

Renata Reisfeld
Christian K. Jørgensen

Lasers and Excited States of Rare Earths

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With 9 Figures
and 26 Tables



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Renata Reisfeld

Department of Inorganic and Analytical Chemistry
Hebrew University, Jerusalem, Israel

Christian Klixbüll Jørgensen

Département de Chimie minérale, analytique et appliquée
Université de Genève, Switzerland

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Preface

The possibility of stimulated light emission was discussed by Einstein in 1917, eight years before the quantum-mechanical description of energy levels of many-electron systems. Though it is imperative to use samples having optical properties greatly different from the standard continuous spectrum of opaque objects ("black body" radiation) it is not always necessary to restrict the study to monatomic entities. Thus, spectral lines can be obtained (in absorption and in emission) from lanthanide compounds, containing from one to thirteen 4f electrons going from trivalent cerium to ytterbium, that are nearly as sharp as the ones from gaseous atoms. However, the presence of adjacent atoms modifies the simple picture of an isolated electron configuration, and in particular, it is possible to pump excited levels efficiently by energy transfer from species with intense absorption bands, such as the inter-shell transitions of other lanthanides and of thallium(I), lead(II) and bismuth(III) or the electron transfer bands of the uranyl ion or other complexes. On the other hand, it is possible to diminish the multi-phonon relaxation (competing with sharp line luminescence) by selecting vitreous or crystalline materials with low phonon energies.

Obviously, one cannot circumvent the conservation of energy by lasers, but they may have **unprecedented** consequences for the future by allowing nuclear fusion of **light elements**, effects of non-linear optics and time-resolved **spectroscopy**, besides the more conventional applications of coherent light beams with negligible angular extension. In this book we attempt to provide **suggestions** for a variety of new laser materials and conceivable use of combined new properties.

Jerusalem and Geneva, January 1977

Renata Reisfeld
Christian K. Jørgensen

C. K. Jørgensen

Oxidation Numbers and Oxidation States

VII, 291 pages. 1969

(Molekülverbindungen und
Koordinationsverbindungen
in Einzeldarstellungen)

Contents: Introduction. – Formal Oxidation Numbers. – Configurations in Atomic Spectroscopy. – Characteristics of Transition Group Ions. – Internal Transitions in Partly Filled Shells. – Inter-Shell Transitions. – Electron Transfer Spectra and Collectively. – Oxidized Ligands. – Oxidation States in Metals and Black Semi-Conductors. – Closed-Shell Systems, Hydrides and Back-Bonding. – Homopolar Bonds and Catenation. – Quanticule Oxidation States. – Taxological Quantum Chemistry. – Author Index, Subject Index. – Bibliography to each chapter.

Electrons in Fluids

The Nature of Metal-Ammonia Solutions

Editors: J. Jortner, N. R. Kestner

271 figures, 59 tables. XII, 493 pages. 1973

From the contents: Theory of Electrons in Polar Fluids. – Metal-Ammonia Solutions: The Dilute Region. – Metal Solutions in Amines and Ethers. – Ultrafast Optical Processes. –

Metal-Ammonia Solutions: Transition Range. – The Electronic Structures of Disordered Materials. – Concentrated $M-NH_3$ Solutions. – Strange Magnetic Behaviour and Phase Relations of Metal-Ammonia Compounds. – Mobility Studies of Excess Electrons in Nonpolar Hydrocarbons. – Metallic Vapors. – Optical Absorption Spectrum of the Solvated Electron in Ethers and in Binary Liquid Systems.

M. W. Breiter

Electrochemical Processes in Fuel Cells

98 figures. XI, 274 pages. 1969

(Anorganische und allgemeine Chemie
in Einzeldarstellungen, Band 9)

In the last few decades the development of different types of fuel cells has greatly stimulated research into basic processes occurring in these cells. It is the aim of this monograph to describe and discuss the progress made in our understanding of these electrochemical processes. Chapters I to III introduce the reader to the general problems of fuel cells. The nature and role of the electrode material which acts as a solid electrocatalyst for a specific reaction is considered in chapters IV to VI. Mechanisms of the anodic oxidation of different fuels and of the reduction of molecular oxygen are discussed in chapters VII to XII for the low-temperature fuel cells and the strong influence of chemisorbed species or oxide layers on the electrode reaction is outlined. Processes in molten carbonate fuel cells and solid electrolyte fuel cells are covered in chapters XIII and XIV. The important properties of porous electrodes and structures and models used in the mathematical analysis of the operation of these electrodes are discussed in chapters XV and XVI.



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Structure and Bonding

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1. Analogies and Differences Between Monatomic Entities and Condensed Matter

(References to this Chapter are found p. 59).

The selective absorption or emission of narrow spectral lines in the visible and in the adjacent, near ultra-violet and near infra-red regions is normally thought to be a characteristic of transitions in individual atoms efficiently isolated from the surroundings by large distances to the nearest neighbour atoms. This phenomenon is of great importance for astrophysics and our conviction that the same elements exist in the Sun and the other stars as in the surface of the Earth is almost exclusively based on coincidences between positions of lines in stellar spectra and in light sources (such as flames, arcs, sparks and electric discharges in gases) available in the laboratory. This idea was established by Bunsen and Kirchhoff in 1860 and atomic light sources such as red neon, yellow sodium and blue-green mercury lamps (frequently combined with luminescent wall materials) have to a great extent replaced the continuous spectra emitted by incandescent solids in oil lamps and candles, and the electric carbon or tungsten filaments. Whereas Newton did not use sufficiently collimated light and a very narrow slit, Wollaston detected 1802 narrow, dark absorption lines in the Solar spectrum (also seen in the scattered light from the blue sky) and these were carefully studied by Fraunhofer since 1814. The line spectra of gaseous atoms and monatomic positive ions (such as M^+ , M^{+2} , ... called M II, M III, ... by atomic spectroscopists because they emit the second, third, ... spectrum of elements, M^0 representing M I) have been intensively studied for more than a century. The Ritz combination principle $h\nu = (E_2 - E_1)$ can be used to determine the energy levels E_1, E_2, \dots relative to the groundstate E_0 of the monatomic entity (only a minority of atoms have well-established long series of levels obeying the Rydberg formula and hence allowing the ionization energy $I = E_0(M^+) - E_0(M^0)$ to be determined with as high an accuracy as the other energy differences) and they are tabulated [1] by Charlotte Moore-Sitterly of the National Bureau of Standards in Washington, D. C. A very important empirical fact is that the individual levels (having the quantum number $J = 0, 1, 2, \dots$ for an even and $J = 1/2, 3/2, 5/2, 7/2, \dots$ for an odd number of electrons; combined with odd (ungerade) or even (gerade) parity) frequently can be classified in terms characterized by S and L in the Russell-Saunders coupling

$$J = S \oplus L = (S + L) \text{ or } (S + L - 1) \text{ or } (S + L - 2) \dots \\ \text{or } (|S - L| + 1) \text{ or } |S - L| \quad (1.1)$$

where $S = 0, 1, 2, \dots$ for an even number of electrons are called singlet, triplet, quintet, ... and $S = 1/2, 3/2, 5/2, \dots$ for an odd number of electrons doublet, quartet, sextet, ... It has no practical importance that q electrons at most can show $S = (q/2)$, already in the lithium atom, the first state with maximum $S (= 3/2)$ occurs in the

continuum about ten times higher than the first ionization energy. The quantum number L is a non-negative integer having traditional names

$$\begin{array}{cccccccccccccccc} L = & 0 & 1 & 2 & 3 & 4 & 5 & 6 & 7 & 8 & 9 & 10 & 11 & 12 & \dots \\ & S & P & D & F & G & H & I & K & L & M & N & O & Q & \dots \end{array} \quad (1.2)$$

and the individual level is denoted 3H_6 , $^4I_{9/2}$, ... where the left-hand superscript indicates the spin multiplicity $(2S + 1)$ equal to 3 ($S = 1$), 4 ($S = 3/2$), ... and the right-hand subscript $J = 6$, $9/2$, ... Frequently, one adds a right-hand superscript small circle for *odd* levels, of which the energies are tabulated [1] with italicized numerals. Seen from the point of view of quantum mechanics [2, 3] each J -level corresponds to $(2J + 1)$ mutually orthogonal wave-functions Ψ and is said to contain $(2J + 1)$ states. A summation of $(2J + 1)$ for each level indicated by Eq. (1.1) gives $(2S + 1)(2L + 1)$ states in a term characterized by a given combination of S and L .

An even more important empirical fact is that the levels and terms can be successfully classified in *electron configurations* where each shell l [having the lower-case traditional names s, p, d, f, g, ... in Eq. (1.2)] contains between 0 and $(4l + 2)$ electrons. l is a quantum number for one-electron wave-functions, *orbitals*, where the number [4] of angular node-planes (node-cones count for two angular nodes) is l and where the orbital can be written as the product of a radial function and an *angular function* which is a normalized linear combination of homogeneous polynomials $x^a y^b z^c / r^l$ in the Cartesian coordinates with the sum of the three non-negative integers $a + b + c = l$. The principal quantum number n (a positive integer not smaller than $l + 1$) is not strictly speaking a quantum number corresponding to a physical quantity (like the square of the momentum of orbital motion being $l(l + 1) \hbar^2 / 4\pi^2$) though the radial function has $(n - l - 1)$ radial nodes for finite, positive distance r from origo of the coordinate system, where the nucleus is situated. There are no such radial nodes for 1s, 2p, 3d, 4f, ... whereas other orbitals (such as 2s, 3s, 3p, ...) have to be orthogonal on the previous shells with the same l by judicious choice of their radial functions. The groundstate of gaseous M^{+2} (where five exceptions are known, $M = \text{La, Gd, Lu, Ac and Th}$) and all known M^{+3} and M^{+4} belong to a configuration obtained by consecutive filling of the shells in the order

$$1s \ll 2s < 2p \ll 3s < 3p \ll 3d < 4s < 4p \ll 4d < 5s < 5p \ll 4f < 5d < 6s < 6p \ll 5f < \dots \quad (1.3)$$

where the double inequality signs indicate configurations containing 2, 10, 18, 36, 54, 86, ... electrons isoelectronic with the noble gases. Thus, Pr^{+3} has its $(Z - 3) = 56$ electrons distributed on the same closed shells [first line of Eq. (1.3)] containing 54 electrons as the xenon atom and two electrons in the 4f shell. This can be written $[\text{Xe}] 4f^2$ where the number of electrons in each shell is written as a right-hand superscript (sometimes omitted when it is one; thus, the next-lowest configuration [5] of Pr^{+3} is $[\text{Xe}] 4f^1 5d^1$ or $[\text{Xe}] 4f 5d$). Seen from this point of view, the behaviour of the neutral atoms is far less regular. A modified version of Eq. (1.3) putting $(n + 1)s$ orbitals before the nd shell has 20 exceptions, and frequently, several configurations partly coincide and it seems somewhat accidental exactly to which configuration the

groundstate of the neutral gaseous atom belongs. Though the lowest level $4I_{9/2}$ of the praseodymium atom belongs to $[Xe]4f^36s^2$ this configuration is represented by 41 levels distributed over more than $40,000\text{ cm}^{-1}$ or 5 eV, whereas the first level belonging to $[Xe]4f^25d6s^2$ already occurs at $4,300\text{ cm}^{-1}$ above the groundstate.

It is worth noting the discrepancy [6, 7] between the *chemical* and the *spectroscopic* versions of the Periodic Table that neodymium is almost exclusively trivalent (written with Roman numerals in parenthesis Nd(III) by chemists, one unit lower than Nd IV without parenthesis used by atomic spectroscopists when speaking about Nd^{+3}) though it has only *two* valence electrons in the sense that the groundstate belongs to $[Xe]4f^46s^2$. This lack of relation between chemical behaviour and lowest configuration occurs frequently; the groundstate of the gaseous uranium atom belongs to $[Rn]5f^36d7s^2$ though U(VI) and U(IV) are more common oxidation states than U(III). A completely extreme aspect of this discrepancy is, that helium and ytterbium are spectroscopic alkaline earths having the last occupied orbital *ns*, whereas the noble gases Ne, Ar, Kr and Xe terminate with a filled *np* shell.

A. The Configuration $4f^q$ as an Instance of Spherical Symmetry

Already in 1857, Gladstone noted that aqueous solutions containing praseodymium(III) and neodymium(III) (this mixture was believed to be an element, didymium, according to Mosander 1842, but was separated in 1885 by Auer von Welsbach by laborious techniques of fractional crystallization) show about ten narrow absorption bands in the visible. This observation is strikingly similar to the Fraunhofer lines and spectral lines in absorption present in monatomic vapours of metallic elements. Extensive studies of all kinds of coloured substances later showed that diatomic and polyatomic molecules in the gaseous state in many cases show band spectra with adjacent narrow lines organized in what is now recognized to be vibrational and rotational structure [8] of electronic transitions, whereas, a few sharp, irregularly distributed absorption bands in condensed matter (solutions, vitreous and crystalline solids) are an almost unique characteristic of the lanthanides. The 3d, 4d and 5d group compounds [6, 9] and the general dye-stuffs and other coloured organic molecules [10] show broad absorption bands, in the latter cases often exhibiting vibrational structure, but very rarely atomic-like sharp lines. After the advent of the "ligand field" theory [3, 11] the rare cases of d group complexes showing sharp lines (even known in emission from ruby $Al_{2-x}Cr_xO_3$ with a small amount of chromium(III) replacing colourless aluminium) in addition to broader bands have been explained as intra-sub-shell transitions where the excited state has almost the same electronic density in our three-dimensional space as the groundstate (however, the average reciprocal value $\langle r_{12}^{-1} \rangle$ of the distances between the electrons in the partly filled shell is different). According to Franck and Condon's principle no extensive co-excitation of vibrational states is expected when the equilibrium internuclear distances are the same in the excited electronic state as in the groundstate. It is very interesting that Ephraïm and Mezener [12] argued that the presence of many narrow absorption bands in uranium(IV) compounds indicates a configuration $[Rn]5f^2$ in analogy with Pr(III) and confirming the suggestion by Goldschmidt that

a new series of rare earths of predominantly quadrivalent elements starts with thorium. Of course, it was not known at that time [7] that $Z = 95$ to 100 are most stable in trivalent compounds, and that Md(II) and No(II) occur at the end of the 5f group.

Though all the elements with the atomic number Z between 57 (lanthanum) and 71 (lutetium) actually were discovered before 1907 (with exception of promethium ($Z = 61$) only having short-lived radioactive isotopes) a certain uncertainty remained about their definite nature until Moseley derived Z from X-ray spectra in 1913. Furthermore, the "Aufbau principle" of the Periodic Table such as Eq. (1.3) was not established before Stoner in 1924 suggested nl -shells containing at most $(4l + 2)$ electrons. The study of absorption spectra was somewhat delayed by the scarcity of high-purity samples obtained by tedious methods of separation, until Spedding developed the ion-exchange resin columns around 1942. In accordance with the present state of knowledge [13], all the M(III) with $q = (Z - 57)$ between 2 and 12 show a definite set of narrow absorption bands corresponding to the transitions from the lowest to a variety of higher J -levels of the configuration $[\text{Xe}]4f^q$. At this point, gadolinium ($Z = 64$) has a special position ($q = 7$) because the first excited levels occur at sufficiently high energy to correspond to absorption (and sometimes emission) bands in the ultra-violet, as first measured by Urbain. Ytterbium ($Z = 70$) was later shown to have a single group of closely adjacent, narrow bands in the near infra-red (close to $10,000 \text{ cm}^{-1}$) which can be identified as the transition from the groundstate $^2F_{7/2}$ to the only other level $^2F_{5/2}$ of $[\text{Xe}]4f^{13}$. One would expect cerium(III) to have a similar transition from $^2F_{5/2}$ to $^2F_{7/2}$ of $[\text{Xe}]4f$, but it occurs at a low wave-number close to $2,500 \text{ cm}^{-1}$ with the result that it is difficult to detect, and is hidden by vibrational spectra in solvents or crystals containing hydrogen. Apart from the narrow bands due to internal transitions in $[\text{Xe}]4f^q$ the M(III) can show other broad bands due to excitations to another configuration $[\text{Xe}]4f^{q-1}5d$ or due to electron transfer, where an electron is lost from one or more reducing neighbour atoms and the lanthanide is reduced to M(II) by being $[\text{Xe}]4f^{q+1}$. Contrary to the case of d groups, the broad absorption bands are not very frequent below $50,000 \text{ cm}^{-1}$ though M(II) generally have more prominent inter-shell and M(IV) electron transfer bands than M(III).

It is very important to note that the internal transitions in the partly filled 4f shells have positions almost independent of the ligands, the neighbour molecules or anions. We discuss below the detailed nature of these weak perturbations, but the main part of the problem has spherical symmetry. Though Sugar [5] found 12 of the 13 possible levels of $[\text{Xe}]4f^2$ in Pr^{+3} in 1965, it had been believed for many years that the narrow band spectra of M(III) are very similar to the excited levels of isolated M^{+3} . We have to make a few more remarks about the coupling schemes which can be represented by the operator \oplus of Eq. (1.1). If a monatomic entity has a configuration with two partly filled shells, it is possible to count the number of terms having the desired combination of S and L by performing the operation $L = L_1 \oplus L_2$ and $S = S_1 \oplus S_2$ on each of the combinations (S_1, L_1) of the first and (S_2, L_2) of the second partly filled shell, using the general definition

$$Q_1 \oplus Q_2 = (Q_1 + Q_2) \text{ or } (Q_1 + Q_2 - 1) \text{ or } (Q_1 + Q_2 - 2) \dots \\ \text{or } (|Q_1 - Q_2| + 1) \text{ or } |Q_1 - Q_2| \quad (1.4)$$

called vector-coupling by Hund [14]. Since this operation is associative (and commutative) the final result of $(Q_1 \oplus Q_2) \oplus Q_3$ is the same as of $Q_1 \oplus (Q_2 \oplus Q_3)$. As simple examples may be mentioned:

$$\begin{aligned} f^1 d^1: & \quad {}^1P, {}^3P, {}^1D, {}^3D, {}^1F, {}^3F, {}^1G, {}^3G, {}^1H, {}^3H \\ f^1 d^1 s^1: & \quad \text{two } {}^2P, {}^4P, \text{two } {}^2D, {}^4D, \text{two } {}^2F, {}^4F, \text{two } {}^2G, {}^4G, \text{two } {}^2H, {}^4H \end{aligned} \quad (1.5)$$

where it is noted that the same combination of S and L can repeat itself twice or more in the same configuration. The operation (1.4) simply multiplies the number of states having the quantum number Q_1 with the number of states having Q_2 . Hence the configurations in Eq. (1.5) comprise a number of states being the product of $(4l+2)$ for each electron or $14 \cdot 10 = 140$ and $14 \cdot 10 \cdot 2 = 280$ in the two examples.

When a partly filled shell contains at least 2 and at most $4l$ electrons, it is not possible to apply Eq. (1.4) before knowing the terms belonging to l^q which is a complicated problem [2, 6] restricted by Pauli's exclusion principle though it is completely resolved in principle [15]. An explicit expression exists for

$$l^2: {}^1S, {}^3P, {}^1D, {}^3F, {}^1G, \dots, {}^3(2l-1), {}^1(2l) \quad (1.6)$$

having all L -values from 0 to $2l$ alternatively combined with $S = 0$ or 1. The number of states in l^2 is $(2l+1)(4l+1)$ to be compared with two non-equivalent electrons $(nl)^1(n'l)^1$ having all the L values of Eq. (1.6) represented both as singlet and as triplet terms with the result that $(4l+2)^2$ states subsist. In the partly filled shell l^q the number of states is the product

$$(4l+2) \cdot \frac{(4l+1)}{2} \cdot \frac{(4l)}{3} \cdot \frac{(4l-1)}{4} \dots \frac{(4l+3-q)}{q} \quad (1.7)$$

which is the result of the permutation theory for the distribution of q *indiscernible* objects on $(4l+2)$ sites. Equation (1.7) is identical for q and for $(4l+2-q)$ electrons in the partly filled l -shell. This identity goes much further in Pauli's theorem of *hole-equivalency* that the number of levels having a given value of J is the same in the two cases, as well as the number of terms having a definite combination of S and L . By the way, the ten terms given for $f^1 d^1$ in Eq. (1.5) are the same for the three configurations $f^1 d^9$, $f^{13} d^1$ and $f^{13} d^9$ related by hole-equivalency. The terms for three electrons or three holes are:

$$\begin{aligned} p^3: & \quad {}^4S, {}^2P, {}^2D \\ d^3, d^7: & \quad {}^4P, {}^4F, {}^2P, \text{two } {}^2D, {}^2F, {}^2G, {}^2H \\ f^3, f^{11}: & \quad {}^4S, {}^4D, {}^4F, {}^4G, {}^4I, {}^2P, \text{two } {}^2D, \text{two } {}^2F, \text{two } {}^2G, \text{two } {}^2H, {}^2I, {}^2K, {}^2L \end{aligned} \quad (1.8)$$

comprising 20, 120 and 364 states, respectively. There are no immediately evident regularities for a greater number of electrons in the shell, though it may be noted that among the 119 terms of f^7 , the groundstate is 8S and the sextet terms 6P , 6D , 6F , 6G , 6H and 6I having the same L values as f^2 in Eq. (1.6). One doublet (2Q) has $L = 12$.

According to Hund [14] the lowest term of l^q has the highest L compatible with the highest $S = S_{\max}$ of the configuration. $S_{\max} = (q/2)$ in the first half of the shell, and $(4l + 2 - q)/2$ for $q > (2l + 1)$. The L value of the ground term is a symmetric function around maxima for quarter and three-quarter filled shells, and is:

$$\begin{array}{llll} f^0, f^{14}: {}^1S & f^1, f^{13}: {}^2F & f^2, f^{12}: {}^3H & f^3, f^{11}: {}^4I \\ f^7: {}^8S & f^6, f^8: {}^7F & f^5, f^9: {}^6H & f^4, f^{10}: {}^5I \end{array} \quad (1.9)$$

Obviously, such results are also symmetric around half-filled shells. This is true to a lesser degree for the relativistic effect usually called *spin-orbit coupling* where another of Hund's rules is that the lowest level has $J = L - S$ for $q \leq 2l$ but $J = L + S$ for the second half of the shell, $q > (2l + 1)$. In the case of more than one partly filled shell, Hund's rules do not always apply. Thus, the lowest level of the gaseous cerium atom is 1G_4 (and distinctly not 3H_4) belonging to $[Xe]4f^15d6s^2$. Whereas, the lowest level of Ce^{+2} is 3H_4 (even parity) belonging to $[Xe]4f^2$ the configuration $[Xe]4f^15d$ starts already at $3,277 \text{ cm}^{-1}$ with 1G_4 (odd parity). The levels belonging to a given configuration have even or odd parity according to whether the sum of the l values of the electrons is even or odd. It is also calculated [6, 15] that the rules of Hund do not apply for all cases of l above 3, such as g^3 .

It should be emphasized that Eqs. (1.5), (1.6) and (1.8) do not indicate the relative energies of the terms, and Hund's rules should not be construed to demand a systematic dependence of energy on L for given S value. The question of relative energies have three parts:

1. Group-theoretical conditions for the existence of definite (S, L) -terms and J -levels.
2. Algebraic relations between coefficients to parameters of interelectronic repulsion and spin-orbit coupling.
3. The numerical question of size of the parameters, either calculated from the radial function in Hartree-Fock approximation or considered as phenomenological parameters are fitted to obtain the best possible agreement with the experiment.

An important aspect of the group-theoretical (symmetry-determined) conditions is that the quantum numbers $S = L = 0$ characterizing a closed shell filled with $(4l + 2)$ electrons is the neutral element of the operation \oplus in Eq. (1.4) always having $({}^1S) \oplus (Q_2) = Q_2$ like zero is the neutral element of addition and 1 the neutral element of multiplication. This means that we can speak about the configuration $4f^3$ of Pr^{+2} or Nd^{+3} without knowing anything about the detailed behaviour of the 54 electrons in closed shells. This remark has profound ramifications in chemistry. It is clear what we mean with *isoelectronic series* of monatomic entities such as the 54-electron series $I^-, Xe, Cs^+, Ba^{+2}, La^{+3}, Ce^{+4}, Pr^{+5}, \dots$ though we must remember that the ground configuration [1] may change along an isoelectronic series. Thus, the 19-electron series is $[Ar]4s$ for K and Ca^+ but $[Ar]3d$ for $Sc^{+2}, Ti^{+3}, V^{+4}, \dots$ and the 68-electron series $[Xe]4f^{12}6s^2$ for the gaseous erbium atom, $[Xe]4f^{13}6s$ for Tm^+ but the closed shells $[Xe]4f^{14}$ for $Yb^{+2}, Lu^{+3}, Hf^{+4}, Ta^{+5}$ and undoubtedly many subsequent elements. Chemists [4] also speak about isoelectronic series such as $Sb(-III), Te(-II), I(-I), Xe, Cs(I), Ba(II), La(III)$ and $Ce(IV)$ whereas $Pr(V)$ is far too oxidizing [16] to exist in compounds, even in fluorides and oxides and gaseous anions such as Sb^{-3} and Te^{-2} spontaneously lose electrons *in vacuo*, as all anions (including O^{-2} isoelec-

tronic with neon) carrying more than one negative charge. The closed-shell segment of the 68-electron series Yb(II), Lu(III), Hf(IV), Ta(V), W(VI), Re(VII) and Os(VIII) is also familiar to chemists though they do by no means argue that the fractional atomic charge approaches +8 (it seems to be closer to +2 in the tetrahedral molecule OsO_4) and not even that the fractional atomic charge is a monotonic function of the oxidation state; it may easily be higher in lutetium(III) fluoride than in osmium(VIII) oxide. The oligoatomic molecules [6] are said to be isoelectronic if they contain the same nuclear distribution with essentially the same atomic core closed-shells, as the linear triatomic species OCO , NCN^{2-} , N_3^- , NNO , fulminate CNO^- and cyanate NCO^- among which the three former possess a centre of inversion and the point-group $D_{\infty h}$ whereas the symmetry of the three latter species is $C_{\infty v}$. The chemist speaks about pseudo-isoelectronic or *isologous* series of such species having a different number of electrons in closed inner shells but analogous distributions of the valence electrons. Remembering the classification of oxygen, sulphur, selenium and tellurium as chalcogens, species such as OCO , SCO , SeCO , SCS , SeCSe , NCO^- , NCS^- and NCSe^- are isologous. The repetition of periods in the Periodic Table is a manifestation of isologous behaviour (though S may vary from high to low values in the d group compounds) and spectroscopists can argue that U(IV) is isologous with Pr(III) and U(III) and Np(IV) with Nd(III).

In Russell-Saunders coupling the individual (S, L) term is predicted [2] to follow the interval rule first proposed by Landé

$$E(J) = E(S, L) + \zeta [J(J+1) - \langle J(J+1) \rangle] / 2 \quad (1.10)$$

where $E(S, L)$ is the average energy of the $(2S+1)(2L+1)$ states belonging to the term, and the average value is

$$\langle J(J+1) \rangle = S(S+1) + L(L+1) \quad (1.11)$$

as can be seen easily by induction and recursion. A corollary of Eq. (1.10) is that the distance between two levels, J and $(J-1)$, of the term is $J\zeta$. Further on, ζ can be evaluated from first principles [2] as a multiple $k\zeta_{nl}$ of the *Landé parameter* ζ_{nl} characterizing all the terms with one partly filled shell of the monatomic entity considered. It is empirically known [17] that ζ_{nl} tends to be proportional to $(z+1)^2 Z^2$ where z is the ionic charge. The coefficient k is particularly simple for terms with S_{\max} . In the first half of the shell, $S_{\max} = q/2$ and $k = 1/q$. In the second half of the shell (q above $2l+1$), k is negative and equals $-1/2S_{\max}$. There is a tradition among magneto-chemists to call $k\zeta_{nl}$ for (the positive or negative) λ . This symbol is also used as a symmetry type in the linear symmetries [6] and we do not use it for the former purpose. Nearly all terms with S_{\max} have $L \geq S_{\max}$ in which case the total width of the term between the two extreme J -values $L + S_{\max}$ and $L - S_{\max}$ is $(L + 1/2)\zeta_{nl}$ exactly like it would be for a single nl -electron outside closed shells.

If there were no correlation effects [3] and no mixing of configurations, the interelectronic repulsion in one partly filled shell l^q can be treated [2] according to a theory first proposed by Slater 1929, where a series expansion (relative to polar coordinates with the nucleus at origo) is performed for the integrated average value

$\langle r_{12}^{-1} \rangle$ of reciprocal interelectronic distances. Fortunately enough, the triangular conditions of Gaunt restrict the number of parameters needed to describe term distances in l^q to l integrals, $F^2, F^4, F^6, \dots, F^{2l}$ which are functions of the radial function of the partly filled shell. Actually, there is one more slightly larger parameter F^0 but it does not contribute to the term distances since its coefficient is $q(q-1)/2$ for all the terms. However, F^0 is a major contribution to the difference between the ionization energy and the electron affinity of the partly filled shell. Though the proportionality constant depends to a certain extent on the shape of the $4f$ radial function, the order of magnitude is $F^k = \varphi_k \langle r^{-1} \rangle$ with

$$\varphi_0 \sim 0.7 \quad \varphi_2 \sim 0.5 \quad \varphi_4 \sim 0.3 \quad \varphi_6 \sim 0.2 \quad (1.12)$$

where the average reciprocal distance from the nucleus $\langle r^{-1} \rangle$ of the $4f$ electrons in hartree/bohr atomic units correspond to $14.4 \text{ eV}/\text{\AA}$ or $115,000 \text{ cm}^{-1}/\text{\AA}$. It is also worth noting that the product $\langle r \rangle \langle r^{-1} \rangle$ which is $(2l+3)/(2l+2)$ for hydrogenic (H, $\text{He}^+, \dots, \text{Ar}^{+17}, \dots$) $1s, 2p, 3d, 4f, \dots$ radial functions without nodes is between 1.3 and 1.25 for most Hartree-Fock radial functions in many-electron atoms.

It is rather tedious [18] to apply the Slater-Condon-Shortley theory to f^q where it is also customary to introduce new, smaller parameters

$$F_2 = F^2/225 \quad F_4 = F^4/1089 \quad F_6 = F^6/7361.64 \quad (1.13)$$

in order to assure integers as coefficients f_k to the individual terms ($f_2 F_2 + f_4 F_4 + f_6 F_6$). It is very fortunate that Racah [19] introduced a much more practical method to obtain the same results as the F_k treatment, but with the new parameters

$$\begin{aligned} E^0 &= F^0 - 10F_2 - 33F_4 - 286F_6 \\ E^1 &= (70F_2 + 231F_4 + 2,002F_6)/9 \\ E^2 &= (F_2 - 3F_4 + 7F_6)/9 \\ E^3 &= (5F_2 + 6F_4 - 91F_6)/3 \end{aligned} \quad (1.14)$$

and at the same time, achieved a very subtle group-theoretical classification of the numerous terms showing the same combination of S and L by introducing new quantum numbers such as the *seniority number* ν and other complicated quantities such as U and W . Since these fascinating results have minor connections with our subject, and since they have been described by Wybourne [20] and Judd [21] we do not consider them here, apart from the comment that the diagonal elements classified with the help of Casimir's group generally have rather large non-diagonal elements of interelectronic repulsion with the result that the new quantum numbers frequently are not particularly "good" when several terms have the same combination of S and L .

One of the many advantages of Racah's parametrization ($e_0 E^0 + e_1 E^1 + e_2 E^2 + e_3 E^3$) is that the energy differences between terms with S_{\max} are definite multiples of E^3 alone, the coefficient e_3 then dependent on L :

$$\begin{array}{llll} f^2, f^5, f^9, f^{12}: & \text{H: } -9 & \text{F: } 0 & \text{P: } +33 \\ f^3, f^4, f^{10}, f^{11}: & \text{I: } -21 & \text{S, F: } 0 & \text{G: } +12 \quad \text{D: } +33 \end{array} \quad (1.15)$$

Both the Hartree-Fock radial functions [22] and the phenomenological values give E^1 very close to $10E^3$. The coefficient e_1 only depends [19] on S and the seniority number ν (which is q for the large majority of terms in the first half of the shell, though it is 0 for 1S of f^2 and 1 for one of the two 2F of f^3 in Eq. (1.8), and 2 for seven terms of f^4) and is:

$$e_1 = \frac{9(q - \nu)}{2} + \frac{\nu(\nu + 2)}{4} - S(S + 1) \quad (1.16)$$

This dependence on $S(S + 1)$ is an expression of a general result of the Slater-Condon-Shortley theory for l^q noted by one of us in 1956 that the energy difference between the *baricentre*, the average energy, of all the states having $S = S_0 - 1$ and the baricentre of all the states having $S = S_0$ turns out to be $2DS_0$ where D is a *spin-pairing parameter* constituting the same linear combination of F^k parameters for all q and S_0 . Hence, one obtains a formal similarity to Eq. (1.10) by writing the average energy of all the states as containing a contribution of interelectronic repulsion

$$q(q - 1)A_*/2 \quad (1.17)$$

to which is added a contribution dependent on the total spin quantum number S :

$$D[\langle S(S + 1) \rangle - S(S + 1)] \quad (1.18)$$

with the average value

$$\langle S(S + 1) \rangle = \frac{3}{4} q \left\{ 1 - \frac{q - 1}{4l + 1} \right\} = \frac{3q(4l + 2 - q)}{16l + 4} \quad (1.19)$$

In the case of f -electrons ($l = 3$) the parameters are

$$\begin{aligned} A_* &= E^0 - (9E^1/13) \\ D &= 9E^1/8 \end{aligned} \quad (1.20)$$

It may be noted that this treatment is aligned with the behaviour of the closed shell f^{14} showing the contribution $91A_*$ (which is smaller than $91F^0$ because of the systematic mutual avoidance of electrons in the anti-symmetrized Ψ in spite of the overall spherical symmetry) whereas, Racah [19] concentrated attention on the first half of the shell (q at most 7) with $e_1 = 0$ of Eq. (1.16) for S_{\max} . This is no longer true in the second half (which one does not need to consider if one is exclusively interested in term distances within f^q) where $e_1 = 63$ for $q = 14$ as also discussed by Johnson [23]. It has been discussed in detail [4, 6] why the spin-pairing energy parameter D contains a factor $(2l + 3)/(2l + 2)$ expressing the average effect of decreased seniority number when S decreases. This is one of the several interesting algebraic results relating the differing coefficients to the parameters of interelectronic repulsion.

Obviously, the lowest term among several terms having a given baricentre has lower energy. This is why the distance $2DS_{\max}$ (with D around $6,500 \text{ cm}^{-1}$ or 0.8 eV)