STRUCTURE AND BONDING

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The Conditions for Total Symmetry Stabilizing Molecules, Atoms, Nuclei and Hadrons

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With Contributions by
R. Englman J. C. Green C. K. Jørgensen
I. Moura J. J. G. Moura K. N. Raymond
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South Parks Road Oxford OX1 3QR, Great Britain

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The Conditions for Total Symmetry Stabilizing Molecules, Atoms, Nuclei and Hadrons

Christian K. Jørgensen

Département de Chimie minérale, analytique et appliquée, Université de Genève,
CH-1211 Geneva 4

Though the totally symmetric (and non-degenerate) wave-function both represents the neutral element of Hund vector-coupling and the origin of the repetitive pattern in the Periodic Table, it has not always low energy, and groundstates having J up to 8 are known. Both in compounds and monatomic entities, Russell-Saunders coupling is usually a good approximation, and classifies the levels correctly (like electron configurations). In nuclei with even Z and N, the groundstate (with I zero) is nearly always followed by an excited state having I = 2 at energies being a function of Z and N clearly connected with M.G. Mayer's shell model. The question of constituents (also α-particles) is further studied in baryons and mesons constructed from quarks. It is still undecided whether quarks and leptons (falling in at least 3 generations) conceivably involve subquarks (such as rishons or preons) and whether an indefinite stratification of further divisibility is suggested by the observed properties. Protons and neutrons are not considered elementary particles any longer.

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1 Electron Configurations and Russell-Saunders Coupling in Monatomic Entities and in Compounds

Monatomic entities M^{+z} consisting of one nucleus (carrying Z times the electric charge e of a proton) surrounded by $K = (Z - z)$ electrons have been one of the major subjects for quantum-mechanical treatment. If the nucleus is treated as a geometrical point, and no attention is paid to its electric multipole moments, nor to its magnetic moments, the energy levels can be characterized by *even* or *odd parity* and by a quantum number J of total angular momentum. If the coordinates $(-x, -y, -z)$ replace (x, y, z) in the total wave-function Ψ (assuming the nucleus at origo), the even Ψ are not changed at all, and the odd Ψ are multiplied by (-1) in each point. For an odd number K of electrons (and also for one electron) J is half an odd positive integer (1/2, 3/2, 5/2, ...) whereas for even K, the J is a non-negative integer.

In the non-relativistic asymptotic limit, where the reciprocal value (1/c) of the velocity of light vanishes, two additional quantum-numbers become valid, the spin angular momentum S and the orbital angular momentum L. Like J, for even K, the former quantum number S is a non-negative integer, whereas S is a half a positive odd integer for odd K. However, in both cases, a higher limit for S is (K/2). On the other hand, L is a non-negative integer for both even and odd K, and there is no higher limit to L. For historical reasons, the various L values have trivial names (which we do not italicize):

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

and the quantity $(2S + 1)$ is called the *multiplicity* and is pronounced:

$$\begin{array}{llll} & \text{even } K & & \text{odd } K \\ S = & 0 \text{ (singlet)} & S = & 1/2 \text{ (doublet)} \\ & 1 \text{ (triplet)} & & 3/2 \text{ (quartet)} \\ & 2 \text{ (quintet)} & & 5/2 \text{ (sextet)} \\ & 3 \text{ (septet)} & & 7/2 \text{ (octet)} \\ & 4 \text{ (nonet)} & & 9/2 \text{ (decet)} \end{array} \tag{2}$$

In many cases, when the relativistic effects are not very pronounced, it is possible to identify *terms*, manifolds of adjacent J-levels characterized by a definite combination of S and L. The J-values belonging to a given term can be found by the operation $S \otimes L$ where the *Hund vector coupling* [1] of the two quantum numbers Q_1 and Q_2 has the results

$$\begin{array}{l} Q_1 \otimes Q_2 = (Q_1 + Q_2) \text{ or } (Q_1 + Q_2 - 1) \text{ or } (Q_1 + Q_2 - 2) \text{ or } \ldots \\ \ldots \text{ or } (|Q_1 - Q_2| + 1) \text{ or } |Q_1 - Q_2| \end{array} \tag{3}$$

It is seen that if S is not larger than L, there occur $(2S + 1)$ different J values, stretching from $(L - S)$ to $(L + S)$. It is a general rule that $(2J + 1)$ independent (mutually orthogonal) Ψ represent the same eigen-value with a definite J. It can be seen from recursion formulae that the number of such *states* is $(2S + 1)(2L + 1)$ providing a second reason for calling $(2S + 1)$ the multiplicity. The situation of recognizable terms is called *Russell-Saunders coupling* and the terms are written with the L-symbol from Eq. (1) having $(2S + 1)$ as left-hand superscript. Thus, ^3H combine $S = 1$ with $L = 5$ and is pronounced "triplet-H". In such symbols, J may be added as a right-hand subscript, the three alternatives in the example being $^3H_4$, $^3H_5$ and $^3H_6$. As described by Condon and Shortley 2) the weak relativistic effects can be simplified into "spin-orbit coupling" with definite multiples of the *Landé parameter* ζ_{nl} (for positive l) characterizing each nl-shell (discussed below). In the frequent case of q electrons in *one partly filled shell*, Hund 1) found that the lowest term has the highest possible S_{max} ($= (q/2)$ for the first half of the shell, with q at most $(2l + 1)$, and $= (4l + 2 - q)/2$ for higher q) combined with the highest L compatible with S_{max}. The first-order width of the distribution of $(2S + 1)$ differing J-levels in a term with S_{max} (and L not smaller than S_{max}) is $(L + \frac{1}{2})\,\zeta_{nl}$ (with opposite sign in the *inverted* terms for q higher than $2l + 1$). According to Hund 1) the groundstate has $J = (L - S_{max})$ for q between 1 and 2l. The lowest term of the half-filled shell has $S = J = (2l + 1)/2$ and $L = 0$ corresponding to only one J-level. For q between $(2l + 2)$ and $(4l + 1)$, the groundstate has $J = (L + S_{max})$.

For a monatomic entity containing only one electron, Russell-Saunders coupling is insured by a special situation. Using lower-case letters for one electron, l is like one of the L-values in Eq. (1), and $j = \frac{1}{2}$ when l vanishes, whereas the relativistic effects otherwise separate $j = (l - \frac{1}{2})$ at lower energy from $j = (l + \frac{1}{2})$ at higher. For one electron, the parity is even, when l is an even integer, and odd, when l is odd. It is noted that a given combination of parity and j corresponds to only one l-value.

It is not generally said in text-books that the approximation of *electron configurations* (assigning from zero to $(4l + 2)$ electrons to each *nl-shell*) has many of the same aspects as the approximation of Russell-Saunders coupling. In both cases, the energy levels can be correctly *classified*, and the number of times a given J-value is represented, does not depend on a moderate extent of mixing of electron configurations. In particular, a definite interval of discrete energy levels containing two or three complete configurations contains all the J-levels predicted. The latter situation was originally supposed by the atomic spectroscopists to prevail generally. Thus, it is important for chemists that in neutral atoms of the transition elements, configurations such as $[18]\,3d^q\,4s^2$, $[18]\,3d^{q+1}\,4s$ and $[18]\,3d^{q+2}$ may overlap, and it may be difficult to tell to which configuration a given level belongs. In the example, the three configurations have the same parity (which is a necessary condition for intermixing due to non-diagonal elements of interelectronic repulsion). It was later 3,4) realized that the largest effects of configuration intermixing (excepting special cases such as $1s^2\,2s^2$ with $1s^2\,2p^2$ in the groundstate of $K = 4$) are due to the substitution of two nl-electrons with two electrons in an orbital belonging to the continuum (by having positive one-electron energy). If the l value is different, the radial extension of this orbital is roughly same as the nl-orbital. If the two l values are identical, the continuum orbital has a radial node in the middle of the nl-radial function (in order to remain orthogonal). This produces far larger energetic effects than e.g. the mixing of [18] $3d^q$ with [18] $3d^{q-2}\,4d^2$. We write closed-shell K-values in rectangular parentheses. It is frequent to write [Ar], [Kr], [Xe], . . . for [18], [36], [54], . . . but since many closed-shell systems with positive charge, such as [28], [68], [78], . . . are not represented by groundstates of neutral atoms, it may be more convenient always to use the K-numbers. The groundstate of gaseous M^{+2} (with the five exceptions M = La, Gd, Lu, Ac and Th), all M^{+3}, M^{+4}, M^{+5} and M^{+6} (but5) not certain z values above 6) belongs to the configuration obtained by the *Aufbauprinzip*1) of filling the shells in the consecutive order

$$1s \ll 2s < 2p \ll 3s < 3p \ll 3d < 4s < 4p \ll 4d < 5s < 5p \ll \\ \ll 4f < 5d < 6s < 6p \ll 5f < 6d \ldots \tag{4}$$

where the double inequality signs indicate the closed-shell systems isoelectronic with the noble gases. In text-books are frequently mentioned a similar series for the groundstate of neutral atoms, where 4 s, 5 s, 6 s and 7 s have moved down to follow immediately after the double inequality signs corresponding to K = 18, 36, 54 and 86. However, such an Aufbauprinzip for neutral atoms is of much less interest than Eq. (4), since twenty exceptions occur among the 99 atoms from hydrogen to einsteinium.

It is an experimental fact6) that the lowest 20 to 400 J-levels of a given monatomic entity can be classified by electron configurations (usually either the same as the groundstate, or obtained by letting one or two electrons change their nl-shell) and there is no clear-cut case of any low-lying level being supernumerary to the low-lying configurations expected. When Russell-Saunders coupling is a good approximation, a single partly filled shell can at most have $S = (l + \frac{1}{2})$ (when half-filled) such as $S = \frac{5}{2}$ for d^5 and $\frac{7}{2}$ for f^7. A few terms are known with S = 5, e.g. belonging to [54] $4f^7\,5d\,6s\,6p$ of the gaseous gadolinium atom7). However, because of the great stability of closed inner shells, no discrete levels of monatomic entities containing more than two electrons have S as high as (K/2).

It should not be neglected that even ^1S terms are not restricted to closed-shell K-values. If *one* partly filled shell contains two or $4l$ electrons, $(2l + 1)$ terms occur, among which ^1S has the *highest* energy. If the partly filled shell contains 4, 6, 8, ..., $(4l - 2)$ electrons, two or more terms ^1S occur, most frequently with rather high energy compared with the other, numerous terms. This is not a question of L = 0 since f^3 and f^{11} have the two first excited terms (at the same energy in Racah's theory) ^4S and ^4F slightly above the lowest term ^4I (agreeing with Hund's rules). Said in other words, ^1S belonging to configurations involving partly filled shells are destabilized, compared with closed-shell situations. This does not prevent that configurations with two partly filled shells may have energies4) below closed-shell configurations, e.g. [18] $3d4s$ in Sc^+ below both [18] $3d^2$ and [18] $4s^2$, and [18] $3d^9\,4s$ in the gaseous nickel atom below [18] $3d^{10}$ and the average energy of [18] $3d^8\,4s^2$ (to which the groundstate belongs).

In molecules and polyatomic complex ions, the equilibrium positions of the nuclei determine point-groups8) which are finite (one of the seven cubic groups, or belonging to one of the seven series D_{nh}, D_{nd}, D_n, C_{nh}, C_{nv}, C_n and S_{2n} including the isolated plane of symmetry C_s, the isolated centre of inversion C_i and, finally, C_1

having only identity as element of symmetry) except when two or more nuclei all are colinear, exemplifying the linear point-groups $D_{\infty h}$ with, or $C_{\infty v}$ without, a centre of symmetry (inversion). If Russell-Saunders coupling is valid in such polyatomic entities, the total spin quantum number S is combined with Λ in the linear point-groups or the symmetry type Γ_n (replacing L in monatomic entities) in the finite point-groups.

Organic chemists emphasize that the large majority of molecules have a groundstate with vanishing S (hence being diamagnetic, or at the most, temperature-independent paramagnetic). They call species with positive S "free radicals". It is inevitable that molecules containing an odd number of electrons (such as NO, O_2^+, O_2^-, ClO_2 or O_3^-) have positive S (and the examples given are not known to dimerize) but it is more striking that the groundstate of O_2 has $S = 1$. The paramagnetism of the oxygen molecule (which was discovered by Faraday) was rationalized by Lennard-Jones on the basis of *molecular orbital* (M.O) theory, the two loosest bound M.O. (able to accommodate four electrons, as they do in the diamagnetic peroxide anion O_2^{-2}) have exactly the same energy for group-theoretical reasons, much like the $(2l + 1)$ orbitals of a nl-shell in spherical symmetry. In polyatomic entities, identical (or almost identical) M.O. energies have many of the same consequences as Hund's rules for a monatomic entity with an electron configuration containing a partly filled shell.

At this point, there is an interesting graduation from p over d to f group compounds[8,9]. Even when p-like orbitals can be recognized, the systems with an even number of electrons generally have $S = 0$. Typical cases are the $(K = 32)$ bromine(III) and $(K = 50)$ iodine(III) and xenon(IV) complexes BrF_4^-, ICl_4^- and XeF_4 containing one lone-pair perpendicular on the molecular plane. In d-group complexes, both high-spin (S according to Hund's rule) and low-spin behaviour is known. For instance, d^5 systems can have $S = \frac{5}{2}$ or $\frac{1}{2}$ in their groundstate, and d^6 systems $S = 2$ or 0. These examples are all four compatible with octahedral symmetry (compare hexaqua and hexacyano complexes of iron(II) and iron(III)). Other cases, such as $(K = 26)$ $3\,d^8$ nickel(II) complexes have a marked correlation with the stereochemistry. Thus, the groundstate of octahedral chromophores, such as $Ni(II)O_6$ in $Ni(OH_2)_6^{+2}$, $Ni_xMg_{1-x}O$, undiluted NiO and $Ni(II)N_6$ in $Ni(NH_3)_6^{+2}$ have $S = 1$ because the two anti-bonding 3 d-like orbitals in "ligand field" theory contain 2 (and not 4) electrons (and the three non-bonding 3 d-like orbitals are filled) whereas diamagnetic behaviour of nickel(II) is found in quadratic, rectangular or tetragonal-pyramidal chromophores (such as $Ni(CN)_4^{-2}$, $Ni(S_2P(OC_2H_5)_2)_2$ or $Ni(CN)_5^{-3}$, respectively) with one of the five 3 d-like orbitals empty. The "ligand field" description had the (somewhat unexpected) consequence that the *isoelectronic series*[5] introduced by Kossel in 1916 where the K-values derived from Eq. (4) for monatomic species

$$2 \ll 4 < 10 \ll 12 < 18 \ll 28 < 30 < 36 \ll 46 < 48 < 54 \ll \\ \ll 68 < 78 < 80 < 86 \ll 100 < \ldots \tag{5}$$

were found (with exceptions of $K = 4$, 12 and 30) to correspond to six to thirteen consecutive oxidation states, such as $K = 10$ from C(– IV) to Cl(VII) or $K = 46$ from Ru(– II) to Xe(VIII), whereas other K-values rarely are represented by as many as four or five consecutive oxidation states. Actually, all the K-values from 19 to 100 are known in at least one well-defined oxidation state of a monomeric complex (excluding catenation between identical atoms, such as F_3CCF_3, O_2^{-2}, $O_3SSO_3^{-2}$, F_5SSF_5, $(OC)_5MnMn(CO)_5$, $(NC)_3NiNi(CN)_3^{-4}$ and Hg_2^{+2}) distinctly different from the definition[4)] of oxidation numbers. Whereas all known cases of K = 21 show groundstates (with $S = \frac{3}{2}$) belonging to a M.O. configuration with three (essentially non-bonding) d-like electrons, we already mentioned that K = 23 with five d-like electrons may show either $S = \frac{5}{2}$ (like gaseous Mn^{+2} and Fe^{+3}) or $S = \frac{1}{2}$. The characteristic difference between the chemistry of elements outside the transition groups at one hand, and the d and f groups on the other hand, is that K (when it is defined) nearly always is an even integer in the former case, whereas the most stable (or most frequent) oxidation state of a transition element readily can have an odd K-value, such as Cr(III), Mn(II), Fe(III) or all the trivalent lanthanides from Ce(III) to Yb(III) with even Z.

In the 4 f group, the situation is rather different from the d-groups, since the deviations from spherical symmetry are smaller[10)] than the first-order relativistic effect "spin-orbit coupling". Hence, the J-values of the groundstate and of nearly all the excited states (excluding accidental near-degeneracies) of $[54]\,4f^q$ remain well-defined, like in monatomic entities. This is true, not only for transparent, isolating compounds (such as MF_3 or M_2O_3) and diluted crystals (such as $M_xLa_{1-x}Cl_3$ and $M_xY_{1-x}VO_4$) and glasses, as well as aqueous solutions[11,12)], but also in black, low-energy semi-conductors such as MSb and in metallic alloys and elements. In the latter case, the *conditional oxidation state*[4)] M[III] is said to occur, when magnetic or other physical properties indicate the number q = (Z − 57) of electrons in the 4 f shell, whereas M[II] is defined by q = (Z − 56). The photo-electron spectra[13,14)] of antimonides and the metallic elements indicate the J-level structure of the M[IV] $4f^{q-1}$ obtained by X-ray ionization of M[III]. The typical separation of the seven one-electron energies of 4 f group compounds[10)] is 400 to 800 cm^{-1} (0.05 to 0.1 eV) which is also the order of magnitude of the width of the distribution of (2 J + 1) states in each level. Finer details of the magnetic behaviour[15)] of metallic alloys and elements show that the (2 J + 1) states of the lowest M[III] level are separated about half as much as in anhydrous lanthanum chloride.

For reasons becoming apparent in the next section, it is interesting to note that lanthanides in condensed matter are sufficiently close to spherical symmetry that Hund's rules all apply to the partly filled 4 f shell. Thus, the highest J-value for the groundstate is 8 (combined with S = 2 and L = 6) in $4f^{10}$ holmium(III) and dysprosium(II). Gaseous Ho^{+3} and Dy^{+2} also have this groundstate $^5I_8$ (consisting of 17 states) belonging to $[54]\,4f^{10}$. It may be noted that the gaseous dysprosium atom[7)] also has this groundstate, but in this case belonging to the configuration $[54]\,4f^{10}\,6s^2$.

In the transthorium elements (with Z above 90) there was around 1955 a controversy[16,17)] whether some 6 d electrons might occur, rather than a partly filled 5 f shell in agreement with Eqs. (4) and (5). The situation seems quite complicated in alloys of protactinium, uranium and neptunium with other metals, whereas plutonium may choose between $5f^4$ Pu[IV] and $5f^5$ Pu[III] in the individual alloys or modifications of the element. On the other hand, americium and curium seem always to occur as 5 f^6 Am[III] and 5 f^7 Cm[III] in the metallic state. It is well-established[16,18) that isolating compounds of transthorium elements contain (Z − 86 − z) electrons in a partly filled 5 f shell when the oxidation state is + z. The "ligand field" separations between the one-electron energies of the seven f-like orbitals are known[19) to be 0.5 to 1 eV in hexahalide complexes of 5 f^1 Pa(IV), 5 f^2 U(IV) and 5 f^1 U(V), approaching the values (1 to 3 eV) typical for the 3 d group. On the other hand, 5 f^3 U(III) recently studied[20) in $U_xLa_{1-x}Cl_3$ have "ligand field" effects only twice as large as the homologous 4 f^3 Nd(III), and similar regularities are observed in the subsequent 5 f group M(III). It is very difficult to oxidize 5 f^{14} nobelium(II) representing the closed-shell K = 100 in Eq.(5). It is likely that lawrencium (Z = 103) and immediately following elements most frequently have the oxidation state (Z − 100) but they soon begin to form certain complexes with a partly filled 6 d shell. The predicted chemistry of heavier elements (up to Z = 184) has been discussed at length[16) and the inner shells are strongly influenced by relativistic effects[21,22). However, the chemistry is much less modified from the non-relativistic behaviour, and mostly by the strong stabilization of 7 s and 8 s orbitals and of the third of the 7 p and 8 p shells having $j = \frac{1}{2}$.

Professor Robert Englman was so kind as to point out to the writer that "non-degenerate groundstate" might be a more suitable word than "totally symmetric groundstate". The argument is that a set of degenerate states belonging to the same eigen-value of the Schrödinger equation behaves collectively as having total symmetry. It is very difficult to say a clear-cut "yes" or "no" to such a suggestion. A simplified analysis can be made of the question whether the boron atom in its lowest configuration 1 s^2 2 s^2 2 p has spherical symmetry or not. There is no doubt that the six degenerate states form a spherically symmetric basis set, but at the same time, they form three Kramers doublets constituting the zero-order wave-functions for a uniaxial perturbation, such as the linear "ligand field" in the chromophore XBX with long B-X internuclear distances[8). Hence, an arbitrarily weak non-spherical (and non-cubic) perturbation is capable of producing energy differences between certain of the 6 states. The situation is intrinsically different in the ^1S groundstate of the beryllium atom, independently of the numerical question of the squared amplitude of the next-largest contribution 1 s^2 2 p^2 to the total wave-function written as a mixture of electron configurations, where 1 s^2 2 s^2 is the predominant contribution. "Accidental" degeneracy between non-totally symmetric wave-functions can have rather unexpected consequences; Epstein was the first to point out that the coinciding energies of 2 s and 2 p (of opposite parity) in the non-relativistic treatment of the hydrogen atom (and other monatomic entities with one electron) produce an electric dipole moment, which is otherwise impossible for a system having a centre of inversion. As far we know[11), the smallest distance to a low-lying J-level with opposite parity of the groundstate in a neutral atom occurs in the lowest level of [54] 4 f^8 5 d6 s^2 at 286 cm^{-1} above the groundstate of the gaseous terbium atom belonging to [54] 4 f^9 6 s^2. In Th^{+2}, the lowest level of [86] 6 d^2 occurs only 63 cm^{-1} above the groundstate belonging to [86] 5 f 6 d. Such closely adjacent levels of opposite parity would show an apparent electric dipole moment saturating at high electric field strengths. Englman[23) argues that the Jahn-Teller effect in polyatomic systems having degenerate sets of groundstates in a given high symmetry may be predetermined by properties of the individual atom, such as boron compared with beryllium. However, it is an empirical fact of great importance for the chemistry of post-transitional elements[8,24] that many molecules and polyatomic ions refuse to exhibit the highest symmetry available to them.

In spherical symmetry (of monatomic entities) there is only one type of non-degenerate level not possessing total symmetry: J zero with odd parity. This is, for instance, true for the first excited state of the mercury atom (and the isoelectronic gaseous ions Tl^+, Pb^{+2} and Bi^{+3}) belonging to [78] 6 s 6 p which plays an interesting rôle in the luminescence[10,25] of bismuth(III) in condensed matter. In the limit of Russell-Saunders coupling, the (rather unfrequent) non-degenerate term ^1S combined with odd parity is predicted in the excited configuration $1s^2\ 2s\ 2p^2\ 3p$ of the carbon atom. A much less hypothetical question is whether a chromophore in a finite point-group may show a non-degenerate groundstate, which is not totally symmetric. Many point-groups[8] certainly allow such states ($^1A_2$, $^1B_1$, $^1B_2$, . . . in contrast to $^1A_1$). A naïve M.O. interpretation suggests that such states cannot be groundstates. If x (absolutely or almost) degenerate M.O. contain less than 2x electrons, Hund's rules seem universally valid that a state with positive S has lowest energy. But if they contain 2x electrons, the totally symmetric $^1A_1$ is the only state obtained. This does not prevent[7] that the ground level (with J = 4) of the gaseous cerium atom (belonging to [54] $4f\ 5d\ 6s^2$) and the lowest odd level of Ce^{+2} (belonging to [54] 4 f 5 d) has more $^1G_4$ than $^3H_4$ character. It is not known whether this exception from Hund's rules for *two* partly filled shells in a monatomic entity may have an analogy in M.O. configurations. It is interesting to note[8] that 3 d group complexes showing *pronounced* Jahn-Teller distortions[26] have unbalanced occupation of M.O. in the high symmetry, by having 0 and 1, or alternatively 1 and 2, electrons in two M.O. which would have the same energy, e.g. in regular octahedral MX_6. However, tetragonally elongated $3d^4$ chromium(II) and manganese(III) complexes have $^5A_1$ and $3d^9$ copper(II) $^2B_1$ groundstates, and distinctly not $^5B_1$ nor $^2A_1$.

2 Nuclear Structure and Properties

Molecular spectroscopists and chemists studying polyatomic systems tend to consider nuclei as geometrical points. In this model, the instantaneous picture[8] of a homonuclear diatomic molecule is invariantly of the symmetry $D_{\infty h}$ whereas a heteronuclear diatomic system cannot loose the symmetry $C_{\infty v}$ and a system with three nuclei cannot have a lower symmetry than the point-group C_s having a plane of symmetry as only element of symmetry besides identity. In the strong sense in which the overwhelming majority of all real numbers are irrational (as shown by Cantor, the cardinality of the rational numbers, and even of the algebraïc roots of polynomials with rational coefficients, is not higher than the denumerable set of integers) an instantaneous picture of four or more geometrical points *almost* always has the lowest possible symmetry C_1. The vibrations of the nuclei (accepting three degrees of freedom of translation to be disregarded, assuming Born-Oppenheimer separability of the wave-function, as well as three degrees of rotational motion in the case of three or more nuclei, and two degrees in diatomic molecules) correspond to a distribution of instantaneous pictures scattered around a set of equilibrium positions, frequently representing a point-group of high symmetry. The cubic point-group T_d found in CH_4, SiF_4, $CoCl_4^{-2}$, ... is only such a mean value of the nuclear positions (this restriction is accentuated in X-ray diffraction of crystals, where only the time-average picture of the average content of the unit cell is determined). Like in molecular absorption spectra, the Franck-Condon principle is satisfied by photo-electron spectra, where the "vertical" ionization energies refer to the average internuclear distances, though a few molecules such as methane$^{27)}$ show some additional structure of the first photo-electron signal (corresponding to removal of one of the six electrons in the three degenerate M.O. consisting of C2p and H1s in the L.C.A.O. model) is due to CH_4^+ and CD_4^+ being Jahn-Teller unstable. For our purpose, it is important to note that the most precisely known$^{28)}$ internuclear distances R with an uncertainty of the order of magnitude 10^{-5} are obtained from rotational spectra (in the micro-wave region) with energy levels $J(J + 1) \langle R^{-2} \rangle$ times an expression dependent on the atomic masses and on constants of Nature. In diamagnetic diatomic molecules, the quantum number J is a non-negative integer. The question of time-scale once more shows up in this evaluation, the average value of R^{-2} of the instantaneous pictures being the precisely determined quantity. Actually, the typical scattering of the instantaneous R is several percent around the average value. In polyatomic molecules, three moments of inertia can be derived from rotational spectra, corresponding to the principal axes of a general ellipsoid. If isotopic substitution can be performed on a polyatomic molecule, the slightly different sets of each three moments of inertia can be used, in fortunate circumstances, to evaluate all the internuclear distances (in the sense defined above). By the way, if the difference between optically active enantiomers is neglected, the manifold of internuclear distances suffice to define the nuclear skeleton, without any reference to the explicit point-group.

The reason why nuclei for many purposes can be approximated by geometrical points is their very small diameters, compared with the internuclear distances. Though the nuclear surface$^{29)}$ is not absolutely sharply defined, the nuclear matter has a roughly constant density close to 10^{14} g/cm^3 and hence, the radius of a nucleus with the atomic mass number A is 1.2 fm (1 fermi = 1 femtometer = 10^{-13} cm) times the cube-root of A. The slightly different volumes of different isotopes of the same element produce shifts of atomic spectral lines (mainly connected with the number of s electrons in the electron configurations of the excited and of the lower level) of the order of magnitude 10^{-5} times the wave-numbers. However, a much more conspicuous isotope effect on spectra of monatomic entities (a comparable structure can be resolved in diatomic molecular spectra) occurs when the nuclear groundstate has a positive spin quantum number I. This quantity is zero for all stable nuclei, if both A and the atomic number Z are even integers. The *hyperfine structure* of atomic spectra can spread over several cm^{-1}, i.e. around 10^{-4} times the wave-numbers, and corresponds to a new quantum number $F = I \otimes J$ obtained by vector-coupling defined in Eq.(3). When J is at least as large as I, a set of $(2I + 1)$ adjacent energy levels is observed. A more direct technique of observing such levels is *nuclear* *magnetic resonance* (studying the Zeeman effect due to an external magnetic field) and also the hyperfine structure (introduced by nuclei having positive I) of electron magnetic resonance of paramagnetic species[30) providing a rather objective technique of evaluating L.C.A.O. delocalization coefficients. Another property of certain nuclei of interest for chemists is the electric quadrupole moment (only having observable consequences, if I is at least 1) allowing *nuclear quadrupole resonance*[31) to be observed between the (closely adjacent) energy levels obtained in an external uniaxial perturbation from neighbour atoms.

Besides the experimental fact that some nuclei (those with positive I) have properties (such as magnetic moments) somewhat incompatible with being geometrical points, the evidence obtained from radioactive isotopes strongly suggested some kind of composition of the nuclei. Since the time of Crookes and Thomson, electrons were recognized to be a constituent of all matter. They had been shown to posses the very low atomic weight 0.00054858 (1 unit of atomic weight has $m_0 c^2 =$ 931.50 MeV) when moving at low velocities. It is easy in a laboratory to let electrons through a potential difference 511 000 V after which their velocity is $(\sqrt{3}/2)$ c and their inertial mass twice as large as their rest-mass m_0. The old hypothesis of Prout of hydrogen being the primordial element was reformulated as protons (a hydrogen atom, including its electron, has the atomic weight 1.007825 relative to an atom of the abundant carbon isotope equal to 12) being the only other, and "massive" constituent, the nuclei "consisting" of A protons and (A – Z) electrons. This model prevailing before 1930 had a great impact on chemists; the two major types of chemical reactions are "redox" (reduction-oxidation) transferring electrons (like phlogiston) and Brønsted acidity, transferring protons. However, this model ran into a difficulty even before the discovery of the neutron. The nitrogen 14 nucleus has a groundstate with I = 1, but it should contain 14 protons and 7 electrons, altogether 21 *fermions* which should produce a system with quantum numbers (such as I or J) being odd positive integers divided by 2. Quite generally, quantum mechanics requires a set of bosons, to combine to a system (with I or J being a non-negative integer) also obeying Bose-Einstein statistics, whereas an *odd* number of fermions (with intrinsic half-numbered spin) obeys Fermi-Dirac statistics, but an *even* number of fermions represent Bose-Einstein statistics. Text-books usually introduce a third "elementary" particle, the *neutron*, and the nucleus is said to contain Z protons and N = (A – Z) neutrons. Thus, nitrogen 14 nuclei are bosons because A is even. The observable properties of the free neutron are slightly disturbing for such a simple picture; it has a magnetic moment about $(-\frac{2}{3})$ of that of the proton, though it has no electric dipole moment ($I = \frac{1}{2}$ prevents higher multipole moments from being observable). The *anti-particles* were established a few years after the neutron was detected. All fermions and some bosons (exceptions are the photon and the neutral pion) have anti-particles with opposite electric charges and magnetic moments. The free neutron is radioactive (with the half-like 10.6 min and the 1.4427 times longer average lifetime 15.3 min) forming a proton, an electron and an anti-neutrino (to be discussed below) whereas the anti-neutron is distinctly different by decaying (with the same half-life) to an anti-proton, a positron and a neutrino. The comparatively slow decay of the neutron was not felt to disqualify it as an elementary particle; once, the neutron is incorporated in a stable nucleus, it is no longer radioactive, and it became usual to say that the nucleus consists of A *nucleons* among which Z are in the state of protons, and N = (A – Z) in the state of being neutrons. However, once the doors were opened for radioactive "elementary" particles, they proliferated, and became nearly as numerous as the hundred elements in the Periodic Table. We return to these entities after having discussed problems more directly related to the structure of nuclei.

Some of the radioactive isotopes isolated from thorium and uranium minerals perform exponential β-decay, i.e. they emit electrons, of which the kinetic energy can be in considerable excess of $m_0 c^2$. Such β-rays have been of great help in verifying the predictions of the special theory of relativity, and provided an obvious argument in favour of (A – Z) electrons occuring inside the nucleus. However, subsequent experience clearly demonstrated that the emission of a particle is no proof of its *pre-existence* in the nucleus. The two major problems with β-decay is that the kinetic energies of the electrons are spread over a large interval, from very small values to a limiting maximum (which could be identified with the energy difference between the groundstates of the original and of the product isotopes corrected for $m_0 c^2$ of the electron) and another being that emission of *one* fermion is not compatible with A remaining even (or odd) during the β-decay, without any change-over between Bose-Einstein and Fermi-Dirac statistics. A third problem is that the kinetic energy of a particle as light as an electron confined in a volume as small as a nucleus would be exceedingly high.

Pauli suggested in December 1930 to remove these three problems by the simultaneous emission of an electron and (what we now call) an anti-neutrino. In 1934, Fermi gave a quantitative theory for the probability of sharing of kinetic energy between the two particles. Cases (such as tritium decaying to helium 3) of marginally low energy of decay available indicate *very* much smaller rest-mass of the anti-neutrino than that of the electron. It is generally agreed today that the behaviour of neutrinos and anti-neutrinos is much more comprehensible, if their rest-masses are exactly zero (like the photons) having the corollary that they are seen by all observers to move with the velocity c. The first artificial radioactive isotope (characterized by Irene and Frederic Joliot-Curie in 1934) was phosphorus 30 (half-life 2.5 min) forming the stable silicon 30 by emitting a positron (soon annihilating together with an electron in the surrounding matter) and a neutrino. An alternative to positron emission is *electron capture* where an electron (normally present in the 1 s shell closest to the nucleus) is absorbed by the radioactive nucleus, at the same time as a neutrino is emitted. It is amusing for ecologically minded persons that a-third of the radioactivity in the Earth's crust (and nearly all their own) is due to the isotope K40 present with an abundance 0.012 percent in potassium. It is energetically unstable both with respect to argon 40 (explaining why one percent of the atmosphere consists of this isotope, far more abundant than both the other four noble gases, and argon 36 and 38) and calcium 40. With a half-life of 1277 million years (corresponding to 16 times higher abundance 5 milliard years ago), it emits (with a probability 89.3 percent) electrons (and anti-neutrinos) to form the most abundant calcium isotope 40, it undergoes electron capture (with the probability 10.7 percent) to form argon 40, whereas the probability of emitting a positron (and a neutrino) is only 0.001 percent[32].

The most striking radioactive decay among the isotopes found in thorium and uranium minerals is the emission of *α-particles*, i.e. helium 4 nuclei. If the arguments about pre-existing entities in nuclei were valid, this would suggest that nuclei are systems containing α-particles. However, with present-day understanding of the quantum mechanics, it is more a question of a nucleus characterized by the proton and neutron numbers (Z, N) dissociating to two or more (spallation) products characterized by (Z_1, N_1), (Z_2, N_2), ... conserving $Z = Z_1 + Z_2 + \ldots$ and $N = N_1 + N_2 + \ldots$ The time-dependent Schrödinger equation describes the rate strongly dependent on the height of the activation barrier, and the empirical findings of Nuttal and Geiger that the logarithm of the half-life of α-decay is a rapidly varying, linear function of the penetration range of α-particles in air, were rationalized by Gamov into a similar logarithmic dependence on the kinetic energy of the emitted α-particle 33). A few short-lived fission products with unusually high N (for their Z) emit neutrons with a half-life of a few seconds (these "delayed neutrons" have an enormous importance for reactor technology) and a few nuclei with unusually low N (such as lithium 5, boron 9 or aluminium 23) rapidly emit protons. However, such an emission of one of the two nucleons is rarely energetically feasible. In the interval of A-values between 2 and 11, helium 4 is by far the most stable nucleus, and since it is so relatively light, spallation producing carbon 12 or heavier products has far longer half-life. This does not prevent that for sufficiently high Z-values, other channels of dissociation become important. The nuclear reaction *fission* of uranium 233 or 235 with slow neutrons (where the binding energy of the neutron to form the isotopes 234 or 236 supplies the activation energy needed) is a division (evolving some 200 MeV) into two nuclei with somewhat differing A. The probability distribution (illustrating the many channels utilized) has a shape of a camel back with maxima close to A = 95 and 138. At the same time, two or three "instantaneous" neutrons are emitted. The first nucleus where *spontaneous fission* has been well-established, is uranium 238 (constituting 99.3 percent of uranium in minerals at present) where one nucleus out of 1835000 α-emitters undergoes fission without precedent neutron capture. Since the half-life for α-decay of this nucleus 32) is 4468 million years, it means that the half-life for spontaneous fission would be $8.2 \cdot 10^{15}$ years, if it was the only mode of decay. In heavier nuclei, spontaneous fission becomes a predominant alternative; thus, the half-life is 2.64 years for californium 252 (however, 96.9 percent is due to α-decay), 60 days for californium 254 (99.7 percent spontaneous fission), 158 min for fermium 256 (92 percent spontaneous fission) and 0.08 s for (Z = 104, A = 260).

Much like two helium atoms do not combine to a diatomic molecule, two α-particles do not form a stable beryllium 8 nucleus (which is known to divide within 10^{-16} s). On the other hand, 3, 4, ..., 10 α-particles oligomerize to the stable nuclei carbon 12, oxygen 16, . . ., calcium 40 which are each time the most abundant isotope of their element (with exception of argon 36 discussed above). Also the abundances34) in the normal stars (such as our Sun) strongly point to a pronounced stability of these oligomers, though the most frequent isotope, by far, is the free hydrogen 1, and about 8 percent of the atoms (and 25 percent of the total mass) is helium 4, of which a major part was formed a few minutes after the "Big Bang", the singularity from which the Universe evolved some 10^{10} years ago 35) and the rest of the helium is the product of the source of energy (by hydrogen fusion) of ordinary stars. Though the Sun only transmutes $9 \cdot 10^{-12}$ of its mass from hydrogen to helium per year (at the moment), other stars are much more prodigalous and can show transmutation rates well above 10^{-9} year $^{-1}$ indicating a duration much shorter than of the Universe. There are good arguments (including the relative abundances of radioactive isotopes with half-lifes in the 10^9 year class) that both the Sun, the Earth and its Moon have condensed as recently as 5 milliard years ago. It is obvious[34,36] that the relative abundances of elements and of their isotopes are determined by kinetics; thermodynamical equilibria at temperatures[35] below 10^9 degrees would produce elements such as iron and nickel; neutron stars with A above 10^{57} and their implosion products, the black holes.[37] The two latter types of entities are determined by the gravitational attraction, which is negligible inside atoms and nuclei, but proportional to $A^{5/3}$ for a constant density of the neutron fluid.

The A-values 2 and 3 are not represented by any strongly bound nuclei, and A = 5 not at all (hydrogen 5 and helium 5 immediately loosing a neutron, and lithium 5 and subsequent isotopes a proton). The binding energies (relative to protons and neutrons) are in MeV for the stable light nuclei:

deuterium	2.225	beryllium 9	58.165	
helium 3	8.500	boron 10	64.751	
helium 4	28.296	boron 11	75.423	(6)
lithium 6	31.994	carbon 12	92.163	
lithium 7	39.244	oxygen 16	127.621	

They are seen to increase more rapidly than the number of mutual interactions $A(A-1)/2$ for A = 2, 3 and 4 and reaching a pronounced saturation in helium 4. Then, the pattern seem to repeat for the two next multiples of 4, the sum of the binding energy 8.482 MeV of tritium and 28.296 MeV of helium 4 being 2.466 MeV below that of lithium 7. By the same token, a triton and two α-particles have their binding energies 10.349 MeV lower than of boron 11. The trimerization energy of α-particles is seen to be 7.275 MeV and the tetramerization energy to oxygen 16 is 24.437 MeV, again showing a ratio 1 : 3.329 closely similar to the ratio 3.359 between the binding energies of helium 3 and 4. On the other hand, there is distinctly no tendency of oxygen 16 to tetramerize to germanium 64 or the other nuclei with A = 64 formed by electron capture or positron emission from this nucleus.

It is the general consensus among nuclear physicists[38] that the "unsaturated" behaviour of nuclei with A below 12 in Eq.(6) is atypical, in sofar the *liquid drop* model becomes a reasonable approximation in heavier nuclei. It may be noted that the smallest drop consisting of A identical spheres, where at least one particle is not in the surface, occurs for (both cuboctahedral and icosahedral) A = 13, related to the fact that $4\pi = 12.56637\ldots$ This model was proposed by C.F. von Weiszäcker in 1935, and one example[39] of the parametrization of the total atomic weight in the unit of 0.001 chemical unit is

$$1008.6650\,A - 0.8400\,Z - 16.72\,A + 18.5\,A^{2/3} + 100\,(A-2Z)^2/4A + \\ + 0.75\,Z^2/A^{1/3} + (-1)^{Z+1}\,\delta(\text{even }A) \qquad (7)$$