



INTERNATIONAL ATOMIC ENERGY AGENCY
UNITED NATIONS EDUCATIONAL, SCIENTIFIC AND CULTURAL ORGANIZATION



INTERNATIONAL CENTRE FOR THEORETICAL PHYSICS
34100 TRIESTE (ITALY) - P.O.B. 586 - MIRAMARE - STRADA COSTIERA 11 - TELEPHONES: 224281/2/3/4/5/6
CABLE: CENTRATOM - TELEX 460392-I

SMR/100 - 11

WINTER COLLEGE ON LASERS, ATOMIC AND MOLECULAR PHYSICS

(24 January - 25 March 1983)

Atomic Spectra

Central-Field Description of Complex Atoms

J. BAUCHE

Laboratoire Aimé Cotton
C.N.R.S. II
Campus d'Orsay, Bâtiment 505
91405 Orsay Cedex
France

These are preliminary lecture notes, intended only for distribution to participants.
Missing or extra copies are available from Room 230.

III. CENTRAL-FIELD DESCRIPTION OF COMPLEX ATOMS

The central-field model for atoms with several "optical" electrons is a generalization of that used for alkalis in lecture II.

1. Central-field model (Slater, 1927)

For reasons of simplicity, an atom can be considered, a priori, as being roughly a spherical cluster centered on the nucleus. Along this view, each electron moves in an average potential which is roughly central.

This potential $V(r)$ approaches the hydrogenic potential $-\frac{a^2}{2}$ when $r \rightarrow \infty$ and the function $-\frac{Ze^2}{r} + C$ when $r \rightarrow 0$,

where C is a positive constant (namely, the potential caused in $r=0$ by the $N-1$ other electrons).

Note: $V(r)$ is actually the potential energy seen by the electron, not the electrostatic potential.

2. The hamiltonian

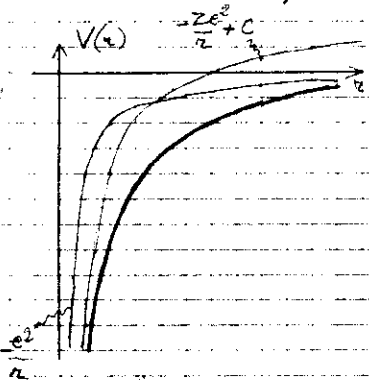
The simplest realistic hamiltonian contains the kinetic energies of the electrons and the electrostatic interactions between the particles:

$$H = -\frac{\hbar^2}{2m} \sum_{i=1}^N \Delta_i - Ze^2 \sum_{i=1}^N \frac{1}{r_i} + e^2 \sum_{i,j=1}^N \sum_{i \neq j} \frac{1}{r_{ij}}$$

In the line of the intuitive idea of the central-field potential, we split H into $H = H_0 + H'$, where

$$H_0 = -\frac{\hbar^2}{2m} \sum_{i=1}^N \Delta_i + \sum_{i=1}^N V(r_i) \text{ is the main hamiltonian, and}$$

$$H' = -\sum_{i=1}^N V(r_i) - Ze^2 \sum_{i=1}^N \frac{1}{r_i} + e^2 \sum_{i,j=1}^N \sum_{i \neq j} \frac{1}{r_{ij}} \text{ is the perturbing hamiltonian, with the hope that the matrix elements of } H' \text{ will really be much smaller than those of } H_0 \text{ if } V(r) \text{ is adequately chosen.}$$



3. Solution for H_0

H_0 is a separable hamiltonian. If we write the Schrödinger equation $H_0 \psi = E \psi$ and we look for solution $\psi = \psi_a(\vec{r}_a) \psi_b(\vec{r}_b) \dots \psi_n(\vec{r}_n)$, all the mono-electron functions ψ are solutions of the equation

$$\hbar \psi_k(\vec{r}_k) = e_k \psi_k(\vec{r}_k) \quad (2)$$

with $\hbar = -\frac{\hbar^2}{2m} \Delta + V(r)$ and $E = \sum_{k=1}^n e_k$

Now, eq. (2) is a central-field equation, for which we know that the angular part of ψ is, like for hydrogen (Lecture I), a spherical-harmonic function $Y_{lm}(\theta, \varphi)$. As for the radial part, which is denoted $R_{nl}(r)$, it is a solution of the radial equation

$$\left\{ -\frac{\hbar^2}{2m} \left[\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{d}{dr} \right) + \frac{l(l+1)}{r^2} \right] + V(r) \right\} \frac{R_{nl}(r)}{r} = e_k \frac{R_{nl}(r)}{r} \quad (3)$$

In order to include the case of hydrogen, we stick to the convention $n \geq l+1$. But e_{np} does not depend on n alone, like in hydrogen: the principal quantum number n is just useful for ordering the eigenvalues of the l -dependent equation (3).

4. Introduction of spin and of the Antisymmetry Principle

It was not necessary to introduce spin above, because H_0 is spin-independent. Now, any ψ solution can be multiplied by any product $\chi_{s_1 m_{s_1}}(\sigma_1) \chi_{s_2 m_{s_2}}(\sigma_2) \dots \chi_{s_N m_{s_N}}(\sigma_N)$ and still be an eigenfunction of H_0 for the same eigenvalue as before.

But a spin-dependent wavefunction must obey the Symmetry Principles. For the electrons, which possess half-integer spins ($s = \frac{1}{2}$) (and, therefore, are called fermions),

(3)

the wavefunction must be antisymmetric with respect to the exchange of any two electrons. Denoting now $\Psi(1, 2, \dots, N)$ an antisymmetric spin-dependent eigenfunction of H_0 , we have

$$\Psi(1, 2, \dots, i, \dots, j, \dots, N) = -\Psi(1, 2, \dots, j, \dots, i, \dots, N).$$

Antisymmetric eigenfunctions are easily built in the form of normalized Slater determinants:

$$\Delta_{a,b,\dots,n} = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_a(1) & \psi_b(1) & \dots & \psi_n(1) \\ \psi_a(2) & \psi_b(2) & \dots & \psi_n(2) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_a(N) & \psi_b(N) & \dots & \psi_n(N) \end{vmatrix}$$

with $\psi_i(\mathbf{r}) = \frac{R_{nl}(r)}{r} Y_{l,m_l}(\theta, \phi) \chi_{s,m_s}(\sigma)$.

Indeed, by expanding this determinant, it is immediately proven to be an eigenfunction of H_0 for $E = \sum_{i=1}^n \epsilon_i$.

5. The Periodic Table of Elements.

The above formalism opens the way to an approximate description of the states of any atom (and ion), and, first, of the ground states, i.e., those lowest in energy. Because the total energy E is the sum of monoelectronic energies ϵ_{nl} , we must first know

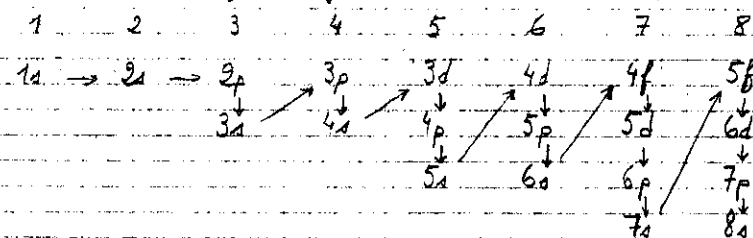
- which is the increasing order of the subshell energies ϵ_{nl}
- how many electrons are allowed in each nl subshell.

(a) Madelung's Rule.

The increasing order of the ϵ_{nl} quantities cannot be determined, in principle, before some $V(r)$ potential is chosen, and eq(3) is solved, which requires the use of a computer. Fortunately, an empirical rule, called Madelung's Rule, has proven to yield generally the correct answer in the case

(4)

of the neutral atoms: it says that ϵ_{nl} increases if $n+l$ increases, and, for a given value of $n+l$, if n increases.



(b) Pauli Principle.

The famous Pauli Principle is a specialized form of the Antisymmetry Principle: two electrons of an atomic system cannot have the same set of quantum numbers. Indeed, it derives immediately from the fact that a determinant with two identical columns is zero, when the wavefunction is a Slater determinant $\Delta_{a,b,\dots,n}$ with sets $k_a = n_a l_a m_{l_a} m_{s_a}, k_b$, etc.

Now, each nl subshell corresponds to $2(2l+1)$ sets, because m_l can take $2l+1$ different values, and m_s two ($\pm \frac{1}{2}$). Therefore, it is said closed when it contains $4l+2$ electrons.

(c) Configurations

For an atomic system, we deal the N electrons over the various subshells. The set of needed subshells is called an electronic configuration, e.g., $1s^2 2s^2 2p^3$ or $1s^2 2s^2 2p^3 4f$ for $N=7$.

The ground configuration for a neutral atom can generally be obtained through the use of Madelung's Rule, trying to put as many electrons as possible in the lowest-energy subshells.

Examples: Carbon ($Z=6$): $1s^2 2s^2 2p^2$.

Titanium ($Z=22$): $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^2$.

Polonium ($Z=84$): $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^{14} 5d^{10} 6p^4$.

⑤

This way of building the ground configuration of the neutral atom meets the experimental result for all but 14 of the 95 lowest values of Z . All the exceptions are linked with the competition between subshells with neighbouring energies, namely $4s-3d$, $5s-4d$, $4f-5d$, and $5f-6d$. The lightest one is Chromium ($Z=24$), with the ground configuration $1s^2 2s^2 2p^6 3s^2 3p^6 4s 3d^5$.

Other configurations are obtained by exciting one or several electrons from the occupied subshells of the ground configuration to subshells with higher energy: n_{el} . Madelung's Rule can still be useful as a hint for finding the lowest excited subshells.

Example: Titanium ($Z=22$), with $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^2$ as its ground configuration, and low excited configurations c.s. $4s 3d^3$, c.s. $4s 4p 3d^2$, c.s. $4p 3d^3$, c.s. $4s 5s 3d^2$, etc., where c.s. (closed subshells) replaces $1s^2 2s^2 2p^6 3s^2 3p^6$ (the "core" of the atom).

① Mendeleev's Table.

Madelung's Rule, although imperfect, gives a physical ground to the building of the Periodic Table of Elements by MENDELEEV (1869). This Table, where the elements appear nearly all in the order of increasing atomic weights, can be arranged so that atoms with similar chemical properties occur in the same column.

Remarkable columns are those of the noble gases ($Z=2, 10, 18, 36, 54, 86$, from Helium to Radon), of the alkalis ($Z=3, 11, 19, 37, 55, 87$, from Lithium to Francium), of the alkaline earths ($Z=4, 12, 20, 38, 56, 88$, from Beryllium to Radium). Remarkable

⑥

III.6

lines are those of the transition elements (where the $3d, 4d$ and $5d$ respective subshells are being filled up), and of the lanthanide and actinide groups (where the $4f$ and $5f$ subshells are being filled up).

The chemical properties derive essentially from the nature of the outermost occupied subshells in the very low configurations of the atom, which can either donate electrons easily (typical cases: the outer s electrons of the alkalis and alkaline earths), or accept electrons donated by neighbouring atoms of the molecule (typical example: the metaloids with open subshells $2p, 3p, 4p$, etc.).

6. First order of the perturbing hamiltonian H' : $H' = -\sum_i V(r_i) = -Ze^2 \sum_i \frac{1}{r_i} + e^2 \sum_{i>j} \frac{1}{r_{ij}}$ can be treated through perturbation theory.

② Degeneracy.

All the configurations which contain at least one incomplete subshell are degenerate. Due to the Pauli principle (5.B), a single incomplete subshell nl^N contains $\binom{4l+2}{N} \equiv \frac{(4l+2)!}{N!(4l+2-N)!}$ states. Examples: the degeneracies of the configurations $3p^3, 4d^2$ and $2p^2 3d$ are respectively equal to 20, 45 and 150.

Problems: determine the degeneracies of $1s^2, 1s 2p, 3d^2 4s 4p, 4f^6$.

③ Adapted functions.

In the first order of perturbation, one must diagonalize H' in the configuration subspace, which may be very large. It is interesting to find the eigenfunctions of this H' submatrix without diagonalizing it, by considering simple angular-momentum operators which commute with H' . These eigenfunctions

(7)

III.7

obtained without difficulty we start with H' adapted to H .

The first two terms in H' are purely radial, so they commute with any angular-momentum operator. The third one represents the electrostatic repulsion between the electrons, and reads

$$G = \sum_{i,j=1}^N \frac{e^2}{r_{ij}} \quad (4)$$

Let us define the total spin of the electrons $\vec{S} = \sum \vec{s}_i$, their total orbital angular momentum, $\vec{L} = \sum \vec{l}_i$, and $\vec{J} = \vec{S} + \vec{L}$.

It is not surprising that $[G, \vec{S}] = 0$ (because G is spin-independent), that $[G, \vec{J}] = 0$ (because $\vec{J}$, the total angular momentum of the system, is a constant vector in Classical and Quantum Mechanics); therefore $[G, \vec{L}]$ is also certainly zero.

Problem: prove explicitly that $[G, L_z] = 0$, using the fact that $L_z = \frac{\hbar}{i} \frac{\partial}{\partial \phi}$ in spherical coordinates.

We deduce that the adapted functions are eigenfunctions of S_z , S^2 , L_z and L^2 (and of J_z and J^2 , but J^2 does not commute with S_z and L_z - see Lecture II).

In Dirac's notation, we write the adapted functions

$|\alpha S M_S L M_L\rangle$, where α stands for all the supplementary quantum numbers which may be necessary for defining completely eigenstates possessing the same S, M_S, L, M_L quantum numbers.

© Russell - Saunders terms.

The symbol αSL above defines a Russell - Saunders (RS) term. This term contains $(2S+1)(2L+1)$ states. These states remain degenerate, because a theorem of Quantum Mechanics says that an operator which commutes with the z -component J_z of an angular momentum $\vec{J}$ and with J^2 has its eigenvalues independent of M .

(8)

III.8

Therefore, we must first find which αSL terms occur in a given configuration.

A general and convenient method is that of the tableau in M_S, M_L (see the Lectures on angular momentum).

- In groups of several equivalent electrons, i.e., electrons of the same subshell, this is the only elementary method for taking the Pauli Principle into account. However, in the frequent case of two equivalent electrons (nl^2), it can be easily proven and memorized that all allowed RS terms, among those obeying the triangular conditions ($S=0$ or 1 , $0 \leq L \leq 2l$), are the terms with $S+L$ even.

- In groups of non-equivalent electrons, i.e., electrons of different subshells, the Pauli Principle does clearly not forbid any association of (m_s, m_l) pairs. Therefore, the usual rules for coupling the angular momenta in both subspaces directly yield the (intermediate and) total values of S and L .

Spectroscopic notation: a term (S, L) is written $^{2S+1}\lambda$, where λ is the symbolic capital letter relevant to the numerical value of L (S for $L=0$, P for $L=1$, D for $L=2$, etc.). When $S=0$, the term is a singlet (because $2S+1=1$); when $S=1/2, 1, 3/2, 2$, etc., it is a doublet, a triplet, a quartet, a quintet, etc.

Example: $2p^1: ^1S, ^3P, ^1D, ^3P, ^1D, ^3P, ^1D, ^3P, ^1D, ^3P$.

$3d^3: ^2P, ^2D, ^2F, ^4P, ^4D, ^4F, ^2P, ^2D, ^2F, ^4P, ^4D, ^4F$ (this configuration contains two terms D). $3d^4 4p: [(3d^4) ^3D, 4p] ^3P, ^3D, ^3F, ^3P, ^3D, ^3F$ and $[(3d^4) ^1D, 4p] ^1P, ^1D, ^1F$.

Problems: determine the RS terms of the configurations $1s 2s, 2p 4f, 2p^2 4s, 2p 3p 4d$. Check that the total degeneracy of each configuration is identical whether computed

directly (see 6. @) or as the sum of the term ligand raises $(2S+1)(2L+1)$.

④ Hund terms

An important case is that of the ground terms of the nl^N configurations, which are frequently encountered, e.g., in crystals. For such terms, an empirical rule proposed by HUND is valid: the ground term of nl^N has the maximum spin S_m allowed in the configuration, and, among the (possibly) several terms with spin S_m , that with the maximum value of L allowed. This term is easily determined from the Slater determinant with the maximum values of M_S and then of M_L .

Example: the Hund term of $3d^6$ is a 5D , corresponding to the determinant: $\{\uparrow\uparrow\uparrow\uparrow\uparrow\downarrow\}$.

Problems: find the Hund terms of $3d^5, 4f^3, 4f^6$; obtain formulae for the values of S and L of the Hund term of nl^N .

7. Term energies.

The separations between the energies of the terms of a given configuration are due to the electrostatic operator G .

The matrix elements of G can be computed exactly for what concerns their angular part, i.e., the integration over the spin and angular variables of the system. The following expansion of $\frac{1}{r_{12}}$ is used:

$$\frac{1}{r_{12}} = \sum_{k=0}^{\infty} \sum_{q=-k}^k \frac{4\pi}{2k+1} (-1)^q Y_{kq}(\theta_1, \varphi_1) Y_{k-q}(\theta_2, \varphi_2) \frac{r_<^k}{r_>^{k+1}}$$

where $r_<$ is the lesser of r_1 and r_2 and $r_>$ the larger. The same expansion can be written

$$\frac{1}{r_{12}} = \sum_{k=0}^{\infty} (C_{(1)}^{(k)} C_{(2)}^{(k)}) \frac{r_<^k}{r_>^{k+1}} \quad \text{for the convenient use of the tensor-operator method.}$$

The integration over the angular variables cannot be made without first determining the R_{nl} , i.e., electronic radial functions (after choosing an explicit form of $V(r)$). Thus, the radial integrals often remain at the end of the calculations as parameters whose values are to be optimized through comparison with the experimental energies. They are called the Slater integrals.

$$\text{(direct integral)} \quad F^k(nl, n'l) = \int_0^\infty \int_0^\infty R_{nl}(r_1) R_{n'l}(r_2) \frac{r_<^k}{r_>^{k+1}} R_{nl}(r_1) R_{n'l}(r_2) dr_1 dr_2$$

and

$$\text{(exchange integral)} \quad G^k(nl, n'l) = \int_0^\infty \int_0^\infty R_{nl}(r_1) R_{n'l}(r_2) \frac{r_<^k}{r_>^{k+1}} R_{n'l}(r_1) R_{nl}(r_2) dr_1 dr_2$$

The energies of the terms of many configurations are given in terms of the Slater integrals by Condon and Shortley in their book.

8. Spin-orbit interaction.

In most atomic spectra, a realistic description of the levels cannot be obtained if one ignores the main perturbing operator to be added to $H_0 + H'$ (eq. (1)), namely, the spin-orbit operator Λ . This operator is an effective operator, which, so to speak, translates in the non-relativistic language some effects initially apparent in the relativistic formalism of DIRAC (see Lecture II, and the book by Bethe and Salpeter). Its effects inside an electronic configuration of the central-field model are exactly reproduced through the expression

$$\Lambda = \sum_{i=1}^N \vec{S}(r_i) \cdot \vec{s}_i \cdot \vec{p}_i$$

where $\vec{S}(r) = \frac{1}{r} \frac{dV(r)}{dr}$, $V(r)$ being the central potential.

@ Quantum numbers.

We have seen above that S, M_S, L, M_L are good quantum numbers for $H_0 + H'$. Unfortunately, Λ does not commute

with $S_z, \vec{S}, L_z, \vec{L}$ when $N > 1$. But we have also seen above (6.⑤) that $H_0 + H'$ commutes with J_z and $\vec{J}$. Because Λ also commutes with J_z and $\vec{J}$ (prove it!), we conclude that J and M_J are the only angular-momentum quantum numbers which can be attributed with certainty to the eigenstates of $H_0 + H' + \Lambda$.

Remark. J and M_J are still valid if the other magnetic interactions (spin-spin, spin-orbit, etc.) are taken into account.

⑥ Russell-Saunders coupling.

Let us suppose that we have obtained the exact solutions of $H_0 + H'$ (this is not true above, where we have treated H' only to the first order of perturbation). From what we have recalled at the beginning of 8 ②, the eigenfunctions can be written $|\alpha S M_S L M_L\rangle$, even if α is not merely the name of a configuration. We say that the eigenfunctions are in Russell-Saunders coupling. Moreover, the αSL term is $(2S+1)(2L+1)$ times degenerate.

If we now treat Λ to the first order of perturbation, we must diagonalize it in the subspace αSL . But we know that the adapted functions are the coupled functions $|\alpha SLJM_J\rangle$ of this subspace, because Λ commutes with J_z and $\vec{J}^2$. Therefore, the first-order contribution of Λ to the energy is $\Delta W_\Lambda = \langle \alpha SLJM_J | \Lambda | \alpha SLJM_J \rangle$.

In the same way as for the term energies (see 7.), the angular part of ΔW_Λ can be computed exactly, and the radial part ends up in radial integrals which are frequently treated as adjustable parameters. For the case of the con-

figuration $n\ell^N$, there will appear only one spin-orbit radial integral, $S_{nl} = \int_0^\infty \xi(r) |R_{nl}(r)|^2 dr$.

A remarkable result can be obtained easily through the use of the tensor-operator method. Because the wavefunctions are antisymmetric with respect to the exchange of any two electrons, we write

$$\langle \alpha SLJM_J | \Lambda | \alpha SLJM_J \rangle = N \langle \alpha SLJM_J | \xi(r) \vec{r} \cdot \vec{p} | \alpha SLJM_J \rangle,$$

and the angular dependence of the remaining matrix element is just the same as that of $\langle \alpha SLJM_J | A_{\alpha SL} \vec{S} \cdot \vec{L} | \alpha SLJM_J \rangle$, where $A_{\alpha SL}$ is independent of J and M_J . Because $\vec{S} \cdot \vec{L} = \frac{1}{2} [\vec{J}^2 - \vec{S}^2 - \vec{L}^2]$, we deduce immediately

$$\Delta W_\Lambda = \frac{A_{\alpha SL}}{2} [J(J+1) - S(S+1) - L(L+1)]$$

This is a very simple formula.

Problems - show that the energy splitting between levels J and $J-1$, in a given Russell-Saunders term, is proportional to J .

- show that the centre of gravity of a Russell-Saunders term does not depend on the spin-orbit interaction.

⑦ Intermediate coupling.

If the spin-orbit (Λ) and electrostatic-repulsion (G) splittings inside a given configuration are of the same order of magnitude, we cannot treat Λ after G , but, instead, together with G . To the first order of perturbation, we must diagonalize $G + \Lambda$ on the basis states of the whole electronic configuration (however, this matrix breaks up in submatrices, each one corresponding to a given (J, M_J) pair). The eigenstates can be written $|\alpha JM_J\rangle$, α meaning here "intermediate coupling".