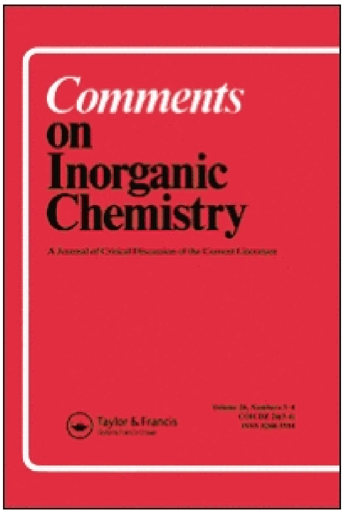

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What Are One-Electron Energies and Electronegativity-Related Parameters?

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What Are One-Electron Energies and Electronegativity-Related Parameters?

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A single Z-nucleus, and K electrons, allow many different, plausible definitions of one-electron energies. The treatment, originally of atomic spectra [of which very high charges $z = (Z - K)$ now are known], has been extended into chemistry studying a mist of indiscernible electrons around several nuclei. Quantum chemistry has revealed many counterintuitive (verified) consequences, and its Achilles heel is the correlation effect for two-digit Z. The present status of electronegativity, M.O. and inner-shell ionization, stabilization of oxides and of unusual oxidation states, heats of atomization, d and f group characteristics, and spin-pairing energy are reviewed.

Key Words: *electron affinity, d group characteristics, ionization energy, lanthanide energy levels, oxidation states, Periodic Table, quantum paradoxes, Schrödinger equation, spin-pairing energy*

INTRODUCTION

The earliest association of ideas with "one-electron energy" for chemists probably involves the standard oxidation potential E^0. In this journal[1] such quantities were discussed for electrochemical

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equilibria in solvents, and between dissolved species and a conducting material. However, the major origin of the close relations to atomic spectra is the formula of Rydberg (1895) originally applied to gaseous alkali–metal atoms, and based on Balmer (1885) for hydrogen atoms. The electron was established in 1897 from studies of the cathode tube invented[2] by Crookes. The series limits of the line spectra start I_1 (the "first" ionization energy) above the ground state of gaseous M^0 atoms (or I_{n+1} above the ground state of gaseous M^{+n}) and were shown twenty years later to represent liberation of an electron with very small kinetic energy, allowed to propagate in empty space. This concept is far less evident for I_n of systems not having only one "Leuchtelektron" outside closed, inert shells, as discussed below. There are many arguments for considering certain energy differences (e.g., between electron configuration barycenters) as better representations for "one-electron energy" than I_n (with negative sign), and quantum mechanics shows a second stratification of problematics: in the presence of several electrons, to what extent are configurations mixed by correlation effects?

The analogy to *nl* shell energy in a monatomic entity (nucleus with charge Z times the protonic charge $+e$ surrounded by K, at most $(Z + 1)$, electrons) is the molecular orbital (M.O.) energy in systems containing two or more nuclei (each having a definite positive integer as Z) and a certain number of (indiscernible) electrons. The M.O. energy combines the problems prevailing in monatomic entities having one or more partly filled shells with the problem that (accepting the Born–Oppenheimer factorization discussed below) 2 nuclei provide a potential curve to each electronic state; and when the number N of nuclei is at least 3, they have $(3N - 6)$ mutually independent internuclear distances, and hence the potential surface [energy as a function of these $(3N - 6)$ distances] of each electronic state subsists in a $(3N - 5)$ dimensional space, 10 dimensions for MX_4, 16 for MX_6 and in a case with 6 protons, 2 carbon and 1 oxygen nuclei (this space includes the ground states of the isomers CH_3CH_2OH and CH_3OCH_3 as well as mutually disconnected H_2O and H_2CCH_2 or the molecules monomeric H_2CO and CH_4) twenty-two dimensions (as any case of 9 nuclei).

Around 1962, perspicacious (and slightly cynical) chemists acquired the feeling that M.O. energies were an exclusively abstract concept derived from unavoidable fuzzy (not to say illusory) approximations to (unobtainable) exact solutions of the Schrödinger equation. Fortunately, David Turner then elaborated a technique of photoelectron spectrometry (cf. Refs. 3–7) where a gaseous molecule is bombarded with 21.2 eV (the strongest spectral line at 58.43 nm from a helium atom) or 40.8 eV (the resonance line 30.38 nm of He^+) photons, the kinetic energy of the ejected photoelectron being the difference between the photon energy and I_b (the "binding energy" of the electron). This method gave quite convincing agreement (and widely extended results) for M.O. energies of diatomic and polyatomic molecules. Frequently, distinction is made between (what is colloquially called) "adiabatic ionization energy" (the lowest I_b observed for a given ionization process, corresponding to the minimum distance from the vibrational ground state of the lowest potential surface up to the vibrational ground state localized around the potential minimum of either the electronic ground state, or excited states under study, of the ionized system) and the "vertical" ionization energy (the somewhat higher I_b going from the non-excited neutral molecule up to the portion of the potential surface for the ionized system having the same set of Z_1 to Z_2 internuclear distances R_{12} as the ground state; this is a corollary to the Franck-Condon principle for optical excitation) close to the maximum (or more precisely, the barycenter) of the photoelectron signal.

Two years later, in 1964, Stig Hagström, Carl Nordling and Kai Siegbahn developed photoelectron spectrometry of non-volatile solids,[8,9] using soft X-ray photons from the $1s2s^22p^6 \rightarrow 1s^22s^22p^5$ transition (1253.6 eV in metallic magnesium, 1486.6 eV in aluminum anticathodes) or, recently, from the continuous emission spectrum from a synchrotron. This technique has superseded X-ray emission and absorption spectrometry at many points. It is used mainly for I_b of inner shells, which show chemical shifts up to 5 or 10 eV (also including the decrease of I_b of gaseous atoms when condensing to metallic elements[10,11] or graphite[11]). However, the valence region (typically I_b between 6 and 25 eV) of samples (insulating or conducting) can also be studied but is impeded by highly differing signal intensities[12–14] for low $l = 0$ and 1 components of the M.O. (written in the L.C.A.O. approximation), although an advantage is that 4f signals are quite strong above $Z = 63$ through 74 compared to the far more numerous "valence" electrons having comparable I_b.The resolution is of order 1 eV (and can be enhanced to 0.2 eV for some metallic samples) to be compared with 0.03 eV for favorable cases of gaseous molecules (which frequently show detailed vibronic structure).

As seen below, these direct relations with measured I_b values have allowed a "consumer-oriented" definition of ionization energies, and also a return to the comparison of compounds with monatomic entities, as had been fashionable around 1930 (cf. the excellent book[15] by Rabinowitch and Thilo). Currently, there are at least three electronegativities used (χ_P introduced by Pauling,[16] χ_M by Mulliken,[17-19] χ_S by Sanderson[20]) with quite disparate conceptual backgrounds. Although the respectful chemist tends to believe (or tacitly submit to the advertizing) that χ *must* be something, since everybody speaks about it, the unexpected (a posteriori) realization that electron transfer spectra of d-group and f-group halide complexes[21-24] and I_b of gaseous and solid (p- or d-group) halides[12,25] show a linear relation (with the proportionality constant 3.7 eV) between the characteristic energy sequence I $<$Br $<$ Cl $\ll$ F and χ_P of the halogen has brought back some confidence, even in the most sceptical chemists. It is discussed below at greater length how the proportionality of all energy differences to Z^2 in one-electron systems ($K = 1$) can be extended to a factor $(z + 1)^2$ in the Rydberg formula, the ionic charge being $z = Z - K$, and to a polynomial for an *isoelectronic series* of monatomic entities with the same K, where the energy differences (excluding the spin-orbit coupling and other, higher-order, relativistic effects) are remarkably close to being proportional to $(v_2Z^2 + v_1Z + v_0)$ or to $(w_2z^2 + w_1z + w_0)$ (these two statements are synonymous for $w_2 = v_2$; $v_1 = w_1 - 2w_2K$; and $v_0 = w_0 - w_1K + w_2K^2$). The restriction to three relevant parameters is gratifying.

For the chemist, the *phenomenological barycenter polynomial*[26-28] is even more useful and surprising than the isoelectronic considerations. For a given *element* (definite Z) we then consider the stripped case with a closed-shell K_c value, such as 4, 12, 18, 30, 36, 48, 54, . . . , indicating a positive ionic charge $z_c = Z - K_c$. Relative to this stripped closed-shell state, all the lower z values have *one* partly filled shell (2p, 3p, 3d, 4p, 4d, 5p, 4f, . . .) containing $(z_c - z)$ electrons. When this number is at least 2, and at most $4l$, the ground state energy is not at all a simple function of z. However, if we evaluate the observed (or, in part, calculated by techniques successful for parametrization of atomic spectra) average energy (barycenter) of *all* (15p^4 or p^4; 20p^3; 45d^2 or d^8; 120d^3 or d^7; 210d^4 or d^6; 252d^5; 91f^2 or f^{12}; . . .) states [each J-level comprises $(2J + 1)$ states; each (S, L) term in Russell–Saunders coupling $(2S + 1)(2L + 1)$ states] it turns out that a helpful polynomial E^* [with the differential coefficient named the *differential ionization energy* I(z)] is obtained (with a highly negative E_0 of the barycenter of the neutral system):

$$E^* = E_0 + a_0 z + \frac{a_1}{2} z^2 + \frac{a_2}{3} z^3,$$

$$I(z) = a_0 + a_1 z + a_2 z^2, \tag{1}$$

$$I_n^* = \int_{n-1}^{n} I(z)dz = a_0 + \left(n - \frac{1}{2}\right)a_1 + \left[n(n-1) + \frac{1}{3}\right]a_2$$

where I_n^* is the energy difference between configuration barycenters [not as I_n between configuration ground state energies]. As discussed below, there is a close relation between I(z) and the electronegativity for each value of $Z = K_c + (z_c - z)$ in the nl-group of monatomic entities considered.

One should not overestimate the homomorphism between the chemical properties of an element with a given Z value and the energy levels of the monatomic entities containing Z with a charge not chosen above z_c. Stoner[29,30] proposed in 1924 a *spectroscopic* Periodic Table based on the electron configuration to which the monatomic ground state belongs (and said in more general wording, in the consecutive filling of nl shells, as also seen in the X-ray spectra studied by Moseley in 1913, who defined Z of the nucleus discovered by Rutherford in 1911). This table is similar, in many ways, to the *chemical* Periodic Table proposed in 1869 by Mendeleev. However, the two tables are distinctly not identical; the chemistry of helium, beryllium, magnesium, . . . is very different, in spite of the lowest electron configuration terminating $(ns)^2$ without partly filled shells, as also zinc, cadmium, ytterbium, mercury (and nobelium). Chromium (I), ruthenium (I), rhodium (I), and platinum (I) are not particularly frequent oxidation states,[27] in spite of one 4s, 5s or 6s electron only in the gaseous atom. This discrepancy was brought to general attention after synthesis of transuranium elements started in 1940. It is known today that the free atoms with $Z = 58$ to 64, and with Z 32 units higher, have ground states belonging to the electron configurations (outside closed shells $K = 54$ or 86): Ce:$4f5d6s^2$, Pr:$4f^36s^2$, Nd:$4f^46s^2$, Pm:$4f^56s^2$, Sm:$4f^66s^2$, Eu:$4f^76s^2$, Gd:$4f^75d6s^2$, Th:$6d^27s^2$, Pa:$5f^26d7s^2$, U:$5f^36d7s^2$, Np:$5f^46d7s^2$, Pu:$5f^67s^2$, Am:$5f^77s^2$, Cm:$5f^76d7s^2$. 4f electrons are seen to occur, starting with cerium, and 5f with protactinium. However, only Ce and Gd correspond to the predominant oxidation states Pr(III) to Yb(III) having spectroscopic properties[30-32] clearly indicating $4f^q$ with $q = (Z - 57)$. The most stable divalent lanthanide is Eu(II) with $q = 7$. On the other hand, La(III), Ac(III) and Th(IV) are almost exclusive, and the closed-shell Pa(V) quite difficult to reduce to $5f^1$ Pa(IV). Belief in strong correlations between the spectroscopic and the chemical Periodic Tables would suggest U(III) and the (unknown) Pu(II) to be common, but actually, U(VI), U(IV), Pu(IV) and Pu(III) are far more frequent.

A closer analysis[27,33,34] shows that the 3d and 4f groups have less varying oxidation states [e.g., Fe and Co mainly (III) and (II); Ni(II)] than the 4d and 5f group prolonging the closed-shell $K = 36$ from Y(III) to Ru(VIII) and $K = 86$ from Ac(III) to Np(VII). After this climax is reached, the 4d oxidation states get, on the whole, lower than in the 3d group, Rh(III), Pd(II) and Ag(I) being the most frequent. By the same token, Am(II) known from black AmI_2 is as reducing[30,35,36] as $4f^{13}$ Tm(II), but $5f^{13}$ mendelevium (II) is less reducing than $4f^7$ Eu(II), and $5f^{14}$ nobelium(II) is as difficult to oxidize in acidic solution as $4f^1$ Ce(III) in contrast to the closed-shell $4f^{14}$ ytterbium(II) nearly as reducing as $4f^6$ Sm(II). This trend can be related to the spin-pairing energy discussed in the section on the Schrödinger equation.

ATOMIC SPECTRA

The sharp Fraunhofer absorption lines have been perceived by Wollaston (who discovered palladium) and thoroughly studied in solar light (also from the blue sky) by Fraunhofer since 1815. In 1860, the chemist Bunsen and the mathematical physicist Kirchhoff showed that these sharp lines have the same wavelength as some (those terminating at low-lying states, or the ground state, according to findings in this century) of the emission lines found in laboratory light sources (arcs, sparks, later Geissler tubes with gaseous samples) from a definite element. All the strong, and many of the weaker, Fraunhofer lines were identified as belonging to about 40 elements, half of which have Z below 30. This work was later extended to other stars than the Sun, and is our most efficient technique of chemical analysis, even at distances[2,37–39] out to 10^{22} km. For the chemist, it is valuable that Bunsen and Kirchhoff discovered rubidium and cesium, based on their emission lines, like Crookes discovered thallium in 1861, and Reich and Richter indium in 1863.

The positions of atomic spectral lines were for 25 years considered pragmatic "fingerprint evidence" until the Swiss high school teacher Balmer proposed a formula for hydrogen which we here transcribe to wavenumbers (going from 10,000 to 40,000 $\mathrm{cm^{-1}}$ from 1000 to 250 nm wavelength)

$$(109678\ \mathrm{cm}^{-1})(1/\mathrm{n}^2 - 1/\mathrm{n}_{\mathrm{high}}^2) \tag{2}$$

where the red line corresponds to this difference from $\mathrm{n_{high}} = 3$ down to $\mathrm{n} = 2$, the blue-green line from 4 to 2, two violet lines from $\mathrm{n_{high}} = 5$ and 6, and a rapidly converging series of lines in the near ultraviolet, with maximum wavenumber a quarter of the constant in Eq. (2), to higher $\mathrm{n_{high}}$ values. In certain stellar photospheres with low pressure, and T about twice the 5800 K (prevailing in the solar photosphere), absorption lines were found of $\mathrm{n_{high}}$ up to 30. Since hydrogen was 7 times lighter than the next-lowest $A = 7$ of lithium, and since Prout had suggested in 1815 that the other elements are polymers H_A in conflict with the paradigm[2,40] of Lavoisier, Eq. (2) might be valid only for hydrogen atoms.

Ten years later, in 1895, Rydberg found a related formula for line spectra of gaseous alkali-metal atoms. In this review, modern symbols are used, both for quantum numbers in spherical symmetry and for energy. In most cases, 1 electron volt is used for the latter purpose, being 8065.48 $\mathrm{cm^{-1}}$ or 96485 Joule/mol or 23.05

kcal/mol. The Rydberg expression can also be extended to energy levels of M^{+n} ions, having one series limit I_{n+1} above the ground state of the ion. In that case, a factor $(z + 1)^2$ is used for M^{+z} ions. It is convenient to name I_{n+1} rather the I_{z+1} (thereby avoiding confusion with the quantum number n) and sometimes to admit instances of two or three closely adjacent series limits I_{z+1} of which the lowest represents the genuine ground state of M^{+z}. Relative to an observed ionization limit, the energy levels are

$$E_{nl} = I_{z+1} - (z + 1)^2 \text{ rydberg}[1/(n - d_l)^2] \quad (3)$$

where 1 rydberg unit (for not very light atoms) is 109737 cm^{-1} or 13.6058 eV. The n value is a positive integer. The *Rydberg defect* is a positive d_l in a given element rapidly decreasing to very small values for g($l = 4$), normally quite small for f($l = 3$) unless Z is above 53 or z very large. Similar conditions occur for d($l = 2$), d_2 being quite moderate[27] for Z below 18. Quite generally, d_1 is much higher than d_0 (although the difference is smaller for lithium than for sodium, rendering Li^0 an intermediate case between H and Na in this respect). For $K = 1$, all d_l vanish, and n is often called the "principal quantum number". This is not strictly true for hydrogen (as seen in the next section), and for K above 1, n is not at all a quantum number like l is.

Most school children have seen a design (frequently serving as logo for nuclear energy establishments) of a fat nucleus surrounded by Keppler ellipses representing electrons. This picture derives from the 1913 model of Niels Bohr of an atom with one electron having an orbit like a planet in celestial mechanics, restricted by novel conditions related to the size of Planck's constant h, and new postulates for quantum mechanics. Since the observed results were so well-known, the model would probably not have been greeted with so much enthusiasm if it had not had a minute corollary that the constant of Eq. (2) increases with A of the nucleus, being 109,722 cm^{-1} for ^4He, and for the rare isotopes (discovered in 1932 and 1939) 109,707 for ^2D and 109,717 for ^3He, with the asymptotic value 109,737 for heavy atoms. In H^0, Lyman found the highest energy series of Eq. (2) with $n = 1$ as ground state. This was a very difficult task because of the strong, detailed absorption spectrum of H_2 in this region, but the lines are observed in stellar spectra outside our atmosphere, in some stars (including our Sun) even as 121.57 nm emission ($n = 2$ down to 1).

Without undue irreverence for a compatriot admired for posing a stepping stone in the middle of a ferocious river, the writer must add that the model of 1913 could not be extended to two or more electrons, and that this was done by Schrödinger in 1926 (as wave functions) in a most counterintuitive way. The analogy between the Balmer–Bohr formula and the Rydberg equation (3) enhanced the expectation that electrons were attracted by a central field U(r) somewhere between the "external" value $(z + 1)/\mathrm{r}$ (in atomic units) and in the nuclear vicinity Z/r, small Rydberg defects d_l suggesting the former limit and large d_l that the electron part of the time is close to the nucleus. For s and p electrons, an ambiguity evolved, that it seemed plausible that d_l can be larger than 1, or 2, ... This has an important bearing on the "Aufbau" principle of the spectroscopic version of the Periodic Table. It was not universally agreed that $K = 55$ has one 6s electron in its ground state, but if it is the case[41,42] $n = 6$ shows $\mathrm{d}_0 = 4.13$ in Cs^0, 3.67 in Ba^+, 3.36 in La^{+2}, 3.11 in Ce^{+3} and 2.89 in Pr^{+4}, to be compared with 2.23 in K^0, 1.86 in Ca^+ and ($K = 19$) ions with 3d ground state, 1.62 in Sc^{+2} and 1.44 in Ti^{+3}. For a 5d electron, $\mathrm{d}_2 = 2.45$ in Cs^0, 2.59 in Ba^+, 2.47 in La^{+2}, 2.32 in Ce^{+3}, and 2.19 in Pr^{+4}. The Rydberg defect d_3 for one 4f electron increases rapidly with Z for $K = 55$, being 0.02 for Cs^0, 0.31 in Ba^+, 1.40 in La^{+2}, and 1.56 both for Ce^{+3} and Pr^{+4}. A given groundstate always has the lowest $(\mathrm{n} - \mathrm{d}_1)$ and is 6s for Cs^0 and Ba^+, 5d for La^{+2}, and 4f for Ce^{+3} and Pr^{+4}. On pp. 28–31 of Ref. 42, d_l for isoelectronic gaseous species having $K = 11$, 19, 37, 55, 69, and 87, and ionic charges 0 to +3. When combined with parameters $A_*\,(nl, nl)$ and $H_*(nl, n'l')$ [cf. Eqs. (16) and (22)] such values allow a consistent treatment of two outer (nl and $n'l'$) electrons in the isoelectronic series $K = 12$, 20, 38, 56, 70, and 88.

It should not be construed that the d_l of Eq. (3) are extremely precise. The Rydberg formula is attractive to atomic spectroscopists because the variation as a function of n usually is weak, and nearly always monotonic (pronounced exceptions may be 4d in the 3d group and 5f in the 4f group).

In one sense, it is tautological to transcribe an observed $I_{z+1} - \mathrm{E}_{nl}$ via Eq. (3) to a definite value of $(n - \mathrm{d}_l)$. It was overdone in literature between 1920 and 1930. Empirically, a distinction developed between "series spectra" with one or even two external electrons, following Eq. (3) very closely, and "multiplet spectra" characterized with groups of closely adjacent spectral lines (today, multiplets[30,43] are groups of closely adjacent energy levels E) and no obvious series convergences. A major breakthrough for atomic spectroscopy was the analysis of the line spectrum of neon by Paschen in 1919, showing (like the four heavier[44] noble gases) the combined features of series and multiplet spectra. Hund[45] wrote a decisive book about the existence of Russell–Saunders (S,L) terms, their coupling schemes, and their spin-orbit coupling to form definite manifolds of J-levels. As long line spectra were the main subject of Eq. (3), the hope for a deep significance of d_l enticed energy levels to be given by their distance from the ionization limit. This was not feasible in most multiplet spectra, where I_1 or I_2 of (say, titanium to nickel of great importance for astrophysics because of their numerous Fraunhofer lines) were less precisely known than 10 or 5 percent. As done in the NBS Tables[46] "Atomic Energy Levels" and their continuation[47] on lanthanides, the energy levels use the ground state of each ionic charge z as zero point, leaving some I_{z+1} much more precisely known than others. At the end, it was only the helium atom that had the various E somewhat below I_1 better known than the distance from the ground state to I_1 (and it is now better known from elaborate quantum mechanics than the experimental uncertainty).

In 1970, Charlotte Moore published a compilation of ionization energies of monatomic entities[48] of great help for chemists. Among additional data may be mentioned I_3 and I_4 of lanthanides[49] also discussed by the writer[30] and in certain cases derived from the spin-pairing energy treatment.[50] I_6 of tantalum[67] was devaluated from 97.34 eV to 94.01 eV, I_6 of antimony[51] from 108 to 98.6 eV and I_7 of tellurium[51] from 137 to 124.0 eV. The high degrees of ionization have played a certain role in the discussion of photoelectron signals of isoelectronic series.[52,53] Brorson and Schäffer[54] discussed a variety of 3d, 4d and 5d group atomic spectra having become available the recent years.

A major part of all academic work in physics was atomic spectroscopy, until the neutron, artificial radioactivity, and Van de Graaf accelerators and cyclotrons became available after 1932. The field was put on the back-burner until attempts of realizing nuclear deuterium–tritium fusion (with gigantic lasers) were developed. It then became clear that the absorptivity of soft X-rays in vapors containing traces of elements above $Z = 10$ can be decisive. Subsequent studies concentrated on certain isoelectronic series, such as $K = 28$ or 11 [cf. the series (4), (5), (6) and neutral atoms (15) below] having very intense transitions of one 3d electron to the empty 4p or 4f shell, or of the single 3s electron to 3p (as in the sodium flame). Typical results[55] are emission lines of Cd^{+37}, In^{+38}, Sb^{+40} and Te^{+41} photographed between 0.5 and 0.92 nm, when emitted from a plasma submitted to a 0.6 nanosecond laser pulse providing 5×10^{14} W/cm^2. The energy levels of the whole $K = 11$ series from Zn^{+19} to Nd^{+49} are discussed.[55] The $K = 12$ series from Mo^{+30} to Cs^{+43} is treated[56] with new results for Mo, Rh, Ag, Cd, In, Sn, Sb, I, and Cs. For several years, the $K = 28$ series (starting with Cu^+ as the closed-shells with n up to 3) has been extensively studied, for instance[47] Sm^{+34}, Gd^{+36} and Dy^{+38} allowing comparison[53] with photoelectron spectra[12] of several Sm(III), Gd(III) and Dy(III) compounds. The transitions from excited $3d^9(nl)$ with nl = 4p, 4f, 5p and 5f were identified[57] in Y^{+11} through Ag^{+19} (except Tc) and the emission from ($K = 28$) $3d^94d$ to $3d^94p$ in several of the ions Hf^{+44} to Th^{+62} can be used[58] for photopumped lasers, the energy transferred from the Lyman line ($n = 2$ to $n = 1$) in $K = 1$, $Z = 17$ through 23, because of the fortunate coincidence that 6f to 3d for a given ($K = 28$, Z) value resonates with ($n = 2$ to 1) for the low Z_1 value $(Z - 21)/3$. More recently,[59,60] the spin-orbit arrays from $K = 28$ (most of the Hf^{+44} to Pb^{+54}, and K = 29, 30, 31, 32, 33, and 34 ending at Pb^{+48}) were studied. $K = 27$ was investigated[30,61] of ions Tm^{+42} to Hf^{+45}. An extensive review[60] discusses the somewhat broad emission bands of laser plasma (and their composition of individual, unresolved spectral lines) of the same element, varying K, e.g., $3d^{(K-19)}4f$ to $3d^{(K-18)}$ in lanthanum, where the emission peaks move smoothly from 1.16 to 1.03 nm from La^{+30} to La^{+34}; or again, $4d^{(K-37)}4f$ from Pr^{+14} ($K = 45$) to Pr^{+22} ($K = 37$). A fascinating variation occurs[60,62] in the $K = 53$ ion Gd^{+11} with $4d^{10}4f^5$ ground configuration, having the five other configurations $4d^{10}4f^{5-a}5p^a$ varying in a characteristic parabolic dependence on a. The ionization limit providing $Gd^{+12}4d^{10}4f^{4}$ is marginally above the configuration $4d^{9}4f^{2}5p^{4}$.

The highly charged ions have ground configurations for K up to 46 following the same order[63] as all transition compounds,[27] and all gaseous ions with charge at least +2:

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

where the double inequality signs indicate the noble-gas configurations $K = 2$, 10, 18 and 36. If we approach the "hydrogenic behavior" with high Z and only a few electrons, it would be more appropriate to put the third double inequality sign between 3d and 4s, hence marking the points of 2 electrons able to have $n = 1$, the 8 having $n = 2$, and the 18 having $n = 3$. In this "quasi-hydrogenic" situation, one would continue the series (4) as

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

where the second closed n value at $K = 60$ is perceived in actual spectra, but $K = 110$ is not at all compatible with the very strong relativistic effects for three-digit Z values.[64,65]

The unfamiliar closed shell situation $K = 60$ is perfectly recognized in energy levels of $K = 61$ for sufficiently high Z values. Eu^{+2} and Gd^{+3} have $4f^{7}$ besides the 54 electrons found in the xenon configuration, extending (4) according to noble gases having double inequality signs:

$$\ll 4d < 5s < 5p \ll 4f < 5d < 6s < 6p \ll 5f < 6d < 7s < 7p \ll 5g \ldots \quad (6)$$

where, for the first time in z above 1 (4s below 3d is commonplace in K^{0} and Ca^{+}), a lower n value (4f) is filled after higher n (5s and 5p). Curtis and Ellis[66] performed Hartree–Fock calculations on several low-lying configurations of $K = 61$ ions, and found

W^{+13} to U^{+31} to have the alkali-metal-like ground state $4f^{14}5s$ as expected from series (5). In W^{+13}: $4f^{13}5s^2$ is quite close to $4f^{14}5s$, but already in Ir^{+16}, $4f^{13}5s^2$ is marginally above $4f^{14}5p$. The stronger of the two $5s \rightarrow 5p$ lines (as in rubidium) moves from 27.7 nm in W^{+13} to 9.6 nm in U^{+31}. In these cases, exorbitant spin-orbit separation makes the weaker line have a wavelength 1.3 and 2 times longer. The extreme of 5s (and a fortiori 5p) getting above 4f is accompanied by the related trend observed in spectra of $K = 67$. Ionization of $K = 68$ Yb^{+2} through W^{+6} provides $5p^64f^{13}$. However, starting with $K = 67$ Re^{+8}, the ground state belongs to $5p^54f^{14}$, the lowest excited level of Re^{+8} $5p^64f^{13}$ has 6.2 eV higher energy. The latter situation[67] of $5p^54f^{14}$ ground configuration persists at least up to Bi^{+14}. Cowan[68–70] reports the most probable Hartree–Fock ground states of Nd^{+z} losing 4f electrons until closed-shell Nd^{+6} $5p^6$. However, 5p electrons transfer to the 4f shell by further ionization: Nd^{+7} $5p^44f$; Nd^{+8} $5p^34f$; and Nd^{+9} $5p4f^2$. The minimum of $4f^4$ in gadolinium is calculated for Gd^{+7} $5p^54f^4$; Gd^{+8} $5p^34f^5$ and Gd^{+9} $5p^24f^5$ (and is found[60] in Gd^{+11} at $4f^5$ and no 5p). The flat minimum is $4f^8$ in erbium: Er^{+7} $5p^54f^8$; Er^{+8} $5p^44f^8$; and Er^{+9} $5p^34f^8$. In all of those ions, K is sufficiently high that $5s^2$ is not opened.

It would seem that about a quarter of the $100 \cdot 101/2 = 5050$ monatomic spectra from hydrogen to fermium ($Z = 100$) have been more or less studied now. As examples, Corliss and Sugar[71] reviewed titanium and gave many J-levels of all charges from Ti^0 to Ti^{+21}. $I_{21} = 6249.42$ eV and $I_{22} = 6625.82$ eV. Unfortunately, I_{16} (1044 eV) to I_{19} (1346 eV) are uncertain with one or a few eV. Further on, Sugar and Corliss studied vanadium[72] with all charges from V^0 to V^{+22}. For inorganic chemists, it may be interesting that both[73] Cr^0 to Cr^{+23} as well as[74] Mn^0 to Mn^{+24} and Co^0 to Co^{+26} were compiled[75] (chemists may note that the "first" spectrum is called Cr I, and that Roman numerals like Cr III and Cr VIII mean Cr^{+2} and Cr^{+7} with a charge one unit lower).

It is quite established that the sum of *one-shot ionization energies* (each time just removing an electron from one of the shells) is very distinctly smaller than the total binding energy, which is the sum of all the K values of I_n (independently of what order the consecutive ionizations take place). As a simple example, the one-shot ionization energy of Ne2s in a neon atom is found by I_b from photoelectron spectra to be 48.47 eV, and of the inner shell 1s 870.3 eV. In these two cases, $1s^22s2p^6$ and $1s2s^22p^6$ remain. The sum of $6 \cdot 21.6 + 2 \cdot 48.47 + 2 \cdot 870.3$ is only 1967.3 eV ($I_1 = 21.6$ is the 2p energy), 1544 eV less than the sum of all consecutive energies 3511.5 eV. For instance[48] $I_7 = 207.27$ eV; $I_8 = 239.09$ eV (last 2s electron leaving); $I_9 = 1195.797$ eV and $I_{10} = 1362.164$ eV (1.6 eV above $Z^2 = 100$ rydberg for relativistic reasons).

When a many-electron system has lost most of its electrons, accentuating the central field, the observed I_n are perceptibly higher than $I_b(nlj)$ of photoelectron spectra. Actually, the X-ray I_b binding energies usually are several eV uncertain, because the absorption bands to an empty, available orbital are broad and the energy of the empty orbital usually not well defined; and the emission lines correspond, to the first approximation, to the difference between two I_b values, but can be quite broad due to very short radiative lifetime or short lifetime of a competing Auger process, for instance $1s2s^22p^6$ ejecting an electron with high kinetic energy, and forming a level of $1s^22s^22p^4$ as residual state. Both the photoelectron and X-ray signals of molecules or solids can be broadened by vibronic coupling (like molecular spectra in the visible), and if one, or both, states involved in an emission process contain partly filled shells, the distribution of transition probability on the many conceivable states is intricate[25,41,76] like in atomic spectra of high ionic charge.[60]

The conventional expression of I_b of a *nl* shell from X-rays

$$(1 \text{ rydberg})(Z - Z_s)^2/n^2 \qquad (7)$$

differs from Eq. (3) by not having the "defect parameter" in the denominator, but considered as a screening constant Z_s subtracted from the central field (for positive charges) Z/r for $K = 1$. There occurs both screening from the part of the electronic density present between the nucleus and the electron in the shell to be ionized and "external" screening from electronic density at distances r longer than r_0 of the test charge (to be integrated in quantum mechanics). Any contribution from external charge density to Z_s is multiplied by (r_0/r). Equation (7) is quite satisfactory for $I_b(1s)$ where Z_s increases from 0.65 for helium to 2.00 for neon, slowly reaching a maximum 2.65 at silver $Z = 47$ and then decreases again (for relativistic reasons), passing 2 at platinum ($Z = 78$) and -0.2 for uranium ($Z = 92$). Equation (7) is not perfectly suitable for the elements lithium to aluminum, where I_b(1s) in photoelectron spectra[12,25] is (9.7 eV) ($Z^2 - Z$) suggesting an approximative $Z_s = 0.5$, but the factor being only 0.71 rydberg.

Since Coster[77] there has been a tradition of plotting the squareroot of I_b, hopefully giving $(Z - Z_s)/n$, but the experimental values for all other shells than 1s wiggle quite a lot. When I_b values have their difference quotient dI_b/dZ plotted[78] it shows a highly nonmonotonic variation with Z. Differentiating Eq. (7) gives $(2Z - 2Z_s)/n^2$. Not only is the slope dI_b/dZ much below 6.8 eV (one-half rydberg) times Z from Eq. (7) [actually, below (3 eV) Z between $Z = 10$ and 33], but intervals of Z values, where a partly filled shell with small average radius is under completion (e.g., 3d for Z around 22 to 29; 4d for 40 to 47; 5d 71 to 79; and, a fortiori, 4f 58 to 70), the slope is much smaller than expected. Both I_b of 3d and 3p would have slopes close to Z times 3.02 eV if Eq. (7) was plausible. Actually, the dI_b/dZ for 3p is below[78,79] the expression (1.5 eV) ($Z - 15$) for Z between 17 and 79. The same is true[78,79] for 3d when Z varies between 28 and 83. The situation is quite unexpected for 4d where Eq. (7) suggests dI_b/dZ close to (1.7 eV)Z. Actually,[79] between $Z = 47$ and 83, it is possible to connect the experimental values of the slope at the two points $Z = 56$ and 82 with a straight line increasing 0.4 eV per unit of Z. However, this straight line is overestimated by a factor 3 in the lanthanides, and by a factor 1.5 between $Z = 71$ and 79. Said in other words, there is an intimate interaction between the 4d and the 4f electrons (and to some extent between 4d and 5d) that makes the concept of Eq. (7) entirely unsuitable.[30] For instance, the photoelectron I_b of the loosest bound ($4d_{5/2}$) increases from 67.5 eV in xenon atoms to 109 eV in La(III), that is, 14 eV per unit of Z, but only to 203 eV in lutetium(III) or 6.7 eV per unit of Z [where Eq. 7) predicts Z times 1.7 eV (one-eighth ry) leaving an "effective Z" as low as 4].

There is overwhelming and multifarious evidence from atomic spectra, also when including X-ray and photoelectron spectra, that "orbital energies" are not directly accessible, if the chemist would like them to be additive. This is particularly true for "one-shot" ionization energies of inner shells. However, entirely "exterior" electrons may also be involved, such as in the variation of d^qs^2, $d^{q+1}s$ and d^{q+2} configuration barycenters as a second-degree polynomial containing the number of s electrons.[36] Thus, in Sc^+, 3d4s is slightly more than 1 eV below *both* $3d^2$ (1.15 eV) and $4s^2$ (1.36 eV); and in the gaseous nickel atom, where $3d^94s$ is 1.12 eV below $3d^84s^2$ (in spite of the latter configuration having 9 *J*-levels, one of which is the actual ground state, 0.17 eV below the barycenter of $3d^94s$) and 1.65 eV below the unique state of 3d.[10] If one asks the question whether 3d or 4s orbitals are the most stable in the 3d group, the approximate answer is that 4s are most readily removed by ionization (all M^{+2} being pure $3d^q$), but that, as a matter of orbital occupation in the ground state, 4s is served first in neutral atoms, all being $3d^q4s^2$ (excepting Cr^0 $3d^54s$ and Cu^0 $3d^{10}4s$). Only the palladium atom has its ground state belonging to $4d^{10}$ (and would be expected naively to be a noble gas, although the metallic element boils at 3400 K).

SCHRÖDINGER EQUATION

Erwin Schrödinger was born in 1887, only two years after Niels Bohr (although his work conceptually looks so much more recent). For our purpose, he published his equations[80] in 1926 and they remain a tool for chemists and spectroscopists to bring a nonrelativistic treatment as far as one probably can hope for. More than 60 years of scrutiny had brought many aspects into the limelight that were not considered essential to textbooks to be read by chemists. The first statement about quantum mechanics is perhaps that identical small systems, or identical "elementary" particles,[2] are *identical* to an extent quite inconceivable to Medieval logicians.[81] Their cardinal number 1, 2, . . . is relevant; their ordinality (No. 1, No. 2, . . . in a catalog) has *no* observable consequences. Chemistry and spectroscopy are profoundly marked by the nuclei happening to be at least 1836 times heavier (as rest-mass) than electrons. This is a convincing argument for the Born–Oppenheimer factorization being an excellent approximation.

In the general sense, wave functions have three Cartesian-type spatial variables per "elementary" particle. Further on, those fermions having $I = 1/2$ (such as electrons, protons, neutrons, ^3He,

^{13}C, ^{15}N, ^{19}F, ^{29}Si, ^{31}P . . . nuclei) have each two exclusive values, $m_s = +1/2$ or $-1/2$ of a spin variable (in a rather metaphysical space). Having heard the good news that everything else (in the following "nuclei") is extremely heavy (relative to electrons), a system with one nucleus and K electrons has its total wave function Born–Oppenheimer factorized in one translational wave function (3 spatial variables) times an electronic function with $3K$ variables. Supposing a kind of fairly empty volume (if its linear extensions are quite small, the translational energy begins to show finely divided energy levels) behaving like a very dilute gas (not interfering with rotation and vibration, and hence producing hybrid motions like librations or nutations) but the system having N (identical or different; from this point of view, isotopes are different) nuclei, the total wave function acquires two additional factors, a rotational with 3 degrees of freedom and a vibrational wave function with $(3N - 6)$ mutually independent *internuclear distances* R_{12} as variables. However, for $N = 2$, there are only 2 degrees of rotation and 1 variable R_{12} (the nuclei are here represented by geometrical points).

In this review, we neglect the vibrational and rotational variables (however important they can be in molecular spectroscopy). Retaining the electronic wave function Ψ only, we concentrate on *stationary states* (technically negative eigenvalues E relative to a continuum at positive E; this statement allows some diplomatic ambiguity; most such states do not last eternally at moderate to low temperature, and the other way around, excited states may be surrounded by a continuum, and still behave the same way as "genuine" stationary states, emitting narrow spectral lines etc., as discussed below for "auto-ionizing" states). Hence, we are resigned to ignore the *time-dependent* Schrödinger equation. This allows a golden fringe benefit: we do not need to keep the possibility open (with a footnote every 8 lines) that the electronic factor Ψ is complex, a linear combination of a real and an imaginary component v + iw of each set of variables describing a point in a multidimensional space. Chemists are so bewitched by textbooks in applied mathematics that they do not always recognize that the only *need* for complex wave functions are *magnetic* fields being present (in the Jargon of the Guild: operators being multiplied by -1 in the case of time reversal require complex Ψ, and the only known ones to occur in laboratories are magnetic fields and other effects of electric currents). Obviously, the imaginary components are indispensable for describing electronic or nuclear magnetic resonance; but the editors did not concede 137 pages to this review. Now, what is the toenail we have kept of the elephant: the *real* (non-complex) *stationary* wave function.

Starting with *one* nucleus, the one-electron function ψ [we also use lower-case symbols for italicized quantum numbers $n, l, j, \ldots$ and non-italic (Roman) symbols s, p, d, f, . . . for $l = 0, 1, 2, 3, \ldots$, to be compared with capital letters for more-electron systems: $S, L, J, \ldots$ and non-italic L values: S, P, D, F, G, H, I, K, L, M, . . .] it is not always realized that ψ *can* be written on *conservative form* (i.e., invariant sum of potential and kinetic energy, like Newtonian mechanics without friction). This was discussed by Klaus Ruedenberg[82] but the idea is older, and occurs in a book by Landau and Lifschitz. Below, we assume a one-valued potential U(x, y, z) in Cartesian coordinates, a stationary state with (negative) eigenvalue E and a local kinetic operator $\mathcal{P}$(x, y, z) behaving conservatively in each point:

$$\mathrm{U(x, y, z)} + \mathcal{P}\mathrm{(x, y, z)} = E. \tag{8}$$

In regions where U is more negative than E, the $\mathcal{P}$ is positive. But unlike classical mechanics (where $mv^2/2$ cannot be negative), $\mathcal{P}$ is negative as soon as U is less negative (or, if it can happen, positive) than E (allowing the quantum-mechanical "tunnel effect"). In the following equations, we are using atomic units (1 hartree = 2 rydberg = 27.2116 eV for energy, 1 bohr = 52.9177 picometer for distance, and $-$e for electric charge), and the symbol $\langle Q \rangle$ for an operator Q multiplied by ψ^2 and integrated over all appropriate variables (the wave function is normalized, having $\langle 1 \rangle = 1$). Thus,the potential energy is $V = \langle U \rangle$ and the kinetic energy $T = \langle \mathcal{P} \rangle$. For stationary states, the *virial theorem* is valid in the same form as in classical mechanics for a solar system held together (E is negative) by gravitation:

$$T = -E, \quad V = 2E, \quad (V/T) = -2. \tag{9}$$

The local kinetic operator[82] depends implicitly on ψ:

$$\mathcal{P} = -\frac{1}{2\psi}\left(\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2}\right). \tag{10}$$

One may worry for a moment that one might commit a division by zero. However, each of the three second differential coefficients vanish when ψ is zero, with one exception: if a nucleus is considered as a geometric point, $\mathcal{P}$ goes infinitely high, with values of U maintaining Eq. (8). We write here potentials for *electrons*, and hence (in atomic units) $U(r) = -Z/r$ if the nucleus is at (0, 0, 0) and $r^2 = x^2 + y^2 + z^2$. In the special case of a *central field* U(r) *only* depending on r, the eigenfunctions (orbitals) for one electron have the property of factorization

$$\psi_{nl} = A_l \cdot R_{nl}(r) \tag{11}$$

where the angular function only depends on l (and, so to say, is the carrier of this one-electron quantum number) and the *radial function* R_{nl} is determined by the detailed shape of U(r). The integrated volume of a spherical shell is $4\pi r^2 dr$ and literature contains several ways of distributing the factors (2), ($\pi^{1/2}$), and (r) of its square root on A_l and R_{nl}. Here, we normalize A_l by being a linear combination of (one or more) homogeneous polynomials $(x^a y^b z^c)/r^l$ [each with a normalization constant], all of degree $l = a + b + c$ (three non-negative integers). Since $(x^2 + y^2 + z^2)/r^2$ is another way of writing 1 (the A_0) there remain only five (and not six) A_2 proportional to $(3z^2 - r^2)$; (xz); (yz); (xy) and $(x^2 - y^2)$. There are $(2l + 1)$ linearly independent A_l; the A_1 look like vectors proportional to (x), (y) and (z). In the spherical symmetry of U(r), the local kinetic operator can be separated into a radial and an angular component:

$$\mathcal{P} = \mathcal{P}_{\text{rad}} + \mathcal{P}_{\text{ang}}, \quad \mathcal{P}_{\text{rad}} = -\frac{1}{2R_{nl}}\frac{\partial^2 R_{nl}}{\partial r^2}, \quad \mathcal{P}_{\text{ang}} = \frac{l(l+1)}{2r^2}. \tag{12}$$

The radial part is an implicit function like Eq. (10) but the angular part is an explicit "pseudo-potential" giving a total angular kinetic energy

$$T_{\text{ang}} = \langle \mathcal{P}_{\text{ang}} \rangle = \frac{l(l+1)}{2} \langle \mathrm{r}^{-2} \rangle \qquad (13)$$

vanishing for $l = 0$. It was immediately recognized[43,65] that the Schrödinger equation for one electron in spherical symmetry can be solved for a pseudo-potential $\mathrm{U(r)} + [l(l+1)/2\mathrm{r}^2]$ having a minimum (when l is positive) at some low r value (and diverging at the nucleus in the opposite direction of U(r) alone, making R_{nl} proportional[27] to r^{l+1} in the immediate vicinity of $\mathrm{r} = 0$). It may be noted that the lowest energy R_{nl} for each l (1s, 2p, 3d, 4f, . . .) has no radial nodes (vanishing R_{nl}) for finite (positive, but not infinite) r values. R_{nl} and $\mathrm{R}_{nl'}$ are always orthogonal, but all R_{nl} with the same l remain orthogonal by acquiring $(n - l - 1)$ radial nodes (they wiggle quite a lot close to the nucleus) and this is the (rather shadowy) sense in which n can be said to be a quantum number for orbitals in general central fields. For the "hyperspherical" symmetry of $\mathrm{U(r)} = -Z/\mathrm{r}$ and $K = 1$, the eigenvalues $E = -Z^2/2n^2$ and do not depend on l. Because of the virial theorem [Eq. (9)], $\langle \mathrm{r}^{-1} \rangle = Z/n^2$, but it has been known since 1927 that

$$\langle \mathrm{r} \rangle = [3n^2 - l(l+1)]/2Z, \quad \langle \mathrm{r} \rangle \langle \mathrm{r}^{-1} \rangle = \frac{3}{2} - [l(l+1)/2n^2] \qquad (14)$$

with the latter, dimensionless, product being 1.5 for 1s; 1.25 for 2p; 1.1666 . . . for 3d; and 1.125 for 4f.

The Schrödinger equation (our definite article indicates in this review "time-independent; real wave functions; (at least) quasi-stationary states") also addresses itself to the structure of the spectroscopic version of the Periodic Table as consecutive filling of nl shells [like Eqs. (4) and (6)] as first proposed[27,29,30] by Stoner in

1924, although the early emphasis on ground states of neutral atoms tended to favor a "pedagogic" sequence[83]

$$1s \ll 2s < 2p \ll 3s < 3p \ll 4s < 3d < 4p$$

$$\ll 5s < 4d < 5p \ll 6s < 4f < 5d < 6p \ll 7s < 5f \ldots \quad (15)$$

having 20 exceptions between the 99 gaseous atoms from hydrogen to einsteinium. The arrangement (15) was described[63] by a rule of E. Madelung, cutting slices each terminating with an s orbital. Each slice has invariant $(n + l)$, starting with the lowest n and highest l, and then regularly increasing n and decreasing l by one unit. Prokofjew[84] (not the composer) used the numerous known $1s^22s^22p^6(nl)^1$ of the sodium atom to evaluate a general[43] central field U(r). However, already in 1928, D. R. Hartree developed a systematic evaluation of ψ in a central field where $(-Z/r)$ is added to a (positive) contribution representing the repulsion of the *other* electrons (not the test electron considered) if their electronic density is smeared out to a spherically symmetric average in each "bubble" between r and r + dr. If each (n_1l_1), (n_2l_2), (n_3l_3), . . . , (n_tl_t) shell contains q_1, q_2, . . . , q_t electrons, the total amount of interelectronic repulsion in a Hartree Ψ is

$$\sum_{w=1}^{t} \frac{q_w(q_w - 1)}{2} A_*(n_wl_w, n_wl_w)$$

$$+ \sum_{w<v} q_wq_vH_*(n_wl_w, n_vl_v). \quad (16)$$

The repulsion parameter A_* is typically 0.6 to 0.7 hartree/bohr times $\langle r^{-1}\rangle$ for the shell [it is exactly $(0.625\ Z/n^2)$ hartree for a hydrogenic radial 1s function] and would get the closer to $\langle r^{-1}\rangle$, the closer to 1 the $\langle r\rangle\langle r^{-1}\rangle$ is, cf. Eq. (14). In case of $H_*(n_wl_w, n_vl_v)$ one of the two shells may have, by far, the larger $\langle r\rangle$, say n_vl_v. Then, the charge density represented for the extended shell by the square of the radial function $R_{nl}(r)$ of Eq. (11) provides H_* slightly greater than $\langle r^{-1}\rangle_v$ quite independent of the exact size of the small w orbital. This represents what X-ray spectroscopists call "external screening." This Hartree treatment can be ameliorated for all K values (excepting the ground state for $K = 2$) by taking *all* the interelectronic repulsion inside a well-defined configuration [i.e., Eq. (16)] into account by adding (frequently negative) contributions by the more detailed aspects of the Schrödinger Ψ, as proposed by Fock.[85] Besides the enhanced amount of calculation (hardly a problem since 1973 for[86] monatomic entities) a conceptual disadvantage of the Hartree–Fock treatment is that the added contributions are *not local* in a definite volume element, because they include "exchange integrals of interelectronic repulsion" representing,[27,65] in the case of one nl-shell, the interaction of the "cross-term" charge density with itself, or between two orbitals $\psi_1\psi_2$ and $\psi_3\psi_4$ [such interactions vanish if the two orbitals do not co-exist in our three-dimensional space, in contrast to the "Coulomb integrals" in Eq. (16)]. The "direct" Coulomb integrals of interelectronic repulsion are determined, e.g., by ψ_1^2 interacting with ψ_3^2 being (only) positive densities.

Slater[87] evaluated, in 1929, the parameters of interelectronic repulsion in the cases where one (or more) nl-shells are partly filled (1 to $4l + 1$ electrons in the general case; 2 to $4l$ for a single shell). This theory got incorporated as a major topic of the famous book by Condon and Shortley[43] (of which the first edition appeared 1935). Inorganic chemists tend to concentrate interest on one partly filled shell co-existing with closed shells. In this case, there are $(l + 1)$ differing F^k integrals $F^0, F^2, F^4, \ldots, F^{2l}$ of interelectronic repulsion separating the (S, L) terms of the nl-shell containing at least 2 electrons, and lacking at most two. The F^0 does not play an overt role in the term distances, but is the major part of the parameter A_* of Eq. (16) (which is actually slightly smaller than F^0 for positive l values). We keep A_* of Eq. (16) with a mildly modified sense, meaning below the quantity that corresponds to the Hartree–Fock average energy of all the l^q states containing the contribution $q(q - 1)A_*/2$ slightly changed by differing H.F. radial functions.

The F^2 and F^4 of d^q were combined by Racah[88] into two new parameters B and C, which subsequently have been quite elaborated.[27,54,89] The F^2, F^4 and F^6 of f^q systems were, even more significantly, transcribed to E^1, E^2 and E^3 by Racah[90] and discussed at length by lanthanide spectroscopists, also in condensed matter.[30,32,42,91,92] For our purpose, the most interesting result[21,27,54,89,93] is that there exists a spin-pairing energy parameter D such that in S.C.S. (Slater–Condon–Shortley) treatment, the average energy of all l^q states with a given $S = S_0$ is situated $2DS_0$ *below* the average of all l^q states with $S = (S_0 - 1)$. Since $2DS_0$ is the difference quotient of $DS(S + 1)$ it is possible to write the negative or positive distance (cf. Table VII in Ref. 93) from the l^q configuration barycenter [hence, not modifying Eq. (16)] as

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

$$\langle S(S + 1)\rangle = 3q(4l + 2 - q)/(16l + 4) \qquad (17)$$

which was subsequently proven by Slater[94] for all l^q in Russell–Saunders coupling. Most typical D have the order of magnitude 1 eV; it is $5(F^2 + F^4)/84 = 7((5/2)B + C)/6$ for d^q and $9E^1/8$ for f^q. As emphasized by Hund[45] the stabilization concomitant with high S values is also seen by the quartet ($S = 3/2$) ground states of N^0, P^0, As^0 and Sb^0 gaseous atoms, but not frequently outside transition-group monatomic entities *and compounds*. The highest $S = S_{max}$ occurs for the ground state of l^q as (q/2) until the half-filled shell ($q = 2l + 1$), and then $S_{max} = (4l + 2 - q)/2$. When several (S, L) terms of d^q or f^q have $S = S_{max}$, the lowest term has lower energy than Eq. (17), typically to the extent of 0.5 eV to 2 eV. For d^q and f^q, the lowest term has the highest L compatible with S_{max}.

The Hartree–Fock (H.F.) many-electron wave function for a given (S, L) term of a given well-defined configuration is obtained by minimizing the S.C.S. energy of interelectronic repulsion, including the spin-pairing energy Eq. (17), and maintaining *one* radial function R_{nl} for each *nl* shell, accepting all consequences of kinetic energy [the operator $\mathcal{P}$ in Eq. (12) prevents the implosion of the atom[82]]. The agreement with term distributions is reasonably close, although F^k parameters tend to be overestimated[93,95] by a factor $(z + 3)/(z + 2)$ in $3d^q$ H.F. *integrals* over R_{3d} as compared to F^k *parameters* optimizing agreement between S.C.S. expressions and observed term distances. If anything, the agreement[96,97] is less good than a factor 1.20 for $4f^q$ in Ln^{+3}, the ratio (integral)/(parameter) rather being 1.5 for E^3 but perhaps 1.4 for E^1. This does not prevent that a given set of parameters is much more precise for the many *J*-levels of Ln(III) compounds (having rather "spherical" spectra[30,32,47] between $4f^2$ and $4f^{13}$) than for the cases[27,43,93] studied early of gaseous $2p^q$ (q = 2, 3 and 4).

A very intricate question related to the moderate discrepancies between H.F. *integrals* and *pragmatic parameters* is why it is not obligatory to perform a new H.F. calculation for each term of a configuration. The utility of parameters is that they are, to a good to excellent degree, *transferable* between two closely related situations. Before cautiously stepping into this minefield, it is worth realizing that stylish quantum chemistry is usually restricted to one-digit Z elements.[98,99] The situation could easily have been worse. The total binding energy of the ten electrons[48] to a neon nucleus is 3511.5 eV. It is already 28 times more in a zirconium atom ($Z = 40$). We may review shortly *heats of atomization per atom*: in metallic elements, it varies from 0.64 eV for mercury to slightly below 9 eV for tungsten. It is 7.5 eV for graphite and diamond. Most compounds atomize at the cost of less than 4 eV per atom (i.e., 10^{-3} of the total binding energy of neon) with the exception of gaseous BF_3, solid BeO and LiF, and very carbon-rich molecules like CO, HCCH and its trimer C_6H_6, all running around 5 eV. If we were not so familiar with daily life, we might consider chemical bonding as an exotic epiphenomenon at low temperatures, since only diatomic CH, CN, SiO, TiO, ZrO, etc. survive in sunspots and in red stars at 4000 K. Contrary to nuclei[100] binding each new nucleon (above $A = 12$) with 6 to 8 million eV, atoms are very feudal, the two first electrons providing more than half the binding energy[98] for Z below 32. In heavier atoms, the eight subsequent 2s and 2p electrons are quite important too. The loosest bound electron has I_1 varying between 3.894 eV for cesium ($Z = 55$) and 24.587 eV of helium. It was reviewed[98] how the total binding energy is marginally higher (by 2 to 4 percent between $Z = 5$ and 61) than

$$E_G = Z^{2.40} \text{ rydberg} \qquad (18)$$

for reasons not fully understood. Preliminary literature has existed since 1951 about this expression (here called E_G and not E_{GG}) but the main evidence was presented by Gaspar.[101,102]

This mnemotechnic device Eq. (18) inspired the question: how significant are *closed-shell effects* in gaseous atoms? As a plausible choice was suggested[98] for $K = 10$

$$I_1(\mathrm{F}) + 2I_1(\mathrm{Ne}) - 2I_1(\mathrm{Na}) - I_1(\mathrm{Mg}) \qquad (19)$$

corresponding[48] to 42.6 eV = 1.57 hartree, or 1.2 percent of the binding energy in neon. Table I gives the analogous results for argon, krypton, and xenon 21.7 eV (about 1.1×10^{-4} E_G). Now since $I_1 = 4.07$ eV of francium ($Z = 87$) has been determined,[103] the influence of astatine on the analogue to Eq. (19) is not large, and the radon closed-shell effect is 17.6 ± 0.3 eV. The noble gas closed-shell effects are not far from (104 eV)$Z^{-0.4}$. Actually, the strongest heats of atomization of compounds per atom, starting around carbon, tend to be one-tenth of the closed-shell effect in the latter approximation. Table I also gives other closed p shell effects for gaseous cations. They are *roughly* proportional to $(z + 1)$ of the entity. Table I was also extended to closure of d($l = 2$) and f($l = 3$) shells by assuming Eq. (19) to be multiplied by $(2l + 1)/3$ because of the closure taking place over more elements:

$$\frac{2l+1}{3}[I_{z+1}(K_0 - 1) + 2I_{z+1}(K_0) - 2I_{z+1}(K_0 + 1) - I_{z+1}(K_0 + 2)]. \qquad (20)$$

Returning to the questions of *the* Schrödinger representation

TABLE I

Closed-shell effects (in eV) as defined from Eqs. (19) and (20) for gaseous atoms and positive ions

K = 10 Ne	42.6	Na^+	87.0	Mg^{+2}	141.5	Al^{+3}	297.6
18 Ar	29.7	K^+	57		–		–
28	–	Cu^+	3.8	Zn^{+2}	34.4	Ga^{+3}	77
36 Kr	25.8	Rb^+	46.0		–		–
46	–	Ag^+	16.2	Cd^{+2}	38.7		–
54 Xe	21.7	Cs^+	37		–		–
68	–		–	Yb^{+2}	20	Lu^{+3}	70
86 Rn	17.6		–		–		–

adopted in this review, the virial theorem[82] in Eq. (9) can be separated for H.F. Ψ:

$$E = T_c + T_f + Q_c + Q_f + C_{cc} + C_{cf} + C_{ff} \qquad (21)$$

where the subscript c refers to completed (closed) shells, and f to *one* partly filled shell (in the example below, the 4f shell of lanthanides). Four among the 7 contributions to the total energy E belong to one-electron operators, and the three last to two-electron operators. The kinetic energy T_c refers to all the K_c closed-shell electrons, and T_f to the $q = (K - K_c)$ electrons in the partly filled shell. The operator Q is the nuclear attraction acting on an electron in an orbital $-Z \langle r^{-1} \rangle$ hartree/bohr, either in closed shells Q_c or in Q_f. (By the way, several authors[104,105] use the less convenient symbol L rather than Q.) The interelectronic repulsion falls (in a H.F.) in three components, C_{cc}, C_{cf} (between the closed shells and the partly filled shell) and C_{ff} inside the partly filled shell, starting with a coefficient $q(q - 1)/2$ like Eq. (16). Among the seven constituents of Eq. (21), only two (Q_c and Q_f) are *negative* and hence the only ones responsible for E being negative.

In 1977, Katriel and Pauncz[104] analyzed the consequences of ascribing term distances in a partly filled shell to increased interelectronic repulsion, Eq. (17) in the S.C.S. treatment[43] which prevents the virial theorem from staying satisfied, because rigid H.F. radial functions R_{nl} (the same for a given shell) entail invariant T but V varying because of its C_{ff} component in Eq. (21). A comparison with previous studies of excited configurations of $K = 2$, and with their own calculations[104] for the terms ^3P and (at higher observed energy) ^1D of $1s^22s^22p^2$ in several monatomic entities with $K = 6$, provided the rather counterintuitive result that the lower term has *higher* overall $\langle r^{-1} \rangle$ and hence more negative Q (and a more positive T), but the contraction of the 2p shell in the lower term has increased the total interelectronic repulsion.

This enigma did not impress most chemists dramatically, but the problem forcefully returned in a H.F. study[105] allowing *different* R_{nl} (for the 11 complete shells in Eqs. (4) and (6), and for 4f) for each value of the total spin quantum number S in Ln^{+3} ($q = 2$ and 12: $S = 1$ and 0; 3 and 11: $S = 3/2$ and 1/2; 4 and 10: $S = 2$, 1 and 0; 5 and 9: $S = 5/2$, 3/2 and 1/2; 6 and 8: $S = 3$, 2, 1 and

0; and for q = 7: S = 7/2, 5/2, 3/2 and 1/2). Taken alone, the R_{nl} extension hardly varies with S. However, the energies involved in these minor variations are enormous. In spite of I_b of a 4f electron in $4f^7$ of various Gd(III) compounds varying between 11 and 15 eV, and I_4 of gaseous[49] Gd^{+3} being 44.0 eV, the angular kinetic energy 6 $\langle r^{-2}\rangle$ hartree/bohr^2 for *each* 4f electron in Eq. (13) turns out to be [535.4 eV + (0.56 eV)$S(S + 1)$]. For all eleven Ln^{+3}, Eq. (17) is nicely confirmed, the distances showing $2DS_0$ with almost the same D (for a given q) even when three distances occur. For Gd^{+3} the calculated[105] value (evaluated as the difference between total energies of two H.F. sets of R_{nl}) of D_{calc} is 1.09 eV, whereas[91,92] the pragmatic value derived from spectra of gadolinium(III) compounds is 0.79 to 0.80 eV and hardly can be above 0.81 eV in gaseous Gd^{+3}. This discrepancy D_{calc}/D_{prag} = 1.36 is quite familiar[21,93] for transition-group H.F. and was predicted by Freeman and Watson.[96] This is nothing compared to the analysis[91,92] of the contribution to D_{calc} from each of the seven quantities in Eq. (21). In units equal to D_{calc}, T_c contributes +3.5 and T_f: −4.5 (hence T: −1 in agreement with the virial theorem), Q_c: −7; Q_f: +13 (hence Q: +6), C_{cc} (+3.5), C_{cf} (−7.9) and C_{ff} (+0.4), and hence C: −4 and $V = Q + C$: +2. The most striking difficulty for the S.C.S. interpretation is that the pragmatic D = 0.80 eV corresponds to 1.84 times the calculated contribution from C_{ff} and to −0.184 times the calculated sum of the C integrals.

In this review, the requirement of stationary states can be just a tiny bit relaxed to include some sufficiently long-living *autoionizing states* above the first ionization limit I_n (the limits for previous electrons already departed do not count, e.g., I_2 for z = +3). Any excited state, even in empty space, performs radiative transitions to lower states and/or to the ground state. The electric dipolar transitions[43] go between states of opposite parity (*odd* if an odd number of electrons have odd l = 1, 3, 5 . . . ; otherwise *even* parity) and have the selection rules that J may change to (J + 1) or (J − 1) or remain the same J (then, at most one of the two states can have J zero). Besides such group-theoretical selection rules, numerical variation of the oscillator strength can exceed a factor 100. *If* Russell–Saunders coupling is less than perfect (and for this purpose, it is not even the case for all one-digit Z), the spin selection rule that S does not change gets mitigated for increasing Z (without modifying the J selection rules). Nearly all spectral lines observed of gaseous monatomic entities are electric dipolar; the categories[43] magnetic dipolar and electric quadrupolar are much less frequent and usually quite weak.

Seen against this background, an exceptionally long-lived auto-ionizing state belongs to the lowest term ^4P of 1s2s2p in the lithium atom (in hot dilute vapor), in spite of being almost at 10 I_1 above $1s^22s$. By the same token, gaseous potassium atoms[46] have excited states of . . . $3p^54s^2$ at 14.5 eV above the ground state . . . $3p^6$ of K^+. Cesium atoms[41,46] have numerous $5p^56s^2$, $5p^56s5d$, $5p^56s7s$, $5p^56s6d$, . . . states at least 8.4 eV above I_1, and even several eV above the first $5p^5$ ionization limit of Cs^0 (situated 107,392 cm^{-1} above the ground state of Cs^+). One of the earliest known auto-ionizing states *close* to I_1 occurs in the calcium atom, where the 12 J-levels of 3d4p (outside the K = 18 closed shells) are distributed between 35,730 and 40,538 cm^{-1} above the $4s^2$ ground state (having $I_1 = 49{,}305$ cm^{-1}). On the other hand, 32 J-levels have been identified[46] between 51,235 and 57,638 cm^{-1} belonging to 3d5p, 3d4d, and 3d5d. Hence, these two sets of J-levels have a second ionization limit $I_1^{(2)}$ due to $3d_{3/2}$ at 62,955 cm^{-1} (or 13,650 cm^{-1} above the 4s ground state of Ca^+). For the chemist, a more intuitive case[46] is the gaseous copper atom having the ground state $3d^{10}4s$ and many $3d^{10}(nl)^1$ behaving according to the Rydberg Eq. (3) with $I_1 = 62{,}317$ cm^{-1}. However, a second set of states $3d^9$ (nl) $(n'l')$ reminds the chemist that Cu(II) is frequent. ^2D of $3d^9$-$4s^2$ occur at 11,202 and 13,245 cm^{-1}; and $3d^94s4p$ starts at 39,019 cm^{-1}. The 8 J-levels of $3d^94s5s$ are just marginally auto-ionizing between 62,403 and 67,972 cm^{-1}, as well as many other configurations, and actually more levels are identified[46] above I_1 than between 0 cm^{-1} and I_1. The (several) secondary limits start at $I_1^{(2)} = 21{,}929$ cm^{-1} above the $3d^{10}$ ground state of Cu^+.

The heavier noble gases have two typical ionization limits[43,46] because of the spin-orbit coupling separating $^2P_{3/2}$ and (the higher) $^2P_{1/2}$ of $(np)^5$ to the extent of 1431 cm^{-1} in Ar^+, 5371 cm^{-1} in Kr^+ and 10,537 cm^{-1} in Xe^+. Conceptually, inner-shell ionization studied by X-ray and photoelectron spectrometry produces auto-ionizing states. In 2p ionization of Mn (Z = 25) to Zn (Z = 30), the excitation is roughly 100 times I_b of the 3d shell in solid compounds, happening to be similar to 100 I_1 of the gaseous atom. On the whole, high-energy auto-ionizing levels are difficult to detect, but they are perceived via the photoelectrons (or Auger electrons) ejected. From a strict quantum-mechanical point of view, even the presence of a long-lived radioactive nucleus in an atom[81] makes all its states quasi-stationary.

This short overview of auto-ionizing states provides arguments for both orbitals and electron configurations playing some deep role in the equation of Schrödinger. Now, we have to turn to the other side of the coin: solutions to this equation, involving two or more electrons, have no obligation to be, not even approximately, well-defined electron configurations. The deviations from a single configuration are called correlation effects.

CORRELATION EFFECTS

Condon and Shortley[43] did not try to hide that the interelectronic repulsion operator e^2/r_{12} besides diagonal matrix elements (including linear combinations like Eqs. (16) and (17), and many, so-called G^k integrals, in the presence of two or more partly filled shells) also have non-diagonal elements between differing configurations of the same (even *or* odd) parity. In Russell–Saunders coupling (neglecting spin-orbit coupling) such non-diagonal elements only occur between terms with the same (S, L) combination [($2S + 1$) is "multiplicity" written as left superscript (^{3}S; ^{2}P; ^{4}D; ^{5}F; ^{2}G; ^{3}H . . .) and pronounced triplet, doublet, quartet, quintet in these examples]. If spin-orbit coupling is perceptible (as always for Z above 4), J is written as lower superscript ($^3S_1$, $^2P_{1/2}$ and $^2P_{3/2}$, ^4D_J with $J = 1/2, 3/2, 5/2$, or $7/2$ . . .) and takes all values (equidistant, one unit apart) between $|S - L|$ and $(S + L)$.

Already Ufford[106] was inspired by the prevailing interest in Fraunhofer lines of neutral atoms between $Z = 21$ and 29 to calculate non-diagonal elements of interelectronic repulsion between (S, L) terms belonging to $3d^{q-2}4s^2$; $3d^{q-1}4s$; and $3d^q$ (with $q = Z - 18$). Gaseous Th^{+2} ($K = 88$ with two electrons[42] outside radon closed shells) has been studied since Racah[107] parametrized 5f6d, 5f7s, 6d7p and 7s7p of odd parity, even $5f^2$ etc., and Klinkenberg and Uylings[108] studied the even "superconfiguration" $6d^2$

+ 6d7s + $7s^2$ + $5f^2$ + 5f7p using 39 parameters (among which 11 were fixed by the authors), the highest percentage of a given (S, L) term in a given J-level varies between 100 and 34 in a table treating 39 J-levels).

Condon and Shortley[43] only mention one case (p. 366) of strong configuration intermixing, in the gaseous magnesium atom, where ^3D (47,957 cm^{-1} above the ground state ^1S) clearly represents 3s3d (outside neon shells) but two ^1D (46,403 and 53,134 cm^{-1}) were shown *both* to contain comparably strong characteristics of 3s3d and of $3p^2$ (having its lowest clear-cut level $^3P_0$ at 57,813 cm^{-1}). The writer (being a kind of chemist) got very anxious reading this page in 1954—if this happens once, what cannot happen to diatomic molecules, narrow J-levels of lanthanide compounds, broad absorption bands of d^q group complexes? However, among the shrinking community of atomic spectroscopists, habits (and a zest for wishful thinking) had forged the opinion that mixed configurations is only a serious problem when the term distribution of two configurations either overlap or at least are not separated to a larger extent than twice the width of the broadest configuration (as one might justify with semi-quantitative perturbation theory). However, this dragon was slain by Löwdin[109] in 1959.

When attempting to solve *the* Schrödinger equation for a complicated system (say, K above 20) no questions are asked about the diligent (and perhaps unfamiliar) algorithms used; only the result counts. This is why one is very cautious (since 1930) to use a method if it is not obeying the *variation principle*. If the method can get *below* the observed E value without warning, it is as impetuous as to jump across Times Square or Place de Concorde in the rush hour on kangaroo flexible stilts. The Variation Principle performs at its best when the calculated E is situated in the interval between the observed ground state [or lowest state of a given symmetry type, such as (S, L) combined with even or odd parity] and the next-lowest state of the *same* symmetry type. Unfortunately, as we see below, all neutral atoms, starting with sodium ($Z = 11$) have I_1 *smaller* than the difference (called *correlation energy* by Löwdin[109]) between the actual ground state (if needed, corrected for relativistic effects) and the (almost perfect[98]) Hartree–Fock ground state. Since this difference is negative, it is easier to speak about $-E_{corr}$.

After Niels Bohr (1913) had his Eq. (2) for $K = 1$ justified by the (1926) Schrödinger equation, there was a great effort to find, at least, the ground state for $K = 2$. The first attempt for states (nl) $(n'l')$ of helium and isoelectronic ions was (ϵ_{nl} being binding energy in the system with one electron less):

$$E = -\epsilon_{nl} - \epsilon_{n'l'} + A_*(nl, n'l') \qquad (22)$$

with $-\epsilon_{nl} = -Z^2/2n^2$ and $-\epsilon_{n'l'} = -Z^2/2(n')^2$ hartree valid for $K = 1$, and the interelectronic repulsion A_* between the two electrons. For the helium ground state, a much more fruitful "Ansatz" was to use a hydrogenic 1s radial function calculated for Z_* not being an integer, but a parameter (equal to $\langle r^{-1} \rangle$ bohr^{-1}). Then, the kinetic energy has to come out in the open as $T = -E$:

$$E = 2T_{1s} + 2U_{1s} + A_*(1s, 1s) = Z_*^2 - 4Z_* + \frac{5}{8} Z_* \qquad (23)$$

having its lowest E for He^0 at $Z_* = 2 - (5/16) = 27/16$, and $-E = (729/256)$ hartree. If $I_2 = 2$ hartree is subtracted, $I_1 = (217/256) = 0.847656$ hartree is predicted (23.066 eV), 1.52 eV less than the observed $I_1 = 24.587$ eV.

Equation (23) is the origin of "Slater screening constants" such as 0.3125 for 1s since all solutions to Eq. (23) have $Z_* = (Z - 0.3125)$ (this is a concept quite difficult to defend for two-digit Z values, as far as the shape of the radial functions goes). It was argued that gaseous H$^-$ may lose an electron spontaneously, since Eq. (23) gives $E = -(121/256)$ hartree, or 7/256 hartree = 0.744 eV *less* stable than a hydrogen atom.

Hylleraas started work[110] on this fascinating problem, and showed by higher-order perturbation treatment (with $1/Z$ as parameter) of the $K = 2$ Schrödinger equation that He^0, Li$^+$ and Be^{+2} have I_{z+1} agreeing with

$$E = -Z^2 + 0.625\, Z - 0.15744 + 0.00876\, Z^{-1} - 0.00274\, Z^{-2} \qquad (24)$$

(in hartree) giving good confidence in a *positive* $I_0 = 0.7$ eV for H^-, in close agreement with recent, very accurate calculations $I_0 = 0.7542$ eV. The gaseous species [also known as H(− I) in many crystalline hydrides like LiH to CsH (all NaCl structure, like CsF), perovskites $BaLiH_3$ and $EuLiH_3$, and the rhenium(VII) complex ReH_9^{-2}] plays an important astrophysical role, infrared radiation maintaining the quasi-stationary concentration of free electrons in stellar atmospheres.

The various strategies for evaluation of correlation energy[109] (explicit use of interelectronic distance r_{12} as variational parameter[110,111]; intermixing of numerous electron configurations; open shell with correlation factor; etc.) were brought to a common forum, introducing orthogonal *natural spin orbitals* (n.s.o.), transcribing the results of the various methods to the most rapidly converging ψ_{nso}. For instance, the helium ground state[109,112] converges to 99.186 percent of the electronic density in the s orbital (we call 1s), 0.390 percent in a p orbital (with highly positive kinetic energy, and belonging to the continuum), 0.385 percent in a continuum s orbital with radial node, and $\langle r \rangle$ comparable with both 1s and the continuum p. The next n.s.o. of continuum d type has only 0.018%. By the same token, H_2 for which James and Coolidge[113] gave the first convincing Schrödinger solution, has undergone several subsequent, sophisticated treatments giving n.s.o.[114] total densities 0.982 for σ_g, 0.010 for σ_u, 0.0043 for π_u and 0.0030 for a second σ_g. It was noted that $-E_{corr}$ is close to 1.1 eV both in He and H_2. This similarity of electron pairs in molecules ($-E_{corr}$ is small only close to the equilibrium[109] internuclear distance) is not likely to be a general feature; it would be surprising if Kr^0 and GeH_4 have comparable $-E_{corr}$.

Linderberg and Shull[115,116] demonstrated that a series of the type (here given for $K = 2$)

$$E = -Z^2 + 0.625\,Z - h_0 + h_{-1}Z^{-1} + h_{-2}Z^{-2} + \dots \quad (25)$$

describes the non-relativistic ground state for any Z. This perturbation result (like so many others) is formally valid, but the analogs for higher K have the problem that the various coefficients h_{-n} can be negative and positive, and do not vanish rapidly. For $K = 2$ with all correlation included, h_0 is 0.1576, for the optimized H.F.

function 0.1110 and for Eq. (23) 0.09765625. The other problem is relativistic effects, starting at the opposite end of Eq. (25) with $-Z^4/(4 \cdot 137^2)$ where 137, as in the following, stands for the speed of light 137.0359 in atomic units. Cohen[117] recently reviewed these Z-expansion methods.

Many facts are established about $-E_{corr}$ for Z below 20. In many systems, like the helium and the neon atom, *two-electron* substitution (e.g., $1s^22s^22p^6$ mixed with $2s^22p^6X_1^2$, $1s^22p^6X_2^2$ and $1s^22s^22p^4X_3^2$) to continuum orbitals X having either the same l, and an additional radial node roughly at the $\langle r \rangle$ of the orbital to be substituted, or otherwise, an additional angular node, because of $(l + 1)$, and comparable $\langle r \rangle$ of its radial function. This provides $-E_{corr} = 10.6$ eV in neon. The moderate $-E_{corr} = 20$ eV in argon (but still above $I_1 = 15.759$ eV) suggests continuum orbitals playing the major role. On the other hand, the isoelectronic series with $K = 4$ has a large coefficient to Z in Eq. (25) and was shown by Watson[93,118] to increase linearly from 2.5 eV for Be^0 in the isoelectronic B^+, C^{+2}, . . . mainly because of "near-orbital-degeneracy" between $1s^22s^2$ and $1s^22p^2$ (giving observable levels[46] known to atomic spectroscopists). The continuum effects vary much less in an isoelectronic series. The total spin quantum number S is far better defined in the beryllium atom ground state and excited states than the electron configuration. Watson gave arguments[93,95] for $-E_{corr}$ increasing somewhat more steeply from $Z = 20$ to 30, mainly because of $3p^63d^q$ substituted to $3p^43d^{q+2}$ (the 3p and 3d orbitals[86] have comparable $\langle r \rangle$; the great change in I_b comes from T_{ang} in Eq. (13): (3 hartree) $\langle r^{-2} \rangle$ decreasing I_b for 3d electrons strongly). The writer is only aware of approximate $-E_{corr}$ not far from 40 eV found for Zn^{+2} and Zn^0. For monatomic entities without exceptional near-degeneracy effects, it was suggested[30,98]

$$-E_{corr} \approx (0.7 \text{ eV}) Z^{1.2} \tag{26}$$

proportional to the square root of E_G of Eq. (18). Some numerical values of Eq. (26) are 41 eV for $Z = 30$; 90 eV for $Z = 60$ (Nd) and 133 eV for $Z = 80$ (Hg). This may not look so spectacular, $-E_{corr}$ being 0.3 percent of the total binding energy for $Z = 10$; 0.09 percent for $Z = 30$; and 0.04 percent for $Z = 60$. However, already in monatomic entities, a prominent problem is likely to occur, since (admittedly rather crude) second-order perturbation estimates (p. 283 of Ref. 30) of "squamp", the squared amplitude of the Hartree–Fock $\Psi_{\mathrm{H.F.}}$ in the complete (non-relativistic) Schrödinger Ψ [the square of the integral of $\Psi_{\mathrm{H.F.}}\Psi$ over all $3K$ relevant variables; for one-electron functions ψ_1 and ψ_2 it would be the square of their overlap integral] is known to be 0.99 for the helium ground state, 0.93 for the neon ground state, and likely to be[30] close to 0.7 for $Z = 30$ and 0.4 for $Z = 60$. If the squamp has the order of magnitude one-half in xenon atoms or lanthanide ions, half of the properties connected with electron densities are determined by the (numerous) small admixtures of many "correlation-induced" configurations. There are good reasons to expect[30] that most of $-E_{\mathrm{corr}}$ in, e.g., lanthanides is related to two-electron substitutions of any 2 electrons from inside one of the 11 filled *nl*-shells to a continuum orbital with comparable $\langle r \rangle$ and l at most modified by one unit. This mechanism makes the looser bound orbitals with about half of the electrons ($n = 4$ and 5) the major source of $-E_{\mathrm{corr}}$ (and decreasing the "squamp"). However, because of the comparable $\langle r \rangle$ of 4d and 4f shells,[86] two-electron substitutions of the kind $4d^{10}4f^q$ to $4d^8 4f^{q+2}$ (closely related to the "near-orbital-degeneracy" of the configurations $1s^2 2s^2$ and $1s^2 2p^2$ in the ground state[93,118] of $K = 4$) may be important, providing an appreciable part of $-E_{\mathrm{corr}}$. The idea[30] of two-electron substitutions has built in a divergent development, where 4-, 6-, 8- . . . electron substitutions eventually become predominant. This situation may already occur around $Z = 80$ or 100. It may not need to modify the electronic density in our three-dimensional space enormously; the need for 240 or 300 spatial variables "dilutes" the H.F.

It does not seem that any physical operator involves more than two electrons (we are not here considering the multifarious apparent 3- and 4-electron operators used as abstract tools for describing deviations from the S.C.S. treatment). If this proposition should be valid, the Schrödinger Ψ contains far too much information (like Ptolemaic epicycles) to be required by observable quantities. There was a feeling around 1960 that the (diagonal and non-diagonal elements of) a *second-order density matrix* subsisting in only 6 (and not $3K$) dimensions might replace[119,120] the wave functions. So far as the writer is aware, no safe criterion has yet been found for rejecting second-order densities (looking like they belong to genuine wave functions) that undershoot the experimental energy E. *If* a replacement for the Variation Principle, or a satisfactory formulation of a new set of conditions, should be found one day, *the* Schrödinger Ψ would have found a worthy successor.

When X-ray induced photoelectron spectra[121] were compared with H.F. calculations, a very curious regularity was found that the ground state, e.g., $1s^22s^22p^6$ of neon, has a calculated $I_b(1s)$ as high as 891.7 eV which is 21.5 eV above the observed $I_b = 870.2$ eV. These discrepancies turn out to be close to 0.8 eV times the square root of the H.F. I_b (in eV), strongly suggesting some correlation phenomenon. On the other hand, if a different H.F. calculation is performed for $1s2s^22p^6$ (achieving differing radial functions R_{nl}), the value is 868.6 eV. Manne and Åberg[122] pointed out that the main photoelectron signal observed at 870.2 eV is accompanied by a satellite structure of many weak signals. The barycenter of this structure plus main signal occurs at 886 eV, closer to the unrelaxed H.F. result 891.7 eV. This situation is analogous to the principle of Franck and Condon in the Born–Oppenheimer factorization of electronic and vibronic behavior that the (very rapid) ejection of a photoelectron leaves the ionized system in alternative *final states* being the *new* eigenvalues, and it should be worthwhile to speak about a Manne–Åberg principle. Distribution of the signal intensity on satellites in photoelectron spectra is a quite intricate subject.[25,76,121,123,124] Like the large shifts toward lower $I_b(nlj)$ of gaseous atoms[10] condensing to metallic elements, the relations between correlation effects and chemical influences remind one of the Pearson concept of hard and soft bases and anti-bases taken up again in the last section.

After having discussed correlation effects, it may be useful to discuss shortly the other deviation in Nature from the Schrödinger treatment, the (various) *relativistic effects*. They are roughly proportional to Z^4 and more than compensate $-E_{corr}$ for the atomic ground state for Z above 13. When it is known[86,98] that the relativistic stabilization reaches one percent (573 eV) at $Z = 32$ (germanium) and 10 percent at $Z = 96$ (curium), it might seem that $-E_{corr}$ is a negligible detail. However, for chemists, the great difference is that the "valence electrons" are percentagewise more, and also in a more unpredictable way, influenced by $-E_{corr}$ than by the relativistic effects. In compounds, the relativistic effects[64] are almost exclusively modifying ns orbitals and the (j = 1/2) component of *n*p orbitals, in both cases[86] showing divergent $\langle r^{-3} \rangle$ values due to their close vicinity to the nucleus. The "classical" relativistic effect is spin-orbit coupling[43] quite precisely proportional to $\langle r^{-3} \rangle$ of (non-relativistic) H.F. To the first approximation, 2s has the same energy as $2p_{1/2}$ (in $K = 1$) representing a splitting of 2p but a downward shift of 2s. The subsequent phenomenon is the *Lamb shift* (1949), where 2s is destabilized a tiny bit relative to $2p_{1/2}$ (0.0353 cm^{-1} in all hydrogen isotopes, not to be confused with the nuclear hyperfine structure of 1s, 0.049 cm^{-1}, induced by a proton; the Lamb shift is 0.468 cm^{-1} in He^+). As seen from the tables[125] for Z up to 40, and extended[126] up to 110, the Lamb shift is roughly proportional to Z^4 and crosses 0.1 eV at $Z = 16$ (sulfur), 1 eV at $Z = 31$ (gallium), 10 eV at 59 (Pr) and 100 eV at 96 (Cm). Experimentally, the details[127] of the $K = 2$ gaseous U^{+90} can be used to derive a Lamb shift 70 ± 8 eV.

Since all of the *n*s electrons are so sensitive to relativistic effects at high Z, the isoelectronic Au(−I) in non-metallic Cs^+Au^-, thallium(I), lead(II) and bismuth(III) (having two 6s electrons in the gaseous ion) show the most striking chemistry.[64] Here, we restrict ourselves to citing two other reviews.[128,129] The Dirac theory for $K = 1$ is divergent for a point nucleus for Z above 137 (the last integer before the speed of light in atomic units). However, there is general agreement that the empirically known density of nuclei[2,100] combined with reasonable estimates of A for a given Z allows a convergent Dirac description up to Z around 172 to 174. The weird aspect of this limit is that the 1s binding energies are comparable to m_0c^2 of an electron 511,000 eV or $(137.036)^2 = 18778.8$ hartree, allowing ephemeric pairs of an electron and a positron to become significant.

In textbooks of group theory, it is considered evident that a general point in empty space is a center of inversion. However, the emission of a (non-preexisting) electron[2] simultaneously with an anti-neutrino from a radioactive nucleus does *not* conserve parity.[130] The corresponding "weak neutral currents" also show up as perceptible effects[131] on atomic spectra of cesium thallium, lead and bismuth. The Aharonov–Bohm effect is a quantum-mechanical phenomenon wherein the motion of a charged particle is influenced by the existence of electromagnetic fields in regions which the particle does not enter.[132] Neutron interferometry[133] demonstrates that rotation of a fermion by 360° multiplies ψ by (-1) but is invariant by 720° rotations.

A major topic is relations with time and gravitation.[134] Wolfgang Pauli felt that gravitation hardly can be quantized because it is the geometrical structure of space-time and the theater where Ψ are played. The Big Bang (when the local time started) hardly can avoid some quantum effects.[135] In recent years, many expect that our local universe may be imbedded in several additional dimensions, perhaps in a foam-bath of other universes having the four Minkowski-like dimensions, but no longer able to communicate with our light-cone. It is a moot question whether they still belong to a single Universe[136] in such a situation. In addition to black holes[134] having a Schwarzschild radius 1.485×10^{-27} m times their mass in kg, through which no information can escape, we may very well have topological connections ("wormholes") between entirely different regions of space-time[137–140] and astounding quantum effects. If it is not only fiction,[141] macroscopic passengers might even take subways in such channels and get off un-squashed, 10^9 light-years (10^{22} km) away, and arrive either 10^9 years before or after their departure. Quantum mechanics is not a stern defender of causality, and even less of local realism and determinism.

OXIDATION STATES AND MADELUNG POTENTIAL

In spite of the highly oxidizing character (enormous electron affinity 15 to 29 eV) of gaseous Be^{+2}, Mg^{+2}, Al^{+3}, Y^{+3}, Er^{+3}, Th^{+4} . . . , the corresponding oxidation states Be(II), Mg(II), Al(III), Y(III), Er(III), Th(IV) . . . are chemically almost invariant. The first explanation was the full Madelung potential[15] of the anions (on the average closer than distant cations) "paying back" the formation of cations.

The idea of such a U_{Mad} (x, y, z) is qualitatively useful, but it cannot be neglected that several mathematical difficulties show up. In diatomic MX with internuclear distance R, full charges $+e$ on M and $-e$ on X produce $U_{Mad} = (14.4 \text{ eV})/(R/100 \text{ pm})$ (where 1

Å = 100 pm = 0.1 nm) stabilizing negative charge on X, and the opposite sign of U_{Mad} stabilizing positive charge on M, each of the two contributions to the total energy giving the sum (14.4 eV) ξ^2/(R/100 pm) if the charge separation is less complete, ξe on M and $-\xi e$ on X. The corresponding values are compiled[26,27] for neutral molecules such as equilateral triangular MX_3, regular tetrahedral or square MX_4, regular octahedral MX_6, and anion complexes MX_4^{-z}, MX_6^{-z}, etc. In this model, the spherically symmetric part of U_{Mad} essentially has an influence as if all the charges on the other atoms were concentrated on their nuclei.

Inorganic crystals with a repeated unit cell would need U_{Mad} (x, y, z) to depend only on the internal coordinates in the unit cell, and be continuous (and in practice differentiable) functions on each point of the surface of the unit cell, contingent to another unit cell. This renders it inconsistent to write an analogy $E = T + Q + C + N$ where Q is the attraction of *all* nuclei on all electrons, C the sum over $q(q - 1)/2$ contributions to repulsion between *all* q electrons and N the sum over repulsion energy between *all* nuclei. However much such a partition of E would remain defined in a molecule, a crystallite with linear dimension d (say, a cube; or approximately spherical) has the three contributions Q, C and N proportional[65,91] (as a predominant quantity) to d^5 (or the volume in the power 5/3) and not like the extensive (in the sense of classical physical chemistry) total energy E and (at least to a very good approximation) extensive kinetic energy T both proportional to d^3 (like the volume).

A related divergence is the original definition of the *Madelung constant* α as the total amount of electrostatic stabilization in units of 1 hartree/(R/bohr) = 14.4 eV/(R/100 pm) inversely proportional to the shortest M–X internuclear distance R (or, in an alternative representation, a characteristic constant for the unit cell). For instance, a cubic 1:1 binary structure (such as NaCl) has the shortest $R = (a_0/2)$, half the unit cell side a_0 and $\alpha = 1.748$ (greater than one, valid for diatomic MX) with the result that the alkali-metal halides in NaCl structure have the total Madelung stabilization varying from 12.53 eV in LiF to 6.87 eV in RbI (inversely proportional to a_0). This expression would be multiplied by ξ^2 if the M charge is $+\xi e$ and the X charge $-\xi e$ (including an extreme such as hypothetically fully electrovalent MgO with $\xi = 2$ and the total Madelung energy −47.9 eV). These results are generally accepted, but slightly suspect to a mathematician. The summation over positive *and* negative charges contributing to U_{Mad} is manifestly only conditionally convergent, if extreme care is not exercised to keep each new shell of summation neutral (or exceedingly close to it) and showing comparable distances in all directions. A conditionally convergent series can be rearranged (also by inadvertence) to give almost *any* positive or negative sum.

The dielectric constant D_{rel} (relative to 1 for vacuum) occurs in contributions to energy as its reciprocal value ($1/D_{rel}$), being 0.013 for water. This may as well be neglected at the scale of precision available when the hydration energy of a cation or anion with radius r_{ion} is evaluated[1,27,30,33,65,157] as

$$E_{hydr} = (7.2\ \text{eV})z^2/(r_{ion}/100\ \text{pm})$$

or (27)

$$E_{hydr}^{Latimer} = (7.2\ \text{eV})z^2/[(r_{ion} + 82\ \text{pm})/100\ \text{pm}]$$

where the former expression appropriate for a perfect dielectric is very satisfactory for the four halide X^-. It *cannot* be used *also* for cations with charge $+z$ if one accepts that $R(=a_0/2)$ can be separated[99] as $R = r_{anion} + r_{cation}$ in NaCl type salts. If the crystals had the Madelung constant $\alpha = 2$ and $r_{anion} = r_{cation}$, they could dissolve without evolution of heat in water. However, $\alpha = 1.748$ leaves a large exothermal excess of order 2 to 1 eV (able to heat 1 kg water at least by 30°C) per mol MX, which is further accentuated by any difference between r_{ion} of M and X, $[1/(1 + x) + 1/(1 - x) = 2/(1 - x^2)$ being larger than 2]. Actually, as pointed out by Fajans (1921), only alkali-metal halides[157] with great disparity of r_{ion} (such as LiCl, LiBr, LiI and CsF) dissolve quite exothermally (though far less than predicted by a perfect dielectric). This discrepancy was removed by Latimer (1955), adding 82 picometers to the *cation* radius in Eq. (27), suggesting that water is not fully efficient as a dielectric for M^{+z} of metallic elements.

The hydration of a single proton is accompanied by large-scale reorganization of the hydrogen bonding in the solvent, but represents actually[1,33] a stabilization 11.3 eV of H_3O^+ and its environment, larger than the Latimer value 8.8 eV for vanishing r_{ion} in Eq. (27). Many, but not all, aqua ions are much more similar to complexes of a definite set of ligands[1,27,99] and are not really expected to be well described by a model involving an (almost) perfect dielectric. With the conceivable exception[99] of Li^+ forming an ephemeric (10^{-11} s) $Li(OH_2)_6^+$ (the average life-time of magnesium(II) and aluminum(III) hexa-aqua ions are 2 microseconds and 6 seconds), alkaline-metal M^+ (and Ba^{+2}) show a rather chaotic instantaneous picture.

It is almost gratifying that the stabilization is 5 or 10 percent larger than the observed enthalpy. The problem here is that U_{Mad} for *non-overlapping spherical ions* would make any stable system collapse, because it is k times more stable, if all distances are divided by k. Even metallic elements would form M^+M^-, $M^{+2}M^{-2}$ . . . in contrast to the observed trend[99] for salts to go metallic at sufficiently high hydrostatic pressure. Born and Haber justified equilibrium M–X distances by a repulsion [from our view, almost certainly related to the kinetic energy Eq. (10)] with high slope (like furniture not going through the floor after a microscopic indentation, in Newtonian mechanics). Chemists no longer recommend a black/white dichotomy between electrovalent and covalent compounds, but the sum $U(r) + U_{Mad}$ of the central field of the ion or atom considered, and the "external" Madelung potential, still plays an important role when describing non-metallic solids.[25-27,65,93]

We meet a conceptual, and a numerical, challenge. The *Kossel oxidation state* (introduced[52,53,142] in 1916) may look superficially reminiscent of an exclusively electrovalent paradigm of Berzelius (1819). A closer analysis[27] shows that spectroscopy, magnetic resonance, and even absence of excited states below 4 eV in "truly colorless" compounds help to construct coherent descriptions, most (but by no means all) non-metallic inorganic solids and molecules having plausible K values of their elements. At one extreme is the 4f group.[30-32] Nobody having recognized the narrow absorption bands assigned to about 10 J-levels of a pink erbium compound, solution or highly diluted glass or crystal can doubt its character of $K = 65$ erbium(III) being a $4f^{11}$ system ($65 = 54 + 11$) quite independently of correlation energy, incomplete electrostatic bonding, etc. The same argument applies to narrow emission lines of $K = 60$ europium(III) from $^5D_0$ to $^7F_2$, $^7F_1$ and (the ground state) $^7F_0$ of $4f^6$ known from photoluminescence (also of doped biological systems) and from cathodoluminescence in red color television.[32,143]

The absorption bands of d^q systems, if not hidden by very intense electron transfer bands[23,24,27] [and even such situations can be of unique help in characterizing $K = 41$ rhodium(IV), a very rare $4d^5$ case, in emerald-green $Cs_2(RhCl_6)_x(PtCl_6)_{1-x}$; and still allowing detection of narrow-band red luminescence of $K = 21$ manganese(IV) in brown mixed oxides, this $3d^3$ system being isoelectronic with chromium(III) known from ruby $Al_{2-x}Cr_xO_3$], use today "ligand field" theory[27,65,144] in the opposite logical order than before 1969. The previous procedure was to select a plausible d^q, a set of conceivable (or crystallographically established as a time-average picture) nearest-neighbor distances ("ligating" atoms) and compare the result of one-electron energy differences [such as Δ (earlier 10 Dq) in the point group O_h between the strongly anti-bonding $(3z^2 - r^2)$ and $(x^2 - y^2)$ of equal energy, and non-bonding (or weakly anti-bonding) (xz), (yz) and (xy) of lower, identical energies] as well as a choice of interelectronic repulsion Racah parameters, such as B and C, Eq. (17), somewhat below the gaseous ion, as classified in the *nephelauxetic* ["cloud-expanding" referring to modified R_{nl} and possibly to breakdown of the factorization Eq. (11)] series, hydrostatic pressure, substitution in colorless crystals or glasses promoting unfamiliar internuclear distances, the Δ vary somewhat, but surprisingly little,[27,144,145] excepting mixed oxides,[27] and in particular[146] quite unrelated to the charges of the ligating atoms, contrary to the Bethe (1929) model of the (small) *non-spherical* part U_{ns} of the Madelung potential $U_{Mad} = U_{Mad}(r) + U_{ns}(x, y, z)$ quite popular until the Solvay meeting in Brussels, May 1956.

For our purpose, the establishment of detailed sets of d^q spectra[27,144] especially in chromophores (formed by the central atom and directly ligating atoms) having high symmetry allowed in nearly all cases to establish $3d^q$ with $K = (18 + q)$ and $z = (Z - K)$, or the $4d^q$ and $5d^q$ with the constant 18 replaced by 36 or 68. Without having been voted one definite year, this has imperceptibly become a major component of defining d^q oxidation states. It should not be neglected that the literature 1954–1984 has to a large extent overestimated high symmetries; the "instantaneous" Franck–Condon picture of (not exactly regular) tetrahedral $3d^7$ cobalt(II) is an instructive example.[147]

In $S = 0$ (colloquially "diamagnetic") p and d group complexes, stereochemistry provides strong suggestions for definite oxidation states, in particular quadratic (or rectangular, with two bidentate ligands, or halide bridges) d^8 Ni(II), Cu(III), Rh(I), Pd(II), Ag(III), Ir(I), Pt(II), Au(III) and $4p^2$ BrF_4^- and $5p^2$ iodine(III) and XeF_4 where one perpendicular "lone-pair" may be largely p(z) or $d(3z^2 - r^2)$.[65,148] Admittedly, some choices of oxidation states[27] may look more arbitrary, as when hydrogen is only H(I) when bound to either F, Cl, Br, I, O, S, Se, Te or N, but otherwise H(−I) with the result that H_2 oxidizes the green cobalt(II) complex $Co(CN)_5^{-3}$ to the colorless cobalt(III) hydrido complex $HCo(CN)_5^{-3}$. Nevertheless, this agrees with some organic chemists, belief that the similarity of halides H_nCX_{4-n} with methane makes C(IV) and H(−I) plausible. A ligand CH_3 may be considered as a carbanion when bound to Mn(I), Co(III), Zn, Cd, Hg . . . [and is C(II)] or a carbonium ion C(IV) bound to N, O, S . . . although it *is not* clear whether $Te(CH_3)_3^+$ contains tellurium(−II) or Te(IV). General sentiments about electronegativity differences[16–20] conduct OF_2 to be our only oxygen(II) compound, but OCl_2 and OH_2 contain Cl(I) and H(I), though admittedly there is no compelling evidence[27] available from positions of excited states nor stereochemistry.

Gaseous monatomic entities can have all K values from 1 to Z, and in most cases, also be anions with $K = Z + 1$. However, compounds are far less asymmetric at this point; if black or metallic solids are disqualified, C(−IV) exists in amber-yellow fluorite-type Be_2C; P(−III) in colorless PAg_6^{+3} and sheer non-metallicity of Mg_2Si, Mg_2Ge and[30] TbSb may assure Si(−IV), Ge(−IV) and Sb(−III). In a list of 309 oxidation states compiled[34] in 1986, going from hydrogen(I) to 105(V), only 20 anions without ligands are given, including[149] Na(−I) and Au(−I). Sixteen other cases[34] of negative oxidation states typically involve CO and/or PF_3 ligands [exceptionally[99] obeying the 18-electron rule that the coordination number is $9 - (q/2)$ for d^q systems like $3d^8$ Cr(−II), Mn(−I), $3d^{10}$ Mn(−III), Fe(−II), Co(−I) . . .]. To the 13 cases[34] of d-group M(0) may be added Ar(0), Kr(0) and Xe(0) ligands[44,146] (with quite high spectrochemical position) leaving 260 positive oxidation states. It is not evident that M(IX) *cannot* exist; the better candidates might be iridium and $Z = 109$ in MO_3F_3; MF_6^{+3} or IrO_4^+ (as known from Mössbauer spectra of an ephemeric species forming in OsO_4 containing a β-active isotope). Since 1968, there has not been characterized more than 1 to 3 new oxidation states each year. However, the winter of 1990/91 saw 13 at a time, having CO ligands[150,151] and all being negative; d^6 $Ti(CO)_6^{-2}$, $Zr(CO)_6^{-2}$ and $Hf(CO)_6^{-2}$; d^8 $V(CO)_5^{-3}$, $Nb(CO)_5^{-3}$, $Mo(CO)_5^{-2}$, $Ta(CO)_5^{-3}$, $W(CO)_5^{-2}$; d^{10} $Cr(CO)_4^{-4}$, $Mo(CO)_4^{-4}$ and $W(CO)_4^{-4}$; and (the somewhat $d^{10}s^2$ like) $Rh(CO)_3^{-3}$ and $Ir(CO)_3^{-3}$. Still, we know only about 3.4 oxidation states, z per element, on the average. The arrival of 29 negative complexes of CO (or PF_3) all together brings the select club of elements (Mn, Ru, Re, Os) able to change their z by 10 units three new members (Cr, Mo and W). There is no doubt that the 10 here is determined by the capacity of a d shell. Abegg pointed out the variation by 8 units from N(−III) to N(V); S(−II) to S(VI); Cl(−I) to Cl(VII) (and their higher homologs); today it seems connected with a coalescence of ns^2np^6 to a quasi-shell. The s^2 systems are not spherical (excepting[149] Na^- and Rb^-) as seen from P(III), S(IV), Cl(V), As(III), Se(IV), Br(V), Sn(II), Sb(III), Te(IV), I(V), Xe(VI), Pb(II) and Bi(III) manifestly lacking a center of inversion,[65] at least on short time-scales.

Obviously, the 34 oxidation states M(−IV), M(−III), and M(−II) now known have no analogy in gaseous ions. The number of monatomic cations is 3 to 4 times larger than the 270 to 280 positive oxidation states. Nevertheless, the writer is not aware of analyzed atomic spectra of Os, Ir and Pt with $z = +4$, $+5$ or $+6$, nor neptunium in any values 3, 4, 5, 6, 7 known chemically.

One might expect negative z values to be more frequent than 15 percent of the known z, although one should not confuse oxidation *numbers*[27] (a most helpful tool for writing stoichiometric coefficients of reactions) with z. On the other hand, the highest monatomic I_0 is 3.61 eV for chlorine, to be compared[152–155] with 3.40 eV for fluorine, 1.46 eV for oxygen and 2.08 eV for sulfur (forming O^- and S^-). Only in compounds are the $K = 10$:O(−II) and $K = 18$:S(−II) very frequent. At sufficient distance,[99] Cs^+ and Cl^- are less stable than Cs^0 and Cl^0. It was realized early[15] that only the Madelung U_{Mad} can stabilize the chalcogenide anions. At this point, the reducing character being 3.7 eV more pronounced (times differences such as 3.9–2.5) as derived from electron transfer spectra[23,30] and photoelectron spectra[25,30] show rather precisely 74 percent of the changes of I_1 among halogen atoms. Oxides are *far less* invariant, get stabilized by the Madelung potential of small, highly charged cations to become almost similar to fluorides, but also, with large, unipositive ions reducing like, say, bromides. Thus, oxygen (free of CO_2 and humidity) can oxidize Cs_2O to the superoxide[156] $Cs^+O_2^-$ and, by moderate heating, BaO to the peroxide $Ba^{+2}O_2^{-2}$. The electric polarizabilities[157] (derived from the refractive index) change by factors above 2 of differing oxides. Sulfides have a strong covalent bonding. The processes $O^{-2} \rightarrow O^- + e^-$ and $S^{-2} \rightarrow S^- + e^-$ are in both cases spontaneous in vacuum. It is possible to extrapolate from quadratic functions like Eq. (1) that O^{-2} has 8 eV *higher* energy[27] than O^- (almost the same values as obtained from the Born–Haber treatment of crystalline oxides like MgO) although small deviations from parabolic behavior *may* decrease the energy of this state (situated in the continuum) to only 7 or 6 eV. Seen from a quantum-mechanical point of view, this auto-ionizing state represents a H.F. required to have *six* equivalent electrons $1s^22s^22p^6$ rather than (the lower energy) $1s^22s^22p^5$ + electron at large distance.

Another source of information is photoelectron spectra of gaseous oxides.[3] The 2p orbital perpendicular on the plane containing the three nuclei in H_2O has its lowest $I_b = 12.61$ eV. In linear OCO, the two loosest, non-bonding oxide-delocalized orbitals have $I_b = 13.8$ eV and CO 14.0 eV (all "vertical" values). Tetrahedral RuO_4 and OsO_4 have been reinterpreted[158]; the detailed assignment of M.O. symmetry types has been discussed for many years.[159–161] The lowest I_b is 12.3 and 12.5 eV in these two molecules (almost like H_2O). For comparison, CF_4 shows[25,76] $I_b = 16.3$ eV; SF_6 15.7; and H_2 16.0 eV.

It would be bringing owls to Athens to emphasize that atomic spectroscopy and chemistry lack interfaces at many subjects. For instance, gaseous Al^{+3} ($I_3 = 28.447$ eV as electron affinity; $I_4 = 119.99$ eV) is able to oxidize monatomic cations[48] Rb^+, Ar^+, Mo^{+2}, C^+, Kr^+, S^+, Cs^+, Ag^+, Xe^+ and Y^{+2} (arranged according to I_n decreasing from 27.98 to 20.46 eV). Al^{+3} can also remove an electron from all[30,47] Ln^{+2} and from helium and all other gaseous atoms. There is a relation with diatomic molecules (p. 427 of Ref. 65) that most MX^+ are rather stable. They dissociate at long internuclear distance R either to M^+ and X^0 or M^0 and X^+ according to whether I_1 is largest for X or for M. Most molecules MX^{+2} tend to have a repulsive potential curve, at least at long R, because M^+ and X^+ repel each other. However, if M has a smaller I_2 than I_1 of X, the asymptotic dissociation is M^{+2} and X^0 (not necessarily being a repulsion). If X is helium, this would be the case for M = Be, C; Mg to Cl; Ca to Kr, etc. Actually, I_3 of most[30,47] Ln^{+2} is below I_1 of helium, with the exception of Eu^{+2} and Yb^{+2}. Hence, Eu^{+3} and Yb^{+3} are too oxidizing to have helium as ligand, wheras the other $LnHe^{+3}$ do not necessarily have a repulsive curve.[44] This type of argument may be relevant for the minority (6 to 8 percent) of Sirius-like A_p stars[37,38] having very strong Fraunhofer lines of one or a few distinct elements with Z above 30. Their accretion on the star seems to be favored[39] if their atom has I_1 (or I_2) situated in the interval between 10.2 eV (the first excited states (2s and 2p) of the ambient interstellar hydrogen atoms) and I_1 = 13.6 eV of hydrogen.

The photoelectron spectra with I_b below 16 eV also show very characteristic differences between the d groups[36] and the 4f group. Among solid $3d^3$ to $3d^9$ (and also $4d^6$, $4d^8$, . . .) compounds, I_b of the partly filled shell show values between 7 and 13 eV, much more dependent on the ligands than on q. On the other hand, the typical[12,34] I_b of closed d^{10} shells are in eV:

$$\begin{array}{llll} \text{Cu(I): 9} & \text{Zn(II): 16} & \text{Ga(III): 26} & \text{Ge(IV): 39} \\ \text{Ag(I): 10} & \text{Cd(II): 17} & \text{In(III): 24} & \text{Sn(IV): 32} \\ \text{Au(I): 11} & \text{Hg(II): 14} & \text{Tl(III): 18} & \text{Pb(IV): 25} \end{array} \qquad (28)$$

showing a *slope* dI_b/dz roughly in the ratio 4:3:2 for 3d:4d:5d. The other way around, the 4f group[30,42] has I_b slightly higher for fluorides than for oxides, but mainly dependent on $4f^q$, increasing in an S-shaped pattern about 5 eV from $4f^1$ to $4f^7$ and then repeating practically the same I_b values for $4f^{7+q}$ as for $4f^q$. The structure, especially $4f^8$ to 4f,[13] reveals the many terms of the ionized system

$4f^{q-1}$ formed according to the Manne–Åberg principle[121,122] with relative probabilities calculated by Cox.[162,163]

The transthorium compounds[30] show an intermediate behavior. The $5f^q \rightarrow 5f^{q-1}$ ionization is perceptible in U(V), U(IV) and higher Z values, but both its I_b and inner shells move much less as a function of the oxidation state z than in the 4f group, and more dependent on the ligands (in a way reminiscent of the d groups). As far as chemistry goes, the closed shell $K = 86$ continues from Ac(III) to Np(VII) in analogy to the $K = 36$ in 4d group Y(III) to Ru(VIII) whereas the lanthanides most frequently are Ln(III) and otherwise, at most, can change to Ln(II) and/or Ln(IV) [cf. the end of the Introduction].

Neither the "main" groups nor the 4f and 5f groups exhibit the very low (or negative) z with ligands such as CO and PF_3 so characteristic for all the d groups. Further on, at the beginning of each d group, oxo ligands are more efficient than fluorine to obtain high z (in spite of E^0 of liberating F_2 being far higher than of O_2). Thus, Mn(VII), Fe(VI), Co(V), Ru(VIII), Os(VIII) show *higher* z of oxo complexes than of (exclusive) fluoro complexes. A test case was the lemon-yellow CrF_6 shown[164] to decompose above −100°C. One might have guessed it to be as unreactive as SF_6. The optical electronegativities and related problems of CrF_6, OsF_7 and $OOsF_5$ were discussed.[165] At the end of the d groups, Cu(IV), Pd(V) Ag(V), Pt(VI) and Au(V) are known in fluoro, but not oxo, complexes.[34] One difference between O(−II) and F(−I) is that the ratio between the π-antibonding and σ-antibonding effect on the d subshell energies already is quite high, 0.3, in fluoride-substituted Cr(III) complexes,[54] but the behavior of OH^- suggests that this trend is even much stronger for oxo complexes.

A permanent dilemma for quantum chemistry is that many properties (heats of formation, photoelectron spectra, . . .) of heteronuclear compounds are *almost* the same if the fractional atomic charges[27] are assumed small (as in Hückel models) or rather large, positive and negative. Admittedly, the easier task was the combination[15] of I_n and the full Madelung potentials; and this approach was overestimated, e.g., by Van Arkel. But the opposite emphasis on the "principle of electroneutrality" according to Linus Pauling cut off fruitful connections with spectroscopy, as initiated by Kossel.[142] The minimization of E of constituent atoms from Eq.

(1) added to appropriate U_{Mad} of fractional charges [or in practice, their differential quotients added to[26-28] I(z)] gave a qualitative picture of gradually varying electrovalent and covalent contributions, and we know *why* the straightforward minimization overestimates the fractional charges. This model is not applicable to the 4f group, where a huge difference (of order 8 eV) between ionization energy and electron affinity in condensed matter assures a substantial premium for the number of 4f electrons keeping close to an integer. The opposite problem is that strongly reducing[27] sulfur-containing ligands, phosphines, arsines (and to some extent hydride) favor some ***high*** *z* because of the covalent stabilization, e.g., of Fe(IV), Co(IV), Ni(IV), Cu(III). . . . Extreme cases of this situation are that the two best known $5d^4$ iridium(V) complexes are IrF_6^- *and* $H_5\,Ir[P(C_6H_5)_3]_2$, and three typical $5d^0$ rhenium(VII) complexes being ReO_4^-, ReF_7 *and* colorless ReH_9^{-2}.

STRATIFICATIONS IN QUANTUM CHEMISTRY

During more than 60 years, quantum chemistry (and the more specific field, atomic spectroscopy) has developed a series of stratifications, some "serious" investigations doing deductive physics with a few equations and constants of Nature; some more parametric, trying a broad bird's eye view, using inductive methods (as seem to be the major difference[83] between chemical and physical thought). Most people consider "ab initio" a quality label; but ascetic restrictions do not necessarily help; *if* there is an excellent theory, it agrees with observable results (within their experimental uncertainty). The main reason why "semiempirical methods" (containing all kinds of parameters) are looked down upon is the risk of undershooting the variation principle; we have to learn that [A implies B] does not imply that [B implies A]; almost perfect agreement does not *prove* the theory; several quite different alternative rationalizations may be as good, be found tomorrow, be more apt to generalization, and our earlier theory may break its neck on a new crucial observation. The doubtful approximations are our living condition; is the weather forecast for a definite week next year available, even if we might be right that it can be derived from high school Newtonian physics?

Chemists should not underestimate quantum intrusions in the macroscopic world. They are not alone seen in liquid helium, when cooled from −269°C to −272°C or in Josephson junctions; the monochromatic lines seen, when looking at an advertizing neon Geissler tube through an optical grating (frequent as replicas in tie-pins) are an intrusion too. Gravity was discussed above as having unexplored quantum sides. Localization is formally inconceivable in quantum mechanics, but [excepting interference patterns of photons, electrons or slow neutrons[133] (though intact H_2 molecules and He^0 were diffracted by Otto Stern on LiF surfaces before 1933)] wave functions delocalized more than 100 nanometers are rarely observed to revolt against the relativistic rule against transmission of information more rapid than c (i.e., 0.3 millimeter in one picosecond). We all have an urge to learn[166] about a "Theory of Everything" but such a title covers many cases, from the identity principle "A is A" to the other extreme of deducing the outcome of a basketball match tomorrow. This review is not allowed to ramify like "Comments on the Collected Works of Leibniz," and the rest of this section is divided into three topics.

The first topic concerns four conceptual points of fixation. One is the multifarious connotations of "one-electron energy in systems with several electrons" which is really the main subject of the whole review. It may be worthwhile to remind chemists that electronic distributions in *six* dimensions are a modest lower limit (it is true for $K = 2$, and there is still hope for second-order density matrices[109,119,120]). The first excited level $^6P_{7/2}$ of $4f^7$ gadolinium(III) is situated 4 eV (or 380 kJ/mol) above the ground state $^8S_{7/2}$ and has quite different chemical properties in aqueous solution[167–170] and usually luminescent for several milliseconds. It must have almost the same set of R_{12} as ^8S as seen from the moderate vibronic co-excitation[167–173] in spite of containing as much energy as the typical heat of atomization per atom. The second conceptual point is the *Periodic Table* on which quantum chemistry [Q.C.] has thrown light, but not explained in a deductive sense.[174,175] As there is a lot of latitude in both the Chemical Version and in [cf. Eqs. (4)–(6) and (15) above] the Spectroscopic Version, looking like the two major styles (realistic and Platonic) in painting and sculpture, there is no absolute Periodic Table anymore than there is an ultimate painting of a sunset over a lake. This situation is obvious to lanthanide chemists,[30] early accepting $4f^q$ ideas. The invasion of d group chemistry by electron configurations was initiated by Henry Taube[176] in a review of substitution kinetics. Central ions were classified as d^qD^{2t} where the t-filled orbitals are bonding and symmetry-wise d-like, called D. There are 2 such D orbitals in $MX_6(O_h)$; 3 in $MX_4(T_d)$; and 1 in $MX_4(D_{4h})$ and several other types of chromophores. If $(q + 2t - 10)$ is positive, e.g., octahedral Ni(II) or planar Cu(II), these "supernumerary" d electrons are anti-bonding (known in p groups from the 4 loosest bound π electrons in O_2^{-2} and F_2; 3 in O_2^-; 2 in O_2 and 1 in NO and O_2^+ also acting as ligands[34,156]) and ascribed by Pauling to 4p orbitals [suggesting ready oxidation to Ni(IV) and Cu(III)] like "d^2sp^3 hybridization" in SF_6.

The third conceptual point is *Electronegativities*. If one wants to correct Mulliken's χ_M for spin-pairing energy, etc., the χ_M^* for M^0 would be $a_0 + (a_2/3)$ in Eq. (1), and χ_M^* for M^{+n} would be $a_0 + na_1 + (n^2 + 1/3)a_2$. It is noted that a_2 is significant, when the *nl* shell considered has an average radius rapidly decreasing with $+z$, and the earliest version of this idea omitted a_2. Though χ_M for N^+ is 22.07 eV (more than twice 10.21 eV for F^0) making N^+ a less attractive constituent of the betaine molecule $(CH_3)_3NCH_2CO_2$, there is some advantage for neutral atoms. In other cases (like Li^+) a closed shell is crossed, and Eq. (1) has highly different parameters on each side of the $K = 2$. Such cases have in a strong sense a moderate χ in the direction of *lower z*, and an exorbitantly high χ in the direction of higher z. This dual χ is persuasive in noble gases[44] where xenon has slightly higher a_n coefficients[26,27] than iodine, corresponding to Xe(VIII) being somewhat more oxidizing than I(VII), but the electron affinities of noble gas atoms vanishing, and probably lower (in the sense of highly charged anions) than magnesium atoms. Hence, these two trends cannot be combined[44] in a definite χ_M nor χ_P. A related problem is the controversy about χ of systems[177,178] having observable $Z = (Z_0 + 1/3)$ or $(Z_0 + 2/3)$ either because of the nucleus containing[100,179-181] a number of quarks not divisible by 3, or having integer Z_0 very close to an orbiting entity with negative, fractional charge. Comparison between known behavior of lanthanides shows χ_M of Ref. 177 to be irrelevant, but it is possible to use more classical chemical arguments[181] to obtain qualitative information on ($Z \pm 1/3$) chemistry. Such species may have astrophysical importance, and may occur in minerals at concentrations in the range 10^{-21} to 10^{-19} per amu, that is, 600 to 60,000 per gram. Pearson introduced Hard and Soft Bases and Lewis acids (Anti-bases, according to Jannik Bjerrum) as a generalization of many previous ideas of complex formation.[157,182–189] More recently, $\chi_M = (I + A)/2$ (e.g., 40.52 eV for Li^+) and an absolute hardness parameter $\eta = (I - A)/2$ was introduced for gaseous ions[190] and in another paper[191] $\chi = I(z)$ of Eq. (1) and $\eta = d^2E^* = d[I(z)]/dz = a_1 + 2a_2$ (the reviewer using barycenters). There is much to say for a hardness parameter being zero if the electron affinity A equals the ionization energy (and actually, it was a new concept[185,187] that metals *ipso facto* are soft). However, these ideas are only applicable to I and A in condensed matter; nobody can see from I(z) for carbon that graphite is a two-dimensional metal, and even[99] Li^+ and Li^- would have a combined $\eta = 2.37$ eV and not the perfect softness 0, due to conduction electrons. This brings up the question of hydration energies of ions[1,157,192] and the concomitant value 4.5 eV or 4.42 eV to be added[193,194] to E^0 per ionized electron to obtain "chemical" I_{chem} of species in water. The lower limit of the range stable toward H_2 evolution varies from 4.4 eV at pH = 0 to 5.4 eV at pH = 15, whereas only species having I_{chem} (after having been reduced by one electron) at most 5.6 to 6.6 eV in this pH range, are stable toward evolution of O_2. The softness parameter of Ahrland[157,188] is closely related to such I_{chem}. Anyhow, Eq. (1) cannot be differentiated at a closed shell. It is possible to take the average of its d^2E^* just before and just after the non-analyticity point. Still, $Li^{+1.01}$ would seem far less relevant to chemists than $Li^{+0.99}$. Pearson's last paper[191] argues that χ is a chemical potential for electrons[21,195] running into a mild problem for χ_S of Sanderson[20] whether the χ really equilibrates for the 13 innermost atoms of $C(CH_2CH_2CF_2CF_2CF_2CF_3)_4$ to a value determined by 36 of the 77 nuclei of the molecule being fluorine. A more inorganic question is how much I^- or $V(OH_2)_6^{+2}$ equilibrates its χ with increasing amounts of water.

We now continue with more "professional" queries: Chemists knowing Q.C. would like to perform significant perturbation calculus. The choice of both *diagonal* and *non-diagonal elements* acts in "strong-field" sub-shell configurations vs. "weak-field" (S, L)

or $[4f^q]$ (S, L, J) starting points, i.e., spherical symmetry. Such descriptions *within* a defined configuration can be perfectly equiconsequential, as known from rediagonalization.[148,196,197] Diagonal I(z) vs. weaker covalent bonding[26] is not a frequent approach (it may be nicer than it looks). Covalent bonding diagonal vs. weaker I(z) quantities is not exactly Extended Hückel Theory (E.H.T.), rather having non-diagonal covalent elements too, vanishing asymptotically for large R_{12}. In everyday chemistry, E.H.T. is probably the "bread and butter" approach.

Solving Eq. (8) directly for orbitals, the Johnson–Slater method $X\alpha$ is quite popular.[198,199] The non-local "exchange effects" of e^2/r_{12} are taken care of by the parameter α given with 5 decimals, differing according to authors. *Pseudo-potentials* are likely to become very helpful, representing inner shells and concentrate interest on outer electrons or 4f electrons.[200,201]

Sub-shell (d or f) energy differences in the *Angular Overlap Model* (A.O.M.) are parametrized with a specific version[65,202–208] of E.H.T. with emphasis on parameters of interelectronic repulsion from d^2 to d^8 and from f^2 to f^{12}. The writer argues[65,209] that $\mathcal{P}$ of Eqs. (10) and (12) provides the major part of the anti-bonding effect, even[207] for the minute (order 0.05 eV) separation of seven 4f one-electron energies. The ratio $e_\lambda/(S^*_{MX})^2$ between e_σ [or e_π] and the squared (one X to M) overlap integral is between 110 and 120 eV in Cu(II) complexes[210] and typically 100 to 200 eV in twenty $4f^3$ Nd(III) and $4f^6$ Eu(III) studied[207,208] in crystals. It is significant that the ratio e_π/e_σ between 0 and 0.3 in $3d^3$ Cr(III) complexes[54] is similar[206–208] in the 4f group, and close to squares of the ratio between S^*_{MX} for π and σ anti-bonding. The ratio considered as an energy is 10 times larger than I_b of the partly filled d or f shell, and is so enormous that the only quantity of this size is Eq. (12). The actual size of each S^*_{MX} is less precise[207,211] (perhaps by 25 percent) because of an effect first revealed in a study of $OV(OH_2)_5^{+2}$ by E.H.T. (as parametrized by Wolfsberg and Helmholz[21]) where the oxygen ligand[212] was reiterated to $z = -0.60$, and the other atoms allowed to vary their fractional charge.[212] Today, the R_{nl} have to be taken *cum grano salis* for another reason, the correlation effects decreasing the "squamp" (the squared amplitude of the H.F. approximation in the Schrödinger ground state) to well below 0.8 in the vanadyl ion, and to the order of 0.5 in the lanthanide compounds.

Finally, we may try to psychoanalyze some more philosophical queries. Can chemistry be reduced to Q.C.? (Can biology be reduced to chemistry?) This is not what makes a chemist enthusiastic; it is very difficult to answer "no", and probably needs an infinite investigation to say "yes". We should look upon half-filled bottles with satisfaction, rather than considering them half empty. Q.C. was derived from atomic spectra and the treatment of one Z nucleus and K electrons. Hund[213] and Mulliken[214] introduced *molecular orbitals*. They are closely analogous to nl shells in spherical symmetry. Their energy differences can vanish asymptotically for large R (like n becomes predominant for E if r times the central field U(r) approaches a constant $[Z = (z + 1)$ for $K = 1])$. Their M.O. configurations can be *strongly* mixed ("weak-field" A.O.M.). Their $-E_{corr}$ may be horrendous[121,215] and is likely to be 1 to 5 times the sum over all the $-E_{corr}$ of the constituent atoms. The "squamp" may lurk below 0.2.

Conceptually, configurations fall into two categories. Either we consider the *observed* J-levels of monatomic entities or $4f^q$ compounds as the object to study[30-32,216-218]; or the (not directly observable) configuration energies before correlation (and relativistic) effects set in. The former method (also used by atomic spectroscopists[42,49-51,55-62,71-75]) would be the obvious choice of chemists, if it was not for the monster of correlation.

In the case of d^q or $4f^q$ systems, approximated by pure configurations, important progress has been made along the lines of Racah[88,90] in the analysis of the (S, L) term energy differences and in suitable methods of comparison with observed (S, L, J) energy levels in complete (or almost completely known) configurations. Thus, the concept of orthonormal operators[54,89,148,197,219] allows the choice of $E = 21\ B/4$, a parameter separating $d^q(S, L)$ terms with given S and seniority number, as the most appropriate partner to D (of which the small part $1/(2l + 3)$ is known[21,65] to represent a decrease of the seniority number ν in the energy average over all l^q states). Also, the two first Trees[220] parameters α and β can be incorporated in the parametrization of d^q terms based on the five d^2 terms. The empirically found (C/B) quite close to 4.25 (for high z closer to 4 and[197] $(D/E) \sim 1.44$) is related to the conclusion that the mean square deviation of terms from the d^q barycenter is due to D to an extent close to 70 percent, and 30 percent because of E contributions.[54]

The good agreement of such a treatment[54,90] with observed atomic levels also emphasizes the lack of one brick in the puzzle: why are elaborate descriptions based on a pure d^q configuration so successful, when it is almost certain that the squared amplitude of the H.F. function has the order of magnitude 0.6, the rest (in particular in compounds) representing other natural-spin-orbital configurations?

The writer does not believe that these problems go away by being ignored; and he does not really share the hope that supercomputers solve these problems (but wait and see the next millennium). Q.C. might take a turn, making it even more counterintuitive. Niels Bohr once said after a seminar: This hypothesis is crazy, but it is not crazy enough to be correct.

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