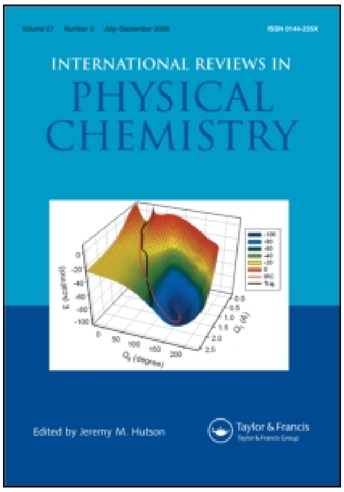

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J-LEVELS AND *S*-VALUES IN MONATOMIC ENTITIES AND CONDENSED MATTER

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ABSTRACT

The electron configurations (in spite of being a debatable approximation to the wavefunction) predict correctly the number of levels with given J value, and in the case of reasonably valid Russell–Saunders coupling, their bunching together in (S, L) terms. The similarity with the energy levels in condensed matter attenuates from the 4f to the 5f group, and in d-group compounds (like those outside the transition groups) usually only S remains a good quantum number. Recent experimental results, such as the Judd–Ofelt treatment of absorption and fluorescence transition probabilities (of importance for lasers), photoelectron and Auger spectra, antiferromagnetic coupling through anion bridges (allowing excitation of two transition-group ions by the same photon) and arguments for definite spectroscopic and conditional oxidation states, are connected with a general analysis of non-totally symmetric states. It is shown that the less frequent occurrence of positive S values in compounds of elements lighter than calcium, distort many opinions about chemical bonding.

MONATOMIC ENTITIES

The system consisting of one nucleus with charge $+Ze$ and $K = (Z - z)$ electrons is always stable against loss of an electron for z positive or zero (the neutral atom). A few elements (such as helium, beryllium, nitrogen, neon, magnesium) are known not to have any affinity for an additional electron (Berry, 1969; Zollweg, 1969), but the majority can form monatomic anions with $z = -1$. No monatomic entity is stable with $z = -2$ or more negative values, not even the most likely candidate, oxygen. The repulsion between M^- and an electron at large distances cannot be compensated by second-order attractions at shorter distances. The gaseous, neutral atoms and positive ions all have a large number of discrete stationary states below the beginning of the continuum of states represented by the groundstate of M^{+z+1} and situated at I_{z+1} (the $(z + 1)$st ionization energy) above the groundstate of the M^{+z} considered. The latter state is used as zero-point of energy in the great compilations of atomic energy levels performed at the National Bureau of Standards (Moore, 1949, 1952, 1958; Martin, Zalubas and Hagan, 1978). In the spherical symmetry of monatomic entities, each level is characterized by the *quantum number J* of total angular momentum, which is a non-negative integer 0, 1, 2, 3, ... for an even number of electrons K, and half an odd positive integer $\frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \ldots$ for odd K, and further by the *parity* which is *even* or *odd* according to whether the total wavefunction remains invariant, or is systematically multiplied by (-1), when the Cartesian coordinate set (having the nucleus at the origin) is changed from (x, y, z) to $(-x, -y, -z)$. Each J-level contains

$(2J + 1)$ states corresponding to mutually orthogonal wavefunctions (Condon and Shortley, 1953).

The characterization of each level by J (and in a sense, also by the positive integer K) and by parity, can be extended in practice in two directions.

1. *Russell–Saunders coupling* introducing the additional quantum numbers S (of total spin) having the same choice of alternatives as J (though at most $K/2$) and L (of total orbital angular momentum) being a non-negative integer (without further restrictions).
2. *Electron configurations* to be discussed below.

In Russell–Saunders coupling, *terms* can be recognized, having a definite combination of S and L. When both of these quantum numbers are positive, more than one J-level is a member of the term. The J values are $S \otimes L$ where the *Hund vector-coupling* operation (Hund, 1927) acting on two quantum numbers Q_1 and Q_2 is

$$Q_1 \otimes Q_2 = (Q_1 + Q_2) \quad \text{or} \quad (Q_1 + Q_2 - 1) \quad \text{or} \quad (Q_1 + Q_2 - 2) \quad \text{or} \ldots$$
$$\text{or} \quad (|Q_1 - Q_2| + 1) \quad \text{or} \quad |Q_1 - Q_2|. \tag{1}$$

The name *multiplicity* given to the quantity $(2S + 1)$ has two origins, that $(2S + 1)(2L + 1)$ states occur in a given term, and that a term contains $(2S + 1)$ differing J-levels in cases where S is not larger than L. The multiplicity is frequently denoted singlet, triplet, quintet,... for $S = 0, 1, 2, \ldots$ (even K) and doublet, quartet, sextet, for $S = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \ldots$ (odd K).

The electron configuration is an *approximation* to the wavefunction, where each nl-shell is allocated 0, 1, 2 to $(4l + 2)$ electrons. The closed shell containing the maximum number of electrons corresponds to only one state (called $^1S_0$ in the notation of the multiplicity as a lefthand superscript, and J as a righthand subscript to the trivial name of the L-value S, P, D, F, G, H, I, K, L, M, N, O, Q,... between 0 and 12) having even parity and $S = L = J$ all zero. This state has the remarkable property of being the *neutral element* of Hund vector-coupling, Eq. (1), as (+1) is the neutral element of multiplication and zero is of addition. One or $(4l + 1)$ electrons in a given shell produce one term with $S = \frac{1}{2}$ and $L = l$ having two J-levels for positive l, viz. $(l - \frac{1}{2})$ and $(l + \frac{1}{2})$, whereas only the latter J-level occurs for one s-electron $(l = 0)$, as known from the groundstate of hydrogenic systems containing one electron. An explicit list can be given of the terms for 2 or $(4l)$ electrons in a given shell.

$$^1\text{S}, {}^3\text{P}, {}^1\text{D}, {}^3\text{F}, {}^1\text{G}, \ldots, {}^3(2l - 1), {}^1(2l) \tag{2}$$

with alternating singlet and triplet multiplicity combined with all the L values from zero to $(2l)$. It is important to note that the terms in Eq. (2) are not necessarily arranged in energetic order; ^{1}S always has the highest energy, and according to Hund's rules (Hund, 1927), the lowest term has the maximum value of S (here 1) combined with the highest value of $L (= 2l - 1)$ compatible with this condition.

For chemists interested in the transition groups, it is useful that complete lists of all p^q, d^q and f^q configurations are available (Condon and Shortley, 1953). Racah (1949) analysed the structure of f^q thoroughly, and Karayianis (1965) found recursive formulae for all l^q. The number of states in *one* partly filled shell is decreased by Pauli's exclusion principle to the permutational expression for distributing q *indistinguishable* objects on $(4l + 2)$ sites,

$$(4l + 2) \cdot \frac{(4l + 1)}{2} \cdot \frac{(4l)}{3} \cdot \frac{(4l - 1)}{4} \cdots \frac{(4l + 3 - \text{q})}{\text{q}}. \tag{3}$$

For instance, the number of states in Eq. (2) is only $(2l+1)(4l+1)$ to be compared with $(4l+2)^2$ for two differing l-shells (such as $3d^1 4d^1$) each containing an electron. In the latter case, each of the L-values in Eq.(2) would be combined with both $S=0$ and 1. In general, the terms formed by several partly filled shells are much easier to count. The combination of a term (S_1, L_1) of one shell with (S_2, L_2) of another shell gives *all* the $S = S_1 \otimes S_2$ values each combined with *all* the $L = L_1 \otimes L_2$. It has no importance in what order one applies the Hund vector-coupling to several partly filled shells, but one has to be careful recognizing that a given combination (S, L) may be repeated a definite number of times. It may be noted that the number of levels with a given J can be evaluated for a given electron configuration assuming Russell–Saunders coupling, independently of whether this classification is a good approximation to the relative energies or not. The same invariant character of the number of levels with given (S, L, J) is also entailed by electron configurations, regardless of how good an approximation this description is to the total wavefunction.

It seems surprising to many physicists to put the validity of electron configurations on the same footing as the approximation of Russell–Saunders coupling. This is because the chemist (Jørgensen, 1979c) proceeds by *induction from facts* whereas the physicist prefers *deduction from axioms*. In a well-ordered deductive description, the electron configuration comes as an earlier assumption than the quality of Russell–Saunders coupling. However, in one sense this neglects the historical development of atomic spectroscopy. The adjacent J-levels are bunched together in (S, L) terms in much the same way as manifolds of terms are bunched together in electron configurations. This process started on a large scale with the analysis of the neon spectrum by Paschen in 1919, and was well established (Hund, 1927) before the quantum-mechanical interpretation of term distances within a given configuration by Slater–Condon–Shortley (S.C.S.) *parameters of interelectronic repulsion*. Even before wavefunctions of reasonable quality were available, it was easy to see (Jørgensen, 1962a, 1962b, 1971) that dielectric effects corresponding to the substitution of two electrons from conventional orbitals to continuum orbitals (with comparable average radii, additional nodes, and positive one-electron energy) contributed quite large squared amplitudes to the wavefunction considered as a configuration interaction. A further problem related to the virial theorem was analysed by Katriel and Pauncz (1977) providing support to the idea that the deviations of terms from the *barycentre polynomial* (Jørgensen, 1969) are approximately described by S.C.S. parameters, but that the F^k integrals evaluated for Hartree–Fock radial functions of the partly filled shell are considerable larger (sometimes by factors 1.5 to 2) than the phenomenological parameters of interelectronic repulsion. This effect is particularly important in lanthanide compounds (Reisfeld and Jørgensen, 1977) containing a partly filled 4f shell, which behave for many practical purposes as monatomic entities. Gaseous ions with z from +2 to +6 (with the exception of M^{+2} for M = La, Gd, Lu, Ac and Th) have their groundstate belonging to the configuration obtained by consecutive filling of shells according to the *Aufbau principle*:

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

where the double inequality signs indicate $K = 2$, 10, 18, 36, 54 and 86 isoelectronic with the noble gases. Textbooks frequently give a similar series for the configuration to which the groundstate of each neutral atom belongs, and where the 4s, 5s, 6s and 7s orbitals follow immediately after K = 18, 36, 54 and 86. However, the 99 gaseous atoms from hydrogen to einsteinium exhibit 20 exceptions to such a series, and for several interesting reasons (Jørgensen, 1969, 1978) such a treatment of neutral atoms is much less relevant for chemistry. The exceptions to Eq. (4) for $z = +7$ and above are connected exclusively with the crossing of 4f and 5p under circumstances restoring the hydrogenic order of *n* values (Jørgensen, 1976b, 1978).

The treatment of monatomic entities as *isolated* is only defensible because of their short-range interaction with other atoms. It is even likely that more paradoxical aspects, such as the non-local and superluminal connections (D'Espagnat, 1976) originally proposed by Einstein, Podolsky and Rosen as an attempt to reduce quantum mechanics ad absurdam, actually have been experimentally verified (Freedman and Clauser, 1972). In spite of such traps opening under our feet, it is also a fact that roughly stationary states can be studied under conditions of splendid isolation. It is worth mentioning that the Born–Oppenheimer approximation consists of writing the wavefunction as a product of four factors describing translational, rotational, vibrational and electronic behaviour. However, monatomic entities lack the second and third of these factors. It is striking how reluctant textbooks are to discuss the translational states of monatomic entities forming almost a continuum (starting at the groundstate) unless the entity is confined in a very small volume. On this basis it is not too alarming that neutral atoms can have *autoionizing states* (e.g. belonging to [18]3d5p and [18]3d4d of the calcium atom, which can ionize to the groundstate [18]4s of Ca^+ although [18]3d has higher energy) in the continuum, and the stationary states of positive ions only subsist if the electrons lost are kept at a safe distance. Actually, many interesting and high resolution techniques of X-ray and of photoelectron spectroscopy involve states far up in the continuum, and in recent years, spectral lines have been identified in the lithium atom (at ten times higher energy than the ionization limit to form the groundstate of Li^+ belonging to $1s^2$) where the excited levels have $S = \frac{3}{2}$ and belong to 1s2s2p and higher configurations. The enormous binding energy of the two 1s electrons removes the practical consequences of the maximum value of S being as high as $(K/2)$.

A problem in monatomic entities is the approximation of considering the nucleus as a geometrical point, though the radius is exceedingly small. Whereas nuclei with even Z 'containing' also an even number of neutrons (Jørgensen, 1981a) have groundstates with I zero (the quantum number corresponding to J in the electronic system) other nuclei have positive I. The J-levels then split into *hyperfine components* with $F = \mathrm{I} \otimes J$ and separated by about 10^{-5} to 10^{-4} of the energy of visible photons. This hyperfine structure can be detected in a few polyatomic species, such as the groundstate (Jørgensen, 1964a; Berg *et al.*, 1965; Kasai and Weltner, 1965) of the diatomic molecules ScO and LaO (which had previously been supposed to have $S = \frac{3}{2}$ but actually have $S = \frac{1}{2}$) and holmium(III) salts at very low temperature (Hellwege, Hüfner and Pelzl, 1967) having $J = 8$ in the electronic groundstate and $I = \frac{7}{2}$ for the only stable isotope 165. However, apart from direct detection in visible and ultraviolet spectra, the hyperfine effects play a conspicuous rôle in nuclear magnetic and nuclear quadrupolar resonance (Lucken, 1969).

LANTHANIDES (WITH A PARTLY FILLED 4f SHELL) IN CONDENSED MATTER

When Newton separated white light into rainbow colours with a prism, he did not collimate the solar light sufficiently, and did not use a very narrow slit, so the absorption lines were first discovered by Wollaston. They are called *Fraunhofer lines* because of the subsequent thorough studies by Fraunhofer. As described by Weeks (1968) it was also known that lithium and sodium (rendering pale blue flames intensively red or yellow) emit emission lines. These two phenomena were connected by Bunsen and Kirchhoff in 1860 to the hypothesis that gaseous atoms emit and absorb characteristic wavenumbers. It is known today that absorption lines only occur due to transitions from the groundstate, from thermally populated low-lying levels, or from metastable states (with very low transition probabilities toward the groundstate) accumulating in electric discharges. On the other hand, incandescent solids and liquids emit a standard continuous spectrum shown by Wien, Stefan and Boltzmann to depend only on the absolute temperature T (and quantum theory started by Planck rationalizing this observation). Though such objects traditionally are called 'black bodies' a better name may be *opaque objects*, because even sufficiently thick layers of a hot gas (as found in the atmosphere of the Sun and other stars) emit such a standard spectrum. It extended our understanding of the Universe in an unprecedented fashion to realize that many of the elements known from our laboratories were present (though with differing abundance) in the stars and even in remote galaxies. The operation of *lasers* (Reisfeld and Jørgensen, 1977) has as a requirement the *population inversion* that during the pumping of energy (directly to E_2 or by rapid transfer from a higher level E_3) the population of E_2 is higher than that of the lower E_1 to which the stimulated emission (predicted by Einstein in 1917) of coherent monochromatic radiation takes place. In three-level lasers, E_1 coincides with the groundstate E_0 whereas the (more easily realized) four-level lasers have E_1 above E_0. It is characteristic of lasers that they are transparent (and distinctly not opaque) over wide intervals of wavenumbers.

Gladstone noted in 1857 that solutions of didymium salts (this supposed element was separated in praseodymium and neodymium by Auer von Welsbach in 1885) show narrow absorption bands, quite similar to Fraunhofer lines. Bahr (1865) wanted to investigate this unexpected 'atomic' feature of non-gaseous systems containing coloured lanthanides, and found the pink sesquioxide of erbium to emit green light in a flame, corresponding to several narrow emission bands. It seems that this *candoluminescence* (Jørgensen, 1975c, 1976a; Jørgensen, Bill and Reisfeld, 1982) corresponds to oxides of trivalent lanthanides approaching the status as opaque objects only inside the narrow absorption bands. The classical Auer mantle $Th_{0.99}Ce_{0.01}O_2$ emits a broad spectrum covering most of the visible (but emitting much less than an opaque object would do in the infrared) due to an intense electron transfer band of cerium(IV). In the following, we write monatomic entities Er^{+3}, Ce^{+4},..., and species with well-defined oxidation state (Jørgensen, 1969) in gaseous molecules and in condensed matter, as erbium(III), cerium(IV),... It is noted that atomic spectroscopists write ErIV and CeV for the monatomic entities, their argument being that the 'first spectrum' of an element belongs to the neutral atom, the second spectrum to M^+, and so on. In order to diminish confusion, Roman numerals without parentheses are not used in this review. The trivalent lanthanides developed the paradoxical situation of having J-levels to be treated by methods of atomic spectroscopy, though the first M^{+3} (containing more than one electron in a partly filled 4f shell) to be analysed was Pr^{+3} (Sugar, 1965). It remained a source of doubt that a few elements outside the 4f group, such as chromium(III), could show narrow absorption bands and red emission lines (by fluorescence) in *ruby* $Al_{2-x}Cr_xO_3$. The latter material was used by Maiman for the first (three-level) laser in the visible. However, it was realized since the work by Finkelstein and Van Vleck (1940) that transitions in d-group compounds are described by 'ligand field' theory (Jørgensen, 1969, 1971) where a few (usually two or one) among the five d-like orbitals are strongly antibonding (their angular functions directed toward the nearest-neighbour ligating atoms) whereas the others are approximately nonbonding. In such a situation, Russell–Saunders coupling usually remains a good description as far as S goes (the first excited state of ruby is a doublet, and the groundstate a quartet) but the individuality of J-levels is completely lost, because the strong antibonding effects remove the degeneracy of the five d-orbitals present in the monatomic entity, and the quantum number L (prevailing in spherical symmetry) is replaced by the symmetry type in the point group of the *chromophore* such as $Cr(III)X_6$ where the equilibrium positions of the six X nuclei relative to the central chromium nucleus exemplify the point-group O_h. Hund's rule for S of the groundstate is not always followed by d-group compounds; most manganese(II) and iron(III) compounds have $S = \frac{5}{2}$ like Mn^{+2} and Fe^{+3}, but some Mn(II) and Fe(III), and all ruthenium(III) and iridium(IV) compounds, have $S = \frac{1}{2}$ with five electrons concentrated in the three lower d-like orbitals in octahedral chromophores.

4f GROUP AQUA IONS AND OTHER COMPLEXES

Since the time of Gladstone, there has been an extensive study of trivalent lanthanides, and the main conclusion was that all M(III) between M = Pr and Tm have groups of narrow absorption bands in the visible, with the exception of Gd(III) which starts in the ultraviolet. Various compounds of the same M(III) have *almost* the same distribution of excited states, and it became obvious that any changes were small details, fairly difficult to detect. Hofmann and Kirmreuther (1910) found that the wavenumbers of Er_2O_3 systematically were 1 to 1.5 per cent lower than in hydrated salts of erbium(III). This trend was found in a large number of solid Pr(III), Nd(III) and Sm(III) compounds (Ephraim and Bloch, 1926, 1928; Ephraim and Rây, 1929; Boulanger, 1952; Jørgensen, 1956) and related to weak covalent bonding increasing along the series: fluorides, double nitrates, aqua ions, anhydrous chlorides, bromides and iodides, and finally (perhaps slightly surprising) oxides. This variation is today called the *nephelauxetic effect* (this word, proposed by the late Professor Barr, meaning 'cloud-expanding') and is much more pronounced in d-group compounds (Schäffer and Jørgensen, 1958; Jørgensen, 1969) where the *nephelauxetic ratio* β between the phenomenological S.C.S. parameters of interelectronic repulsion in compounds and in M^{+z} is defined. In the d-groups β varies between 0.94 in MnF_2 containing the octahedral chromophore $Mn(II)F_6$ (to be compared with 0.56 in MnF_6^{-2}) down to values below 0.4 in the most covalent complexes.

Hund (1927) concluded from interpolation between the known groundstates of lanthanum and lutetium atoms that the other lanthanides have groundstates belonging to $[54]4f^q5d6s^2$ because of their almost invariant trivalency. However, this opinion turned out to be valid only for cerium and gadolinium (Martin *et al.*, 1978), the rest belonging to $[54]4f^{q+1}6s^2$ being 'barides'. It is also true that the groundstate of the neutral atom may be rather irrelevant for the chemical properties of the element (Jørgensen, 1979a) and it was established by magnetic measurements (Van Vleck, 1932) that the groundstate of M(III) has a J-value agreeing with Hund's rules applied to $[54]4f^q$ where $q = (Z - 57)$. In spherical symmetry, assuming Russell–Saunders coupling, the *gyromagnetic factor*

$$g = \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)} \tag{5}$$

is of considerable help identifying J-levels (Condon and Shortley, 1953). The *magnetic susceptibility* is proportional to $g^2J(J+1)/3kT$ on the condition that the $(2J+1)$ states forming the J-level have nearly equal Boltzmann population. In compounds at lower T, deviations can occur, to be discussed below.

Anyhow, the first constructive attempt to identify excited J-levels of M(III) was done by Gobrecht (1937, 1938) studying infrared absorption spectra of M_2O_3 dissolved in beads of molten borax $Na_2B_4O_7$. This procedure avoids interference from the vibrational spectra of OH groups (such as water) also consisting of narrow bands. The key to this interpretation was the detection of an excited J-level of ytterbium(III) slightly above 10 000 cm^{-1}. This transition is now known to occur in Yb^{+3} at 10 214 cm^{-1} (Kaufman and Sugar, 1976). The 'spin-orbit coupling' energy difference between $J = \frac{7}{2}$ and $\frac{5}{2}$ for a single 4f electron is $\frac{7}{2}\zeta_{4f}$ where the *Landé parameter* in atomic units (the velocity of light in vacuo being 137.036 ...)

$$\zeta_{nl} = \left\langle \frac{1}{r} \frac{\partial U(r)}{\partial r} \right\rangle \frac{\text{rydberg}}{(137.036)^2} \tag{6}$$

is the average value (taken over the *nl*-radial function) of the radial gradient of the *central field U*(*r*), divided by *r*. Contrary to S.C.S. parameters of interelectronic repulsion, which are always considerably smaller than the F^k integrals evaluated for Hartree–Fock radial functions, the computed values of Eq. (6) are between 1.2 and 0.8 times the observed values (Blume, Freeman and Watson, 1964) indicating compensating second-order effects. In hydrogenic systems with one electron, Eq. (6) gives Landé parameters proportional to Z^4, and Gobrecht (1938) interpreted the smooth increase among the M(III) up to Yb(III) as a proportionality to $(Z - 35)^4$. However, this cannot be the whole truth, as already seen from $^2F_{5/2}$ at 8774 cm^{-1} above the groundstate $^2F_{7/2}$ of Tm^{+2}, and from the seven *J*-levels of ^7F being spread 1.22 times as much in Eu(III) as in Sm^{+2} and Sm(II) compounds (Dupont, 1967). The fact that the *J*-levels of the lowest term of the samarium atom belonging to [54]4f^{6}6s^2 have wavenumbers only 0.2 per cent below those of Sm^{+2} (and about 0.3 per cent above those of $Sm_xLa_{1-x}Cl_{3-x}$) brings up the point emphasized by Dunn (1961) that external electrons have a very small influence on Landé parameters. Thus, ζ_{3d} is almost identical for [18]3d^{q}4s^2 of M, [18]3d^{q}4s of M$^+$ and [18]3d^q of M^{+2}, whereas it increases by several tenths from the latter ion to [18]3d^{q-1} of M^{+3}. In other words (Jørgensen, 1969) it is *the conditional oxidation state* M[II] or M[III] defined from the number q of electrons in the shell with the smallest average radius that counts. Other examples of Tm[II] and Yb[III] with q = 13 are the first excited level at 8771 cm^{-1} belonging to [54]4f^{13}6s^2 of the thulium atom, or the separation 10 149 cm^{-1} of the two *J*-levels of the excited configuration [54]4f^{13}6s^2 of Yb$^+$.

In Russell–Saunders coupling, the distance between the levels *J* and (*J* — 1) within the same term having $S_{\max}$ in a partly filled shell containing $q < (2l + 1)$ electrons is $J\zeta_{nl}/q$. In the second half of the shell, the same expression is valid with opposite sign (the terms are 'inverted' with the higher *J* values at lower energy) and replacing q by $(4l + 2 - q) = 2S_{\max}$. A corollary of this result is that the total width of a term with $S_{\max}$ (and *L* at least as large as $S_{\max}$) is $(L + \frac{1}{2})\zeta_{nl}$ in the first half of the shell, and the same expression with the opposite sign for $q > (2l + 1)$.

The deviations from Russell–Saunders coupling expressed as *intermediate coupling* correspond to eigen-values of determinants having diagonal elements with the *same J* (but not necessarily with the same *S* and *L*) and non-diagonal elements being definite constants times ζ_{nl}. The lower levels of the lanthanides are most frequently fairly close to Russell–Saunders coupling. An interesting exception are two levels with $J = 4$ of the lowest configuration [54]4f^{12}6s^2 of the erbium atom, [54]4f^{12} of Er^{+2} and of Tm(III) (Martin *et al.*, 1978) (all in cm^{-1}):

	$^3H_6$	$^3H_5$	$^3H_4$	$^3F_4$	$^3F_3$	$^3F_2$	
Er	0	6958	10 751	5035	12 378	13 098	
Er^{+2}	0	6970	10 785	5082	—	—	(7)
Tm(III)	0	8300	12 700	5800	14 500	15 100.	

In all three cases, ^3H and ^3F overlap considerably, and the squared amplitude of the ^3F character of the lower level with $J = 4$, and of the ^3H character of the second level with $J = 4$ (the third $^1G_4$ occurs in Tm(III) at 21 300 cm^{-1}) has the order of magnitude 0.6.

The terms of Eq. (2) are split by 'spin-orbit coupling' to a relatively small extent in $4f^2$Pr(III) and to a larger extent in $4f^{12}$Tm(III). The first attempts to apply S.C.S. theory to these two systems (Spedding, 1940; Bethe and Spedding, 1937) agree with present-day ideas as far as the positions of the triplet levels is concerned, but not at all with the singlets. The origin of this problem (Jørgensen, 1955b) is that a very low ratio between F^6 and F^2 in the highly excited configuration [54]$4f^2$ of La^+ (Condon and Shortley, 1953) had been uncritically accepted as a rule, whereas this ratio is close to 0.5 in actual M(III). Since the distances between terms with S_{max} only depend on one linear combination E^3 of the three F^k in the streamlined theory of Racah (1949), the disagreement can always be exported to terms with lower S. The same mistake was made in pioneer work by Satten (1953) on $4f^3$Nd(III) where the doublets were placed much too low relative to the quartets having the correct order. The first large-scale calculations of all the many terms (e.g. 73 for q = 5 and 9, 119 for q = 6, 7 and 8) was performed by Elliott, Judd and Runciman (1957) but quite a complete calculation in intermediate coupling was made by Carnall, Fields and Rajnak (1968). The identification of J-levels is largely finished below 25 000 cm^{-1} (cf. Reisfeld and Jørgensen, 1977) but the high density of J-levels in the ultraviolet (especially for q = 6, 8 and 9) makes it necessary to take the Judd–Ofelt theory of absorption band intensities into account (as discussed below). It may be noted that only 46 J-levels of $4f^6$Eu(III) and 36 J-levels of $4f^8$Tb(III) are calculated to occur below 40 000 cm^{-1}. According to Carnall *et al.* (1968), 37 and 23 have been safely identified. The search for the 249 J-levels at higher energy in Eu(III) is rendered difficult by electron-transfer bands, and for the 259 J-levels above 40 000 cm^{-1} in Tb(III) by transitions to the next configuration $4f^75d$.

Besides the unique excited J-level of Ce^{+3} (at 2253 cm^{-1}) and of Yb^{+3}, the only M^{+3} (having a ground configuration with a partly filled 4f shell) for which reliable evidence exists (Martin *et al.*, 1978) is Pr^{+3} in which Sugar (1965) located the first twelve J-levels of [54]$4f^2$ (the position of the very high $^1S_0$ is still controversial) as well as twenty J-levels of [54]4f5d (starting at 61 171 cm^{-1}). The difference $22\,007 - 6415 = 15\,592$ cm^{-1} between $^3P_1$ and $^3F_3$ is independent of ζ_{4f} in intermediate coupling. The corresponding difference (in cm^{-1}) and the nephelauxetic ratio is:

$$\begin{array}{lll} Pr_xLa_{1-x}F_3 & 14\,954 & \beta = 0.959 \\ [Pr(OH_2)_9](C_2H_5SO_4)_3 & 14\,933 & 0.958 \\ Pr_xLa_{1-x}Cl_3 & 14\,739 & 0.945 \\ Pr_xLa_{1-x}Br_3 & 14\,686 & 0.942 \end{array} \tag{8}$$

β is close to 0.92 for $BaPr_2S_4$. For comparison, the distance is $16\,524 - 4765 = 11\,759$ cm^{-1} in the isoelectronic Ce^{+2}. In a pure L.C.A.O. (linear combinations of atomic orbitals) model of the nephelauxetic effect, the parameters of interelectronic repulsion are expected to decrease twice as much as the Landé parameter, and ζ_{4f} does not vary as much as that in the trivalent lanthanides. As indicated by the J-level positions, two other contributions to the nephelauxetic effect (all pulling in the same direction) also operate.

1. The expanded radial functions due to the modified central-field $U(r)$.
2. The Watson effect (Jørgensen, 1962a,b) due to dielectric decrease of the interelectronic repulsion by mixing of small amounts of configurations having two electrons substituted into continuum orbitals with comparable radial extension.

A clear-cut case is the Racah parameter E^3 decreasing more by chemical bonding than E^1. The position of $^1I_6$ above the groundstate $^3H_4$ of $4f^2$ is mainly determined by E^1, whereas the ^3P levels are mainly dependent on E^3. The energy difference between $^1I_6$ and $^3P_1$ is 205 cm^{-1} in Pr^{+3}, 253 cm^{-1} in the ennea-aqua ion in Eq. (8), 340 cm^{-1} in the chloride, 380 cm^{-1} in the bromide, and has increased to 897 cm^{-1} in Ce^{+2} (where $^1I_6$ is even situated 104 cm^{-1} above $^3P_2$, though it is 949 cm^{-1} below $^3P_2$ in Pr^{+3}). One way of looking at the crossing of $^1I_6$ with the ^3P levels is the Pr(III) compounds in Eq. (8) representing some effective charge, say 2.83 in the aqua ion and 2.76 in the bromide from β of Eq. (8), but 2.93 and 2.70 from the interpolation of $^1I - {}^3P$ crossing. There is also evidence from the fine details of the variation of complex formation constants with q (Jørgensen, 1970b; Nugent, 1970; Fidelis, 1981) that chemical bonding decreases E^3 to a larger extent than E^1.

Unfortunately, no relevant data about Nd^{+3} and Er^{+3} are available (Martin *et al.*, 1978) but a large number of Nd(III) and Er(III) compounds have had their nephelauxetic ratio relative to the salts of the ennea-aqua ion evaluated, either by direct identification (at low T) of all the $(2J + 1)$ states belonging to each J-level (reviewed by Jørgensen, 1976c, 1979a) or by a less accurate technique (Jørgensen *et al.*, 1965; Jørgensen and Rittershaus, 1967) of comparing intensity baricenters in the absorption bands measured in reflection spectra. In both cases, it is established that β decreases 0.03 from $M(OH_2)_9^{+3}$ to M_2O_3 for M = Nd and 0.016 for M = Er. The effect is much weaker in $M_xLa_{1-x}Cl_3$ (0.007 for Nd and 0.004 for Er) though chlorides with lower coordination number (and concomitantly shorter M–X distance in the chromophore) such as MCl_6^{-3} having 0.022 for Nd and 0.012 for Er. On this basis, it is likely that β of Eq. (8) is close to 0.97 for Nd(III) aqua ions, and 0.985 for Er(III).

Energy-wise, considering the minute chemical variations of the parameters of interelectronic repulsion, and even smaller changes of the Landé parameter, the J-levels of M(III) compounds provide a remarkable imitation of a monatomic entity. For some obscure reason, the Slater–Condon–Shortley and Racah treatment gives much better agreement with $4f^q$ (Carnall *et al.*, 1968) than with gaseous ions $[18]3d^q$. It should not be forgotten, however, that the phenomenological parameters of interelectronic repulsion E^k (or F^k) are considerably smaller than the integrals obtained for Hartree–Fock 4f radial functions (Freeman and Watson, 1962). As far as *intensities* of absorption bands go, M(III) obviously differ from M^{+3}. In atomic spectra (except when measured at relatively high gas pressures) the *selection rules* are very severe. Electric dipolar transitions *only* go between two states of opposite parity (if a J-level is well described as belonging to a definite configuration, the parity is even or odd, according to whether the sum of the l-values of all the electrons is even or odd). Further on, J_1 changes at most one unit (J_2 of the other level can be $(J_1 + 1)$, J_1 or $(J_1 - 1)$; and transitions are forbidden if both J_1 and J_2 are zero). In the approximation of Russell–Saunders coupling, S does not change, and L changes at most by one unit. With these selection rules, it is clear that many atoms (some of them important for electric discharge lamps) have *metastable* states. For instance, the mercury atom and the isoelectronic Tl^+, Pb^{+2} and Bi^{+3} have the first excited configuration [78]6s6p with the four levels $^3P_0$, $^3P_1$, $^3P_2$ and $^1P_1$ (among which the two J-levels with $J = 1$ are strongly mixed by intermediate coupling) and in spite of its odd parity, the lowest level $^3P_0$ cannot go down to the even groundstate $^1S_0$ exemplifying $[78]6s^2$. It is interesting to discuss (Jørgensen, 1971; Reisfeld and Jørgensen, 1977; Boulon, Jørgensen and Reisfeld, 1980) to what extent the luminescent levels of bismuth (III) in condensed matter are related to $^3P_0$ and $^3P_1$ of Bi^{+3}. The first excited configuration $1s^22s^22p^53s$ of the neon atom (analogous behaviour is found in the heavier noble gases) also has four J-levels, among which $J = 2$ has the lowest energy, and it cannot go down to $^1S_0$. The stationary concentration of the metastable $^3P_2$ allows ready excitation to the ten J-levels of $1s^22s^22p^53p$ and the strong emission lines from this configuration to the first excited configuration provide the familiar red light.

Not only are there restrictive selection rules operating in monatomic entities, but the *oscillator strength P* (called f by many authors) can be highly different for various allowed transitions. The strongest spectral lines typically have P between 0.1 and 1.5 (thus, the two lines in the yellow of the sodium atom connecting the groundstate [10]3s with the two levels of [10]3p having $J = \frac{1}{2}$ and $\frac{3}{2}$ have $P = 0.33$ and 0.65, whereas the transitions in the ultraviolet to [10]4p and [10]5p are far weaker) but the product of the radial functions of the even and odd l-values may provide large or small electric dipole moments according to detailed conditions (Sobelman, 1979). Einstein proved in 1917 that the *radiative lifetime* of an excited state E_2 to a lower state E_1 is inversely proportional to the product of P and the square of the photon energy. If E_2 (containing e_2 states) exclusively decays to E_1 (containing e_1 states) the half-life (as for a radioactive process) is

$$t_{1/2} = \frac{e_2}{e_1} \cdot \frac{1.6 \times 10^{-8}\,\mathrm{s}}{P(h\nu/\mathrm{eV})^2} \tag{9}$$

with 1 eV = 8065.48 cm^{-1}. In condensed matter, P of an absorption band can be evaluated as a constant of Nature times the area (the molar extinction coefficient ε as a function of the wave-number). If the absorption band is a Gaussian error-curve with maximum $\varepsilon_{\mathrm{max}}$ and the half-width (half the width at half height) δ (in cm^{-1}), $P = 9.20 \times 10^{-9}\delta\varepsilon_{\mathrm{max}}$. P for organic dye-stuffs can be close to 1, but the strongest transition in the visible known for an inorganic species is the first electron-transfer band of PtI_6^{-2} at 20 250 cm^{-1} having $\varepsilon_{\mathrm{max}} = 12\,800$ and $\delta = 1600$ cm^{-1}, and hence $P = 0.19$ (the corresponding electron-transfer band in the green of permanganate is ten times weaker). For a compilation of P values and other characteristics of (mainly) d-group complexes, *see* Jørgensen, 1963.

It turns out that most of the narrow absorption bands of trivalent lanthanides have P between 10^{-7} and 10^{-5}. In one way, this is too little, and in another, too much. The only transitions permitted in monatomic M^{+3} inside the configuration [54]4f$^{\mathrm{q}}$ are magnetic dipolar. In Russell–Saunders coupling, they occur in absorption mainly from the groundstate to the first excited J-level (in the infrared) but small contributions to P of other transitions can be calculated (Carnall *et al.*, 1968) with great precision, since no radial functions, nor material parameters are involved. By far the largest amount of the P observed has electric dipolar character, but is induced by the presence of the neighbour atoms. Broer, Gorter and Hoogschagen (1945) analysed this situation in terms of the *hemihedral* part of the Hartree field (with the lanthanide nucleus at the origin)

$$U_{\mathrm{hem}} = [U(x, y, z) - U(-x, -x, -z)]/2 \tag{10}$$

mixing the 4f$^{\mathrm{q}}$ to a very small extent with one (or more) configurations of the opposite parity. If the intrinsic P of transitions to such a configuration is 0.1 to 1, agreement might be obtained with non-diagonal elements of U_{hem} of the order of 100 cm^{-1} if the excited configuration is situated some 50 000 to 100 000 cm^{-1} above the groundstate. Judd (1962) and Ofelt (1962) proposed independently a more quantitative treatment, where three squared matrix elements $|U^{(t)}|^2$ with $t = 2$, 4 and 6 (in the following called U_t for simplicity) can be evaluated once and for all from the groundstate to the excited J-levels of a given M(III), as tabulated by Carnall *et al.* (1968). Since the positions of J-levels hardly depend on the surrounding atoms, this is an acceptable approximation. On the other hand, each M(III) in a given molecule, polyatomic complex ion, or solid, has three *material parameters* Ω_t (to be evaluated from optimized agreement with the Judd–Ofelt theory). Hence, the transition with frequency ν from the J state has

$$P = \frac{8\pi^2 m\nu}{3h(2J+1)} \cdot \frac{(n^2+2)^2}{9n} (\Omega_2 U_2 + \Omega_4 U_4 + \Omega_6 U_6) \tag{11}$$

where the first of the three factors contain constants of Nature and the ratio $\nu/(2J + 1)$, the second factor depends on the refractive index n of the system, and the third is linearly additive in the three parameters. A convenient unit for Ω_t is 10^{-20} cm^2. Besides special selection rules (one can only go to $J = 2$, 4 and 6 from $J = 0$) a corollary of Eq. (11) is that J cannot change by more than 6 units. It is very rare in spectra of condensed matter that one knows that a given J-level is situated in an open region without other interfering absorption bands, and then cannot be detected. This exceptional forbiddenness of transitions occurs for $^5L_9$ and $^5L_{10}$ of Eu(III) calculated at 28 200 and 28 800 cm^{-1}, $^6F_{1/2}$ of Dy(III) very reliably predicted at 13 700 cm^{-1}, and $^5F_1$ of Ho(III) close to 22 400 cm^{-1}. In all of these cases, not the slightest absorption has been observed.

For the chemist, the variation of the three Ω_t is of great interest. In aqua ions, and in other, rather electrovalent cases, such as solid fluorides, Ω_2 is quite small, and almost within the experimental uncertainty. There is, obviously, an uncertainty in each Ω_t, since a large number of transitions is brought on the Procrustes bed of the overdetermined set of linear equations of the form of Eq. (11) (with the exception of Yb(III) showing only one transition, which further is magnetic dipolar to a significant extent). The Ω_4 and Ω_6 for aqua ions and fluorides have a comparable size, some 2 to 7 × 10^{-20} cm^2 for the aqua ions, and about one-third of these values in crystalline fluorides. Technically, the Ω_4 and Ω_6 correspond to 16- and 64-polar transitions. The situation is entirely different for other kinds of ligands. It was noted by Moeller and Ulrich (1956) that one or two of the absorption bands of tris-acetylacetonates increased the oscillator strength (relative to the aqua ion) by a factor 10 to 50. Jørgensen and Judd (1964) generalized this situation of very large Ω_2 to *hypersensitive pseudoquadrupolar transitions*. They are hypersensitive because small changes of the ligands intensify one definite transition (in Russell–Saunders coupling going from the (S, L, J) groundstate to $(S, L-2, J-2)$) having a very large squared matrix element U_2. Holmium(III) has two such transitions, to $^5G_6$ at 21 100 cm^{-1} and to $^3H_6$ at 27 700 cm^{-1} having $U_2 = 1.52$ and 0.22, respectively, and erbium(III) also two, to $^2H_{11/2}$ at 19 200 and $^4G_{11/2}$ at 26 400 cm^{-1} with $U_2 = 0.71$ and 0.92. All the three transitions to levels with $J = 4$ in thulium(III) have rather large $U_2 = 0.54$, 0.24 and 0.05. These transitions are called 'pseudoquadrupolar' because the genuine P values of electric quadrupolar transitions would be proportional to U_2 but the observed values are thousands of times the calculated P (Broer, Gorter and Hoogschagen, 1945). 'Conjugated' ligands such as nitrate, carbonate and acetate (which seem generally to be bidentate) and polycarboxylates, besides the classical cases of β-diketonates, specialize in the high Ω_2 values. However, gaseous halides also have huge Ω_2 and the largest of all known (180 × 10^{-20} and 275 × 10^{-20} cm^2) occur for gaseous $NdBr_3$ and NdI_3 (Gruen and DeKock, 1966) and the transition to $^4G_{5/2}$ of the vapour $CsNdI_4$ (Liu and Zollweg, 1974) shows $P = 2.6 \times 10^{-4}$, about half the value for NdI_3, whereas $P = 10^{-5}$ for Nd(III) aqua ions. Also volatile adducts of $ErCl_3$ with $AlCl_3$ or $GaCl_3$ show large Ω_2 (Papatheodorou and Berg, 1980). The Judd–Ofelt parameters have been reviewed several times (Peacock, 1975; Henrie, Fellows and Choppin, 1976; Reisfeld and Jørgensen, 1977). It seems that the origin of the large Ω_2 may indeed be the oversimplification of describing the matter (consisting of atoms) as a homogeneous dielectric (Judd, 1979).

The analogy of trivalent lanthanides to monatomic entities has brought configurations such as $4f^{q-1}5d$ and $4f^{q-1}5g$ (of opposite parity to the ground configuration) into the Judd–Ofelt theory. It is likely that the neighbour atoms play a more active rôle than just supplying an external field. However, it is beyond doubt that electron-transfer spectra are less important in the trivalent lanthanides (perhaps because of rather low intrinsic P) than in the d-group complexes having a centre of inversion, where it is generally true (Jørgensen, 1963) that the spin-allowed internal transitions in the partly filled 3d, 4d or 5d shell have P values inversely proportional to the square of the energy difference to the closest strong electron-transfer bands. However, a few central atoms (Jørgensen, 1975a) such as copper(II) and palladium(II) have unexpected large P, in the region 0.001 to 0.01. It must also be realized that the Judd–Ofelt description of Pr(III) does not work if the unusually intense transition to $^3P_2$ (the aqua ion has $P = 1.5 \times 10^{-5}$) is included. A rather *ad hoc* explanation would involve configuration intermixing between [54]4f^2 and [54]5d^2. With the exception of such rare cases, the situation of only three Ω_t describing a large number of transitions, is entirely different from monatomic entities having their intrinsic P values derived from specific electric dipole moments. Thus, the transition to [10]4p is 80 times weaker in the sodium atom than the 'resonance lines' to [10]3p. The additional factor of *spin-forbiddenness* is quite similar in monatomic entities, f- and d-group compounds. When the spin-allowed transition for whatever reason has a given P value, the adjacent spin-forbidden transitions (changing S by one unit) have P multiplied by a small multiple of the square of the ratio between ζ_{nl} and the energy difference to the closest level (same J in the 4f group and in monatomic entities) with S of the groundstate.

It is worth noting that keeping the neighbour atoms constant, the Ω_t values vary quite smoothly from Nd(III) to Tm(III). Whereas this trend is a decrease, the parameters of interelectronic repulsion increase almost linearly with q. Thus, the distance between ^3P and ^3F given in Eq. (8) is $33E^3$. Hence, Pr(III) aqua ions have $E^3 = 450$ cm^{-1} and Tm(III) aqua ions $E^3 = (36\,500 - 14\,500)/33 = 670$ cm^{-1}. The M(III) with q = 3 to 11 are situated roughly on a straight line between these two points (Carnall *et al.*, 1968). Such regular variations are indeed expected from the smooth decrease of the radial extension of the 4f shell in Hartree–Fock calculations (Freeman and Watson, 1962).

LANTHANIDES IN GLASSES AND TRANSPARENT CRYSTALS

The overall distribution of J-levels of trivalent lanthanides dispersed in vitreous or crystalline solids is the same as for aqua ions or other complexes in solution. However, the solids are much more apt to *luminescence.* The classical cases (Gobrecht, 1937, 1938) of excited levels fluorescing in the visible are $^4G_{5/2}$ of Sm(III) at 17 900 cm^{-1}, $^5D_0$ of Eu(III) at 17 250 cm^{-1}, $^5D_4$ of Tb(III) at 20 500 cm^{-1} and $^4F_{9/2}$ of Dy(III) at 21 100 cm^{-1}. Several fluorescence lines may be observed, due to transitions to the lower J-levels of the lowest term ^6H in Sm(III) and Dy(III) and ^7F in Eu(III) and Tb(III). It is noted that these four lanthanides are disposed symmetrically (q = 5, 6, 8, 9) around the half-filled shell. The major reason (Reisfeld and Jørgensen, 1977, page 93) is that a large gap (7400 to 14 800 cm^{-1}) occurs between two consecutive J-levels in the visible. The situation is more extreme in Gd(III) having the first excited level $^6P_{7/2}$ at 32 200 cm^{-1} whose ultraviolet luminescence was discovered by Urbain in 1905.

It is a truism that excited states not decaying in some non-radiative way (producing heat or performing photochemical reactions) all luminesce. The competing multiphoton deexcitation is, under equal circumstances, the less important, the higher the ratio between the energy difference between two adjacent J-levels and the highest phonon energy (i.e. the normal vibration energies of the condensed matter). Thus, anhydrous lanthanum chloride (Dieke, 1968) and bromide have unusually low phonon energies, and many J-levels of most substituted M(III) are known to luminesce. These crystalline materials are difficult to handle, because of their strong hygroscopicity, and Reisfeld (1973, 1975, 1976) selected glasses with high atomic weights and small force constants (the two conditions favouring low phonon energies) such as germanates and tellurites. It was later found (Reisfeld and Bornstein, 1977; Reisfeld *et al.*, 1977, 1979) that sulphur-containing glasses of composition close to $LaAl_3S_6$ or $LaGa_3S_6$ and certain fluoride glasses are also excellent for fluorescence. This problem became of considerable technical importance, when the transition in the near infrared (close to 9500 cm^{-1}) from $^4F_{3/2}$ to the first excited level $^4I_{11/2}$ of Nd(III) was shown to be an efficient four-level laser in crystalline garnet $Y_{3-x}Nd_xAl_5O_{12}$, perovskite $Y_{1-x}Nd_xAlO_3$ or pentaphosphate $La_{1-x}Nd_xP_5O_{14}$ (where even undiluted NdP_5O_{14} works). The SHIVA system of twenty neodymium(III) silicate glass lasers delivering synchronous 10^{-9} s pulses (each in the 10^{12} to 10^{13} W range) for inducing nuclear fusion in imploding deuterium-tritium pellets, has actually been functioning since January 1978 in the Livermore laboratories in California. However, according to a private communication from Dr. W. F. Krupke, it is likely that such large-scale lasers in the future may be made from the rutile-type $Mg_{1-x}V_xF_2$ where the near-infrared luminescence from the first excited quartet state of the chromophore $V(II)F_6$ to the quartet groundstate has almost the full radiative mean lifetime ($=t_{1/2}/ln2$) according to Einstein, Eq. (9), close to 2 ms.

The Judd–Ofelt theory originally applied to M(III) absorption intensities in Eq. (11) can also describe the lifetime via the oscillator strength in Eq. (9) for purely radiative decay, and the *branching-ratios* for a given *J*-level fluorescing down to various lower-lying *J*-levels, including the groundstate. Thus, Reisfeld and Eckstein (1975) investigated the luminescent properties of erbium(III) in various glasses, and Reisfeld and Hormadaly (1976) holmium(III). Recently, Blanzat *et al.* (1980) compared the luminescence of europium(III) in various oxide- and fluoride-type glasses with the Judd–Ofelt results for lifetimes and branching-ratios. It is expected that one cannot predict these quantities better than with a scattering of some 20 per cent of their values, but the Judd–Ofelt parameterization allows valid prediction of laser characteristics with a much smaller amount of experimental effort (Reisfeld and Jørgensen, 1977).

The *crystal-field theory* of Bethe (1929) was the explanation of the energy differences in partly filled d- and f-shells in compounds by the electrostatic perturbation of $V(r) - V(x, y, z)$, the *non-spherical part* of the *Madelung potential* produced by electric charges on the atoms other than the transition-group atom considered. There is no doubt that the spherical part $V(r)$ of the Madelung potential (which can be calculated in the case of spherically symmetric, non-overlapping ions as if their charges were situated on their central point) has important and experimentally verifiable effects (Rabinowitch and Thilo, 1930; Jørgensen, 1969, 1971) but the non-spherical part is very small, and it was realized before 1956 that the ordinary effects of covalent bonding on the d-like orbitals are far more important. Orgel and Sutton in a meeting in Copenhagen in 1953 suggested using the word *ligand field theory* for the MO treatment of the five d-like orbitals as (approximately) nonbonding or antibonding. However, until the introduction (Jørgensen, Pappalardo and Schmidtke, 1963) of the *angular overlap model* (A.O.M.) there was a general opinion prevailing that the nearest neighbours (the 'ligating atoms') had so small an energetic influence on the partly filled 4f shell that it might as well be an electrostatic effect of the non-spherical part of the Madelung potential. This approach has been renovated by Hellwege (1948) and systematized further in the monograph by Prather (1961). However much the numerical predictions of energy differences may have been unsatisfactory, one has to realize that electrostatic perturbations cannot split sets of states (always an even number of states 'Kramers doublets' in the case of an odd number of electrons) that have to remain degenerate for fundamental reasons, and further that such perturbations nearly always separate all states that do not *have* to have the same energy. 'Ligand field' theory is to a large extent a question of applied group theory.

In the simplest version of A.O.M. only σ-antibonding due to the filled orbitals of the ligating atoms is considered. It can be shown that the calculated σ-antibonding energy (given as a multiple of a radial parameter) can be obtained more readily from an equi-consequential contact potential perturbing the squared angular part of the d- or f-functions at the positions of the nuclei of the ligating atoms. It is possible to introduce the (smaller)

π-antibonding energy (Schäffer and Jørgensen, 1965; Schäffer, 1968, 1970, 1973) as the perturbation of Kronecker dipoles on the differential quotient of the angular function perpendicular to the M–X axis. In the limit of considering all the λ values $(0, 1, 2, \ldots, l)$ and alternating (plus and minus) regular 2λ-polygons as the source of perturbation close to the X nucleus, one obtains exactly the same number of parameters as the electrostatic crystal-field model. The latter model has several features in common with A.O.M. Thus, a fundamental assumption is that the perturbations of the ligands can be incorporated exclusively in one-electron energies (relative to a zero-point of non-bonding behaviour, or relative to the average energy of the seven f-like orbitals). For $q = 2, 3, 4, \ldots, 12$ the $91, 364, 1001, \ldots$ states of Eq. (3) provide a far larger number of *sublevels* than the one-electron parameters. In octahedral symmetry (O_h), as known (Morrison, Leavitt and Wortman, 1980) from the elpasolites Cs_2NaMCl_6, there are only two independent energy differences, because three different symmetry types are represented by 1, 3 and 3 f-like orbitals. The point-group D_{3h} realized (at least to a close approximation) by the chromophores $M(III)X_9$ in $LaCl_3$, $LaBr_3$, $M(OH)_3$ and many salts of $M(OH_2)_9^{+3}$ have four independent energy differences, because 1, 2, 2, 1 and 1 f-like orbitals occur. The point-group D_{2d} for $Zr(IV)O_8$ in zircon ($ZrSiO_4$) type xenotime YPO_4 and the orthovanadate (known from the red cathodoluminescence in colour television) $Y_{1-x}Eu_xVO_4$ has five parameters, because two sets of two f-like orbitals have a non-diagonal element of one-electron energy. In the lowest possible symmetry, six $(=7 - 1)$ diagonal and 21 non-diagonal parameters occur. Another common feature is that energy levels (not certain other properties, such as the Judd–Ofelt Ω_t) within a single f^q configuration are determined by the *holohedrized symmetry* (Jørgensen, 1971) the point-group (including a centre of inversion) of U_{hol} (which is Eq. (10) with a plus in the middle, or $U = U_{hol} + U_{hem}$ in other words).

As with the overdetermined sets of linear equations of the type of Eq. (11), it is not possible to discuss A.O.M. or other versions of 'ligand field' theory as a question of solving n linear equations (without singularities in the determinants) for n unknowns. It is rather a question of judgment of the overall agreement between a large number of experimental data and a small number of parameters. It is not wise to minimize the square of the deviations (as if they had a Gaussian distribution), and direct visual comparison, or minimizing the absolute deviations, may be more realistic. The advantage of purely σ-antibonding A.O.M. (if it works) is that $e_\sigma = \sigma^*(2l + 1)$ should be *transferable* from one chromophore MX_N to another, having a different (holohedrized) symmetry or a different coordination number N, or both. If the M–X internuclear distance R changes, σ^* is ideally some exponentially decreasing function of R (Jørgensen, 1971) but it seems empirically verified (Burns, 1967) that σ^* increases some 6 to 10 per cent, when R decreases by 1 per cent. It also seems established (Linares, Louat and Blanchard, 1977; Urland, 1977, 1978, 1979, 1981) that halides and hydroxides have π-antibonding effects e_π about one fifth of e_σ, much like the d-group compounds. One should not forget that the parameters of the electrostatic crystal-field model are only *one* among many ways of presenting the more fundamental one-electron energy differences, and it is in this sense that it is meaningful to ask whether this model or A.O.M. (with e_σ alone, or including a small e_π) is the more appropriate. If the group-theoretical consequences of the site symmetry in the crystal are taken into account (as one has to do in both models) there is very little hope of *determining* the electrostatic parameters from the positions of the ligating atoms. There is a long series of unconvincing attempts to explain what went wrong with the electrostatic parameters, whereas A.O.M. with transferable e_σ (and a bit of e_π) actually works. Faucher (1981) has made a fascinating attempt at combining both models for the two sites (point groups S_6 and C_2) for $M(III)O_6$ in cubic C-type M_2O_3. However, in the writer's opinion, it is far more appealing to start with A.O.M. and let the non-spherical part of the Madelung potential explain what cannot be explained by A.O.M. than to proceed in the opposite direction.

It is worthwhile to consider the numerical quantities involved. In octahedral d-group complexes, the energy difference Δ (called 10 Dq in the older literature) between the two antibonding and the three roughly nonbonding orbitals varies (in a very predictable way as a function of the central atom in a definite oxidation state, and of the ligands) between 5000 and 40 000 cm^{-1} (Jørgensen, 1969). The A.O.M. description with pure σ-antibonding is $\Delta = 3e_\sigma = 15\sigma^*$. The σ^* values in 4f-group compounds decrease slightly from Pr(III) to Tm(III) and are generally between 15 and 50 cm^{-1} (Reisfeld and Jørgensen, 1977), that is 50 times smaller than typical values for 3d-groups M(III). The total σ-antibonding effect on *all* seven f orbitals in MX_N is $7N\sigma^*$ and the typical spreading of their energies is 300 to 700 cm^{-1}. Because of the smallness of this spreading compared with the typical distance between (at least the lower) J-levels, the total spreading of sublevels belonging to a given J-level tends to be even smaller. Crosswhite *et al.* (1976) made a thorough study of $Nd_xLa_{1-x}Cl_3$ (at liquid helium temperature) and succeeded in identifying 101 among the 182 Kramers doublets. The ground level $^4I_{9/2}$ is split by 249 cm^{-1} and the following $^4I_{11/2}$ by only 85 cm^{-1}. Both $^4F_{3/2}$ and $^4F_{5/2}$ are only split to the extent of 30 cm^{-1}, $^4G_{9/2}$ and $^2D_{3/2}$ 28 cm^{-1}, $^4D_{3/2}$ 3 cm^{-1} and $^4S_{3/2}$ 2 cm^{-1}. Among the 32 J-levels identified below 33 000 cm^{-1}, 18 have their sublevels distributed over less than 100 cm^{-1}. The total spreading of one-electron energies should be close to 350 cm^{-1}.

It is tempting to ask about the physical origin of σ^*. It seems well established (Jørgensen, 1971) that the effect of the local operator of electronic kinetic energy *at least* has the same order of magnitude as the energy differences induced by potential energy. The writer suspects (but has not been able to prove) that the contribution from the kinetic operator (before adaptation of the closed shells to the virial theorem) are considerably larger than the potential contribution. This is why he puts quotation marks when writing 'ligand field' theory.

LANTHANIDES IN BLACK SEMICONDUCTORS AND METALLIC ELEMENTS AND ALLOYS

Whereas 11 of the lanthanides have neutral atoms with groundstate belonging to $[54]4f^{q+1}6s^2$ and hence showing the conditional oxidation state M[II], and only four are M[III] corresponding to $[54]4f^q5d6s^2$, the situation is different for the crystalline metallic elements. Twelve are M[III] without discussion, europium ($S = \frac{7}{2}$) and ytterbium (S zero) are M[II], and whereas the hexagonal and the lower-density cubic cerium stable at higher T are Ce[III], the higher-density isotypic cubic form may contain Ce[IV] alone, or mixed with some Ce[III] (Jayaraman, 1965). It is more surprising to the chemist that not only do the magnetic properties characterize the ground J-level (many europium or ytterbium alloys contain Eu[III] or Yb[III]) but it is possible (Wallace, Sankar and Rao, 1977) from finer details of the dependence of the magnetic properties on T to evaluate the spreading of sublevels of the ground J-level, and it is generally one third to one half of the corresponding M(III) aqua ions.

After this manifestation of 'ligand field' effects in the metallic elements, it may be mentioned that *photoelectron spectra* (cf. Jørgensen, 1977) allow the nephelauxetic ratio β to be determined for the M[IV] obtained by ejection of a photoelectron. The ionization energies I are *defined* from Einstein's photoelectric equation

$$I = h\nu - E_{\mathrm{kin}} \tag{12}$$

for the sharp maxima (*signals*) in the probability distribution of the ejected electrons as a function of their kinetic energy. The monochromatic photons used on solid samples are generally $h\nu = 1253.6$ or 1486.6 eV originating in 2p → 1s transitions in either magnesium or aluminium anticathodes. The metallic lanthanides can show a quite complicated structure (Cox, Baer and Jørgensen, 1973) in the region corresponding to the ionization $4f^q \rightarrow 4f^{q-1}$ especially for q = 8 to 13. The structure is due to several J-levels of the ionized system, but their probability of formation is not simply proportional to the number of states $(2J+1)$. As shown by Cox (1975), the symmetry-determined and the numerical selection rules correspond to the square of the coefficient of fractional parentage of (S, L, J) in the ground level (S_0, L_0, J_0) of the un-ionized system.

As discussed by Campagna, Wertheim and Bucher (1976) both the metallic elements and the semiconducting NaCl-type antimonides MSb have almost the same signals (both energy- and intensity-wise) with I systematically about 1 eV higher in the latter case. Seen from the point of the chemist, the most unexpected feature is that I for the filled Sb5p shell is always *lower* than for the partly filled 4f shell. This difference (up to the first M4f signal) increases from 2.6 eV in PrSb to 7.1 eV in GdSb, and then after a downward jump at the half-filled shell, from 1.2 eV in TbSb to 3.5 eV in TmSb. A closer analysis (Jørgensen, 1975b, 1979a) shows that these large differences (much like the distance 8.0 eV from the Fermi level to the 4f signal in metallic gadolinium) reflect the electron affinity of the 4f shell being *much* smaller than the ionization energy. This creates an enigmatic situation for 'ligand field' theory (Jørgensen, 1973b, 1974a, 1975b; Ferreira, 1976) that we are accustomed to covalent bonding being the most pronounced, when the ionization energies of the orbitals involved on two adjacent atoms are identical, or roughly comparable. Nevertheless, it is an experimental fact that the I(M4f) and I(X2p) approximately coincide in M_2O_3 and MF_3 for M = Sm, Eu, Tm and Yb, and that I(Gd4f) is distinctly higher than I(X2p), like the general rule for the antimonides. In view of the very moderate nephelauxetic effect in the oxides and fluorides, it seems that the negligible extent of covalent bonding (involving the 4f shell) is determined by the electron affinity of the lanthanide being lower than the ionization energy of the ligands.

Perhaps an even more surprising observation (Cox *et al.*, 1973; Jørgensen, 1975b) is the moderate nephelauxetic effect in the M[IV] obtained by ionization $4f^q \rightarrow 4f^{q-1}$. For instance, the difference between ^8S and ^6H is found to be 8.0 eV in the photoelectron spectrum of metallic terbium, and 7.9 eV in TbSb, to be compared with 7.3 eV derived from the absorption spectra of Gd(III) (Carnall, Fields and Rajnak, 1968). By the same token, the difference between $^4I_{15/2}$ and $^2L_{17/2}$ derived from the photoelectron spectrum of metallic thulium is 5.5 eV, and of TmSb 5.7 eV, to be compared with 5.2 eV obtained from absorption spectra of erbium(III). A comparison of the term distances in Pr^{+2} and Nd(III) (Jørgensen, 1969) and general regularities among M^{+3} and M^{+4}, combined with the nephelauxetic ratio β of the aqua ions having the order of magnitude 0.99 from Gd(III) to Tm(III) allow the conclusion that M^{+4} ought to have the term distances close to 1.20 times those of M(III) aqua ions formed by the preceeding element. Hence, β is 0.92 in metallic terbium, 0.89 in metallic thulium and 0.91 in TmSb. One would have expected covalent bonding in M[IV] to be more impressive, and the sublevel broadening of the individual J-signals to have been larger than the experimental higher limit 0.5 eV. A particularly interesting case is the NaCl-type thulium telluride TmTe containing comparable amounts (on an instantaneous picture) of $4f^{12}$Tm[III] and of $4f^{13}$Tm[II] (Campagna *et al.*, 1976). The Tm[IV] formed by ionizing the former constituent shows $\beta = 0.91$ (like TmSb) but the $4f^{12}$ states (from ionizing $4f^{13}$) indicate the marginal nephelauxetic effect $\beta = 0.99$.

The variation of redox properties (being comparable for q and (7 + q) 4f electrons) can be rationalized by the *refined spin-pairing energy* description originally developed

(Jørgensen, 1962c) for explaining the positions of electron-transfer bands of M(III) bromide complexes in ethanol, but later shown to be applicable to many other properties varying in a characteristic way with q. Thus, the position of the ground (S_{max}, L, J) level below the baricenter of all $4f^q$ states of Eq. (3) consists of a major contribution

$$\left[\frac{3q(14-q)}{52} - S(S+1)\right]D \tag{13}$$

where the spin-pairing energy parameter D is $(9E^1/8)$ in Racah's notation. Eq. (13) for the average energy of all the states having a given S, has to be further supplemented for the groundstate of q = 2, 3, 4, 5, 9, 10, 11 and 12 (where S_{max} can be combined with differing L values) by a negative multiple of E^3 according to Racah (1949), and for all the groundstates from q = 1 to 13 (except q = 7) a small negative constant times ζ_{4f}. This theory agrees with the standard oxidation potentials E^0 of M(II) aqua ions, and with the systematic variation of ionization energies of gaseous M^{+2} and M^{+3} and I determined from photoelectron spectra of a definitive type of solid (varying q). It was pointed out earlier (Jørgensen, 1964a; Hulliger, 1968) that the choice of NaCl-type MS, MSe and MTe between metallic behaviour and M[III] (M = La, Ce, Pr, Nd, Gd, Tb, Dy, Ho, Er and Lu) and low energy-gap semiconductors M[II] (M = Sm, Eu and Yb) can be rationalized by the refined spin-pairing energy treatment. Jørgensen (1976c) and Johnson (1977) noted that the tendency toward M[III] increases

$$M^{+2} < \text{gaseous } M < MI_2 < MTe < MSe < MS < \text{metallic } M \tag{14}$$

as a function of decreasing M–M distances in the solids. It may also be noted that dense alloys (Wertheim, 1980) of ytterbium such as $YbNi_5$ contain Yb[III], and the $4f^{13} \rightarrow 4f^{12}$ photoelectron spectrum (which is less well-resolved in non-conducting Yb_2O_3 and YbF_3) is compared with the Tm[II] component of TmTe.

One may ask the general question what parameter determines the monatomic behaviour of the lanthanides. It would seem that it is related to the average radius of the partly filled shell being so much smaller than the internuclear distances to the ligating atoms. In spite of the contraction of ionic radii from Ce(III) to Yb(III), this argument would make the latter atom the most 'isolated' known. However, it seems beyond doubt (Jørgensen, 1971, 1975d) that there is a component of the huge angular part of the kinetic energy (according to a private communication from Dr. R. E. Watson, 540 eV for the Hartree–Fock function of Gd^{+3}) counteracting any chemical attempt at modifying the radial extension of the partly filled 4f shell.

TRANSTHORIUM (5f GROUP) ELEMENTS

As an interesting example of how difficult it is to decide certain questions by exclusively chemical arguments, the position of uranium in the Periodic Table may be mentioned (Jørgensen, 1973a, c). As seen on a Russian stamp issued in 1969, Mendeleev at first put this element in the third column (starting with boron and aluminium) accepting the oxidation states U(II) and U(III) and the atomic weight 119. Then, he needed this position for the newly discovered indium, and he moved uranium to the sixth column, forming U(IV) and U(VI) compounds such as the *uranyl ion* UO_2^{+2}. This homologue to chromium, molybdenum and tungsten was not chemically worse off than so many other homologues, and certainly more convincing than the fifth column between nitrogen and bismuth. The only dissenting voice against this view in the next sixty years was the geochemist Goldschmidt who argued that the mineral ThO_2 has such a propensity for incorporating not only cerium(IV) but also trivalent lanthanides (leaving statistically distributed oxide vacancies, Jørgensen and Rittershaus, 1967) and uranium(IV), and though genuine transuranium elements were not synthesized before 1940, Goldschmidt suggested that thorium might be the first of a series of predominantly quadrivalent elements. This hypothesis was defended by Ephraim and Mezener (1933) with a surprisingly modern argument that the green U(IV) salts show narrow absorption bands like Pr(III), and hence contain two 5f electrons. However, this argument was neglected (probably because Cr(III) compounds also have narrow bands) until the groundstate $^5L_6$ belonging to [86]$5f^36d7s^2$ was established for the gaseous uranium atom in 1946. Connick (1949) was the first to point out that the most frequent oxidation states have very little to do with the groundstate of the neutral atom. Thus, Nd(III) is exceedingly difficult to reduce to Nd(II) in spite of the fact that five *J*-levels below 6764 cm^{-1} of the neutral atom all belong to ^5I of [54]$4f^46s^2$, whereas U(III) is far less frequent than U(IV) and U(VI).

It is now known that the groundstate of Th^{+2} belongs to [86]5f6d, but only 63 cm^{-1} below the lowest *J*-level of [86]$6d^2$. On the other hand, the groundstate $^2F_{5/2}$ of Th^{+3} belongs to [86]5f, whereas the first of the two levels of [86]6d occurs at 9193 cm^{-1}. The Landé parameter ζ_{5f} is 1236 cm^{-1} in Th^{+3}. The analysis by Racah (1950) of the (excited) configuration [86]$5f^2$ of Th^{+2} indicates $\zeta_{5f} = 1035$ cm^{-1} and $E^3 = 290$ cm^{-1}, two-thirds of the value for $4f^2$ of Pr(III). Kaufman and Radziemski (1976) find $\zeta_{5f} = 2174$ cm^{-1} for the ground configuration [86]5f of U^{+5}.

Unfortunately, no direct evidence is available for [86]$5f^2$ of U^{+4}. The uranium(IV) aqua ion has its last visible absorption band at 23 300 cm^{-1} (connected with $^3P_2$) followed by $^1S_0$ at 40 800 cm^{-1} (Jørgensen, 1955a; Cohen and Carnall, 1960) again suggesting that the parameters of interelectronic repulsion are 60 per cent as large in the 5f group as in the 4f group, under equal circumstances, but ζ_{5f} about twice as large as ζ_{4f}, producing much stronger deviations from Russell–Saunders coupling. This picture has now been confirmed all the way up to trivalent curium, berkelium, californium and einsteinium. However, the uncertain aspect of the absorption spectra of 5f-group compounds is the relative size of 'ligand field' effects and term distances. The most constructive work has been done on octahedral UCl_6^{-2} and UBr_6^{-2} (Johnston *et al.*, 1966) where 21 sublevels have been identified among the 40 sublevels formed by the 91 states of $5f^2$ in the point-group O_h. Thus, the two sublevels of $^3P_2$ occur at 23 329 and 24 700 cm^{-1} in the chloride, and 22 817 and 24 152 cm^{-1} in the bromide. A comparison between two complexes suggest β around 0.8. The 'ligand field' effects have been compared by Edelstein, Brown and Whittaker (1974) and Warren (1980) with the octahedral $5f^1$ systems PaX_6^{-2}, UF_6^-, UCl_6^-, UBr_6^- and NpF_6 where σ^* is close to 250 cm^{-1} for M(IV) but 800 to 400 cm^{-1} for U(V) and perhaps as large as 1600 cm^{-1} in NpF_6. At the same time e_π/e_σ is unusually large, above 0.3. It is likely that the aqua ion is $U(OH_2)_9^{+4}$ (Folcher *et al.*, 1978). The photoelectron spectra (Green, 1981) of the gaseous 16-coordinated U(IV) compounds $U(C_5H_5)_3Cl$ and $U(C_8H_8)_2$ show distinct 5f signals at 7.0 and 6.2 eV, respectively, of the same order of magnitude as $I = 6.88$ and 7.23 eV of the 3d-like orbitals (two and one) of the 10-coordinated iron(II) cyclopentadienide $Fe(C_5H_5)_2$.

There seems to be little doubt that comparatively large 'ligand field' effects in the 5f group are connected only with M(IV) and higher oxidation states. Recently, Gruber, Morrey and Carter (1979) demonstrated that $5f^3$ U(III) in $U_xLa_{1-x}Cl_3$ shows 'ligand field' effects only twice as large as in the isologous Nd(III), joining previous evidence for the following elements Np(III), Pu(III), Am(III), ... Nugent *et al.* (1973) used the refined spin-pairing energy theory for rationalizing the variation of E^0 for aqua ions, and electron-transfer bands.

Obviously, the *electron-transfer spectra* (Jørgensen, 1963, 1969, 1970a) have relatively little connection with our subject of *J*-levels, except the rather isolated case of Eu(III), which must form essentially $^8S_{7/2}$ (since the next level of Eu^{+2} occurs at 28 200 cm^{-1} higher energy, and has been observed of Eu(II) in certain double fluorides, starting parity-allowed transitions to $4f^65d$ at higher wave-number) and the iodides discussed below. However, the fluorescent (and photochemically very active) first excited state of UO_2^{+2} (Jørgensen and Reisfeld, 1975, 1981; Jørgensen, 1979) has quite specific properties related to the large ζ_{5f} close to 2000 cm^{-1} and involves an essentially nonbonding state $^2F_{5/2}$ of U[V] combined with a hole in the electronic density of the two oxo ligands.

FILLED VALENCE SHELLS AND PENULTIMATE MOLECULAR ORBITALS

Turner started in 1962 to apply Eq. (12) to gaseous molecules (at low pressure) irradiated by $h\nu = 21.2$ eV (by far the strongest spectral line of helium) or 40.8 eV (of He^+) to confirm energies of penultimate MOs (Turner *et al.*, 1970; Rabalais, 1977) with much greater resolution than can be obtained with solid samples. Again, most of these fascinating results are rather remote from our subject, as the gaseous molecules have local symmetries strongly deviating from spherical. The closest analogy is perhaps the filled 3d shell of zinc(II), 4d of cadmium(II) and 5d of mercury(II) which has been reviewed (Jørgensen, 1976b). In the monatomic Zn^{+3}, Cd^{+3} and Hg^{+3}, the 'spin-orbit' separation between $J = \frac{5}{2}$ (at lower energy) and $J = \frac{3}{2}$ of d^9 is 2759 cm^{-1} (Moore 1970), 5812 cm^{-1} (Moore, 1958) and slightly above 15 038 cm^{-1} known in $[68]5d^96s^2$ of Hg^+. These separations have the same order of magnitude as the separations of one-electron energies $d\sigma(3z^2 - r^2) > d\pi(xz, yz) > d\delta(x^2 - y^2, xy)$ in linear XMX. In spite of the higher I of the d shell than that of the loosest bound X orbitals, it is seen that the order follows conventional 'ligand field' arguments, as in the 4f group. These systems represent an intermediate case much like U(IV) and U(V); there is a recent review by Creber and Bancroft (1980).

The 'spin-orbit coupling effects' in *bromide* and *iodide* have attracted attention since Franck and Scheibe (1928). In order to understand the excited states of these anions, it is useful to consider the isoelectronic krypton and xenon atoms:

	$J = 2$	$J = 1$	$J = 0$	$J = 1$
Kr: $[30]4p^55s$	79 973	80 918	85 192	85 847
$[30]4p^56s$	99 628	99 895	105 092	105 147
Xe: $[48]5p^56s$	67 068	68 046	76 197	77 186
$[48]5p^67s$	85 189	85 441	95 721	95 801.

(15)

The two configurations are members of Rydberg series, the first two sets of J-levels converging toward the groundstate $^2P_{3/2}$ of Kr^+ ($I_1 = 112\,915$ cm^{-1}) and of Xe^+ ($I_1 = 97\,834$ cm^{-1}) and two other sets (to the right) converging towards the first excited state $^2P_{1/2}$ at 5371 cm^{-1} higher energy in Kr^+ and at 10 537 cm^{-1} in Xe^+. The 'resonance lines' allowed as electric dipolar transitions go to the two levels with $J = 1$. It is noted that in spite of the contribution of interelectronic repulsion being about a thousand cm^{-1} separating $J = 2$ and 1, or 0 and 1, in the lowest excited configuration, the main effect is the $\frac{3}{2}\zeta_{np}$ of Kr^+ and Xe^+. In the isoelectronic bromine and iodine atoms, this splitting is 3685 and 7603 cm^{-1}, respectively. Halide ions in cubic crystals (not separating the one-electron energies of the three p orbitals) and in roughly spherical symmetry (in polar solvents) behave quite closely to the ideas of Franck and Scheibe, as has been reviewed (Jørgensen, 1967b, 1975b) though it is noted that such iodides have the configuration $[48]5p^55d$ at lower energy than $[48]5p^57s$ of Eq. (15), as in the xenon atom. It is important for the chemist to realize that 'electron transfer to the solvent' is a description of the temporal evolution of the excited state having photochemical consequences (such as formation of solvated electrons, or molecular H_2) whereas the original optical excitation (following the Franck–Condon principle) is rather to $5p^5 6s$. Katzin (1955) argued that similar $\frac{3}{2}\zeta_{np}$ effects can be detected in electron-transfer spectra of bromide and iodide complexes, but a closer scrutiny (Jørgensen, 1967b, 1970a; Jørgensen, Preetz and Homborg, 1971) shows that the undoubted 'spin-orbit coupling effects' rather are of the ζ_{np} type (two-thirds as large) characterizing linear MX groups deviating strongly from spherical symmetry. On the other hand, Kosower *et al.* (1960) demonstrated that the electron-transfer band from iodide to alkylpyridinium cations (of which the position characterizes the polar character of the solvent) is followed at some 6000 cm^{-1} higher energy by a second strong band, agreeing better with Franck and Scheibe's description, though aqueous and acetonitrile solutions of ionic iodides are at 7200 cm^{-1} (Jørgensen, 1967b).

INNER SHELLS STUDIED BY X-RAY, AUGER AND PHOTOELECTRON SPECTRA

The X-ray emission and absorption spectra allow the difference between the two ionization energies $I(nlj)$ belonging to the two j-values of a positive l value to be measured. This difference can be many eV, and several per cent of I (it is 10.7 per cent for Xe5p) due to very steep gradients of the central field in Eq. (6). The previous tables (Cauchois, 1952, 1956; Bearden and Burr, 1967) can be made much more precise by *photoelectron spectra* using Eq. (12) on 600 non-metallic compounds containing 77 elements (Jørgensen and Berthou, 1972) and it has been customary for metallic elements (Fuggle and Mårtensson, 1980) to indicate ionization energies of inner shells relative to the Fermi level. As long as the sample is diamagnetic, it is striking how invariant the separations $(l + \frac{1}{2})\zeta_{nl}$ are for different compounds (invariant within the experimental uncertainty of 0.05 eV) as reviewed for the 4f signals from lutetium to bismuth (Jørgensen, 1976b). The same behaviour is found for monatomic entities, as long as electrons are not removed from shells with the same or smaller average radii than the shell for which ζ_{nl} is determined. Thus, as reviewed (Jørgensen, 1978) the 'spin-orbit coupling' separation of the sulphur 2p signal in a large number of compounds is 1.2 eV to be compared with 1.256 eV in S^{+7}. However, in the hydrogenic S^{+15} it is 2.97 eV. On the other hand, the 2p separation is decreased from 2.91 eV in K^{+10} to 2.65 eV in potassium(I) salts, and from 3.72 eV in Ca^{+11} to 3.5 eV in several calcium(II) compounds (Jørgensen and Berthou, 1972). The separation 24.40 eV in Zn^{+21} (Behring *et al.*, 1976) can be compared with 23.1 eV obtained from X-ray spectra (Bearden and Burr, 1967) and 23.15 eV from photoelectron spectra of zinc(II) compounds (Jørgensen and Berthou, 1972).

It is a diagnostically useful observation that the apparent 2p separation in 3d-group compounds increases with S of the groundstate. Thus, it is 17.2 eV in diamagnetic nickel(II), but 17.5 to 18.1 eV when $S = 1$. There are more striking variations, such as 9.7 eV in Cr(III) ($S = \frac{3}{2}$) and 9.2 eV in diamagnetic chromates(VI), 13.7 in iron(II) with $S = 2$ to be compared with 12.9 eV for diamagnetic Fe(II), 16.0 eV in cobalt(II) ($S = \frac{3}{2}$) but 15.0 eV for Co(III) ($S = 0$). There is little doubt that these variations are due to interelectronic repulsion differing in the multiple states of a configuration containing $2p^5 3d^q$ (Jørgensen, 1975d) and that they are of the same character as the deviations of Eq.(15) from the simple conditions prevailing in Kr^+ and Xe^+. Since the average radii of 3s, 3p and 3d orbitals are quite similar (their I are so different because of the angular part of the kinetic energy), it is not surprising that ionized configurations such as $[10]3s3p^6 3d^q$ and $[10]3s^2 3p^5 3d^q$ show a broad interval of energy levels, though an additional problem is the *satellite signals* of enigmatic and controversial origin (Jørgensen, 1975d). Calculations (Spector *et al.*, 1976) in intermediate coupling of the 910 states of $3d^94f^2$ forming 107 J-levels, and of the 3640 states of $3d^94f^3$ forming 386 J-levels (among which 61 have $J = 3$ and 61 have $J = 4$) have been compared with the 3d region of the photoelectron spectrum of metallic praseodymium and neodymium.

Excepting such manifolds of states, which can be quite wide in the lanthanides, the X-ray spectra are normally dominated by energy levels which can be described as *one* hole in *one* shell. The situation is entirely different in *Auger spectra* where an initial state lacking an electron in a strongly bound shell decays to a state lacking *two* electrons, of which the total sum of binding energies is smaller than in the original shell. One of the electrons is ejected with a kinetic energy determined by the energy difference between the initial and the final states. The final Auger states in zinc(II) and in metallic zinc (Wagner, 1976) and in gaseous zinc atoms (Aksela, Väyrynen and Aksela, 1974) may belong to configurations such as $3p^53d^9$ (neglecting filled shells) or $3d^8$ already known from the Auger spectra of krypton atoms. The (S, L, J) levels of such configurations are spread over 10 to 25 eV and can be parameterized by S.C.S. calculations. It is perhaps more striking that an Auger state in metallic copper (Kowalczyk *et al.*, 1973) lets *one* atom become a kind of 'impurity', and that the nephelauxetic ratio β for the term distance of $[18]3d^8$ relative to Cu^{+3} is somewhat *higher* than $\beta = 0.54$ in the copper(III) complex CuF_6^{-3}.

However, it is not all Auger states that have approximately spherical symmetry. The $1s^22s^22p^4$ final states of several fluorides (Jørgensen and Berthou, 1974) show essentially spherical behaviour on cubic local sites, but their energy and intensity distribution changes in uniaxial situations, removing the degeneracy between the three 2p orbitals.

If all the inner shells of a given atom have the same chemical shift of I from one compound to another (as suggested by the wavenumbers of X-ray emission lines varying 10 to 20 times less than absorption edges) Wagner (1976) pointed out that the difference of kinetic energy E_{kin} of the Auger electron and of the photoelectron in Eq. (12) for the initial ionization should be a reliable measurement of the *interatomic relaxation energy* (Jørgensen, 1974) known to have the order of magnitude 5 eV. Wendin (1981) discussed interesting cases of breakdown of the one-electron description.

RUSSELL–SAUNDERS COUPLING IN CHEMISTRY

The large majority of all samples consisting of distinct molecules are diamagnetic and have a groundstate with the total spin quantum number S equal to zero. This statement is true because the overwhelming majority of organic compounds fall in this category. Organic chemists recognize that the first excited (and the following) MO configuration has triplet states below singlet states, but the lowest MO configuration contains only the singlet groundstate. Inorganic compounds differ in several respects; the vitreous and crystalline solids, more often than not, are constituted by a large network of interconnected atoms, without distinct isolated molecules, and there is a concomitant tendency toward non-stoichiometry. This was already well known from minerals, where substitution of central atoms in the same oxidation state (such as the mutual miscibility of corundum-type Al_2O_3, Cr_2O_3 and Fe_2O_3), substitution by charge compensation (such as a given amount of Na(I) and Si(IV) being replaced by Ca(II) and Al(III) in many rocks; or traces of Gd(III) and O(−II) simultaneously entering CaF_2), non-stoichiometry with anion excess (such as $Ca_{1-x}Y_xF_{2+x}$ and UO_{2+x}) and anion deficit (such as $Th_{1-x}La_xO_{2-0.5x}$ or the Nernst lamp materials fluorite-type $Zr_{1-x}Y_xO_{2-0.5x}$ and $Zr_{1-x}Mg_xO_{2-x}$) or cation deficit (such as $Fe_{1-x}O$ and $Fe_{1-x}S$, ironically enough used as an example of a stoichiometric compound in schools).

However, the major difference regarding S values occurs at another point: when a set of approximately or (for group-theoretical reasons) completely degenerate MOs are partly filled, containing at least two electrons, and at most, 2 electrons less than twice the number of orbitals, several S values occur, and the groundstate has the *highest possible* S_{max}. The physical mechanism behind this preference for high S values is Eq. (13) showing that it costs, on the average, $2DS_0$ to go from S_0 to $(S_0 - 1)$ in a monatomic entity. The spin-pairing energy parameter D is inversely proportional to the average radius of the partly filled shell. The situation just described can occur outside the transition groups, not only in chemically reactive species (such as nitrogen and phosphorus atoms with quartet groundstate) but in the relatively unreactive O_2 having the MO configuration containing the two weakest bound electrons in *two* equally π-antibonding orbitals, with the result that the triplet groundstate is followed by two singlet states producing several of the 'terrestrial Fraunhofer lines' in the red, filtering the solar spectrum strongly at sunrise and sunset. However, this situation is far more frequent in the d-groups, as we have seen, and universally prevailing in the 4f group. Whereas monatomic entities can present terms with S as high as 5, e.g. belonging to the excited configuration [54]4f^{7}5d6s6p of the gaseous gadolinium atom (Martin *et al.*, 1978), condensed matter having $S = \frac{7}{2}$ is known for Eu(II), Gd(III) and Tb(IV), as well as instances of metallic samples containing Eu[II] and Gd[III]. This is already less true for the $J = \frac{7}{2}$ groundlevel of 5f^7 curium(III) having a squared amplitude 0.79 of octet character only because of a higher ratio between ζ_{5f} and the term distances (Carnall and Rajnak, 1975). In the 4d and 5d group with highly antibonding d-like orbitals empty, there is a tendency toward even numbers K of electrons, as exemplified by gold forming Au(V), Au(III), Au(I) and Au(−I) (Jørgensen, 1978) and, at the same time, diamagnetic groundstates. The excited states may show considerable deviations from Russell–Saunders coupling, spin-forbidden transitions in octahedral Ir(III) and Pt(IV) and quadratic Pt(II) complexes having 10 to 20 per cent of the oscillator strength of the corresponding spin-allowed 5d^6 and 5d^8 transitions (Jørgensen, 1963). This mixing of triplet and singlet character is even more pronounced in thallium(I), lead(II) and bismuth(III), where the description of the excited configuration as 6s6p is subject to some caution (Jørgensen, 1971; Boulon, Jørgensen and Reisfeld, 1980).

Because of the very weak coupling between the d^{q+1} states (still showing positive S) with the hole in the MO delocalized on the ligands, at most comparable to the moderate interaction between p and s electrons in Eq. (15), excited states of electron-transfer bands (Jørgensen, 1970a) do not very frequently show a well-defined S, though triplet states seem to be perceptibly lower than the first singlet state in vanadate, chromate and permanganate (Blasse, 1980). The situation is particularly intricate in the *uranyl ion* (Jørgensen and Reisfeld, 1975, 1981) where four (if not six) of the empty 5f orbitals have almost the same one-electron energy. Combined with the energy difference close to 7000 cm^{-1} between $^2F_{7/2}$ and $^2F_{5/2}$ of U[V] in the excited state, the first electron-transfer bands represent transitions to almost pure states among $^2F_{5/2}$ (as europium(III) selects Eu[II] states $^8S_{7/2}$) and it has absolutely no physical significance to ask whether they are triplet or singlet states.

Systems containing more than one paramagnetic species show a large number of states, which can be assigned S values (at least for accounting purposes) by $S_1 \otimes S_2 \otimes S_3 \otimes \ldots$ according to Eq. (1). If the interaction between the paramagnetic subsystems is much smaller than kT, the Boltzman population of each resultant S state is proportional to $(2S + 1)$. In this asymptotic limit, it can be shown (Jørgensen, 1971) that if the paramagnetic susceptibility of the whole system is proportional to $S(S + 1)$, it is additive, on the average, from contributions $S_1(S_1 + 1)$ or $S_2(S_2 + 1)$, ..., for the subsystems. If the interaction between the paramagnetic subsystems is perciptible, we frequently have *antiferromagnetic coupling* with the lowest energy for the lowest S, and highest energy for $S = S_1 + S_2 + \ldots$ One of the many consequences of antiferromagnetic coupling is the observation of two adjacent paramagnetic subsystems being excited by the same photon. Thus, $(H_3N)_5CrOCr(NH_3)_5^{+4}$ has low-lying states (distributed over 2700 cm^{-1}) with $S = 0$, 1, 2 and 3, and sharp absorption bands in the near ultraviolet due to simultaneous quartet → doublet excitation of both Cr(III) become induced spin-allowed, because $S_1 = S_2 = \frac{1}{2}$ can couple to $S = 0$ and 1 like the two lowest-lying alternatives of $S_1 = S_2 = \frac{3}{2}$ (Glerup, 1972). This phenomenon of *simultaneous pair-excitation* was discovered in ruby $Al_{2-x}Cr_xO_3$ (Linz and Newnham, 1961) where the narrow bands in the near ultraviolet have intensities proportional to x^2 since the probability of encountering CrOCr groups increases that way for low x. A quite striking effect is simultaneous excitations of two ytterbium(III) in the green of Yb_2O_3 (Schugar *et al.*, 1975) having an oscillator strength around 10^{-9}. It is conceivable (Jørgensen, 1980a, 1981b) that such antiferromagnetic coupling through anion bridges between trivalent lanthanides (having positive S_1 and S_2) may allow four-level lasers with favourable conditions of population inversion, and it may contribute to the mechanism of *energy transfer* (Reisfeld, 1976; Reisfeld and Jørgensen, 1977).

The question of more or less well-defined S in many-electron systems is not formally conditioned by the validity of electron configurations. Taking an example among monatomic entities, the totally symmetric groundstate of the beryllium atom has a squared amplitude close to 0.90 of the (optimized) configuration $1s^22s^2$ and close to 0.08 of $1s^22p^2$ (Jørgensen, 1969, 1978). This does not prevent the singlet character of the groundstate being close to 0.99999999 because of the small ζ_{2p} around 2 cm^{-1}. On the other hand, because of the detailed mathematics of intermixing with configurations substituted by two electrons in a continuum orbital (Jørgensen, 1962a,b) there is a growing suspicion that the conventional configuration, used for the classification in Eq. (4), has a squared amplitude well below 0.5 in atoms with Z above 36 (if not already above 18). Examples of a more general character (than the beryllium atom) of much better defined S than electron configuration can be found among many J-levels belonging to the overlapping configurations $[18]3d^q4s^2$ and $[18]3d^{q+1}4s$ (of the same parity) in the gaseous titanium, vanadium and chromium atoms.

PREPONDERANT ELECTRON CONFIGURATIONS IN CHEMISTRY

Though Condon and Shortley (1953) specifically mention one example of strong configuration interation (between $[10]3s3d$ and $[10]3p^2$ of the magnesium atom) the general feeling among atomic spectroscopists was that such mixing was only important for overlapping or adjacent configurations of the same parity. Racah (1950) did pioneer work on parameterization of such cases, using Klinkenberg's data for Th^{+2}. Unfortunately, the number of S.C.S. parameters is almost as large as the number of J-levels, and attempts to evaluate the integrals for radial functions are frequently wrong by a factor of 2. The writer (Jørgensen, 1969) proposed consideration of the manifold of low-lying J-levels (rather than the groundstate alone), establishing a *preponderant configuration* of the groundstate, from which the other J-levels can be obtained by substituting zero (in the case of partly filled shells), one or two electrons by other nl-values. It is with purpose that the adjective used is not 'predominant' which rather alludes to the largest squared amplitude in a configuration interaction. For instance, the beryllium atom is a spectroscopic alkaline-earth (like helium, zinc, ytterbium and mercury) with the preponderant configuration $1s^22s^2$ in spite of the squared amplitude of $1s^22p^2$ being one tenth as large as that of $1s^22s^2$ in the groundstate. Thus, the lowest excited levels (Moore, 1949) are three ^3P close to 21 980 cm^{-1} and $^1P_1$ at 42 565 cm^{-1} (all belonging to $1s^22s2p$), $^3S_1$ at 52 082 and $^1S_0$ at 54 677 cm^{-1} (both $1s^22s3s$). The first level which may have problems (related to the magnesium case discussed above) is $^1D_2$ at 56 432 cm^{-1}. It is also noted that the two subsequent ^3P terms (ascribed to $1s^22s3p$ and $1s^22p^2$) are separated by only 900 cm^{-1}. Nevertheless, we are three-quarters of the distance up to $I_1 = 75\,193$ cm^{-1} corresponding to $1s^22s$ of Be^+. A more transparent case is the isoelectronic C^{+2} having the configurations $1s^22s^2 < 1s^22s2p < 1s^22p^2 < 1s^22s3s < 1s^22s3p < 1s^22s3d$ arranged neatly (without overlap) and constituting all the J-levels within 75 per cent of I_3. The writer is interested in properties of classes (Jørgensen, 1964b) and in three-valued logic (Jørgensen, 1967a) and this is how he focused the interest on the manifold of low-lying J-levels having properties belonging more to the manifold than to the individual levels. The mathematics applied to comparing sets of wavefunctions is to a large extent the algebra of inequality signs, with fairly trivial theorems of the kind that if one squared amplitude is larger than 0.5, it is the largest. Fortunately, the physical problems with many-electron wavefunctions (about which we speak as of locomotives made of iridium—we do not possess them, but we can think about them) with a multitude of 2, 4, 6, ... electron-substituted configurations having tiny squared amplitudes, do not seem (in the large majority of cases) to prevent the preponderant configuration from also being the predominant component with, by far, the largest squared amplitude, though perhaps well below 50 per cent.

One of the reasons why atomic spectroscopy is so fascinating for chemists (Jørgensen, 1980b) is the rôle of the closed-shell $^1S_0$ as a neutral element of Hund vector-coupling Eq. (1) causing columns of the Periodic Table to have such similar atomic spectra. In spite of the small, but highly significant, differences (e.g. helium, neodymium and uranium) between the *chemical* and the *spectroscopic versions* of the Periodic Table, one can forget about the closed shells, when counting the J-levels. The 'ligand field' treatment of chromophores containing a partly filled 4f, 5f, 3d, 4d or 5d shell has as a basis the non-totally symmetric levels provided by the l^q, disregarding the filled MOs everywhere else. Exactly as in monatomic entities, S is a reasonably well-defined quantum number, when ζ_{nl} is not large, nor comparable, with distances between energy levels having differing S. The *spectroscopic oxidation state* $z = (Z - K)$ is defined from the low-lying energy levels indicating K as a sum of q electrons in the partly filled shell discussed, and $(K - q)$ electrons hidden away in a plausible set of 'inert' filled orbitals (to be located by photoelectron spectra, if need be). If only the groundstate is available (e.g. in black semiconductors, or in metallic samples) one may sometimes succeed in determining the *conditional oxidation state* written in square brackets M[III] from the integer q (rather than any other integer) of f (or less frequently d) electrons, accounting correctly for S and other properties of the groundstate having observable consequences. The opposite extreme is the colourless molecule or solid having no readily accessible excited states, and being in a totally symmetric groundstate (e.g. CH_4,CF_4,$N(CH_3)_4^+$, fluorite-type non-metallic Be_2C containing 8-coordinated carbon, but containing less than $2N$ electrons for N 'bonds') where the oxidation state needs strong arguments of analogy with *oxidation numbers* defined according to rules of standard closed-shell constituents (Jørgensen, 1969). This way, it is defensible to say that the oxidation states are C(IV) and F(–I) in CF_4, and C(–IV) and Be(II) in Be_2C, but such classifications do not stand on the same firm basis as the thoroughly elaborated ramifications of non-totally symmetric systems. Thus, octahedral nickel(II) with triplet groundstate has several characteristic absorption bands (typically due to three other triplets, and to two singlets) having excited levels formed among the 45 states of eight d-like electrons. The classification (being far more evident in lanthanides) is perhaps slightly more debatable in quadratic, rectangular (two bidentate ligands), and tetragonal-pyramidal, diamagnetic nickel (II) complexes. However, real troubles would only start if the ligands are not *innocent*, lacking a standard closed-shell modification, as sometimes found for maleonitrilodithiolate, deprotonated 2-mercaptoaniline, or NO. The rules for symmetry types in 'ligand field' theory have turned out to be of far greater utility than any of the physical models of the antibonding effects.

There is a certain parallelism in the development of atomic spectroscopy (Hund, 1927) and 'ligand field' theory (Jørgensen, 1971, 1980b). In the former case, normal thinking was centred around semi-classical models with quantum conditions, and the characteristic quantum-mechanical situation (outlined in this essay) was slowly recognized. By the same token, the non-spherical part of the Madelung potential, was a red herring during the process of induction from transition-group properties.

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