Closed-Shell and Chemical Bonding Effects are Almost Negligible in Two-Digit Z Elements**

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Abstract: In an atom, the total binding energy of Z electrons is close to $E_{GG} = Z^{2.4}$ rydberg, with observed (available up to $Z = 17$) and calculated non-relativistic values decreasing from $1.036\,E_{GG}$ for $Z = 5$ to $0.996\,E_{GG}$ for $Z = 90$; and relativistic values going through a shallow minimum $1.022\,E_{GG}$ ($Z = 26$) back to $1.083\,E_{GG}$ ($Z = 90$). Hence, closed-shell effects are about one percent of E_{GG} for neon ($Z = 10$), below 0.1 percent for krypton ($Z = 36$), and a few times 10^{-5} for radon ($Z = 86$). Typical chemical bonding is 10 to 20 times weaker per atom than the closed-shell effects. The correlation energy (in atoms) is roughly $-(0.7\ \mathrm{eV})Z^{1.2}$ (proportional to the square-root of E_{GG}). It is minute, but may well modify the radial extension (in compounds) and the LCAO model a lot. The virial theorem and spin-pairing energy are shortly reviewed. The feasibility of quantum-chemistry for compounds involving two-digit Z values is critically reconsidered.

Already in 1913, *Moseley* pointed out that the inner shells of a typical atom (say with two-digit atomic number Z) have far higher one-shot ionization energies $I(nlj)$ than the ionization energy I_1 of the loosest bound electron in an atom. Thus, if the one-shot $I(2p) = 21.6$ eV, $I(2s) = 48.47$ eV, and $I(1s) = 870.3$ eV of the neon atom are multiplied by the occupation numbers 6, 2, and 2 in the configuration $1s^2 2s^2 2p^6$, the sum 1967.4 eV is only 56 percent of the total binding energy 3511.5 eV obtained[1] as the sum of the ten consecutive ionization energies I_n (each time going from the ground state of Ne^{+n-1} to the ground state of Ne^{+n}). In eV, $I_7 = 207.27$; $I_8 = 239.09$; $I_9 = 1195.797$; and $I_{10} = 1362.164$. The reason why the one-shot ionization energies (except I_1) are smaller, is the electrostatic repulsion from the other ($Z - 1$) electrons; this repulsion disappears gradually in direction of I_{10}.

For (not fully understood) reasons, it is a remarkably good approximation for all atoms (at least for Z up to 100) that the binding energy of the Z electrons is close to

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$$E_{GG} = Z^{2.4} \text{ rydberg} \qquad (1)$$

where 1 rydberg $= 13.6058$ eV is half of the atomic unit of energy 1 hartree $= 27.2116$ eV. This fact is mentioned by *Foldy*[2] and connected by *Scott*[3] to the first-order corrections to the Thomas-Fermi model[4–6] where the exponent 2.4 is known asymptotically to be $7/3 = 2.3\overline{3}$ in the (slightly unrealistic) limit of very large Z and vanishing reciprocal velocity of light $(1/c)$. The binding energy in equation (1) is usually called the Gombas-Gaspar energy[7,8] following the explicit discussion by *Gaspar* of a suggestion by *Gombas*. As shown below, the overall agreement would be better if equation (1) was multiplied by a constant 1.03 (or perhaps 1.02 if expressed

as 0.51 hartree). But the introduction of a second parameter is not necessarily an amelioration, and without this factor, E_{GG} is at present certain to be a lower limit to the binding energy. On the other hand, the exponent 2.40 cannot be chosen strongly different. For instance, if it were 2.41, E_{GG} for $Z = 100$ would be 4.616 percent larger. Quite generally, the ratio between E_{GG} for $10\,Z_0$ and (any positive integer) Z_0 changes by 2.305 percent for any change of the exponent by 0.01. Rather than to use E_{GG} as a viable approximation, the trend after 1970 has been to construct refinements modifying the Thomas-Fermi model[5,9].

All the Z consecutive ionization energies I_n are known[1] for the 17 first elements, and their sum E_{obs} given in Table 1 (in eV and in hartree) and compared with E_{GG}. Recently, Hartree-Fock binding energies E_{HF} have been evaluated for $Z = 5$ to 20 by *Sekiya* and *Tatewaki*[10] with a precision between 10^{-6} and 10^{-7}. These values refer to the (S, L) ground term of the gaseous atom. We return below to the correlation energy $- E_{corr}$ defined by *Löwdin* as the energy difference between the Hartree-Fock ground state (with the lowest term of a definite electron configuration) and the non-relativistic wave-function of lowest possible energy compatible with the Schrödinger equation. Though E_{corr} is, by far, the predominant part of $E_{obs} - E_{HF}$ in Table 1 for He, Li, Be, and B, the relativistic effects (intrinsically proportional to Z^4) grow up with higher Z, and represent one half of $E_{obs} - E_{HF}$ for $Z = 13$. In order to assure a continuity with the Z values between 20 and 100 treated in Table 2, it is useful to consider the relativistic energy E_R (evaluated by *Desclaux*[11]). However, in the case of ground states belonging to a configuration containing one (or more) partly filled shells, these E_R (corresponding to the average energy[12] of all the states of the configuration) are not directly comparable to E_{HF} (the ground state[10] if neglecting spin-orbit coupling) as can already be seen from the fact that E_R is smaller than

Table 1. Observed total energies for gaseous atoms (sum of Z consecutive ionization energies I_n), Gombas-Gaspar total energies, ground state Hartree-Fock energies according to *Sekiya* and *Tatewaki*[10], and relativistic energies according to *Desclaux*[11].

Z	E_{obs} [eV]	E_{obs} [hartree]	E_{GG} [hartree]	E_{obs}/E_{GG}	E_{HF} [hartree]	E_{HF}/E_{GG}	E_R [hartree]	E_R/E_{GG}
2 (He)	79.003	2.903284	2.63901	1.10014	2.86167	1.08437	2.86175	1.08440
3 (Li)	203.48	7.47769	6.9833	1.07080	7.43273	1.06436	7.43327	1.06444
4 (Be)	399.14	14.6680	13.9288	1.05307	14.57302	1.04625	14.5752	1.04641
5 (B)	670.97	24.6575	23.7957	1.03622	24.52906	1.03058	24.5350	1.03107
6 (C)	1030.08	37.8544	36.8581	1.02703	37.68862	1.02253	37.6732	1.02211
7 (N)	1486.05	54.610	53.3587	1.02345	54.40093	1.01953	54.3229	1.01807
8 (O)	2043.79	75.108	73.517	1.02027	74.80939	1.01757	74.8172	1.01768
9 (F)	2715.79	99.803	97.533	1.02327	99.40935	1.01923	99.4897	1.01993
10 (Ne)	3511.5	129.044	125.594	1.02747	128.54709	1.02351	128.674	1.02452
11 (Na)	4419.8	162.423	157.875	1.02881	161.8589	1.01890	162.053	1.02013
12 (Mg)	5450.56	200.303	194.538	1.02966	199.6146	1.02610	199.901	1.02757
13 (Al)	6604.36	242.704	235.740	1.02948	241.8767	1.02603	242.286	1.02776
14 (Si)	7887.5	289.86	281.629	1.02922	288.8543	1.02565	289.403	1.02760
15 (P)	9304.61	341.935	332.345	1.02886	340.7188	1.02520	341.420	1.02654
16 (S)	10858.0	399.02	388.024	1.02835	397.5049	1.02443	398.503	1.02701
17 (Cl)	12554.4	461.362	448.794	1.02800	459.4821	1.02381	460.821	1.02680
18 (Ar)	–	–	514.78	–	526.8175	1.02339	528.540	1.02673
19 (K)	–	–	586.11	–	599.1648	1.02227	601.352	1.02600
20 (Ca)	–	–	662.89	–	676.758	1.02092	679.502	1.02506

Table 2. Gombas-Gaspar total energies for selected gaseous atoms from $Z = 20$ to 100, and comparison with non-relativistic ground configuration energies, and with relativistic energies, both according to *Desclaux*[11].

Z	E_{GG} [hartree]	E_{NR} [hartree]	E_{NR}/E_{GG}	E_R [hartree]	E_R/E_{GG}
20 (Ca)	662.89	676.76	1.02092	679.50	1.02506
24 (Cr)	1026.78	1043.14	1.01593	1049.21	1.02185
25 (Mn)	1132.47	1149.63	1.01515	1156.87	1.02154
26 (Fe)	1244.25	1262.29	1.01450	1270.88	1.02140
27 (Co)	1362.21	1381.31	1.01402	1391.42	1.02144
28 (Ni)	1486.45	1506.82	1.01370	1518.64	1.02165
30 (Zn)	1754.13	1777.85	1.01352	1793.78	1.02260
32 (Ge)	2048.00	2075.34	1.01335	2096.42	1.02364
36 (Kr)	2717.40	2752.06	1.01275	2787.28	1.02572
40 (Zr)	3498.76	3538.97	1.01149	3594.81	1.02745
50 (Sn)	5977.20	6022.92	1.00765	6171.21	1.03246
60 (Nd)	9258.34	9283.70	1.00274	9615.86	1.03862
70 (Yb)	13403.10	13391.5	0.99934	14051.9	1.04841
80 (Hg)	18466.6	18409.0	0.99688	19623.5	1.06265
90 (Th)	24449.2	24359.6	0.99634	26471.9	1.08273
100 (Fm)	31547.8	31282.7	0.99172	34806.3	1.10329

E_{HF} for carbon and nitrogen in Table 1. Under equal circumstances[12] the ground term of p³ (N and P atoms) are three times more stabilized by this effect than the p² and p⁴ atoms C, O, Si, S, agreeing with the trend in E_R. Taking this situation into account, E_{corr} is fairly well represented by $E_{obs} - E_R$ in Table 1, increasing smoothly (but not linearly) from 0.041 hartree for $Z = 2$ to 0.54 hartree for $Z = 17$.

As far as comparison with E_{GG} goes, the E_{obs} values in Table 1 show a mild oscillation between 1.03 E_{GG} and 1.02 E_{GG} for all the elements between $Z = 6$ and 17. If the tiny effect of the ratio between the electron rest-mass and the atomic weight of the nucleus is neglected, equation (1) is exactly valid for $Z = 1$, but shows the large $E_{obs} = 1.10 E_{GG}$ for helium. The effect of the closed shell at $Z = 10$ is far smaller, when compared to E_{GG}. Since $E_{obs} - E_{GG}$ is roughly (0.24 hartree) $(Z - 0.9)$ for helium, lithium, and beryllium, this difference cannot be ascribed in a simple manner to the closed shell at $Z = 2$. For the chemist, it is far more interesting that the total energies (even in the absence of precise E_{obs} above $Z = 17$) remain slightly above E_{GG} for gaseous atoms (and, as we shall see, in all materials of concern to chemists) in the whole Periodic Table.

Table 2 compares E_{GG} with the non-relativistic (E_{NR}) and relativistic (E_R) total energies evaluated by *Desclaux*[11] for all Z values from 1 to 120 (here, 16 elements are selected with Z from 20 to 100). At the scale of percentage adopted here, the E_{NR} of Table 2 must be quite close to E_{HF} values; and arguments are given below that the E_{obs} values probably run 1 to 6 hartree above (as far E_{corr} goes) from $Z = 25$ to 100. It is noted that the ratio (E_{NR}/E_{GG}) monotonically decreases, crossing unity close to $Z = 68$, and still is above 0.99 for $Z = 100$. The situation is somewhat different for E_R/E_{GG} (showing three, probably not particularly significant minima for $Z = 8$, 11, and 15 in Table 1) having a shallow minimum at 1.0214 located at $Z = 26$ in Table 2, and then smoothly reaching 1.10 for $Z = 100$ (the same value as E_{obs}/E_{GG} for $Z = 2$). In other words, E_{GG}

is a better approximation to the non-relativistic E_{HF} and E_{NR} than to E_R (especially for $Z > 40$). Recently, *Loeser*[13] applied an ingenious technique for evaluating non-relativistic total energies for gaseous atoms from $Z = 1$ to 127. The results are compared with «reference energies» that are very close to E_{NR} of *Desclaux*, though even closer to E_{obs} of Table 1, at least up to $Z = 14$. It turns out that the difference between the values (for Z at most 120) of *Loeser* and of *Desclaux* are quite close to (0.04 hartree) Z suggesting that E_{corr} is assumed to be approximately proportional to Z (vide infra).

The first question to be answered by Tables 1 and 2 is the numerical importance of closed-shell effects in gaseous atoms. It may be noted that within a factor 1.15, the binding energy of nuclei relative to protons and neutrons[14] is proportional to the quantum number A (an integer close to the atomic weight on the ¹²C scale) for $A > 12$. The effects of closed protonic (such as $Z = 2, 8, 20, 28, 50, 82, 114, 126, \ldots$) or neutronic $(A - Z)$ shells in the theory of *Goeppert-Mayer* is to achieve binding energies about 1 percent larger than of adjacent nuclei. The situation is entirely different in the electronic structure of atoms, where nearly all the binding energy is provided by the 1s, and to a smaller extent, 2s and 2p inner shells. Actually, if a binding energy $2Z^2$ rydberg were ascribed to the two 1s electrons, this would be above half of E_{GG} for $Z < 32$, and still a-third of E_{GG} for $Z = 90$. It is not easy to give a clear-cut quantitative definition of closed-shell effects[15,16] for the number of electrons $K = 2, 10, 18, 28, 36, 46, 54, 68, 78, 80, 86, 100, \ldots$ but for $K = 10$ in gaseous atoms, a plausible suggestion is

$$I_1(F) + 2 I_1(Ne) - 2 I_1(Na) - I_1(Mg) \qquad (2)$$

taking into account six electrons, and attenuating the weighting of elements further removed from neon. This expression is 42.6 eV or 1.57 hartree, that is 1.2 percent of the electronic binding energy in neon. The analogous expression is 29.7 eV for argon, 25.8 eV for krypton, and 21.7 eV (or 0.8 hartree) for xenon. Comparison with

E_{GG} in Tables 1 and 2 show 0.2 percent for argon, below $6 \cdot 10^{-4}$ for krypton, and $1.1 \cdot 10^{-4}$ for xenon. Though equation (2) cannot be extended at present to radon, the closed-shell effects can only be a few times 10^{-5} for $Z = 86$. These, rapidly vanishing, closed-shell effects for $K > 10$ are a major reason why equation (1) having $dE_{GG}/dZ = 2.4 Z^{1.4}$ rydberg is good for both noble-gas and alkali-metal atoms. This forms a most striking contrast with the wildly varying dI/dZ of one-shot ionization energies of inner shells (excepting 1s) as a function of Z[17,18]. These arguments about almost negligible closed-shell effects in the heavier atoms are not fundamentally modified, even if a quantity twice as large as equation (2) is chosen.

The heat of atomization of metallic elements scatters between 0.64 eV for mercury and 8.8 eV for tungsten. The dissociation energies of compounds to atoms are nearly all below 4 eV per atom concerned. Hence, chemical bonding is usually less than a-tenth of the closed-shell effects expressed in equation (2). The very fact that dissociation energies to (a few) gaseous atoms vary in the compounds of two-digit Z elements from a few times 10^{-3} to about 10^{-5} E_{GG} going along from $Z = 11$ to 99 might be taken as argument that chemical bonding is a very weak perturbation on the atoms involved. However, this would be neglecting the enormous difference in stability of external electrons and of typical inner shells. The ionization energy I_1 of gaseous atoms[1] oscillates in a characteristic way in the Periodic Table, the two extremes being 24.587 eV for helium and 3.894 eV for caesium. The lowest «vertical» (i.e. following the Franck-Condon principle) ionization energy of gaseous molecules[19] varies between 16.46 eV in SiF_4 and 5.4 eV in $Cr(C_6H_6)_2$ (disregarding marginally lower values in similar organometallic molecules). It is rather surprising that the LCAO model is relatively successful for most delocalized molecular orbitals. The decline of other chemical ideas, such as two electrons per «chemical bond», was discussed[20,21] in 1984.

The virial theorem has many important consequences for chemistry. Any solution (with a negative eigen-value E) to the time-independent Schrödinger equation has the exact relations

$$2E = V = -2T \qquad (3)$$

to the potential energy V and the total kinetic energy T (which can be evaluated along three orthogonal axes, if so desired). *Ruedenberg*[22] discussed how bonding MOs have a decreased local contribution to T along the internuclear axis, and antibonding MOs (as known from «ligand field» theory[23,24]) highly increased kinetic energy. In both cases, the virial theorem is restored by minor contractions (increasing T) or expansions (not necessarily by a scale factor) of the atomic orbitals (in the case of the LCAO model). It is possible in a mono-

atomic entity to write $V = Q + C$ where Q is the nucleus-electron attraction (several authors use the symbol L, but it may induce confusion with the term quantum number) and C is the interelectronic repulsion. In most atoms[5], C is roughly $(-Q/7)$. In the Hartree-Fock wave-function for a monoatomic entity with one or more complete shells (subscript c) and one partly filled shell (subscript f) it is possible[25] to write

$$E = T_c + T_f + Q_c + Q_f + C_{cc} + C_{cf} + C_{ff} \quad (4)$$

In the Slater-Condon-Shortley treatment of atomic spectra, one assumes identical radial functions for closed and for partially filled shells in the various (S,L)-terms belonging to the same configuration. Hence, the first six contributions to equation (4) remain constant, and the term distances are ascribed solely to differing interelectronic repulsion C_{ff}. Actually, this description does not work too badly for d-group gaseous ions, nor for 4f-group gaseous ions and compounds, though there is a tendency[26] for the integrals of interelectronic repulsion evaluated from Hartree-Fock 3d radial functions to be $(z+3)/(z+2)$ times the pragmatic Condon-Shortley parameters (giving the best fit of the observed term energies above the ground state) where z is the ionic charge. If anything, this discrepancy is a somewhat larger factor in the 4f group. Anyhow, the Condon-Shortley treatment does not satisfy the virial theorem (3) since T is the same for various terms, but $V = Q + C$ is less negative in higher terms because of larger C. *Katriel* and *Pauncz* [27] analyzed the rather counter-intuitive consequences of modifying radial functions in such a way that T of a higher term decreases half as much as V increases. As main example were used the carbon atom and the isoelectronic gaseous ions with $K = 6$ and the ionic charge $z = (Z - K)$.

Since lanthanoide compounds show narrow absorption and emission bands[18,28] corresponding to the J-levels of a partly filled 4f shell, it is very helpful that *Vanquickenborne* et al.[25] performed $4f^q$ Hartree-Fock calculations with flexible radial functions for differing S values of this, total spin quantum number. For our purpose, the eleven gaseous $Ln^{3\oplus}$ able to show two or more S values are all instructive, but the most interesting is the gadolinium ion with its ground state $(S = 7/2)$ and the higher terms $S = 5/2, 3/2,$ or $1/2$. It is known since 1957[12,18,26] that the average energy of all states [each term comprising $(2S+1)(2L+1)$ states] with a given S_0 is situated $2DS_0$ below the average energy of all states with $S = (S_0 - 1)$, where the spin-pairing energy parameter D is the Racah parameter $9 E^1/8$ (or another combination of Condon-Shortley parameters in the d-groups). Actually, the calculated distances[25] follow closely the ratio 7:5:3, though the calculated D value 1.09 eV is perceptibly higher than the pragmatic parameter close to 0.8 eV[18]. The average

radius $\langle r \rangle$ of the 4f shell[25,29] shrinks as a function of increasing S, being proportional to $1 + kS(S + 1)$ with $k = -0.00116$. All the filled shells expand marginally, the strongest expansion in the 5p shell has $k = +0.00019$. At the first glance, these results suggest that the freedom of selecting flexible radial functions (for differing S) hardly has any practical importance. However, the relative contributions from the seven E components in equation (4) produce an almost surrealistic impression[29]. The resulting D receives the contribution $+3.5\ D$ from T_c; $-4.5\ D$ from T_f (and hence $-D$ from the kinetic energy T); $-7D$ from Q_c; $+13\ D$ from Q_f (and hence $+6\ D$ from the nucleus-electron attraction Q); $+3.5\ D$ from C_{cc} (almost identical to the T_c contribution); nearly $-8\ D$ from C_{cf}; and finally $+0.4\ D$ from C_{ff}. One baffling conclusion is that the contribution of interelectronic repulsion C is approximately -4 times the calculated D, and is ten times larger (with opposite sign) than the Condon-Shortley result (ascribing D exclusively to C_{ff}). It has previously been emphasized[19,23] that the angular part of the kinetic energy $6 \langle r^{-2} \rangle$ hartree/bohr^2 is huge for a gadolinium 4f electron (and plays a role in the tiny «ligand field» effects[24]); it turns out[25,29] to be 535.4 eV + (0.56 eV)$S(S + 1)$ out of all proportion with $I_4 = 44$ eV of the gaseous ions, and I(4f) between 11 and 15 eV found by photo-electron spectra of solids.

The techniques of computer chemistry, and their judicious evaluation, have made such progress possible[25] as illustrated by equation (4). It is particularly fortunate that these results have been obtained for a cation with $K = 54 + 7 = 61$ electrons, allowing for flexible radial functions. They disclose a quite unexpected physical mechanism behind the spin-pairing energy, a concept that has been elaborated further by *Schäffer* and *Brorson* along the lines of thought of *Racah,* both in d-group gaseous ions[30] and compounds, related to the rediagonalization of «ligand field» determinants[31].

The two major effects not taken into account in Hartree-Fock wave-functions are relativistic effects (of which the oldest known is spin-orbit coupling) and correlation effects. Though the difference $(E_R - E_{NR})$ taken from the tables by *Desclaux* [11] increases dramatically with higher Z, and is 1 percent of E_{NR} for $Z = 32$ and 10 percent for $Z = 96$, the conspicuous effects on chemistry are concentrated (for Z below 100) on rather specific topics[32-35] such as the difficulty of oxidizing the $(K = 80)$ systems thallium(I), lead(II), and bismuth(III). The impact on chemical behaviour is essentially due to the relativistic contraction of *all* (not only 1s and 2p) ns and np $(j = 1/2)$ radial functions. *Desclaux* [11] gives for each (nlj) combination the average values $\langle r^k \rangle$ in the unit bohr^k for $k = 6$, 4, 2, 1 (the «average» radius), -1 (this value, when multiplied by Z, gives the contribution of each electron to Q), -2 (deter-

mining the angular part of the kinetic energy when multiplied by 1, 3, or 6 for p, d, or f electrons) and -3 (except the divergent values for $j = 1/2$). Indirectly, *Desclaux* also gives $\langle r^k \rangle$ for non-relativistic Hartree-Fock nl (electron configuration to which the ground state of the gaseous atom belongs) since the ratio between relativistic and non-relativistic values is tabulated. The spectroscopic properties of the uranyl ion[35,36] are also strongly modified by relativistic effects.

The correlation effects are far less spectacular on the total energy. In the Condon-Shortley treatment, they are due to non-diagonal elements of interelectronic repulsion between the Hartree-Fock configuration and the (infinite number of) higher-lying configurations. *Löwdin* [37] pointed out that most of the significant admixed configurations are two-electron substitutions to a suitably optimized continuum orbital (with positive one-electron energy). Nearly all the $-E_{corr} = 0.041$ hartree of the helium atom (slowly increasing to 0.046 hartree in the isoelectronic series $Li^\oplus$, $Be^{2\oplus}$, ...) is due to two such configurations situated in the continuum, one s^2 with an additional radial node, and one p^2 with node-plane, and both having $\langle r \rangle$ similar to 1s. Such continuum orbitals are quite analogous to the polarization orbitals used in one-electron substitutions for describing electric dipolar polarizability. The lithium atom has only a marginally stronger correlation, but $-E_{corr} = 0.09$ hartree of the beryllium atom has a major contribution[26] of $1s^2\ 2p^2$ (a more «classical» configuration[12] known from atomic spectra). Since $-E_{corr} = 0.13$ hartree for the boron atom, $1s^2\ 2p^3$ is likely to be important too. On the other hand, $-E_{corr} = 0.40$ hartree (10 times larger than in helium) for the neon atom is almost exclusively due to continuum two-electron substitutions.

All neutral atoms having Z at least 11 (sodium) have $-E_{corr}$ *larger* than the ionization energy I_1. This is not the most pernicious aspect for a chemist, but it takes out the backbone of the variational principle. For Z above 10, there is an infinite number of levels with identical symmetry situated in the closed interval from the actual ground state to the Hartree-Fock eigen-value (though the open interval is supposed empty in textbooks). Hence, we have no guarantee that a nice looking stepwise amelioration starting with the Hartree-Fock wave-function does not converge to the seventeenth excited state. A much more serious problem for the chemist is the squared amplitude of the Hartree-Fock function in the total wave-function (assumed non-relativistic). This «squamp» is 0.99 for the helium atom[37] and ions with $K = 2$, and mildly oscillates between 0.88 and 0.93 for $Z = 4$ to 10. Because of the numerical aspects of the two-electron substitutions, there is no universal biunique relation between $-E_{corr}$ and the squamp. Good reasons can be found[18] for the approximate expression

$$-E_{corr} = (0.7 \text{ eV})Z^{1.2} \qquad (5)$$

proportional to the square-root of E_{GG} and corresponding to 38 eV for $Z = 30$, 90 eV for $Z = 60$, and 133 eV for $Z = 80$. Since 4d and 4f orbitals have rather comparable average radii[11] between $Z = 59$ and $Z = 68$, it is likely that the substitution of $4d^{10}4f^q$ to $4d^8 4f^{q+2}$ contributes significantly to E_{corr}. An (admittedly quite rough) second-order perturbation model[18] suggests the squamp to have the order of magnitude 0.7 for $Z = 30$ (zinc) and 0.4 for $Z = 60$ (neodymium). It is conceivable that the higher-order 4-, 6-, 8-, ... electron substitutions diverge for Z above 80, and that the squamp then rapidly vanishes. This may not have very dramatic physical consequences. The total Schrödinger wavefunction for K electrons has $3K$ spatial variables, but so far we know, all observable quantities can be described in a six-dimensional second-order density matrix (but unfortunately, there seems at present little hope to find a variational principle, or a substitute condition for it). The electronic density in our three-dimensional space seems well represented by Hartree-Fock functions (as well as the diamagnetism indicating $\langle r^2 \rangle$) and the dilemma culminating in equations (4) and (5) must be hidden in some aspect of the interelectronic distances.

Until now, we have mainly discussed monatomic systems containing one tiny nucleus (characterized by Z) and K electrons. Every problem we have mentioned, will be inherent in quantum chemistry treating K electrons surrounding two or more nuclei, in addition to any further problems. Now, when subject is 60 years old, it is clear that the major successes have been obtained by extension of what was the triumph of the time-independent Schrödinger equation, the rationalization of line spectra, X-ray spectra (and later photo-electron spectra) of essentially unperturbed monoatomic entities. All these processes are so rapid in compounds that the nuclei retain their spatial distribution in the ground state (or the excited state prior to luminescence). This Franck-Condon quantum chemistry is not without difficulties, but is in a reasonably satisfactory shape, and can be assisted by pseudo-potentials representing inner shells. On the other hand, chemical reactions take place in a $(3N - 5)$-dimensional space (energy as a function of the mutual positions of N nuclei, assuming the Born-Oppenheimer approximation of translational, rotational, vibrational, and electronic factors). Though chemistry intrinsically modifies nuclear positions, it is clear that a deductive treatment for three or more nuclei is tedious, and only can be applied to gaseous systems at low pressure (and not to solutions). It should be remembered that «ab initio» is not an unconditional label of quality, but only indicates an ascetic reluctance to include empirical facts (such as atomic energy differences). This restraint

may be conceptually satisfactory, but one should not forget that experimental quantities (within their limits of precision) agree with any perfectly valid theoretical treatments (if such are feasible).

The main conclusion of this paper is the formidable problems expected for compounds involving elements with two-digit Z values. The typical effects of chemical bonding (per atom involved) are about a-tenth of the closed-shell effects, and show a trend roughly like $Z^{-0.2}$. Hence, their order of magnitude decreases from $10^{-3} E_{GG}$ (at $Z = 11$) to $10^{-5} E_{GG}$ for gadolinium ($Z = 64$). Not only is this a small proportion of the total energy but it also decreases from 30 to 3 percent of the correlation energy of the isolated atoms according to equation (5). Disregarding any effects of the correlation on the extent of delocalization in the LCAO model of covalent bonding, it is imperative to look for pragmatic regularities in the correlation energy, such as the quaint observation[15] that *intra*-atomic relaxation effects decrease one-shot ionization energies I of inner shells (relative to Hartree-Fock results retaining ground state radial functions) to the extent 0.8 eV times the square-root of I (in eV). There is strong evidence from photo-electron spectra[19] that interatomic relaxation effects also can be quite large, a clear-cut example being I of inner shells of gaseous magnesium, calcium, strontium, and barium atoms[38] decreasing 5 to 7 eV by condensation to the metallic elements. It is highly likely that correlation effects systematically are larger in molecules (especially for long internuclear distances) and in 15 selected molecules[39] of one-digit Z elements, it is argued that correlation energy is proportional to exchange energy with a constant 1.6 times that for atoms. If we exclusively consider quantum chemistry as an adaptation to the variational principle, we tend to concentrate attention on the 10 inner-most electrons in the two-digit Z elements, and it would seem that (excluding innovating breakthroughs) quantum chemistry (in the strictly deductive sense) is not a particularly appropriate tool in this field. On the other hand, recent computers (and human ingenuity) may help in the numerous H, C, N, O-containing molecules. A particularly fertile area is helium chemistry[40,41]: molecules such as HeLiH and HeBeO are calculated to be stable relative to bond-breaking in the gaseous state; $HeH^\oplus$, $He_2^\oplus$, $HeNe^\oplus$, $HeCN^\oplus$, $HeW^{2\oplus}$, $HePt^{2\oplus}$, and $He_2Pt^{2\oplus}$ are known from mass spectra; $HeC^{2\oplus}$ (having the dissociation energy 0.8 eV to He and $C^{2\oplus}$, like all $HeLn^{3\oplus}$[18] are stable relative to helium atoms and lanthanoide(III) ions, here excepting $HeEu^{3\oplus}$ and $HeYb^{3\oplus}$ dissociating to $He^\oplus$ and $Ln^{2\oplus}$ because the coordinated base helium is too strongly reducing), $HeCCH^\oplus$ (not linear as the isoelectronic HCCH), $He_2C^{2\oplus}$ (singlet ground state, in contrast to the triplet ground state of HCH). Further on $HeF^\oplus$ is known to be repulsive, what is neither the case for calcu-

lated $ArF^\oplus$ nor for $KrF^\oplus$ and $XeF^\oplus$ forming stable salts, which are colourless, in contrast to dark green $Xe_2^\oplus$. Chemistry is exuberant, and novel phenomena are largely unpredictable.

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