Rewrite it as

$$\begin{cases} \phi_1(r) = \cos \delta \phi_{\text{reg}}(r) + \sin \delta \Phi(r) & (18) \\ \text{where } \Phi(r) \text{ asymptotically goes to } \phi_{\text{irr}}(r) \text{ [see Eq.(12)]} & (19) \\ \phi_2(r) = \cos \delta \frac{\langle \phi_0 | V_{12} | \phi_{\text{reg}} \rangle}{E - E_R} \phi_0(r) & \end{cases}$$

Eq.(19) can be rewritten as [use (15) and (17)]

$$\phi_2(r) = -\frac{\sin \delta}{\pi \langle \phi_0 | V_{12} | \phi_{\text{reg}} \rangle} \phi_0(r) \quad (20)$$

Let the “internal channel functions” be  $\Psi_{\text{int}}^{(1)}$  and  $\Psi_{\text{int}}^{(2)}$ , then the total wavefunction is written as

$$\begin{aligned}\Psi_E &= [\cos \delta \phi_{\text{reg}} + \sin \delta \Phi(\mathbf{r})] \Psi_{\text{int}}^{(1)} + \Psi_{\text{int}}^{(2)} \phi_2(\mathbf{r}) \\ &= \cos \delta \phi_{\text{reg}}(\mathbf{r}) \Psi_{\text{int}}^{(1)} \\ &\quad - \frac{\sin \delta}{\pi \langle \phi_0 | \mathbf{V}_{12} | \phi_{\text{reg}} \rangle} \left[ \Psi_{\text{int}}^{(2)} \phi_0(\mathbf{r}) - \pi \langle \phi_0 | \mathbf{V}_{12} | \phi_{\text{reg}} \rangle \Psi_{\text{int}}^{(1)} \Phi(\mathbf{r}) \right]\end{aligned}\quad (21)$$

This shows that channel coupling is more than the coupling of the naked states, but the channel function  $\phi_0(\mathbf{r})$  is modified due to coupling with the open channels.

Equation (21) could be the final state of the photoabsorption. For example, the dipole transition matrix element with respect to the ground state  $|0\rangle$  can be obtained from

$$\begin{aligned}\mathbf{d}_E &= \langle \Psi_E | \bar{\mathbf{D}} | 0 \rangle \\ &= \mathbf{d}_1 \cos \delta - \mathbf{d}_2 \frac{\sin \delta}{\pi \langle \phi_0 | \mathbf{V}_{12} | \phi_{\text{reg}} \rangle}\end{aligned}\quad (22)$$

where  $\mathbf{d}_1$  and  $\mathbf{d}_2$  are clearly defined following (21).

The oscillator strength

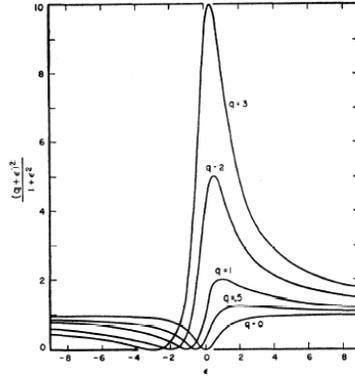
$$\frac{df}{dE} \square |\mathbf{d}_E|^2 = \left( \frac{df}{dE} \right)_0 \left( 1 - \frac{\mathbf{d}_2}{\mathbf{d}_1} \frac{\tan \delta}{\pi \langle \phi_0 | \mathbf{V}_{12} | \phi_{\text{reg}} \rangle} \right)^2 \cos^2 \delta \quad (23)$$

Define	$\varepsilon = \frac{E - E_R}{\Gamma/2}$	$q = \frac{\mathbf{d}_2}{\mathbf{d}_1 \pi \langle \phi_0   \mathbf{V}_{12}   \phi_{\text{reg}} \rangle}$	(24)
	reduced width	shape parameter	

Then

$$\frac{df}{dE} = \left( \frac{df}{dE} \right)_0 \frac{(\varepsilon + q)^2}{1 + \varepsilon^2} \quad (25)$$

The function  $F(q, \varepsilon) = \frac{(\varepsilon + q)^2}{1 + \varepsilon^2}$  is called Beutler-Fano profile



It describes the asymmetric shape of a resonance. Note that the energy away from the resonance  $E_R$  is measured in units of  $\Gamma/2$ . For  $q < 0$  it is just a reflection with respect to  $\varepsilon = 0$

Two limits:  $|q| \gg 0$  Lorentzian Shape  
 small  $q$  Window resonances

The discussion is for one bound state interacting with a single continuum channel. Generalization to more complicated one like one bound + two continuum ; one bound series + single continuum.

Note that the form (25) for the Feshbach resonance was first derived by Fano, Phys. Rev. 124, 1866 (1961) using a somewhat different method. The Fano profile can be seen in many different areas in physics. It is the second "two-channel" problems that we have encountered so far. In this case, it is one bound and one continuum channels.

In the following we will focus on the Feshbach resonances in He.

#### Additional remarks on Fano's resonance theory

If there is more than one background continuum interacting with one bound state, then the general formula for the resonance is

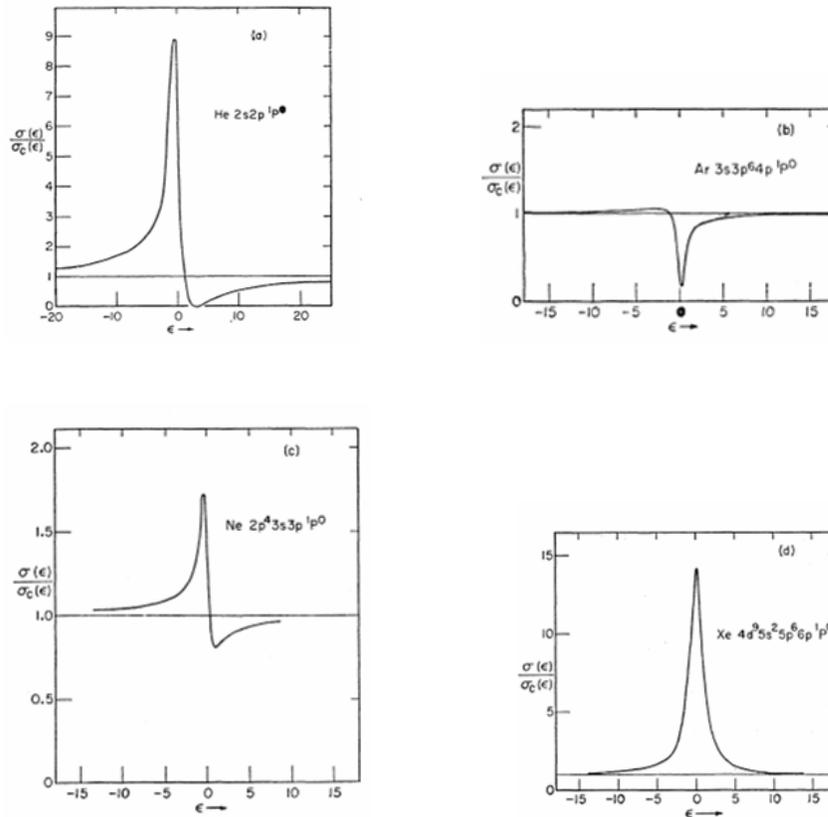
$$\sigma(E) = \sigma_c \left[ \rho^2 \frac{(q + \varepsilon)^2}{1 + \varepsilon^2} + 1 - \rho^2 \right]$$

where  $\rho$  measures the overlap between the continuum state that is generated by autoionization to the state generated by direct photoionization.

Here are examples of Fano resonances from the photoabsorption of rare gas atoms from earlier studies.

(a) He:  $q = -2.8$ ,  $\rho^2 = 1$ ; (b) Ar:  $q = -0.22$ ,  $\rho^2 = 0.86$ ;

(c) Ne:  $q = -2.0$ ,  $\rho^2 = 0.17$ ; (d) Xe:  $q = 200$ ;  $\rho^2 = 0.0003$ .



Many examples of Fano resonances occur in other areas of physics. You can search examples on the web.

### Note-13. Doubly excited states of He--experimental

#### 5. Examples from He photoabsorption

##### 5.1. Experimental spectra in the past half a century for $2lnl'$ states

(a) Photoabsorption spectra: The early days—60's through 80's with first generation synchrotron radiation

Madden and Codling, PRL 10, 516 (1963), Astrophys. Journal 141, 364 (1965).

Fig. 1. Schematics of He spectrum

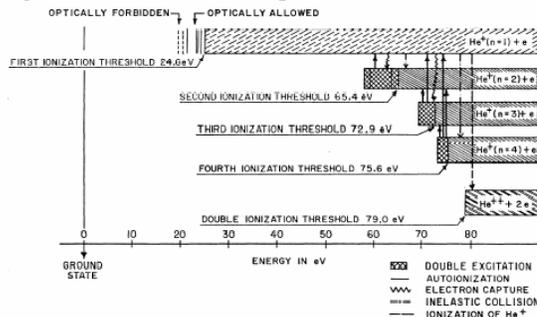
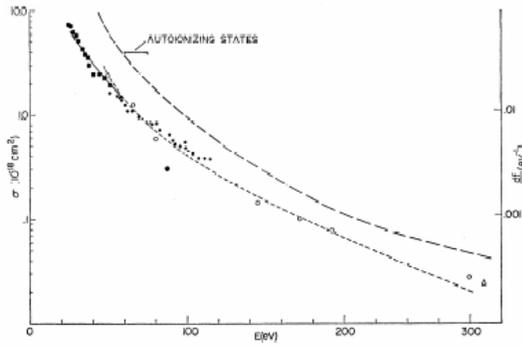


Fig.2. Global photoionization spectra of He



The 90's with third generation light sources

Domke et al, PRL 66, 1306 (1991); Domke et al PRL,1992;

Fig.3 Photoabsorption spectra—autoionizing region showing the + and – series of doubly excited states below the N=2 threshold of He<sup>+</sup>.

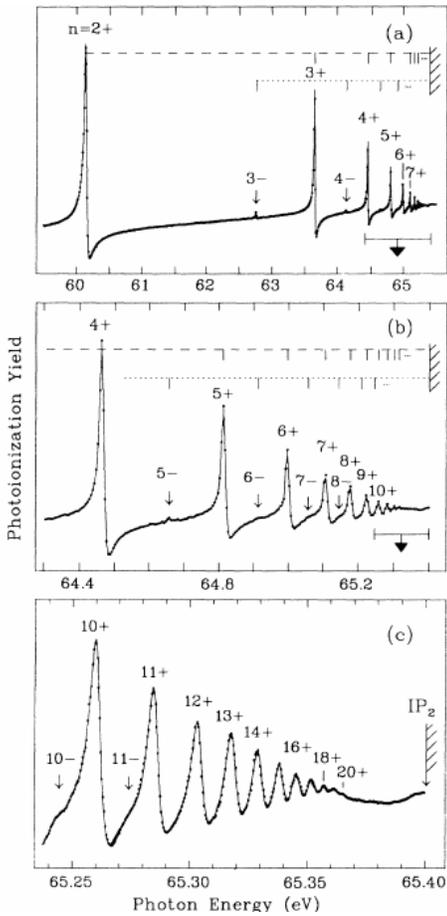
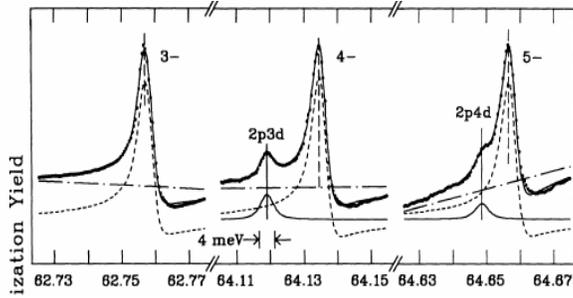


Fig.4. Experiment showing the “-” states and the “pd” states. Domke et al PRL,1992.



The highest resolution up to date: PRL 77, 3086 (1996).

Note that the 2p3d and the 4- states are now well separated. The energy resolution has now been improved to 1 meV from the 4 meV in the 1992 data. But even here the widths for the narrow resonances are due to the resolution of the instrument.

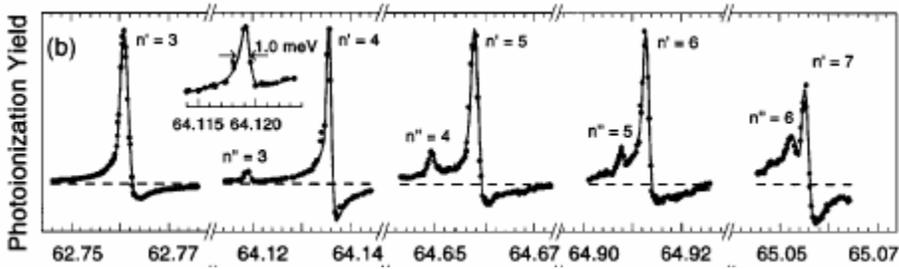


Fig.5. The pd series and the “-” series are now resolved.

**(b) What does the theory predict? –more details later**

**Doubly excited state properties of Helium from theoretical calculations.** From Rost et al, JPB30, 4663 (1997)

Data for  $^1P^o$  states below the  $He^+(N=2)$  threshold.

Note that (1) states have to be classified differently (2) the reduced decay width  $\Gamma^*$  is nearly constant along the series but they are very different for the three series (3) The q parameters are nearly the same.

(c) Radiative decay of these states: From PRL 84, 2598 (2000)

Table A1. Theoretical resonance parameter as defined in section 2 in atomic units converged to the given digits, 7.698e-05 stands for  $7.698 \times 10^{-05}$ .

$N, K$ $[N_1 N_2 m]^A$	$n$	$-E$	$\Gamma/2$	$v$	$\Gamma^*$	$(B^*)^2$	$q$	
2, 0 [001] <sup>+</sup>	2	0.693 134 920	6.866 25e-04	1.6090	5.7202e-03	2.38e-02	-2.77	
	3	0.564 085 188	1.505 94e-04	2.7932	6.5638e-03	2.10e-02	-2.58	
	4	0.534 363 144	6.417 3e-05	3.8145	7.1235e-03	2.15e-02	-2.55	
	5	0.521 504 666	3.289 8e-05	4.8219	7.3766e-03	2.17e-02	-2.54	
	6	0.514 733 994	1.899 8e-05	5.8254	7.5112e-03	2.19e-02	-2.53	
	7	0.510 726 795	1.192 6e-05	6.8273	7.5906e-03	2.19e-02	-2.52	
	8	0.508 158 54	7.96e-06	7.8285	7.6380e-03	2.25e-02	-2.58	
	9	0.506 413 84	5.59e-06	8.8293	7.6952e-03	2.24e-02	-2.5	
	10	0.505 175	4e-06	9.829	7.5966e-03			
	2, 1 [010] <sup>-</sup>	3	0.597 073 804	1.923e-06	2.2695	4.4958e-05	4.00e-04	-4.25
4		0.546 493 257	1.014e-06	3.2704	7.1522e-05	3.67e-04	-3.32	
5		0.527 297 770	4.91e-07	4.2798	7.6980e-05	3.83e-04	-3.31	
6		0.517 937 328	2.67e-07	5.2797	7.8589e-05	3.88e-04	-3.31	
7		0.512 679 987	1.60e-07	6.2795	7.9237e-05	3.80e-04	-3.32	
8		0.509 435 853	1.03e-07	7.2794	7.9460e-05	3.94e-04	-3.3	
9		0.507 294 315	6.8e-08	8.2793	7.7182e-05			
10		0.505 806 96	1.0e-07	9.2792	1.5979e-04			
2, -1 [100] <sup>-</sup>		3	0.547 092 709	5e-09	3.2584	3.4596e-07	9.29e-05	-23.4
		4	0.527 616 338	7e-11	4.2550	1.0785e-08	8.75e+00	-133
	5	0.518 118 268	1.7e-11	5.2532	4.9290e-09	8.66e-05	197	
	6	0.512 791 034	4.7e-11	6.2522	2.2973e-08	8.66e-05	91	
	7	0.509 508 462	4e-11	7.2515	3.0506e-08	8.65e-05	72	
	8	0.507 344 240	5e-11	8.2511	5.6174e-08			
	9	0.505 842 69		9.2509				
	10	0.504 759 0		10.250				

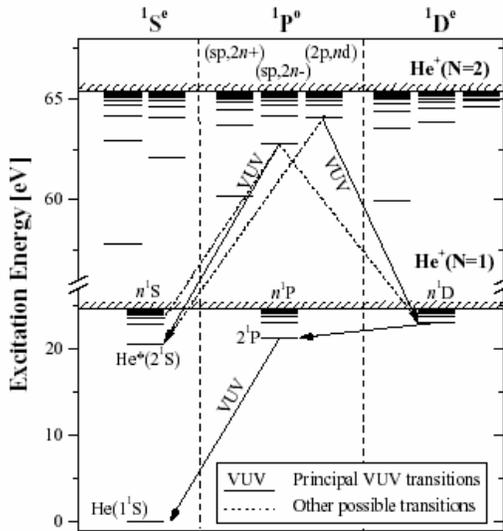


Fig.6. The radiative decay scheme for VUV photons and metastable atom yield.

Experimental results.

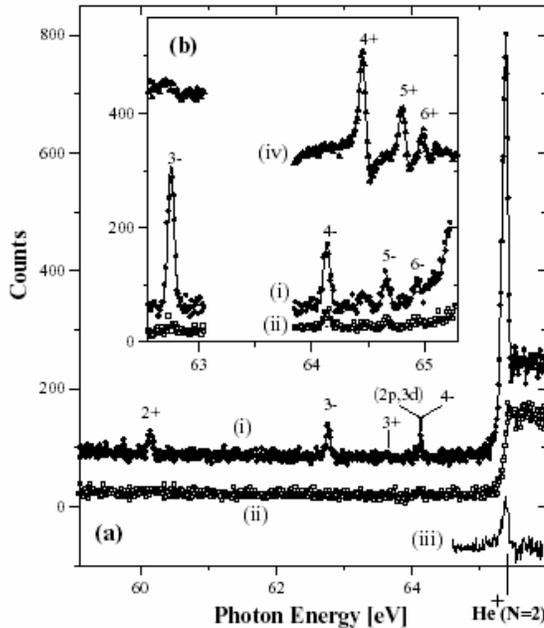


FIG. 2. Metastable atom (i), VUV photon (ii) and (iii), and photoelectron (iv) spectra in the energy region of doubly excited states converging on the  $\text{He}^+ (N = 2)$  ionization threshold. Short form notation is used where, e.g.,  $2+ = (sp, 22+)^1P^o$ . The photon spectrum (iii) is shown following subtraction of the signal arising from the VUV  $\text{He}^+ (2p \rightarrow 1s)$  transition. Spectra shown in (b) are of significantly improved statistical accuracy over those shown in (a). The metastable atom spectrum in (a) has been offset by 50 counts. The photoelectron yield in (b) has been divided by a factor of 15.

(Fig.7)

The “ $2p3d$ ” state has very small Auger width, it decays mostly by radiative transitions. The lifetime has been measured to be  $190 \pm 30$  ps (Phys. Rev. Lett. **90**, 153004 (2003) which is to be compared to the  $2p \rightarrow 1s$  lifetime of 100ps for  $\text{He}^+$ . (The dipole allowed spontaneous radiative rate goes like  $Z^4$  and remember for hydrogen the  $2p$  lifetime is 1.6 ns?). According to C. Liu *et al*,

[Phys. Rev. A 64, 010501 \(2001\)](#), the lifetime of this state is due to the radiative channel rather than by the Auger process. It was calculated to be 207ps.

(d) Observation of triplet states. See PRL 86, 2758, (2001).

Note that triplet states are observed in the radiative channels. These observations show the violation of LS-coupling and made possible only because the intense photon sources that became available recently

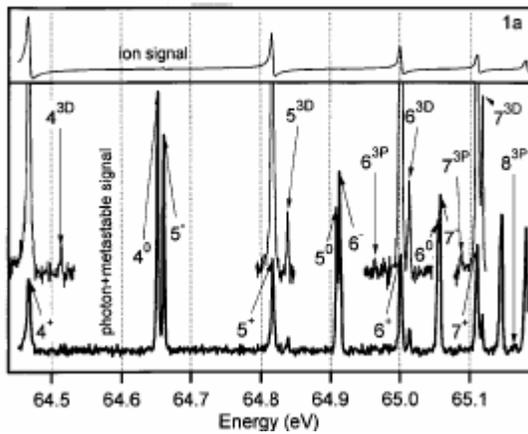


Fig.8. The triplet states can be observed in the photon channel.

(e) Other singlet states can be observed by photoabsorption in a DC electric field PRL 90, 133002 (2003).

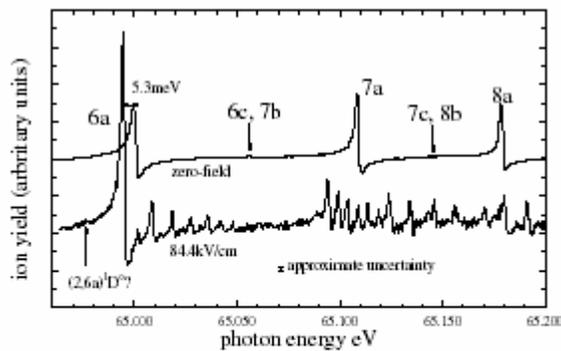


FIG. 2. Photoion spectrum at zero field and with an applied field of 84.4 kV/cm in the region of excitation to the 6a, 7a, and 8a states. Scales and offsets are chosen for maximum clarity. Some saturation is visible in the zero-field spectrum; see text. The statistical uncertainty of the high-field data is shown.

(Fig.9)

We have provided a theoretical interpretation of these data, Tong and Lin PRL92, 223003 (2004).

(see <http://www.phys.ksu.edu/~cdlin/research/pauli.html> for correlation in singly excited states)

## 6. Theoretical models for doubly excited states

The basis for describing singly excited states of helium, as we have discussed earlier, is based on the independent electron model or the shell model. According to this model, double photoabsorption from the ground state  $1s^2\ ^1S^0$  of helium will result in three Rydberg series,  $2snp$ ,  $2pns$  and  $2pnd$  ( $^1P^0$ ). To begin with, these states are not populated by the electric dipole operator if these designations are correct (why?). The experiment of Madden and Codling in 1965 observed only one dominant series, with a weak one and a third series was missing completely. This observation prompted Fano and coworkers to raise the issue that the shell model fails completely for doubly excited states and a new theoretical framework and a new set of approximate quantum numbers are needed to describe these doubly excited states.

### A. The classification of $2\ell n\ell'$ doubly excited states

It was clear from the beginning to Fano and coworkers that  $2snp$ ,  $2pns$  and  $2pnd$  designations are inappropriate. These states are degenerate when the e-e interaction is neglected. They suggested that a better designation is  $2snp+2pns$ , or the “+” series,  $2snp-2pns$ , or the “-“ series and the  $2pnd$  or “pd” series. The “+” series is the one that was observed, the “-“ series is the one that was barely observable and the “pd” series was not seen at all. From perturbation theory this is obvious but the contribution of Fano et al was to provide it with a “physical” interpretation. For the “+” series, the two electrons perform motion akin to the symmetric radial “vibration” with respect to the nucleus. Thus the two electrons have the chance of approaching the nucleus together and leaving from it together. When the two electrons reaches near the nucleus together, it would interact via e-e interaction and the energy exchange between the two electrons results in autoionization. Thus the “+” states have larger Auger widths. For the “-“ states their radial motion is out of phase and they have less e-e interaction and thus are more stable. For the “pd” states they hardly approach each other and thus they have the smallest widths.

Note that in this connection, the autoionization widths are viewed as a consequence of having both electrons approaching the nucleus together. This concept is not in the shell model. Thus a new theoretical basis is needed.

### B. Theoretical and Computational methods for doubly excited states

#### Computational methods

One can separate all the theoretical methods in the literature into these general frameworks. Let us understand the very basic.

#### b.1. The configuration interaction approach—

The continuum part is not considered. Use basis functions of your choice and then diagonalize the whole Hamiltonian. This is like a bound state problem.

#### b.2. The complex coordinate rotation approach-

Replace the real radial coordinate  $r$  by  $re^{i\theta}$  and then diagonalize the resulting complex Hamiltonian. Change the rotation angle  $\theta$  till the complex eigenenergies are converged. The real part is the resonance energy and the imaginary part gives the total half width.

#### b.3. The close-coupling (CC) method

Expand the total wavefunction in the form

$$\Psi(\vec{r}_1, \vec{r}_2) = A \sum F_i(r_1) \Phi_i(\hat{r}_1, \hat{r}_2)$$

where  $A$  is the antisymmetrization operator,  $F_i$  is the radial function of the outer electron and  $\Phi_i(\hat{r}_1, \hat{r}_2)$  is the channel functions including the angular variables of the inner electron. Plug this

expansion into the time-independent Schrodinger equation would result in a set of coupled integrodifferential equations similar to the Hartree-Fock form. The expansion is often truncated to a few terms. The wavefunctions in  $\vec{r}_2$  coordinates are called target functions. Thus a five-state close coupling calculation includes 5 target states (do not count the m-degeneracy). If one obtains the target wavefunction in a finite space then the continuum states are discretized. They are the pseudostates which have positive energies. These states can be viewed as a wavepacket.

The CC method is general and can be used to obtain scattering solutions like the phase shifts or the resonances.

#### b.4. The R-matrix method

This method separates the whole space into the inner region and the outer region. In the inner-region one can solve the problems like the bound states. The solutions are then matched to the solutions in the outer region which are known analytically. This allows a very efficient method to trace out the theoretical spectra. In the inside region one can do the problem using basis sets like the CI method or the CC method. This allows an efficient method to solve the problem over a broad energy regime. In the resonance region the whole spectrum is traced out.

#### b.5. The grid method

The grid method in general would expand  $\Psi(\vec{r}_1, \vec{r}_2) = A \sum F_i(r_1, r_2) \Phi_i(\hat{r}_1, \hat{r}_2)$  where

$\Phi_i(\hat{r}_1, \hat{r}_2)$  is the coupled orbital angular momentum of the two electrons. Using discretized  $r_1$  and  $r_2$ , or with B-spline functions or the finite-element method, we would end up with equations that are quite large. This method is not widely used since the computing load is still too heavy.

These approaches can be used to obtain accurate wavefunctions but do not provide new conceptual interpretations of doubly excited states

### Theoretical Methods

#### b.6. The group theoretical approach—approximate quantum numbers K, T

Mathematically this is equivalent to a limited CI calculation by keeping only basis functions (or eigenstates) to within the same degenerate hydrogenic basis functions. Instead of diagonalizing the full Hamiltonian, one diagonalizes  $B^2 = (\vec{b}_1 - \vec{b}_2)^2$  and  $(\vec{L} \bullet \vec{r}_{12})$  exactly within the (N,n) manifold, where  $\vec{b}_i$  is the Runge-Lenz vector of electron i and  $\vec{r}_{12}$  is the vector joining the two electrons. The eigenstates, obtained semi-analytically, are

$$|(Nn)KT^2S^+1L^\pi\rangle = \sum_{i,i'} |Nl, nl'; 2S^+1L^\pi\rangle D_{Ni,ni'}^{KTL^\pi},$$

where

$$D_{Ni,ni'}^{KTL^\pi} = (-)^{l'} [(P+T+1)(P-T+1)(2l+1)(2l'+1)]^{1/2} \times \begin{pmatrix} \frac{1}{2}(N-1) & \frac{1}{2}(n-1) & \frac{1}{2}(P+T) \\ \frac{1}{2}(N-1) & \frac{1}{2}(n-1) & \frac{1}{2}(P-T) \\ l & l' & L \end{pmatrix} M(T, \pi). \quad (3)$$

where  $P=n-1+K$ . For the details, see PRA 11,97 (1975). The key point here is that two new quantum numbers K and T are introduced. Each state is now labelled by  $|nNKT\rangle$  in addition to the L, S and  $\pi$  quantum numbers. Note that the “shells” n and N are still used and K and T replace the original orbital angular momentum of each electron. The next job is to understand what is the physical meaning of K and T.

Recall that the Runge-Lenz vector  $\vec{b}$  is proportional to the average of the dipole moment  $\langle \vec{r} \rangle$ , one can see approximately that  $B^2$  is a measure of the average of  $\vec{r}_{12}$ . More rigorous analysis shows that K is a measure of the average of the angle of the two electrons with respect to the nucleus, and T is a projection of the total angular momentum L along the line between the two electrons. Thus if K and T are good quantum numbers then the inter-electronic axis is like the internuclear axis of a diatomic molecule, or one of the principal axes of an YXX linear molecule. Thus doubly excited states of an atom are more like a molecule, than what the shell model would imply. These initial understanding also lead to the next two models of doubly excited states.

#### b.7. The molecular YXX model—bending vibrational motion

#### b.8. The $H_2^+$ model

These models provide qualitative models for the motion of electrons but do not provide a means to perform accurate quantitative calculations.

### C. Unified Approach: The hyperspherical (HS) approach.

The hyperspherical approach provides conceptual and computational methods for treating any three-body systems. I will introduce this subject briefly and you should consult original papers for more complete description.

#### C1. The coordinates and the adiabatic expansion

For helium atom, it is very simple. Replace  $r_1$  and  $r_2$  by

$$R = \sqrt{r_1^2 + r_2^2} \quad \text{and} \quad \tan \alpha = \frac{r_2}{r_1}$$

where R is called the hyperradius and  $\alpha$  is the hyperangle. The other spherical angles are retained. Thus in hyperspherical coordinates, there is only one radial distance and the rest are all angles, called  $\Omega$  for simplicity. In HS approach, one does not talk about each electron separately. An idea similar to the Born-Oppenheimer approximation is to treat R as an adiabatic parameter, thus the two-electron wavefunction is expanded as

$$\psi(R; \Omega) = \sum_{\mu} F_{\mu}(R) \Phi_{\mu}(R; \Omega).$$

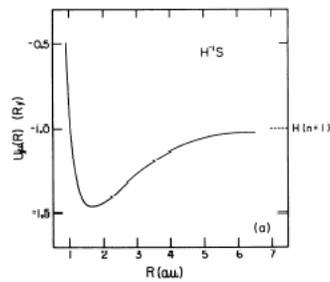
where

$$\begin{aligned} & \left[ \left( \frac{d^2}{dR^2} + \frac{1/4}{R^2} + 2E \right) \underline{\mathbb{I}} - \underline{\mathbb{U}}(R) + \underline{\mathbb{W}}(R) \right] \underline{\mathbb{F}}(R) = 0 \\ U_{\mu, \nu}(R) &= \frac{1}{R^2} \left( \Phi_{\mu}(R; \Omega) \left| -\frac{d^2}{d\alpha^2} + \frac{\mathbb{I}_1^2}{\cos^2 \alpha} + \frac{\mathbb{I}_2^2}{\sin^2 \alpha} - RC \right| \Phi_{\nu}(R; \Omega) \right), \\ W_{\mu, \nu}(R) &= 2 \left( \Phi_{\mu}(R; \Omega), \frac{d}{dR} \Phi_{\nu}(R; \Omega) \right) \frac{d}{dR} \\ & \quad + \left( \Phi_{\mu}(R; \Omega), \frac{d^2}{dR^2} \Phi_{\nu}(R; \Omega) \right). \end{aligned}$$

These expressions are similar to the BO expansion. The U's are the adiabatic potential curves and W are the nonadiabatic coupling matrix elements. At large R where one electron is far away from the other, the potential curves should approach the eigenstates of  $He^+$  which are known exactly.

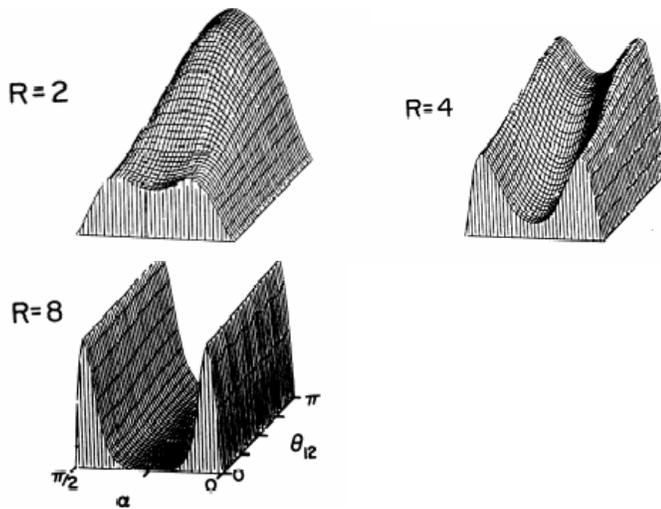
#### C2. The potential curves and channel functions—the lowest curve

The examples below are for  $H^-$  which is isoelectronic to He. Consider  $^1S^e$ , we obtain the lowest potential curve as below



If you solve this potential curve to find the bound state energy, you get almost the right ground state energy. Note that in the Hartree-Fock theory, it predicts no bound states for  $H^-$ .

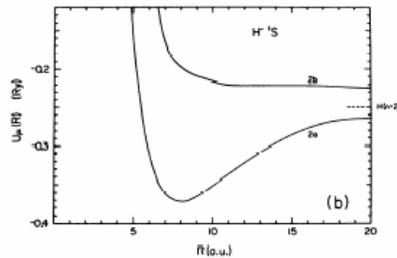
One can get information about the distributions of the two electrons by looking at  $|\Phi(R; \alpha, \theta)|^2$  where  $\theta$  is the angle between the two electrons with respect to the nucleus.



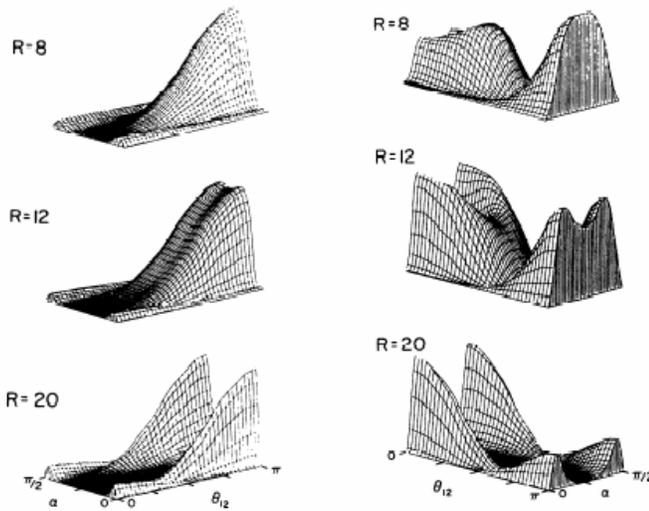
This shows how the “channel functions” evolve smoothly as  $R$  increases, confirming the adiabatic nature.

### C3. The doubly excited states

There are two curves, so two sets of eigenenergies converging to the  $H(N=2)$  limit.



Here are the “channel functions” look like.



Note that the two-electron density peaks near  $\theta = \pi$  on the left column and near  $\theta = 0$  on the right.

#### C4. Fully classification

With these introductions now you are ready to read this paper **C.D. Lin, Phys. Rev. A29, 1019 (1984)** where the classification of doubly excited states are first made completely.

#### C5. Hyperspherical close-coupling method

A practical way to obtain accurate predictions.

### D. General three-body systems

D1. Coulomb systems: From  $H$ ,  $Ps^-$  to  $H_2^+$ , muonic systems, antiprotonic systems

D2. Helium trimers and molecular systems; three-body recombinations; ion-atom collisions

### note-15. Many-electron atoms-1

#### 1. The hierarchy of approximate description of an atom

No one will ever tries to solve the structure of an atom exactly. The description of an atom or a many-body system requires different degrees of approximations, depending on the problems on hand.

Based on  $H$  and  $He$ , one can write down the approximate Hamiltonian of a many-electron system according to the relative magnitudes of the interactions seen by the electron:

(a) Coulomb interactions

$$H = \sum_i \left( -\frac{1}{2} \nabla_i^2 - \frac{Z}{r_i} \right) + \sum_{i>j} \frac{1}{r_{ij}} \quad (1)$$

(b) Spin-orbit interactions

(c) spin-spin, other relativistic corrections, mass polarization; QED effects

The first part of the effort is to solve eq. (1). This is already a monumental task. The approximate solution of (1) can be expressed as

$$\Psi_\alpha = \Psi_\alpha(1,2,\dots,N) \quad (2)$$

where the index  $i=1, \dots, N$  indicates the position and spin of the electron  $i$ . The total wavefunction should be constructed such that it is an eigenstate of  $L^2$ ,  $S^2$  and parity. The wavefunction should also be antisymmetric under the interchange of any two electrons. Once (2) is obtained, the inclusion of the smaller interactions (b) and (c) is done using first order perturbation theory. Of course it is understood that degenerate or near-degenerate perturbation theory will be used when there are states that are very close to each other in energies.

## 2. The central field approximation

If one approximates

$$\sum_{i>j} \frac{1}{r_{ij}} \rightarrow \sum_i S_i(r_i) \quad (3)$$

Then Eq. (1) is separable and each electron sees a central field potential

$$V(r) = -Z/r + S(r) \quad (4)$$

In this approximation,  $S(r_i)$  is the effective central potential on electron  $i$  by all the other  $(N-1)$  electrons.  $S(r)$  describes the screening effect.

Clearly the effective central field potential has the properties:

$$\begin{aligned} V(r) &\rightarrow -Z/r \quad \text{for } r \rightarrow 0 \\ V(r) &\rightarrow -(Z - N + 1)/r \quad \text{for } r \rightarrow \infty \end{aligned} \quad (5)$$

where  $N$  is the number of electrons in the atom or ion.

With the effective potential  $V(r)$ , the Hamiltonian  $H$  can be written as

$$H = \sum_i \left[ -\frac{1}{2} \nabla_i^2 + V(r_i) \right] + H_1 = H_c + H_1 \quad (6)$$

The expression for  $H_1$  is easily written down. Now that  $H_c \Psi_c = E_c \Psi_c$  is clearly separable and can be expressed as

$$\Psi_c = \pi_{i \in N} \{ \phi_{\alpha_i}(i) \} \quad (7)$$

where  $\alpha_i$  is the quantum number representing the spin-orbital of electron  $i$ . Clearly  $\alpha \equiv (n, \ell, m_\ell, m_s)$  for each electron.

The solution of (7) is still not correct since antisymmetry is not imposed yet. There are a few more steps:

(i) Pauli exclusion principle: construct the Slater determinant, see (8.22) and (8.23) of BJ.

(ii) Eigenstates of  $L^2$  and  $S^2$ . To do this, one has to take the linear combination of the Slater determinants like (8.22) or (8.23) such that they are eigenstates of  $L^2$  and  $S^2$ . The linear combination sums over the magnetic substates only. Note that the parity is a good quantum number but it is decided by  $\pi = (-1)^{\sum \ell_i}$  and it is even or odd.

After all these steps, we now have eigensolutions of  $H_c$  which are also eigenstates of  $L^2$ ,  $S^2$ ,  $L_z$ ,  $S_z$ , and parity. The electronic configuration is given by the collection of  $\{ n_i \ell_i \}$  of all the  $N$  electrons.

Using  $\Psi_c$  one can use the first order perturbation  $\langle \Psi_c | H_1 | \Psi_c \rangle$  to obtain the energy of each state for the different possible  $L$  and  $S$ . Note that this procedure is very similar to what we did for the two-electron atoms. At this level the wavefunctions are written as  $\Psi_c = | n_1 \ell_1, n_2 \ell_2, \dots, {}^{2S+1}L \rangle$ . For example, the ground state of Be is  $| 1s^2 2s^2 {}^1S^e \rangle$ , and an excited state is  $| 1s 2s^2 4p {}^3P^o \rangle$ . The latter is said to have a hole in the K-shell. Note that parity is specified once the orbital angular momentum of each electron is specified.

Note that the procedure is just a simple extension of what we did for the two-electron atom.

Some terminologies used:

The set  $\{n_1\ell_1, n_2\ell_2, \dots\}$  is called the **configuration**.

Each fixed L and S from the given configuration is a **term**.

Once the spin-orbit interaction and other small terms are included, each term is splitted into **multiplets of different J's**.

The wavefunction we have constructed so far is based on the central field approximation, and the eigenstate of an atom is approximately represented by  $\Psi_c = |n_1\ell_1, n_2\ell_2, \dots, {}^{2S+1}L\rangle$ , where the approximate quantum numbers  $|\alpha\rangle = |n_1\ell_1, n_2\ell_2, \dots, {}^{2S+1}L\rangle$  are to be used to **designate** exact eigenstates of the atom.

The configuration and the term of the ground states of neutral atoms are given in Table 8.3 of BJ. For the excited states one has to refer to the data on the NIST website.

### 3. The Hartree-Fock method and the self-consistent field

(I have skipped the Thomas-Fermi model)

In the central-field approximation, we talked about a central-field potential  $S(r)$  which has not yet been defined. In principle, it is possible to define any  $S(r)$ , so long that the remaining  $H_1$  is taken into account later. On the other hand, the "next" step in general is very complicated, thus one would like to have the "best"  $S(r)$  available. Thus the  $S(r)$  has to be obtained variationally-- this is the idea behind the Hartree-Fock method.

In the Hartree-Fock method, the wavefunction is expected to be expressed as a Slater determinant. We can write it as a trial wavefunction

$$\Phi(q_1, q_2, \dots, q_N) = \frac{1}{\sqrt{N!}} \sum_P (-1)^P P u_\alpha(q_1) u_\beta(q_2) \dots u_\nu(q_N) \quad (8)$$

where P is the permutation operator of the N identical particles. Using the Hamiltonian (1), we want to vary the u's such that the expectation value  $\langle \Phi | H | \Phi \rangle$  is a minimum, under the constraint that the orbitals u's are orthogonal to each other.

Write

$$H = H_1 + H_2$$

where  $H_1$  includes only the one-electron operator, and  $H_2$  is the total electron-electron interaction. One can show that

$$\langle \Phi | H_1 | \Phi \rangle = \sum_\lambda I_\lambda$$

and 
$$\langle \Phi | H_2 | \Phi \rangle = \frac{1}{2} \sum_\lambda \sum_\mu (J_{\lambda\mu} - K_{\lambda\mu})$$

where I, J, K are defined by

$$I_\lambda = \langle u_\lambda(q_i) | \hat{h}_i | u_\lambda(q_i) \rangle$$

$$J_{\lambda\mu} = \left\langle u_\lambda(q_i) u_\mu(q_j) \left| \frac{1}{r_{ij}} \right| u_\lambda(q_i) u_\mu(q_j) \right\rangle$$

$$K_{\lambda\mu} = \left\langle u_\lambda(q_i) u_\mu(q_j) \left| \frac{1}{r_{ij}} \right| u_\mu(q_i) u_\lambda(q_j) \right\rangle$$

The idea is that one varies  $u$ 's with the constraint of orthogonality  $\langle u_i | u_j \rangle = \delta_{ij}$ , and thus one obtains the **Hartree-Fock integro-differential equations**

$$\left[ -\frac{1}{2} \nabla_{\mathbf{r}_i}^2 - \frac{Z}{r_i} \right] u_\lambda(\mathbf{q}_i) + \left[ \sum_{\mu} \int u_\mu^*(\mathbf{q}_j) \frac{1}{r_{ij}} u_\mu(\mathbf{q}_j) d\mathbf{q}_j \right] u_\lambda(\mathbf{q}_i) - \sum_{\mu} \left[ \int u_\mu^*(\mathbf{q}_j) \frac{1}{r_{ij}} u_\lambda(\mathbf{q}_j) d\mathbf{q}_j \right] u_\mu(\mathbf{q}_i) = E_\lambda u_\lambda(\mathbf{q}_i),$$

$\lambda, \mu = \alpha, \beta, \dots, \nu$

Since the spin part of the spin-orbital for each  $u$  is known, one can obtain the HF equation for the spatial orbitals,

$$\left[ -\frac{1}{2} \nabla_{\mathbf{r}_i}^2 - \frac{Z}{r_i} + \sum_{\mu} V_{\mu}^d(\mathbf{r}_i) - \sum_{\mu} V_{\mu}^{\text{ex}}(\mathbf{q}_i) \right] u_\lambda(\mathbf{q}_i) = E_\lambda u_\lambda(\mathbf{q}_i)$$

where the direct and exchange potentials are given by

$$\begin{aligned} V_{\mu}^d(\mathbf{q}_i) &= \int u_{\mu}^*(\mathbf{q}_j) \frac{1}{r_{ij}} u_{\mu}(\mathbf{q}_j) d\mathbf{q}_j \\ &= \int u_{\mu}^*(\mathbf{r}_j) \frac{1}{r_{ij}} u_{\mu}(\mathbf{r}_j) d\mathbf{r}_j \equiv V_{\mu}^d(\mathbf{r}_i) \\ V_{\mu}^{\text{ex}}(\mathbf{r}_i) f(\mathbf{r}_i) &= \left[ \int u_{\mu}^*(\mathbf{r}_j) \frac{1}{r_{ij}} f(\mathbf{r}_j) d\mathbf{r}_j \right] u_{\mu}(\mathbf{r}_i) \end{aligned}$$

Once the HF wavefunctions are obtained, the total energy is

$$E_{\text{HF}} = \langle \Phi_{\text{HF}} | H | \Phi_{\text{HF}} \rangle$$

The orbital energy corresponding to the HF orbital  $u_\lambda$  is given by

$$E_\lambda = I_\lambda + \sum_{\mu} [J_{\lambda\mu} - K_{\lambda\mu}]$$

Sum over the orbital energies,

$$\sum_{\lambda} E_\lambda = \sum_{\lambda} I_\lambda + \sum_{\lambda} \sum_{\mu} [J_{\lambda\mu} - K_{\lambda\mu}] = E_{\text{HF}} + \langle \Phi_{\text{HF}} | H_2 | \Phi_{\text{HF}} \rangle$$

You need to pay attention to the last equality. Thus the total HF energy is not the sum of all the HF orbital energies.

If we assume that the orbitals and the orbital energies do not change for taking an electron out, then

$$E_N - E_{N-1} = I_\lambda + \sum_{\mu} [J_{\lambda\mu} - K_{\lambda\mu}] = E_\lambda$$

Thus  $E_i$  is the energy required to remove the electron from the  $i$ -orbital. This is known as the **Koopman's theorem**. This relation is approximately correct only since the orbitals will change somewhat in general after an electron is removed.

### Hartree-Fock Potentials

Since the angular part and the spin part of a spin-orbital are well-known functions, use

$$u_\lambda = \frac{1}{r} P_{n\ell}(r) Y_{\ell m}(\theta, \phi) \chi_{1/2, m_s}$$

We can reduce the HF equations to a set of coupled integro-differential equations in  $r$  for the radial wavefunctions. In this equation the first term is the direct potential, and the second term is the exchange potential. BJ has worked out an example of the coupled radial HF equations for the ground state of Be, for example,

$$\left[ -\frac{1}{2} \frac{d^2}{dr^2} + \frac{l(l+1)}{2r^2} - \frac{4}{r} + V_{1s}^d(r) + 2V_{2s}^d(r) - V_{2s}^{ex}(r) \right] P_{1s}(r) = E_{1s} P_{1s}(r)$$

$$\left[ -\frac{1}{2} \frac{d^2}{dr^2} + \frac{l(l+1)}{2r^2} - \frac{4}{r} + V_{2s}^d(r) + 2V_{1s}^d(r) - V_{1s}^{ex}(r) \right] P_{2s}(r) = E_{2s} P_{2s}(r)$$

**Additional comments:**

- (1) The present derivation includes one Slater determinant only, thus it works for the closed-shell atom or one-electron outside a closed shell.
- (2) For open-shell atoms, the trial function should be constructed such that they are eigenstates of  $L^2$  and  $S^2$ . Since the number of radial wavefunctions remain the same, the dimension of the coupled radial HF equations remains the same, but the effective direct and exchange potentials will depend on  $L$  and  $S$ .
- (3) The coupled radial wavefunctions can be solved using “Slater orbitals”, see BJ 398. The exponents of the Slater orbitals and the mixing coefficients are obtained variationally. They can also be obtained numerically.
- (4) One can implement configuration interaction wavefunctions following the procedure of HF to obtain multi-configuration HF method. The latter would give much better wavefunctions and total energy.
- (5) If the exchange is not imposed, one obtain the **Hartree equations**.

**note-16--**

**4. Corrections to the central field approximation**

(i) Even with the Hamiltonian given by (1), the central field approximation is not exact. There are many different approaches that can go beyond the central field approximation. Methods used for two-electron atoms, such configuration interaction, many-body perturbation theory, and close-coupling method and R-matrix method have been used. There are big packages for such calculations.

(ii) inclusion of the spin interactions

The dominant spin-orbit interaction can be written as

$$H_2 = \sum_i \xi(r_i) \vec{\ell}_i \cdot \vec{s}_i \tag{1}$$

where

$$\xi(r_i) = \frac{1}{2m^2 c^2} \frac{1}{r_i} \frac{dV(r_i)}{dr_i} \tag{2}$$

Note that one can prove that contribution to  $H_2$  is zero from closed-shell orbitals. Thus one needs to consider (1) for open-shell electrons only.

**LS-coupling scheme:**

*(1) equivalent and non-equivalent electrons*

For the open-shell atoms, the allowed values of L (and S) can be calculated by adding all the orbital (spin) angular momentum of each of the electrons successively. However, due to the Pauli exclusion principle, the angular momentum addition involving equivalent electrons is more complicated.

For the equivalent electrons you can work out the allowed L and S followed the example of Table 8.7 of BJ, but the process is tedious. For p and d electrons, the results are given in Table 8.8 of BJ. The situation for the d electrons becomes very complicated for  $d^3$ ,  $d^4$  and  $d^5$ . Note that in these latter cases, the final L and S are not enough. An additional quantum number, called **seniority**, is needed. The integers in Table 8.8 are the seniority. Note that the allowed L and S are identical whether you have n extra electrons or n holes for a given  $n\ell$  subshell.

**(2) The Hund's rules:**

The relative energy levels for the different L and S for a given configuration of equivalent electrons in general satisfy the Hund's rules:

*The term with the largest S is lowest. For the same S, the term with the larger L is lower.*

Fine structure of terms in L-S coupling. Multiplet splitting and the Lande's interval rule

For each L and S, the spin-orbit interaction splits the term energies into different J levels—forming a multiplet. The spin-orbit interaction for a given term can be written as

$$\langle \gamma LS | H_2 | \gamma LS \rangle = A \langle \gamma LS | \vec{L} \cdot \vec{S} | \gamma LS \rangle = \frac{1}{2} A [J(J+1) - L(L+1) - S(S+1)] \quad (3)$$

Using this relation

$$E(J) - E(J-1) = AJ \quad (4)$$

This is the Lande' interval rule.

If A is positive, according to the above equation, higher J will have higher energy and the energy separation between two neighboring levels is proportional to the J of the upper level.

It is empirically shown that if the shell is more than half-filled then the fine structure level is inverted.

jj-coupling (omitted)

Problem 23:

- (1) Enumerate the possible L and S of the  $2s2p3p$  configuration.  
Find the possible L and S for the  $2p^23p$  configuration.
- (2) Go to the web to look for the mean term energy ( $\langle E \rangle$  = weighted averaged of  $E_J$ ) of the ground state configuration of C, N, O atoms and confirm that the terms do satisfy the Hund's rule.
- (3) Go to the web to find out the mean energy levels of the  $2\ell 2\ell' 2\ell''$  intrashell states of O IV. The convention for atoms is that the neutral oxygen is written as O I. Thus O IV is  $O^{3+}$ . Intrashell states mean that the principal quantum numbers of the open shell orbitals are identical. Thus the possible configurations in this case is  $2s^2 2p$ ,  $2s 2p^2$  and  $2p^3$ . Find out all the possible L and S for each configuration (you can even just look them up) and the mean energies of all these states according to the configurations. Check if the Hund's rules are satisfied for the  $2p^3$ .

Follow the example of Fig. 5 of Morishita and Lin, J. Phys. B31, L209 (1998) and order the energy levels you found in the similar way. The energy pattern in this new ordering show the rotational level structure of a symmetric top. ( Will be further discussed briefly in the class.)

(4) In the class we talked about the Lande interval rule, and we have said " It is empirically shown that if the shell is more than half-filled then the fine structure level is inverted." Check this statement by looking at the fine-structure energy levels of  $1s^2 2s 2p^3 P_1$  of Be. Check the same for the term  $1s^2 2s^2 2p^5 ^2 P$  of Ne II.

## 5. Density Function Theory

The HF theory described in this chapter can in principle be extended to large systems like molecules and solids. However, as the systems become large, the HF method is too complicated. It is desirable to be able to replace the many-electron problem by an exactly equivalent set of self-consistent one-electron equations. This is the idea behind the Density Function Theory (DFT).

The DFT was first started by Hohenberg and Kohn who proved that the total energy of a system in the ground state including that of the many body effects of electrons (exchange and correlation) in the presence of static external potential (for example, the atomic nuclei) is a **unique functional** of the charge density. The minimum value of the total energy functional is the ground state energy of the system. The electronic charge density which yields this minimum is then the exact single particle ground state energy.

For a many-electron system with known wave function  $\Phi(1,2,3\dots N)$ , the charge density is defined by

$$\rho(\vec{r}) = \int d\vec{r}_2 d\vec{r}_3 \dots d\vec{r}_N |\Phi(1,2,\dots N)|^2 \quad (5)$$

It was then shown by Kohn and Sham<sup>[29]</sup> that it is possible to replace the many electron problem by an exactly equivalent set of self consistent one electron equations. The total energy functional can be written as a sum of several terms:

$$E[\rho(\vec{r})] = \int d\vec{r} U(\vec{r})\rho(\vec{r}) + \frac{1}{2} \int \frac{\rho(\vec{r})\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r} d\vec{r}' + T[\rho(\vec{r})] + E_{xc}[\rho(\vec{r})] \quad (6)$$

for a fixed set of atomic nuclei. In this equation,  $U(\mathbf{r})$  is the "external" potential. In the case of atoms, this is just the electron-nucleus interaction. The second term is the electron-electron interaction. The T term is supposedly the kinetic energy term and the last term gives the many-body effect, including exchange and correlation. The functional for T and the last exchange-correlation terms are not known and various approximations have been proposed and used.

Following the work of Kohn and Sham, if the N-electron system is represented by single electron orbitals  $u_i(\vec{r})$ , the single electron density of the system is given by

$$\rho(\vec{r}) = \sum_{i=1}^N |u_i(\vec{r})|^2 \quad (7)$$

and the expectation value of the kinetic energy is

$$T[\rho] = \sum_{i=1}^N \int d\vec{r} \frac{1}{2} |\nabla_{\vec{r}} u_i(\vec{r})|^2 \quad (8)$$

Note that the true kinetic energy operator cannot be written in this way. Minimizing (6) with respect to  $\rho$  one can obtain the **Kohn-Sham equation**

$$\left[-\frac{1}{2}\nabla^2 + V_{eff}(\vec{r})\right]u_i(\vec{r}) = E_i u_i(\vec{r}) \quad (9)$$

where  $E_i$  is the Lagrange multiplier ensuring normalization as in the HF theory.

The effective potential entering eq (9) is given by

$$V_{eff}(\vec{r}) = U(\vec{r}) + \int \frac{\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}' + V_{xc}(\vec{r}) \quad (10)$$

where the last term is called the exchange-correlation potential which is not known but can be approximated in different ways.

The simplest of them is the LDA—**local density approximation** where the exchange-correlation term is from that of the electron gas evaluated at the local density.

More advanced DFT theories have been proposed. The advantage of the DFT is that it reduces the problem to that of three degrees of freedom, say x,y and z, rather than the 3\*N degrees of freedom. DFT is widely in use, especially for the large systems, such as big molecules or solid-state systems and computational packages have been developed.

## note-17-- Atoms in external electric and magnetic fields

### 1. Hydrogen atoms in static electric and magnetic fields

The external electric and magnetic fields are expressed in terms of vector and scalar potentials and enter the Hamiltonian through

$$(1) \quad H = \frac{1}{2m} (\vec{p} + \frac{e}{c} \vec{A})^2 - e\Phi + V(r)$$

#### a. Hydrogen atom in a homogenous static electric field

For a constant electric field E along the z-direction,

$$(2) \quad \Phi(r) = -Fz$$

In atomic units, the static electric field of, say  $10^5$  V/cm, is still only about  $10^{-4}$  a.u. Thus perturbation theory can be applied if we consider the effect on the ground state of a typical atom.

- If a state has well-defined parity, then the first order perturbation is zero and the energy shift due to the electric field is given by the 2<sup>nd</sup> order perturbation. The energy shift is given by

$$(3) \quad \Delta E = -\frac{\alpha_d}{2} F^2$$

in terms of dipole polarizability. For H(1s), its dipole polarizability is 9.0 in atomic units.

- For the n=2 states, the 2s and 2p degeneracy gives the linear Stark effect. This is equivalent to saying that there exists a permanent electric dipole moment. The eigenstates are given by  $(2s \pm 2p_0) / \sqrt{2}$ , or in terms of Stark states,  $(n_1, n_2) = (1, 0), (0, 1)$ . For m=1 or -1, 2<sup>nd</sup> order perturbation theory gives the quadratic Stark effect.

Clearly this can be extended to higher n's. However, for higher n, mixing from different n-manifolds become important. This will introduce the crossing or avoided crossing of the Stark Map.

Another problem is that the electric field will induce the ionization of the atom. Since the Hamiltonian of hydrogen atom in an electric field is separable each state also acquires a width, or it has a **field-dependent lifetime**.

b. Hydrogen atom in a homogeneous magnetic field

The vector potential for a constant B field along the z-direction can be expressed as

$$(4) \quad A(\vec{r}) = \frac{1}{2} \vec{B}_z x \vec{r}$$

The Hamiltonian can then be expressed as

$$(5) \quad H = \frac{p^2}{2m} + V + \omega(L_z + 2S_z) + \frac{m\omega^2}{2}(x^2 + y^2)$$

where  $\hbar\omega = \frac{e\hbar B_z}{2mc} = \mu_B B_z$  with  $\mu_B$  being the Bohr magneton =  $5.788 \times 10^{-5}$  eV/Tesla

If the magnetic field is considered to be small, then the quadratic term is not important and the perturbation can be expressed as

$$(6) \quad W_B = \mu_B B_z (L_z + 2S_z) \quad (\text{angular momentum in units of } \hbar)$$

This is the perturbation relevant to the Zeeman effect that are treated in standard textbooks.

- (1) Without electron spin—
- (2) Spin-orbit interaction is large compared to magnetic interaction
- (3) Magnetic interaction is large compared to the spin-orbit interaction
- (4) Full treatment
- (5) subjects not covered:
  - \*\*High-B field limit—Quasi-Landau levels (see Friedrich p177-180)
  - \*\*Quantum Chaos (see Friedrich pp287-94)

## 2. Hydrogen atom in a weak electromagnetic field-radiative transitions

### (A) Basic formulation

From the Hamiltonian

$$H = \frac{1}{2m} \left( \vec{p} + \frac{e}{c} \vec{A} \right)^2 - e\Phi + V(r) \quad (2.1)$$

In the Coulomb gauge,  $\nabla \cdot \vec{A} = 0$  and  $\Phi = 0$ , the Schrodinger equation can be expressed as

$$H | \Psi \rangle = \left\{ -\frac{\hbar^2}{2m} \nabla^2 + V(r) + \left[ \frac{-ie\hbar}{mc} \vec{A} \cdot \nabla + \frac{e^2}{2mc^2} |A|^2 \right] \right\} | \Psi \rangle \quad (2.2)$$

where  $\vec{A} = A_0 \vec{\epsilon} \cos(\omega t - \vec{k} \cdot \vec{r})$  represents a plane wave. The  $A^2$  term is not important and first order perturbation theory can be used to evaluate the transition rates.

For an oscillating field like the present one, the transition probability from  $|a\rangle$  to  $|b\rangle$  at time t is given by

$$P_{ba}(t) = \left| \frac{V_{ba}}{\hbar} \right|^2 \frac{\sin^2\left(\frac{1}{2}(\omega - \omega_{ba})t\right)}{(\omega - \omega_{ba})^2} \quad (2.3)$$

where  $V_{ba} = \langle b | H' | a \rangle$  and  $H' = \frac{-ie\hbar}{mc} \vec{A} \cdot \nabla$ . Here we assume that emission and absorption can be treated independently.

If the radiation field is governed by a frequency distribution  $g(\omega)$ , then one has to integrate the P above over  $\omega$  to obtain

$$P_{ba}(t) = 2\pi \left| \frac{V_{ba}}{\hbar} \right|^2 g(\omega_{ba})t \quad (2.4)$$

and the transition rate W is

$$W_{ba}(t) = 2\pi \left| \frac{V_{ba}}{\hbar} \right|^2 g(\omega_{ba}) \quad (2.5)$$

In order for the transition to occur there must be nonvanishing spectral density at the resonant frequency.

The matrix element  $V_{ba}$  is given by

$$V_{ba} = \frac{e\hbar}{mc} A_0 \langle b | e^{i\vec{k}\cdot\vec{r}} \vec{\epsilon} \cdot \nabla | a \rangle = \frac{e\hbar}{mc} A_0 M_{ba} \quad (2.6a)$$

where M defines the matrix element

$$M_{ba} = \langle b | e^{i\vec{k}\cdot\vec{r}} \vec{\epsilon} \cdot \nabla | a \rangle \quad (2.6b)$$

The transition rate W, after integrating over the frequency, from (2.5), is then given by

$$W_{ba} = \frac{2\pi}{\hbar^2} \left(\frac{e\hbar}{mc}\right)^2 A_0^2 |M_{ba}|^2 \quad (2.7)$$

This transition rate can be expressed in terms of the light intensity,

$$W_{ba} = \frac{4\pi^2}{m^2} \frac{e^2}{c\omega_{ba}^2} I(\omega_{ba}) |M_{ba}|^2 \quad (2.8)$$

This equation was derived using semiclassical theory. If  $|b\rangle$  is higher than  $|a\rangle$ , this equation gives the absorption rate. If  $|a\rangle$  is higher than  $|b\rangle$ , it gives the emission rate.

One can define **absorption cross section**. It is defined by the rate of energy absorbed  $\hbar\omega_{ba} W_{ba}$  divided by  $I(\omega_{ba})$ ,

$$\sigma_{ba} = \frac{4\pi^2 \hbar e^2}{m^2 c \omega_{ba}} |M_{ba}(\omega_{ba})|^2 \quad (2.8a)$$

Since the electromagnetic field should also be quantized, we can express the intensity in terms of the number of photons. For a photon with energy  $\hbar\omega$ ,

$$I = \frac{N}{V} \hbar\omega \cdot c \quad (2.9)$$

Thus

$$W_{ba} = \frac{4\pi^2}{m^2} \frac{e^2}{\omega_{ba}} \frac{N\hbar}{V} |M_{ba}|^2 \quad (2.10)$$

where  $N/V$  is the photon number density. According to QED, the correct expression (2.10) is to replace  $N$  by  $N+1$  for the emission process. Thus when there is no external EM waves, the excited state  $|b\rangle$  has **spontaneous emission rate**

$$W_{ba}^s = \frac{4\pi^2}{m^2} \frac{e^2}{\omega_{ba}} \frac{\hbar}{V} |M_{ba}|^2 \quad (2.11)$$

This is the rate for emitting one photon. We want to calculate the total rate for emitting all photons with energy  $\hbar\omega$  in the range  $d\omega$  and in the angular direction  $d\Omega$ . Thus we need to find the density of states of these photons. Use box normalization, the number of modes for a cube box of volume  $V=L^3$  is given by

$$k_x = \frac{2\pi}{L} n_x, \quad k_y = \frac{2\pi}{L} n_y, \quad k_z = \frac{2\pi}{L} n_z$$

The density of states

$$dn_x dn_y dn_z = \left(\frac{L}{2\pi}\right)^3 k^2 dk d\Omega = \rho(\omega) d\omega d\Omega \quad (2.12)$$

Integrating over  $d\omega$  for all the photons emitting into  $d\Omega$  and sum over the two polarizations, the **total spontaneous emission rate is**

$$W_{ba}^s = \frac{\hbar e^2}{2\pi m^2 c^3} \int d\Omega \sum_{\lambda=1,2} \omega_{ba} |M_{ba}^\lambda(\omega_{ba})|^2 \quad (2.13)$$

### (b) Electric dipole approximation--allowed transitions

For wavelength much less than the atomic size,  $kr \ll 1$  such that the  $e^{ik \cdot r} \approx 1$  and from (2.6) we can write

$$M_{ba} = \vec{\epsilon} \cdot \langle b | \nabla | a \rangle \quad (2.14)$$

From the operator identity (work out  $\langle b | [H, x] | a \rangle$  where  $H$  is the atomic Hamiltonian), one can obtain easily

$$\langle b | \vec{\nabla} | a \rangle = -\frac{m}{\hbar} \omega_{ba} \langle b | \vec{r} | a \rangle \quad (2.15)$$

**Exercise** : Prove eq. (2.15)

Thus within the dipole approximation, the absorption rate is given by

$$W_{ba} = \frac{4\pi^2}{c\hbar^2} I(\omega_{ba}) |\vec{\epsilon} \cdot \vec{D}_{ba}|^2 \quad (2.16)$$

where  $\vec{D} = -e\vec{r}$  is the electric dipole moment of the electron. If the angle between the electron position with respect to the polarization axis is  $\theta$ , then

$$|\vec{\epsilon} \cdot \vec{D}_{ba}|^2 = e^2 |r_{ba}|^2 \cos^2 \theta \quad (2.17)$$

where  $|r_{ba}|^2 = |x_{ba}|^2 + |y_{ba}|^2 + |z_{ba}|^2$ . (2.17a)

If the light is *not polarized*, then the **absorption rate** is given by taking the average to obtain

$$W_{ba} = \frac{4\pi^2}{3c\hbar^2} I(\omega_{ba}) |D_{ba}|^2 \quad (2.18)$$

and the **spontaneous emission rate** is

$$W_{ba}^s(\Omega)d\Omega = \frac{1}{2\pi\hbar c^3} \omega_{ba}^3 |\vec{\epsilon} \cdot \vec{D}_{ba}|^2 d\Omega \quad (2.19)$$

which is the spontaneous emission rate to an angle at particular polarization. The total spontaneous emission rate is obtained by integrating over the angles and sum over the two polarizations ,

$$W_{ba}^s = \left(\frac{4}{3}\right) \frac{1}{\hbar c^3} \omega_{ba}^3 |\vec{\epsilon} \cdot \vec{D}_{ba}|^2 = \left(\frac{4}{3c^2}\right) \alpha \omega_{ba}^3 |r_{ba}|^2 \quad (2.20)$$

This last equation allows us to calculate the spontaneous emission rate of an excited state if it is dipole allowed(E1). The inverse of W gives the lifetime of the state.

Note that (2.20) is written in terms of length gauge, (2.15) is in terms of velocity gauge. There is also an acceleration gauge, not discussed here.

### (c). Einstein Coefficients (BJ pp201)

Initially derived by Einstein in 1916.

For two nondegenerate states 1 and 2 with 2 being higher, the number of atoms making the transition from 1 to 2 is

$$\dot{N}_{21} = B_{21}N_1\rho(\omega_{21}) = W_{21}N_1 \quad (2.21)$$

where  $\rho$  is the energy density at the frequency  $\omega_{21}$  and  $N_1$  is the number of atoms in 1. The last equality follows from the definition since  $W_{21}$  is the absorption rate per atom. Since  $\rho = I/c$ , this gives

$$B_{21} = \frac{4\pi^2}{3\hbar^2} |D_{21}|^2 \quad (2.22)$$

which is a constant for a particular atomic transition. For transitions from 2 to 1, we need to add the spontaneous transition

$$\dot{N}_{12} = B_{12}N_2\rho(\omega_{21}) + A_{12}N_2 \quad (2.23)$$

Since the number of atoms making transitions in either direction should be identical at equilibrium, and the numbers  $N_1$  and  $N_2$  are related by Boltzmann equation, and that the radiation energy density is given by

$$\rho(\omega) = \frac{\hbar\omega^3}{\pi c^3} \frac{1}{e^{\hbar\omega/kT} - 1} \quad (2.24)$$

These allow one to derive

$$\begin{aligned} B_{12} &= B_{21} \\ A &= \frac{\hbar\omega^3}{\pi^2 c^3} B \end{aligned} \quad (2.25)$$

in agreement with the derivations from the semiclassical quantum theory. For states that are degenerate, the first eq. of (4.25) is replaced by multiplying the degree of degeneracy of the initial state.

#### (d) Dipole transitions, Oscillator Strength, Atomic Lifetimes

For dipole transitions, it is common to introduce a dimensionless quantity  $f_{ka}$ , called oscillator strength,

$$f_{ka} = \frac{2m\omega_{ka}}{3\hbar} |\bar{r}_{ka}|^2 \quad (2.26)$$

where  $f > 0$  for absorption and  $f < 0$  negative for emission. The oscillator strength satisfies the Thomas-Kuhn-Reiche sum rule,

$$\sum_k f_{ka} = 1 \quad (2.26a)$$

where the sum is over the complete Hilbert space, including the continuum states.

**Exercise :** Prove the Thomas-Kuhn-Reiche sum rule.

For the many-electron system, the total oscillator sum is equal to the number of electrons  $Z$ . The sum rule is valid only within the nonrelativistic theory. For relativistic theory, see W.R. Johnson and C. D. Lin, J. Phys. B10, L331 (1977). The sum is less than  $Z$ .

The calculation of oscillator strength is straightforward for atomic hydrogen since the initial and final state wavefunctions are known analytically. Since the magnetic levels are degenerate for a free atom, one define the **average oscillator strength** by

$$\bar{f}_{n'\ell',n\ell} = \frac{1}{2\ell+1} \sum_{m,m'} f_{n'\ell'm',n\ell m} \quad (2.27)$$

i.e., averaged over the initial magnetic states and sum over all the final magnetic states. The average spontaneous transition rate in the dipole approximation is then given by

$$\bar{W}_{ka} = \frac{2\omega_{ka}^2 e^2}{mc^3} |f_{ka}| \quad (2.28)$$

The atomic lifetime is

$$\tau^{-1} = \sum W_{kb}^s$$

by summing over all the rates to the lower states. For typical optical transitions in atoms the lifetime is in the order of nanoseconds. From the uncertainty principle, lifetime is inversely proportional to the natural width of the level  $b$ . For H(2p) level, its lifetime is 1.6 ns, giving to a width of  $3.32 \times 10^{-3} \text{cm}^{-1}$ , or about 100 MHz. The line shape takes the Lorentzian form for an isolated atom. The spectral width of a state can get additional width from Pressure broadening which is understood as due to collisional deexcitation of the excited state from the surrounding medium, and from Doppler broadening when the emitting atoms have a velocity distribution in accordance with Maxwellian law.

If the photon energy is higher than the ionization threshold, then we have photoelectric effect, or in general, photoionization. See later.

#### (e) Selection rules and Multipole transitions

The cross section or oscillator strength is proportional to the square modulus of the dipole matrix element  $r_{ba}$ . If  $r_{ba}$  does not vanish, we have allowed transitions. It is important to see when the matrix element

$r_{ba} = \langle \Psi_b | \vec{r} | \Psi_a \rangle$  is zero. Since both states are eigenstates of the total angular momentum, and  $\vec{r}$  is a dipole operator, the selection rules for dipole allowed transitions are :

- (1) the angular momenta of initial and final states ( $J_a$  and  $J_b$ ), and the dipole ( $=1$ ) can form a triangle
- (2) The parities of initial and final states are different.

These rules can be extended to any complex systems since the argument come from the overall symmetry, not specific expressions of the wavefunctions.

If the dipole moment is zero, then higher order terms have to be considered.

There are two types of higher order terms.

- (i) Higher multipoles: In eq. (4.6) we set  $e^{ik \cdot \vec{r}} = 1$ . Higher multipoles can be obtained by expanding the vector operators in (4.6) in terms of electric and magnetic multipoles. A rigorous treatment requires relativistic formulation such that spin effect can be added. The successive multipoles are E1, M1, E2, M2, ..., for electric multipoles or magnetic multipoles. Both EJ and MJ are tensorial operators of order J, with parity given by  $(-1)^J$  for EJ and  $(-1)^{J+1}$  for MJ. The selection rules for multipole transitions are that (1)  $J_a$ ,  $J_b$  and J can form a triangle, and (2) the parity for EJ operator is  $(-1)^J$  and for MJ operator is  $(-1)^{J+1}$ .
- (ii) Multiphoton transitions. This results from treating  $H'$  using higher order perturbation theory. For example, one can have two photon transitions. The two photons could be two E1, or two M1, or even E1+M1. The selection rules can be worked out for one-photon transition each time.

We will not discuss how to calculate these multipole transitions or multiphoton transitions, but you should be familiar with the selection rules.

Examples:

- In the Schrodinger picture,  $np \rightarrow 1s$  is allowed, or by E1 transitions.  $2s \rightarrow 1s$  can go by two-photon (E1+E1 type) transition only. Its lifetime is 1/8 sec. In comparison, 2p lifetime is 1.2 ns.
- For an excited state, one needs to include all the possible routes of decay to the lower states. Since the photons emitted are important signature for determining that excited states are formed, one needs to be able to estimate the relative strengths of all the possible decay paths. For a Rydberg state that has the highest  $\ell$ , it decays successively by decreasing n by one unit and  $\ell$  by one unit in each step, such transitions form the Lyman lines.

**Exercise .** Confirm that the lifetime of the 2p state is indeed 1.6 ns.

(e) Photoionization and angular distribution of photoelectrons

### Theory of Photoionization

We will consider the photoionization of a one-electron atom. The differential cross section is given by

$$I(\theta) = \left| \langle \phi_f | T | \phi_i \rangle \right|^2 \quad (2.29)$$

where the transition operator T is

$$T = \vec{r} \cdot \hat{z} = r C_0^1(\theta, \phi) \quad (2.30)$$

if we have a linearly polarized light along the z-direction. The initial state is given by

$$|\phi_i\rangle = R_{n\ell'} |\ell' m'\rangle \quad (2.31)$$

with well-defined angular momentum. The final state, in the asymptotic region, is given by the sum of a plane wave and an incoming spherical wave. It can be written as

$$|\phi_f\rangle = \phi_k^{(-)} = 4\pi \sum_{\ell, m} (i)^\ell e^{-i\delta_\ell} Y_{\ell m}^*(\hat{k}) Y_{\ell m}(\hat{r}) G_{k\ell}(r) \quad (2.32)$$

where  $\hat{k}$  is the direction of the unit vector in the direction of the outgoing electron. Rewrite the equation above in the form

$$\phi_k^{(-)} = \sum_{\ell, m} a(\ell, m) Y_{\ell m}(\hat{r}) G_{k\ell}(r) \quad (2.33)$$

where

$$a(\ell, m) = 4\pi (i)^\ell e^{-i\delta_\ell} Y_{\ell, m}^*(\hat{k}) \quad (2.34)$$

The transition matrix element now becomes

$$\langle \phi_f | r C_0^1 | \phi_i \rangle = \sum_{\ell, m} a(\ell, m) S_\ell \langle \ell m | C_0^1 | \ell' m' \rangle \quad (2.35)$$

where the radial dipole matrix element is

$$S_\ell = \int_0^\infty r R_{n\ell'} G_{k\ell} dr \quad (2.36)$$

Using the Wigner-Eckard theorem

$$\langle \ell m | C_0^1 | \ell' m' \rangle = (-1)^{\ell-m} \left( \ell \parallel C^1 \parallel \ell' \right) \begin{pmatrix} \ell & 1 & \ell' \\ -m & 0 & m' \end{pmatrix} \quad (2.37)$$

where

$$\langle \ell \parallel C^1 \parallel \ell' \rangle = (-1)^g \sqrt{\ell_>}$$

with  $g = (\ell' - \ell + 1)/2$  and  $\ell_>$  is the greater of  $\ell$  and  $\ell'$ . Thus the dipole matrix element can now be written as

$$\langle \phi_f | r C_0^1 | \phi_i \rangle = \sum_{\ell, m} a(\ell, m) (-1)^{\ell-m+g} \sqrt{\ell_>} S_\ell \begin{pmatrix} \ell & 1 & \ell' \\ -m & 0 & m' \end{pmatrix} \quad (2.38)$$

The differential cross section is obtained by adding up all the final states and averaged over the initial states,

$$I(\theta) = \frac{1}{2\ell'+1} \sum_{m'} \sum_{\ell_1=\ell_2} a(\ell_1, m') a^*(\ell_2, m') (-1)^{\ell_1+\ell_2+g_1+g_2} \ell_{1>}^{1/2} \ell_{2>}^{1/2} S_{\ell_1} S_{\ell_2} \begin{pmatrix} \ell_1 & 1 & \ell' \\ -m' & 0 & m' \end{pmatrix} \begin{pmatrix} \ell_2 & 1 & \ell' \\ -m' & 0 & m' \end{pmatrix}.$$

with the 3-j symbols limits the range of angular momentum to  $\ell \pm 1$  where we now use  $\ell$  to represent the angular momentum of the initial state.

$$\begin{pmatrix} \ell+1 & 1 & \ell \\ -m & 0 & m \end{pmatrix} = (-1)^{\ell-m-1} \left[ \frac{(\ell+1)^2 - m^2}{(2\ell+1)(2\ell+3)(\ell+1)} \right]^{\frac{1}{2}}$$

and

$$\begin{pmatrix} \ell-1 & 1 & \ell \\ -m & 0 & m \end{pmatrix} = (-1)^{\ell-m} \left[ \frac{\ell^2 - m^2}{(2\ell+1)(2\ell-1)(\ell)} \right]^{\frac{1}{2}}$$

we then obtain

$$I(\theta) = \frac{16m^2}{2\ell+1} \sum_m \left\{ S_{\ell-1}^2 \left[ \frac{\ell^2 - m^2}{(2\ell+1)(2\ell-1)} \right] |Y_{\ell-1,m}|^2 + S_{\ell+1}^2 \left[ \frac{(\ell+1)^2 - m^2}{(2\ell+1)(2\ell+3)} \right] |Y_{\ell+1,m}|^2 \right. \\ \left. + S_{\ell+1} S_{\ell-1} \left[ \frac{\ell^2 - m^2}{(2\ell+1)(2\ell-1)} \right]^{\frac{1}{2}} \left[ \frac{(\ell+1)^2 - m^2}{(2\ell+1)(2\ell+3)} \right]^{\frac{1}{2}} \left[ Y_{\ell+1,m}^* Y_{\ell-1,m} e^{-i(\delta_{\ell+1} - \delta_{\ell-1})} \right. \right. \\ \left. \left. + Y_{\ell+1,m} Y_{\ell-1,m}^* e^{-i(\delta_{\ell+1} - \delta_{\ell-1})} \right] \right\}$$

Skipping steps, one can simplify the equation above to

$$I(\theta) = \frac{2\pi}{(2\ell+1)^2} \left\{ \ell(\ell+1) \left[ S_{\ell-1}^2 + S_{\ell+1}^2 + 2S_{\ell+1}S_{\ell-1} \cos(\delta_{\ell+1} - \delta_{\ell-1}) \right] \right. \\ \left. + \left[ \ell(\ell-1) S_{\ell-1}^2 + (\ell+1)(\ell+2) S_{\ell+1}^2 - 6\ell(\ell+1) S_{\ell+1}S_{\ell-1} \cos(\delta_{\ell+1} - \delta_{\ell-1}) \right] \cos^2 \theta \right\} \quad (2.39)$$

Let  $\sigma_{tot}$  is the total ionization cross section, obtained by integrating the above expression over all the angles of the electrons, then we can write the differential cross section in the form

$$I(\theta) = \frac{\sigma_{total}}{4\pi} [1 + \beta P_2(\cos \theta)] \quad (2.40)$$

where the  $\beta$  parameter is given by

$$\beta = \frac{\ell(\ell-1)S_{\ell-1}^2 + (\ell+1)(\ell+2)S_{\ell+1}^2 - 6\ell(\ell+1)S_{\ell+1}S_{\ell-1} \cos(\delta_{\ell+1} - \delta_{\ell-1})}{(2\ell+1) \left[ \ell S_{\ell-1}^2 + (\ell+1) S_{\ell+1}^2 \right]} \quad (2.41)$$

The value of  $\beta$  ranges from -1 to 2. For  $\beta=2$ , the angular distribution has a  $\cos^2 \theta$  dependence, with the peak in the direction of the polarization. For  $\beta = -1$ , it is a  $\sin^2 \theta$  dependence, ie., has a peak at  $90^\circ$  with respect to the polarization axis. For  $\ell = 0$ , clearly  $\beta=2$ , and the angular distribution has  $\cos^2 \theta$  dependence.

## Appendices

Review 3j symbols at <http://mathworld.wolfram.com/Wigner3j-Symbol.html>

For specific 3j,6j and 9j symbols, use <http://plasma-gate.weizmann.ac.il/369j.html>

Elementary Clebsch-Gordon coefficients <http://www.physics.udel.edu/~msafro/HTML/L6.pdf>

Calculate specific CG coefficients: <http://www.gostick.co.uk/cleb/cgjava.html>

A website to view hydrogenic wavefunctions:

[http://www3.ltu.edu/~s\\_schneider/physlets/main/hyd\\_radial2.html](http://www3.ltu.edu/~s_schneider/physlets/main/hyd_radial2.html)

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**Essential angular momentum algebra-- essential equations**

$$J_+|jm\rangle = \sqrt{(j-m)(j+m+1)\hbar}|jm+1\rangle$$

$$J_-|jm\rangle = \sqrt{(j+m)(j-m+1)\hbar}|jm-1\rangle$$

$$Y_{lm}(\theta, \varphi) = (-1)^m \left( \frac{(2l+1)(l-m)!}{4\pi(l+m)!} \right)^{1/2} P_l^m(\cos(\theta)) \exp(im\varphi)$$

$$C_q^{(k)} = \left( \frac{4\pi}{2k+1} \right)^{1/2} Y_{kq}$$

### Adding two angular momenta

$$|\gamma j_1 j_2 JM\rangle = \sum_{m_1+m_2=M} |\gamma j_1 j_2 m_1 m_2\rangle \langle j_1 j_2 m_1 m_2 | j_1 j_2 JM\rangle$$

sum rule

$$\sum_{m_1 m_2} \langle j_1 j_2 m_1 m_2 | j_1 j_2 JM\rangle \langle j_1 j_2 J' M' | j_1 j_2 m_1 m_2\rangle = \delta_{J'J} \delta_{M'M}$$

$$\sum_{JM} \langle j_1 j_2 JM | j_1 j_2 m_1 m_2\rangle \langle j_1 j_2 m'_1 m'_2 | j_1 j_2 JM\rangle = \delta_{m'_1 m_1} \delta_{m'_2 m_2}$$

Wigner 3-j symbols

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} = (-1)^{j_1-j_2-m_3} (2j_3+1)^{-1/2} \langle j_1 j_2 m_1 m_2 | j_1 j_2 j_3 - m_3\rangle$$

symmetry properties of 3-j symbols

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} = (-1)^{j_1+j_2+j_3} \begin{pmatrix} j_2 & j_1 & j_3 \\ m_2 & m_1 & m_3 \end{pmatrix}$$

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} = (-1)^{j_1+j_2+j_3} \begin{pmatrix} j_1 & j_2 & j_3 \\ -m_1 & -m_2 & -m_3 \end{pmatrix}$$

$$\begin{pmatrix} j & j & 0 \\ m & -m & 0 \end{pmatrix} = (-1)^{j-m} (2j+1)^{-1/2}$$

### Adding three angular momenta and Recoupling coefficients

$$\mathbf{J} = (\mathbf{J}_1 + \mathbf{J}_2) + \mathbf{J}_3 = \mathbf{J}_1 + (\mathbf{J}_2 + \mathbf{J}_3)$$

$$|\gamma(j_1 j_2) j_{12} j_3 JM\rangle \quad |\gamma j_1 (j_2 j_3) j_{23} JM\rangle$$

They are related by

$$|\gamma(j_1 j_2) j_{12} j_3 JM\rangle = \sum_{m_{12} m_3} |\gamma(j_1 j_2) j_{12} j_3 m_{12} m_3\rangle \times$$

$$\langle \gamma(j_1 j_2) j_{12} j_3 m_{12} m_3 | \gamma j_1 (j_2 j_3) j_{23} JM\rangle$$

--recoupling coeffs

$$\langle (j_1 j_2) j_{12} j_3 J | j_1 (j_2 j_3) j_{23} J\rangle = (-1)^{j_1+j_2+j_3+J} \begin{Bmatrix} j_1 & j_2 & j_{12} \\ j_3 & J & j_{23} \end{Bmatrix}$$

$$\left\{ \begin{array}{ccc} j_1 & j_2 & j_3 \\ j_4 & j_5 & j_6 \end{array} \right\} = \sum_{m_1 m_2 m_3 m_4 m_5 m_6} (-1)^{j_4+j_5+j_6+m_4+m_5+m_6} \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \times \begin{pmatrix} j_1 & j_5 & j_6 \\ m_1 & m_5 & -m_6 \end{pmatrix} \begin{pmatrix} j_4 & j_2 & j_6 \\ -m_4 & m_2 & m_6 \end{pmatrix} \begin{pmatrix} j_4 & j_5 & j_3 \\ m_4 & -m_5 & m_3 \end{pmatrix}$$

For nonzero 6-j the elements marked below should form a triangle

$$\left\{ \begin{array}{ccc} - & - & - \end{array} \right\}, \left\{ \begin{array}{ccc} \backslash & - & - \end{array} \right\}, \left\{ \begin{array}{ccc} / & - & \backslash \end{array} \right\}, \left\{ \begin{array}{ccc} - & - & / \end{array} \right\}$$

### Adding up four angular momenta

$$\mathbf{J} = (\mathbf{J}_1 + \mathbf{J}_2) + (\mathbf{J}_3 + \mathbf{J}_4) = (\mathbf{J}_1 + \mathbf{J}_3) + (\mathbf{J}_2 + \mathbf{J}_4)$$

$$|\gamma(j_1 j_2) j_{12} (j_3 j_4) j_{34} J M\rangle \quad |\gamma(j_1 j_3) j_{13} (j_2 j_4) j_{24} J M\rangle$$

$$|\gamma(j_1 j_3) j_{13} (j_2 j_4) j_{24} J M\rangle = \sum_{j_{12} j_{34}} |\gamma(j_1 j_2) j_{12} (j_3 j_4) j_{34} J M\rangle \times \langle (j_1 j_2) j_{12} (j_3 j_4) j_{34} J | (j_1 j_3) j_{13} (j_2 j_4) j_{24} J \rangle$$

$$\langle (j_1 j_2) j_{12} (j_3 j_4) j_{34} J | (j_1 j_3) j_{13} (j_2 j_4) j_{24} J \rangle = \sqrt{[j_{12}][j_{34}][j_{13}][j_{24}]} \times \sum_{j_{234}} (-1)^{2j_{234}} [j_{234}] \left\{ \begin{array}{ccc} j_1 & j_2 & j_{12} \\ j_{34} & J & j_{234} \end{array} \right\} \left\{ \begin{array}{ccc} j_3 & j_4 & j_{34} \\ j_2 & j_{234} & j_{24} \end{array} \right\} \left\{ \begin{array}{ccc} j_1 & j_3 & j_{13} \\ j_{24} & J & j_{234} \end{array} \right\}$$

### 9-j symbol

$$\langle (j_1 j_2) j_{12} (j_3 j_4) j_{34} J | (j_1 j_3) j_{13} (j_2 j_4) j_{24} J \rangle = \sqrt{[j_{12}][j_{34}][j_{13}][j_{24}]} \left\{ \begin{array}{ccc} j_1 & j_2 & j_{12} \\ j_3 & j_4 & j_{34} \\ j_{13} & j_{24} & J \end{array} \right\}$$

### jj coupling to LS coupling

$$|\gamma(s_1 l_1) j_1 (s_2 l_2) j_2 J M\rangle = \sum_{SL} |\gamma(s_1 s_2) S (l_1 l_2) L J M\rangle \times$$

$$\langle (s_1 s_2) S (l_1 l_2) L J | (s_1 l_1) j_1 (s_2 l_2) j_2 J \rangle =$$

$$\sum_{SL} |\gamma(s_1 s_2) S (l_1 l_2) L J M\rangle \sqrt{[S][L][j_1][j_2]} \left\{ \begin{array}{ccc} s_1 & s_2 & S \\ l_1 & l_2 & L \\ j_1 & j_2 & J \end{array} \right\}$$

convention:  $[x] = 2x+1$

### Tensor Operators

$$[J \cdot \hat{n}, T_q^{(k)}] = \sum_{q'} T_{q'}^{(k)} \langle kq' | J \cdot \hat{n} | kq \rangle$$

$$[J_z, T_q^{(k)}] = \hbar q T_q^{(k)}$$

$$[J_{\pm}, T_q^{(k)}] = \hbar \sqrt{(k \mp q)(k \pm q + 1)} T_{q \pm 1}^{(k)}$$

product of two tensor operators

$$X_Q^{(K)} = \left( T^{(k_1)} U^{(k_2)} \right)_Q^{(K)} = \sum_{q_1 q_2} T_{q_1}^{(k_1)} U_{q_2}^{(k_2)} \langle k_1 k_2 q_1 q_2 | k_1 k_2 K Q \rangle$$

scalar product of two tensor operators

$$\begin{aligned} S &= (T^{(k)} \cdot U^{(k)}) = \sum_q (-1)^q T_q^{(k)} U_{-q}^{(k)} \\ &= -T_{-1}^{(1)} U_1^{(1)} + T_0^{(1)} U_0^{(1)} - T_1^{(1)} U_{-1}^{(1)}, \end{aligned}$$

### Wigner-Eckart Theorem

$$\langle \gamma' j' m' | T_q^{(k)} | \gamma j m \rangle = (-1)^{j'-m'} \begin{pmatrix} j' & k & j \\ -m' & q & m \end{pmatrix} \langle \gamma' j' || T^{(k)} || \gamma j \rangle$$

matrix elements involving spherical harmonics

$$\langle l' m' | Y_{kq} | l m \rangle = (-1)^{l'-m'} \begin{pmatrix} l' & k & l \\ -m' & q & m \end{pmatrix} \langle l' || Y_k || l \rangle$$

$$\langle l' m' | Y_{kq} | l m \rangle = (-1)^{m'} \sqrt{[l'][k][l]/(4\pi)} \begin{pmatrix} l' & k & l \\ -m' & q & m \end{pmatrix} \begin{pmatrix} l' & k & l \\ 0 & 0 & 0 \end{pmatrix}$$

$$\langle l' || Y_k || l \rangle = (-1)^{l'} \sqrt{[l'][k][l]/(4\pi)} \begin{pmatrix} l' & k & l \\ 0 & 0 & 0 \end{pmatrix}$$

$$\int Y_{l_1 m_1} Y_{l_2 m_2} Y_{l_3 m_3} \sin \theta d\theta d\varphi = \sqrt{[l_1][l_2][l_3]/(4\pi)} \begin{pmatrix} l_1 & l_2 & l_3 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_1 & l_2 & l_3 \\ m_1 & m_2 & m_3 \end{pmatrix}$$

### Matrix elements of tensor products

$$\langle \gamma' J' M' | X_Q^{(K)} | \gamma J M \rangle = (-1)^{J'-M'} \begin{pmatrix} J' & K & J \\ -M' & Q & M \end{pmatrix} \langle \gamma' J' || X^{(K)} || \gamma J \rangle$$

$$\langle \gamma' J' || X^{(K)} || \gamma J \rangle = \sqrt{[K]} \sum_{\gamma'' J''} (-1)^{J+J'+K} \left\{ \begin{matrix} k_1 & k_2 & K \\ J & J' & J'' \end{matrix} \right\} \times$$

$$\langle \gamma' J' || T^{(k_1)} || \gamma'' J'' \rangle \langle \gamma'' J'' || U^{(k_2)} || \gamma J \rangle$$

If  $T^{(k)}$  operates only in the subspace of "1" and  $U^{(k)}$  on the subspace of "2", then

$$\langle \gamma' j'_1 j'_2 J' || T^{(k)} || \gamma j_1 j_2 J \rangle = \delta_{j'_2 j_2} (-1)^{j'_1 + j'_2 + J + k} \sqrt{[J][J']} \left\{ \begin{matrix} j'_1 & j_1 & k \\ J & J' & j_2 \end{matrix} \right\} \langle \gamma' j'_1 || T^{(k)} || \gamma j_1 \rangle$$

$$\langle \gamma' j'_1 j'_2 J' || U^{(k)} || \gamma j_1 j_2 J \rangle = \delta_{j'_1 j_1} (-1)^{j_1 + j'_2 + J' + k} \sqrt{[J][J']} \left\{ \begin{matrix} j'_2 & j_2 & k \\ J & J' & j_1 \end{matrix} \right\} \langle \gamma' j'_2 || U^{(k)} || \gamma j_2 \rangle$$

### Some useful applications for two-electron atoms

define:

- i)  $H_{el} = C \cdot 1/r_{12}$  (electrostatic interaction)
- ii)  $H_{SO} = \sum_i \zeta s_i \cdot l_i$  (spin - orbit interaction)
- iii)  $H_{cf} = C \cdot r^t Y_{tp}$  (crystal field interaction)
- iv)  $H_m = \mu_B B (L_z + 2S_z)$  (Zeeman effect)

#### 1. Electrostatic interaction

$$\frac{1}{r_{12}} = \sum_{k=0}^{\infty} \sum_{\substack{r' < r \\ r' > r}} \frac{r'^k}{r^{k+1}} (C_1^{(k)} \cdot C_2^{(k)})$$

$$\langle l_1 l_2 L' S' M'_L M'_S | (C_1^{(k)} \cdot C_2^{(k)}) | l_1 l_2 L S M_L M_S \rangle = \delta_{S' S} \delta_{M'_S M_S} \delta_{L' L} \delta_{M'_L M_L} \times (-1)^{l_1 + l_2 + L} \left\{ \begin{matrix} l_1 & l_1 & k \\ l_2 & l_2 & L \end{matrix} \right\} \langle l_1 || C_1^{(k)} || l_1 \rangle \langle l_2 || C_2^{(k)} || l_2 \rangle,$$

$$\langle l || C^{(k)} || l \rangle = (-1)^l [l] \begin{pmatrix} l & k & l \\ 0 & 0 & 0 \end{pmatrix}$$

For the more general case:

$$\begin{aligned} & \langle l'_1 l'_2 L' S' M'_L M'_S | P_k(\cos \theta_{12}) | l_1 l_2 L S M_L M_S \rangle \\ &= \langle l'_1 l'_2 L' S' M'_L M'_S | (C_{(1)}^{(k)} \cdot C_{(2)}^{(k)}) | l_1 l_2 L S M_L M_S \rangle \\ &= (-1)^{l_2 + l'_2 + 1} \delta_{l_1 l'_1} \delta_{m_1 m'_1} \left\{ \begin{matrix} 1 & l'_2 & l'_1 \\ k & l_1 & l_2 \end{matrix} \right\} [(2l_1 + 1)(2l'_1 + 1)(2l_2 + 1)(2l'_2 + 1)]^{1/2} \\ & \quad \times \begin{pmatrix} l_1 & k & l'_1 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_2 & k & l'_2 \\ 0 & 0 & 0 \end{pmatrix} \end{aligned}$$

#### 2. Spin-orbit interaction

$$\langle \gamma' L' S' J' M' | l_i \cdot s_i | \gamma L S J M \rangle = \delta_{M' M} \delta_{J' J} (-1)^{L + S' + J} \left\{ \begin{matrix} L' & L & 1 \\ S & S' & J \end{matrix} \right\} \times \sum_{\gamma} \langle \gamma' L' || l_i || \gamma L \rangle \langle \gamma S' || s_i || \gamma S \rangle$$



