

# DIFFERENTIAL IONIZATION ENERGIES AND NON-CLASSICAL ASPECTS OF QUANTUM ELECTROSTATICS

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## ABSTRACT

The local kinetic operator (in the conservative form of the Schrödinger one-electron equation) prevents implosion of matter and provides very rigid 4f orbitals, and the anti-bonding character of d-like orbitals. Nevertheless, major aspects of quantum chemistry involve the Madelung potential from surrounding charged atoms; and the differential ionization energy as a diagonal element, when varying the fractional charge has somewhat stronger influence than covalent bonding. The unexpected redistribution of kinetic and potential energy (required by the virial theorem) in chemical bonding, and in the term distances (and the spin-pairing energy) in partly filled shells is analyzed. The correlation effects (also observed in photo-electron spectra of inner shells) leave little hope for strictly deductive quantum chemistry involving two-digit atomic numbers. The Gombas-Gaspar expression for total energy is remarkably precise.

## INTRODUCTION

Quantum chemistry is now 60 years old. It was started in the climax of triumph of the rationalization of line spectra of monatomic entities with a very small nucleus carrying  $Z$  times the protonic charge  $e$ , and surrounded by  $K$  electrons. The ionic charge  $z = Z - K$  is zero for neutral atoms and can assume all positive values from 1 to  $(Z - 1)$ , and for most (but not all) elements  $(-1)$ , but never more negative (not even oxygen). The molecular spectra of diatomic and polyatomic species, the absorption spectra and luminescence spectra of complex cations and anions [1,2] in condensed matter, X-ray emission and absorption spectra and later photoelectron spectra [3-7] all continued the strategy feasible in atomic spectra of characterizing the groundstate (having the most negative  $E$  for a given ionic charge) and the numerous excited quasi-stationary states (living for a sufficiently long time to be perceived with sharply defined  $E$  values). This restriction to Franck and Condon processes (not moving the nuclei) is the origin of many of the dilemmas in quantum chemistry [8]. Even assuming the factorization of the total wave function according to Born and Oppenheimer in a translational and an electronic factor [9], and in the case of more than one nucleus, a rotational and a vibrational factor, the potential surface for  $N$  (at least 3) nuclei involve  $(3N-6)$  mutually independent internuclear distances, and hence takes place in a  $(3N-5)$  dimensional space with the energy as one varia-

ble. Chemical reactions essentially modify internuclear distances, and the groundstates of isomers are relative (and absolute) minima of the  $(3N-5)$  dimensional surface. Optically active enantiomers have the same manifold of internuclear distances  $R$ , and are not, strictly speaking, eigenstates of the Schrödinger equation. We return below to significant differences between one-digit (hydrogen to fluorine) and two-digit  $Z$  values, but the negligible effect (compared to  $E$ ) of chemical bonding for elements with  $Z$  above 10 is illustrated by the empirical result by Gombas and Gaspar that the binding energy for  $Z$  electrons to a  $Z$  nucleus is  $Z^{2.4}$  rydberg ( $1 \text{ ry} = 1/2 \text{ hartree} = 13.61 \text{ eV}$ ) within a factor 1.03 [the factor is 1.10 for helium and 1.07 for lithium] down to 1.01 and then up again to 1.04 going from  $Z = 6$  (carbon) to 80 (mercury). Hence, this binding energy is larger than the rest-mass of an electron 511000 eV for  $Z$  above 80; and is predicted to be 897.6 ry and known from atomic spectra to be 922.7 ry = 12554 eV for  $Z = 17$  (chlorine). It is noted that the proportion of binding energy of the two first 1s electrons is  $2Z^{-0.4}$  in this approximation, above half of the total binding for  $Z$  below 32. Quantum chemistry bases exclusively on the variational principle (minimizing  $E$ ) tends to become a theory for the 10 innermost electrons.

## KINETIC AND POTENTIAL ENERGY OF ELECTRONS

There is a long-standing tradition to consider quantum chemistry as minimizing the electrostatic potential energy  $V$  in a way taking into account the size of the Planck constant and Pauli's exclusion principle (the original demand of, at most, two electrons per orbital has been refined to the requirement of anti-symmetric total wave functions [10]) e.g. in the non-relativistic case by finding good numerical approximations to solutions of the many-electron Schrödinger equation. The writer argues [11] that chemistry is at least as much determined by the total kinetic energy  $T$ , what may seem contradictory in view of the virial theorem ( $V$  and  $E$  are negative):

$$V = -2T = 2E$$

valid for gravitational, and electrostatic, and other attractions having a potential inversely proportional to the distance. The cancellation of half of the potential energy by kinetic energy is valid for the perfectly accurate wavefunction, but can be grossly distorted in approximate wavefunctions giving  $E$  values slightly above the observed value.

Kinetic energy cannot be neglected, one reason being that a stable electrostatic system (e.g. a crystal consisting of spherically symmetric, non-overlapping cations and anions) becomes  $k$  times more stable if all distances are divided by  $k$ . However, the Schrödinger equation provides  $T$  proportional to  $k^2$  (preventing implosion) and the question why the hydrogen atom (or any other quantum-chemical system) is not smaller (or larger) is answered by minimization of  $E = T+V$  as a function  $(k^2 - 2k)$  of this scaling factor. By the way, eq.(1) is only valid for stationary states, and hence only for the potential minima of systems with several nuclei.

The treatment of many-electron systems seems to be the least difficult by introducing one-electron functions  $\psi$  (orbitals) though it entails the (frequently underestimated) effects of correlation energy and intermixing of electron configurations. Real (not complex)  $\psi$  with negative  $E$  allow the Schrödinger equation to be written on a conservative form (like Newtonian motion without friction) with a potential  $U(x,y,z)$  in atomic units (length: 1 bohr; energy: 1 hartree; . . .):

$$E = U(x,y,z) + \zeta(x,y,z)$$

$$\mathcal{P} = -\frac{1}{2\psi} \left[ \frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} \right] \quad (2)$$

where the local kinetic operator  $\mathcal{P}$  is negative in volume elements with  $U$  less negative than  $E$ . There are no problems involving division by zero.  $\mathcal{P}$  only diverges toward infinity when  $U$  goes to  $-\infty$ , and is zero on the nodes with  $\psi = 0$ , once it is multiplied with the orbital electronic density  $\psi^2$ . Ruedenberg [12] discusses eq. (2) but the writer does not know who expressed the idea first; it can be found in the much earlier book by Landau and Lifschitz, interested in the prevention of implosion of matter. In monatomic entities,  $U(r)$  is a "central field" only dependent on the distance  $r$  of the electron from the nucleus, and the one-electron functions are then products of an angular function  $A_\ell$  (normalized linear combination homogeneous polynomials of degree  $\ell$  in Cartesian coordinates) and a radial function. Here,  $A_\ell$  is normalized to  $4\pi r^2 dr$  on a spherical shell, and the integral of  $R_{n\ell}^2 dr$  from  $r=0$  to infinity is 1:

$$\mathcal{P}_{\text{rad}} = -\frac{1}{2R_{n\ell}} \frac{\partial^2 R_{n\ell}}{\partial r^2} \quad (3)$$

$$\mathcal{P}_{\text{ang}} = 1(1+1)/2r^2$$

The radial part  $\mathcal{P}_{\text{rad}}$  of the local kinetic operator is similar to eq. (2) but the angular part  $\mathcal{P}_{\text{ang}}$  does not depend explicitly on  $\psi$  and is hence called a "pseudo-potential" (a concept used in other approximate solutions to the Schrödinger one-electron equation) contributing  $\ell(\ell+1) \langle r^{-2} \rangle / 2$  to the total energy  $E$ , like  $T = \langle \mathcal{P} \rangle$  and  $V = \langle U \rangle$ . The Hartree-model for  $K$  electrons determines  $U(r) + (Z/r)$  as the average repulsion from the  $(K-1)$  other electrons. In the Hartree-

Fock approach (with less interelectronic repulsion for  $K$  above 2) the influence of the  $(K-1)$  other electrons cannot be represented by a local potential, but takes effects of the cross-term densities  $\psi_1 \psi_2$  into account [10].

We are here treating shortly two paradoxes related to eq. (1). Hellmann pointed out in 1937 that the kinetic energy in a bonding M.O. (molecular orbital) is less than in the isolated atoms, because there is no node-plane between the atoms at normal bond length  $R$ , decreasing the second differential quotient of eq. (2). On the other hand, bonding M.O. with an additional node are usually several times more anti-bonding than the bonding M.O. are bonding, corresponding to the monotonic repulsion between two helium atoms or between two neon atoms (or between  $\text{Li}^+$  and  $\text{F}^-$  at sufficiently short  $R$ ). The situation of  $\text{H}_2$  [12] and  $\text{H}_2^+$  [13] was carefully analyzed, and it turns out that the  $z$ -component of eq. (2) along the bond axis indeed represents a decrease in  $\langle \mathcal{P}_z \rangle$  closely similar to the observed dissociation energy of the diatomic species (by the way, it is legitimate in quantum mechanics to choose three Cartesian axes and to evaluate the three separate  $\langle \mathcal{P}_w \rangle$  components of kinetic energy). The virial theorem eq. (1) is satisfied by relatively minor modifications (a shrinking of the orbital, not necessarily by pure scaling) finally increasing  $T$  by the dissociation energy, and decreasing  $V$  twice as much. We return below to the related paradox of term distances in a partly filled shell.

## PARTLY FILLED d AND f SHELLS

In the 3d, 4d and 5d group compounds, "ligand field" theory rationalizes the complicated absorption spectra by the occurrence of two (or less frequently, one or three) strongly anti-bonding d-like M.O. Before 1956, this behaviour was usually ascribed to (the quite small) non-spherical part  $V(x,y,z) - V(r)$  of the Madelung potential  $V(x,y,z)$  discussed below, but for many reasons [e.g. that all oxygen-bound ligands show comparable energy differences between the two anti-bonding and the three lower d-orbitals in octahedral complexes of a given d-group ion, independently of whether the ligand is neutral (as water, alcohols, ethers or urea) or carry one or two negative charges] the "angular overlap model" invoking eq. (3) is much more convincing [1,11,14-16]. This had also been suspected [11,17] for the 20 to 50 times weaker "ligand field" effects in 4f group compounds, and is now firmly established [18,19]. The narrow absorption (and luminescence) bands due to a partly filled 4f shell of a lanthanide compound correspond closely to J-levels of a monatomic entity [2,20].

Each level of a monatomic entity corresponds to  $(2J+1)$  "states", mutually orthogonal total wave-functions having the same  $E$ . Levels can be classified in electron configurations (also when correlation effects render the many-electron wave-functions quite different from Hartree-Fock results). When all  $n\ell$ -shells are complete, each with  $(4\ell+2)$  electrons, there is only one state. If one  $n\ell$ -shell contains from 1 to  $(4\ell+1)$  electrons, there are 6 states for  $p^1$  and  $p^5$ ; 10 states for  $d^1$  and  $d^9$ ; and the numbers derived from permutation theory [10] for  $q$  indiscernible objects: 15 for  $p^2$  and  $p^4$ ; and in general  $(2\ell+1)(4\ell+1)$

for two electrons (or two electrons lacking) in an  $n\ell$ -shell; 20 for  $p^3$ ; 120 for  $d^3$  and  $d^7$ ; 364 for  $f^3$  and  $f^7$ ; . . . ; 3003 for  $f^6$  and  $f^8$ ; . . . If a configuration contains two or more partly filled shells, the number of states is the product of the numbers characterizing each shell. Thus,  $3d^9 4p$  has 60 states and  $3d^9 4d$  100.

When we need the barycentre, the average energy of all the states belonging to a given configuration, it is frequently possible to find most or all J-levels in the "Atomic Energy Levels" tables of National Bureau of Standards, weight them with  $(2J + 1)$  and obtain the average energy relative to the groundstate of the monatomic entity. The lacking energy levels can be extrapolated by rather reliable parametrized treatments, SCS (Slater-Condon-Shortley [10]) streamlined for 4f electrons by Racah [21] and generalized by Schaffer and Brorson [22]. Nevertheless, for our purpose it is more practical to consider regularities, in particular related to the total spin quantum number S. It turns out that all the states of  $n\ell q$  having a given value of  $S = S_0$  have an average energy that is situated  $2DS_0$  below the average energy of all states having  $S = (S_0 - 1)$ . The spin-pairing energy parameter D is a definite linear combination (independent of q) of SCS or Racah parameters for a given  $\ell$ -value, and is quite large, some 0.8 eV in 3d and 4f group compounds, and about 0.4 eV in 4d and 5d. These statements are equivalent [1,11,23,24] to an energy difference relative to the  $\ell q$  barycentre:

$$D [ \langle S(S+1) \rangle - S(S+1) ] \quad (4)$$

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

The importance of spin-pairing energy is particularly striking in the 4f group, where the first line of eq. (4) easily can be higher than the ionization energy of the neutral atom for  $q = 6, 7$  and 8. It is possible [1,20] to introduce further refinements describing the energy difference between the average energy of all states with maximum S and the lowest J-level (providing the groundstate).

In the SCS treatment, the mechanism separating the (S,L) terms of  $\ell q$  is stronger interelectronic repulsion in the higher terms, corresponding to identical  $\langle r^{-1} \rangle$  (average value of the reciprocal distance from the nucleus) of the  $\ell$  shell, but larger  $\langle r_{12}^{-1} \rangle$  determined in the six-dimensional space organized by the interelectronic distance  $r_{12}$  in the partly filled shell. Since  $R_{n\ell}$  of eq. (3) remain unchanged, T is invariant, and the less negative V in the higher terms disagrees with eq. (1). Katriel and Pauncz [25] analyzed this discrepancy carefully, and concluded that the decreased T demanded by the virial theorem is mainly compensated by larger  $\langle r \rangle$ , smaller  $\langle r^{-1} \rangle$  and concomitant smaller nucleus-electron attraction  $Z\langle r^{-1} \rangle$  in the higher term; or said in other words, the groundstate shows contracted  $\langle r \rangle$  and more negative  $Q = Z\langle r^{-1} \rangle$  (this quantity is usually called L [25,26], but this capital letter may induce confusion with (S,L) terms) and the virial theorem is here written:

$$E = T + Q + C \quad 2T = -Q - C \quad (5)$$

with the positive C representing as earlier, the total interelectronic repulsion. Marking the higher term with asterisks, and the lowest term as in eq. (5), the difference is:

$$E^* - E = T^* - T + Q^* - Q + C^* - C \quad (6)$$

Actually, the monatomic entities [25] with  $K = 6$  have a greater contribution to the (positive) energy difference between  $^1D$  and  $^3P$  belonging (in a classificatory way [1]) to  $1s^2 2s^2 2p^2$  from  $(Q^* - Q)$  (i.e. stronger nucleus-electron attraction in  $^3P$ ) than from  $(C^* - C)$  and, more surprisingly,  $(C^* - C)$  is negative for the carbon atom and for  $N^+$ , but positive for  $O^{+2}$  and subsequent elements. The SCS treatment is asymptotically valid for very high Z values [25]. Much in analogy to the ambiguous question whether typical chemical bonding is initiated by decreasing kinetic energy along the bond axis, as proposed by Hellmann and Ruedenberg [12,13], and the virial theorem subsequently restored by minor alterations, one may ask whether the prime cause of the lower energy of the term with maximum S (and among such terms, the one with highest L) is indeed less interelectronic repulsion. It would rather be raising a tempest in a teapot to deny this, and to argue that the lowest term is selected by having the most negative Q. Quantum mechanics present many cases of concomitant events A and B without and asymmetric cause-effect relation, and as Niels Bohr said, a profound truth is characterized by the converse proposition also being a profound truth. Anyhow, Fig. 9 of ref. [25] shows that the Hartree-Fock function of a higher term, keeping its radial functions, can decrease its energy by decreasing the interelectronic repulsion, forming a higher S etc., and then, subsequently, relax by forming the Hartree-Fock radial functions of the lower term, obtaining even lower energy. Katriel and Pauncz say "The energetic ordering of the levels is, therefore, a direct consequence of the difference in the interelectronic repulsion, forming a higher S etc., and then, subsequently, relax by forming the Hartree-Fock radial functions of the stable component of the suggested rationale".

Recently, Vanquickenborne et al. [26] investigated Hartree-Fock functions for different S (each time with slightly differing radial functions) of  $4f q$  from  $q = 2$  (gaseous  $Pr^{+3}$ ) to 12 ( $Tm^{+3}$ ). In such a treatment, C of eq. (5) can be dissected in three contributions:

$$C = C_{cc} + C_{cf} + C_{ff} \quad (7)$$

of interelectronic repulsion between filled shell (core) electrons, between core and 4f electrons, and between 4f electrons. This separation would not be defined in total wave functions including correlation effects. One of the goals is to calculate the spin-pairing energy parameter  $D = (E^* - E)/2S_0$  going from  $S_0$  to  $(S_0 - 1)$ . Compared to the SCS prescription ("frozen" radial functions) the D values obtained for flexible radial functions are up to 0.5 percent higher (low  $S_0$  values) and down to 1.4 percent lower ( $S_0 = 7/2$ ). As discussed at the end of this paper, the D values are approximately 30 percent higher than the parameters derived from observed energy levels.  $\langle r \rangle$  values are given [26] for all the  $n\ell$ -shells in the case of the four S values feasible in  $Gd^{+3}$ . The 4f shell contracts for increasing S by a factor  $(1 + kS(S + 1))$  where  $k = -0.00116$ . The 5s and 5p shells ex-

pand with the  $k = +0.00016$  and  $0.00019$ , respectively. The 4s, 4p and 4d shells also expand with  $k$  close to  $0.00006$ , and 3s, 3p and 3d with  $k$  around  $10^{-5}$ . No modification was reported for 1s, 2s and 2p shells. Compared with these minute changes, it is impressive to see the contributions to  $D$  (compared with its calculated value  $1.1$  eV in  $Gd^{+3}$ ) being  $(Q^* - Q)$  almost  $6D$  (consisting of a core-part  $-7D$  and 4f part  $+13D$ );  $(T^* - T) - D$  (consisting of a core-part  $+3.5D$  and 4f part  $-4.5D$ );  $(C_{cc}^* - C_{cc})$  of eq. (7) being  $3.5D$  (almost equal to the changed  $T$  of the core), and  $C_{cf}^* - C_{cf}$  of eq. (7) nearly  $-8D$ , and  $(C_{ff}^* - C_{ff})$  only  $0.4D$ , showing a total contribution of interelectronic repulsion to  $D$  almost  $(-4)$  times the calculated  $D$ . These results show beyond discussion the dramatic redistribution of  $D$  on its various components in the case of Hartree-Fock with flexible radial functions.

It should not be neglected that the angular part of the kinetic energy  $6\langle r^{-2} \rangle$  hartree/bohr<sup>2</sup> of eq. (3) is about  $540$  eV per 4f electron in the Hartree-Fock function for  $Gd^{+3}$  kindly communicated by Watson [4]. Though  $\langle r^{-2} \rangle$  values are not given in [26], a contraction  $1.74$  percent of  $\langle r \rangle$  going from  $S = 1/2$  to  $7/2$  is expected to increase the kinetic energy  $19$  eV per 4f electron, to be compared with  $69$  eV reported [26] for the 4f part of  $(T - T^*)$ . Perhaps small changes of  $\langle r^{-2} \rangle$  are not minus twice the  $\langle r \rangle$ .

## IONIC CHARGES AND MADELUNG POTENTIAL

It is frequently felt that compounds consist of atoms. It is beyond doubt that the perennial character of elements is based on the persistence of nuclei with definite  $Z$ , and that quantum chemistry describes a given number of electrons surrounding a given set of nuclei. It is also true that photo-electron spectra [3 - 7, 20] have shown the presence of inner shells in all elements starting with lithium, though the chemical variation (frequently  $5$  to  $10$  eV) of the one-shot ionization energies  $I$  is due, not only to differing oxidation state and varying fractional atomic charges discussed below, but also to strong effects of relaxation. It might be argued that with exception of hydrogen, the total binding energy of atoms (close to  $Z^{2.4}$  rydberg) is so much larger than chemical dissociation energies (nearly always below  $1$  ry) that chemical bonding is a weak perturbation on isolated atoms. This argument would have been valid in the model (prevalent 1932 - 1964) of nuclei consisting of  $Z$  protons and  $(A - Z)$  neutrons [27] where the binding energy (for  $A$  above  $12$ ) is roughly  $0.8$  percent of the rest-mass, and hence roughly proportional to  $A$ . Actually, the effect of closed shells of Maria Goeppert-Mayer quantum numbers can be above  $1$  percent of this binding energy, comparable with the  $10$  electrons of the neon atom (binding energy  $258$  ry), whereas it is below  $10^{-3}$  of the electron binding energy in krypton, and only a few times  $10^{-5}$  in radon.

The problem with electrons in atoms is that nearly all the binding energy is provided by inner shells, whereas the loosest bound electrons (forming the M.O. in the L.C.A.O. model) have ionization energies not much larger than chemical bond energies. Actually, the first ionization energy  $I_1$  of gaseous atoms varies between  $24.59$  eV in helium and

$3.89$  eV in caesium ( $Z = 55$ ), oscillating in a very characteristic way in the Periodic Table, and only seven elements (He, Ne, F, Ar, N, Kr and O) have  $I_1$  above  $1$  ry. The photo-electron spectra of gaseous molecules [4,5,28,29] provide clear-cut evidence for penultimate M.O., and the smallest "vertical  $I$ " (leaving the nuclei at their distribution in the groundstate) vary between  $16.46$  eV in  $SiF_4$  ( $16.3$  eV in  $CF_4$  having weak F-F anti-bonding in the loosest bound M.O., and  $15.8$  eV of  $F_2$  shows that this molecule contains four  $\pi$  - anti-bonding electrons, and might perhaps be oxidized to  $F_2^+$  like salts of  $O_2^+$ ) and  $5.4$  eV in  $Cr(C_6H_6)_2$  (and marginally lower  $I$  in substituted analogs). The  $I$  values found in solids are  $1$  to a few eV lower (mainly due to stronger inter-atomic relaxation) and are frequently  $3$  to  $eV$  in semi-conductors. The Fermi level (relative to vacuo) of metals is typically  $2$  to  $5$  eV, and for alkali-metals about half  $I_1$  of the gaseous atoms.

Gaseous ions with charge  $+z$  are extremely oxidizing (it is now recognized [1, 20, 30, 31] that the "adiabatic  $I$ " of species in aqueous solution correspond to the standard oxidation potential  $E^\circ$  added to a quantity between  $4.4$  and  $4.5$  eV) since the ionization energy  $I_n$  (from the groundstate of  $M^{+n-1}$  to the groundstate of  $M^{+n}$ ) is roughly proportional to  $n$  (as long a closed shell is not crossed by the ionization process) and hence, the energy is approximately proportional to  $(z + z^2)$  relative to the groundstate of the neutral atom. Charlotte Moore [32] compiled a revised list of  $I_n$  values. It attracted early attention [33] that certain elements, such as calcium (II), aluminium (III), thorium (IV). . . are only known in one oxidation state (in non-metallic compounds) in spite of the high  $I_n$  of  $Ca^+$ ,  $Al^{+2}$ ,  $Th^{+3}$ , . . . and  $315$  oxidation states are known [34] of the first  $103$  elements in non-catenated (e.g.  $F_5SSF_5$ , dithionate, mercurous ions, . . . are excluded) non-metallic compounds. The rationalization [33] was the Madelung potential provided by surrounding ions [1, 11] in electrovalent solids, and the hydration energy [1, 30, 35] of aqua ions. The reciprocal dielectric constant  $0.013$  of water is so small that it might equally well be zero (at this level of precision) and indeed, halide anions  $X^-$  have the hydration energy  $z^2$  ( $7.2$  eV)/ $r_{ion}$  appropriate for this case, though for cations, one must add  $0.82$  Å to the Goldschmidt ionic radius  $r_{ion}$  for this purpose, as first pointed out by Latimer in 1955.

The quantitative treatment of  $I_n$  of gaseous ions attenuated by the Madelung potential  $V(x, y, z)$  goes through the observation that the barycentre of configurations such as  $p^q$  and  $d^q$  varying  $q$  (and hence the ionic charge  $z$ ) for a given  $Z$  are represented to a very high precision [1] by a polynomial of third degree:

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

$$\frac{dE}{dz} = I(z) = a_0 + a_1 z + a_2 z^2 \quad (8)$$

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

The differential quotient  $I(z)$  is called the differential ionization energy.  $E_0$  is a zero-point corresponding to the configuration barycentre in the neutral atom, and  $(E - E_0)$

is the integral of  $I(z)$  from zero to  $z$ , and  $I_n^*$  the integral of  $I(z)$  from  $(z-1)$  to  $z$ . The polynomial  $E$  is obtained by comparison with observed  $I_n$  values corrected (via the barycentre positions relative to the groundstates) in order to obtain  $I_n^*$ .

Iczkowski and Margrave [36] proposed the electronegativity  $x$  of monatomic entities to be  $dE/dz$  of eq. (8) as a generalization of the definition by Mulliken  $x_M = (I_1 + I_0)/2$  for neutral atoms. Space is not available here to discuss the many problems for the latter definition [11], a major difficulty is the extension to exorbitant values of  $(I_2 + I_1)/2$  for  $Li^+$  and  $N^+$ . The main purpose of introducing  $I(z)$  is to add the Madelung potential [23] and minimize the sum of  $E$  [derived from eq. (8) for the constituent atoms] and the Madelung energy of a given compound as a function of the ionicity  $\xi$ . Thus, in binary compounds  $MX_N$  the fractional charges are  $z_M = +N\xi$  and  $z_X = -\xi$  ( $\xi$  is at most +1 in halides, but might be up to +2 in oxides). In crystalline  $MX$ , it is possible to define a physically consistent (though apparently only conditionally convergent) Madelung constant  $\alpha$  ( $= 1.638$  for tetrahedrally coordinated  $CuCl$ -type cubic crystals;  $1.748$  for octahedral  $NaCl$ -type;  $1.763$  for cubical  $CsCl$ -type; etc.) such that the Madelung potential (for electrons) is at the  $M$  sites  $+\alpha \xi \mu$  and at  $X$  sites  $-\alpha \xi \mu$  (stabilizing electrons with  $\mu = e/R$  (the shortest internuclear  $M-X$  distance  $R$ ) in the unit  $14.4 \text{ eV/\AA}$ ). In binary molecules  $MX_N$  (with all  $N$  values of  $R$  identical) the Madelung potential is  $+N \xi \mu$  for the central  $M$  atom and  $-\mathcal{H} \xi \mu$  for  $X$  having for instance [1,11]  $\mathcal{H} = 1.5$  for linear  $XM_X$ ,  $2.1628$  for regular tetrahedral  $MX_4$ , the slightly smaller  $2.0858$  for quadratic  $MX_4$ , and  $2.6716$  for regular octahedral  $MX_6$ . As numerical examples, Table 1 gives ionicities  $\xi$  and  $z_M$  values for 42 (mainly d-group) binary molecules and complex anions [1,37]. Values in rectangular brackets correspond to minimum energy for full ionicity. The trends between different  $M$  (and differing halides) look plausible, as well as the tendency toward almost invariant  $z_M$  when keeping  $X$  constant and increasing the oxidation state of  $M$ . However, there is little doubt that the  $z_M$  are somewhat overestimated, and a closer analysis [1,37] and comparison between observed heats of atomization and calculated total energy at optimized ionicity indicate that covalent bonding further decreases the energy minimum, and that  $z_M$  would only be 0.5 to 0.8 times as large as the computed values. The major problem in the 3d group is the neglect of the empty 4s orbital, and in the main-group elements the unrealistic break between ns and np orbitals. Thus,  $z_C$  in  $CF_4$  stays put at exactly 2.00 because 1.99 would mean unfavourable transfer of C 2s electronic density, and 2.01 with remaining C 2p is less stable. It may be noted [1] that the  $2p^4$  barycentre of oxygen is situated at  $+8000 \text{ cm}^{-1}$ , the  $2p^5$  of  $O^-$  at  $-11000 \text{ cm}^{-1}$  but  $2p^6$  of  $O^{2-}$  at  $+53000 \text{ cm}^{-1}$  relative to the groundstate of the oxygen atom. Textbooks frequently cite such a strongly negative electron affinity (close to  $-8 \text{ eV}$ ) of  $O^-$  derived from the Born-Haber treatment of  $NaCl$ -type  $MgO$ , assuming full ionicity. It is clear that a gaseous monatomic entity cannot show a negative electron affinity (it can always chase away the electron) but it is also clear that a Hartree-Fock function for  $Z = 8$  and  $K = 10$  constrained to have six 2p electrons show a less negative  $E$  than with five. The full Madelung potential in  $MgO$  would stabilize  $O^{2-}$  to the extent  $24 \text{ eV}$ .

## ELECTRONEGATIVITY AS DIAGONAL ELEMENT OF L.C.A.O. DESCRIPTIONS

Ferreira [38] reviewed "Electronegativity and Chemical Bonding" in a very thorough way. He pointed out that the parabolic interpolation of energies in an analytic function of  $z$  of the kind of eq. (8) cannot be valid for gaseous atoms of a given element at large internuclear distances. A system containing equal amounts of  $M^+$  and  $M^0$  has no opportunity to become more stable as equivalent  $M^{+0.5}$ . The quantum-mechanical reason is that (in spite of extended electron densities having many of the properties of clouds rather than points) systems of  $K$  electrons show only  $K(K-1)/2$  interelectronic repulsion quantities, each electron interacting only with the  $(K-1)$  other electrons, but not with itself (short of the rest-mass  $137^2$  hartree of the electron). Hence, the  $q^2$  term is not a simple series  $1, 4, 9, 16, \dots$  but is a residual of the progression  $0, 2, 6, 12, \dots = q(q-1)$ . This has rather dramatic effects in the hydrogen atom having no interelectronic repulsion. The hydrogenic 1s orbital with the effective charge  $Z_* = \langle r^{-1} \rangle \text{ bohr}^{-1}$  would have a J-integral of interelectronic repulsion  $5Z_*/8$  hartree which would minimize the energy when  $Z_* = 3/8$  (assuming the conventional nuclear attraction  $-Z_*$  and kinetic energy  $(Z_*)^2$  hartree/2) at only  $-9/32$  rydberg. This is a caricature of the textbook treatment of the helium groundstate, where the optimized  $Z_*$  is  $2-(5/16)$  for related reasons, with one J-integral, providing a total energy  $-(27/16)^2$  hartree.

Equation (8) would be less ludicrous for a high density of gaseous atoms. This situation might be similar to the Mott transition [39-41] from an insulating to a metallic state by decreasing internuclear  $R$ . Disregarding the formation of  $Na_2$  molecules (having the dissociation energy  $0.8 \text{ eV}$ ) a dilute gas of sodium atoms would show no tendency to form  $Na^+$  ( $I_1 = 5.14 \text{ eV}$ ) and  $Na^-$  ( $I_0 = 0.54 \text{ eV}$ ). But assuming the dielectric constant 1, and the full Madelung attraction  $14.4 \text{ eV/R}$ , the difference  $(I_1 - I_0) = 4.6 \text{ eV}$  can be compensated for by  $R$  below  $3.13 \text{ \AA}$  somewhat smaller than the observed  $R = 3.72 \text{ \AA}$  in metallic sodium. However, because of the larger Madelung constant  $\alpha = 1.748$ , hypothetical  $NaCl$ -type  $Na^+Na^-$  with full Madelung potential would be stable relative to the metal (heat of atomization of metallic sodium  $1.12 \text{ eV}$ ) for  $R$  below  $3.68 \text{ \AA}$ , and stable in the sense of the electrons not jumping back for  $R$  below  $5.47 \text{ \AA}$ . The likely conclusion is that the transition from ionic crystal to metal is a collective phenomenon (as also suggested by the fact that most Mott transitions take place within a very narrow temperature interval by heating). It may be noted that crystalline salts, and strong solutions of sodium in liquid ammonia, can contain the strongly coloured, spherical  $Na^-$  of radius comparable to iodide [42]. Based on a criterion of the molar volume achieving the Lorentz volume of refractivity [35] proposed by Herzfeld in 1927, there has recently been great interest [43,44] in the pressure needed to render weak semiconductors metallic. It may also be mentioned that amorphous mixtures  $Cs_xXe_{1-x}$  at  $6 \text{ K}$  (essentially statistically disordered) are metallic for  $x$  above 0.55, and strongly coloured for lower  $x$  [45].

It is very important in quantum chemistry to treat important effects before minor perturbations, in order to maintain a moderately realistic insight. In this sense, the differential ionization energy (including the Madelung potential) provides acceptable diagonal elements in cases where covalent bonding between elements of highly differing  $I(z)$  functions still is a relatively pronounced effect. Since the interelectronic repulsion in a partly filled shell  $lq$  is proportional (in the SCS treatment multiplied by  $\langle r^{-1} \rangle$ ) to  $q(q-1)$  and not to  $q^2$ , quantum mechanics pays a premium to localized orbitals, the system being stabilized to the extent of some  $0.3 q \langle r^{-1} \rangle$  hartree/bohr relative to a classical electrostatic description of extended electron densities. It was pointed out [46] at a summer school in Milano 1963 that homonuclear diatomic molecules lose half of this non-classical stabilization relative to separate atoms, being destabilized roughly  $0.25 a_1$  of eq. (8), and this is the reason why the first-order L.C.A.O. description of the  $H_2$  groundstate dissociates at large  $R$  to  $H^+$  and  $H^-$  (at  $13.61 - 0.76 = 12.85$  eV higher energy than two atoms) with 50 percent probability. Said in other words, L.C.A.O. configurations can be unsound energy-wise for  $I_1$  much higher than  $I_0$ .

It would be easy to imagine atoms of a given element to become indifferent to their local charge in a high-temperature plasma (full of electrons) or dissolved in mercury (as a liquid amalgam). But it seems also to be true that sufficiently strong chemical bonding (at comparatively short  $R$ ) let the atoms use  $I(z)$  of eq. (8) as an analytical function of a  $z$  value somewhat higher than their fractional charge occurring. There is no requirement of metallic behaviour; the molecule or the solid compound may even be colourless. The situation is rather comparable to the "strong-field" diagonal elements of "ligand field" treatment of  $dq$  complexes, corresponding to a definite number of anti-bonding electrons in the M.O. configuration, but having diagonal elements of interelectronic repulsion corresponding to a mixture of  $dq$  (S,L) terms in spherical symmetry. In this sense, the  $I(z)$  treatment is somewhat similar to a re-diagonalization of "ligand field" matrices [47] except that adjacent  $q$  values are allowed to mix. It is highly instructive that transition-group compounds exhibit quite differing types of behaviour, showing how quantum chemistry to a large extent is a compromise between counteracting effects. Thus, most octahedral manganese (II) and iron (III) complexes have a groundstate  $S = 5/2$  and one electron in each of the five  $d$ -like orbitals (and hence two anti-bonding electrons) but a few have  $S = 1/2$  and all five electrons in the lower sub-shell of three orbitals. Some iron (II), nearly all cobalt (III) and all known nickel (IV) complexes have  $S = 0$  and six electrons filling the lower sub-shell, whereas most iron (II) complexes show  $S = 2$  having 4 and 2 electrons in the two sub-shells. The clear-cut choice between the low and high  $S$  values of the groundstate plexes have  $s = 0$  and six electrons filling the lower sub-shell, whereas most iron (II) complexes show  $s = 2$  having 4 and 2 electrons in the two sub-shells. The clear-cut choice between the low and high  $s$  values of the groundstate depends on whether twice the value of the sub-shell energy difference is larger or smaller than the change of spin-pairing energy,  $8D$  in the case of  $d^5$  and  $6D$  for  $d^6$ .

The opposite extreme occurs in lanthanide com-

pounds having identifiable  $J$ -levels or  $4f^q$  [2,20] but tiny "ligand field" effects, normally well below 0.1 eV [17-19]. It may be worthwhile to stress that (with exception of the long-distance correlation of the polarization direction of two photons, supporting the Copenhagen interpretation in contrast to the paradox of Einstein, Podolsky and Rosen) atomic spectra are remarkably insensitive to long-distance interactions. Sharp line-spectra are obtained at gas pressures, where the typical interatomic distance is 100 Å, and even at 8 times higher concentrations of atoms with average distance 50 Å (in spite of frequent collisions) the lines are only slightly broadened. It may be mentioned that the symbols  $s$  ( $l = 0$ ) and  $d$  ( $l = 2$ ) derive from the two series in alkali-metal atoms, where "sharp" lines are obtained when an electron jumps from one  $s$  orbital down to the first excited configuration involving the  $np$  shell, whereas "diffuse" lines are obtained by the corresponding jump from the five  $d$  orbitals marginally separated in energy by the surrounding atoms.

The sum of the Madelung potential  $V(x,y,z)$  and  $I(z)$  of eq. (8) is closely similar to a chemical potential for electrons, and the minimization of the total energy [1,37] is conceptually an equalization of this chemical potential for all atoms in the compound. Sanderson [48-50] has extensively developed the hypothesis of electronegativity equalization, which has also been used [51] for rationalizing chemical shifts [3-7] of one-shot ionization energies  $I$  of inner shells, obtained from photo-electron spectra. However, this cannot be the whole explanation of chemical shifts because of interatomic relaxation effects. Thus, the gaseous Mg, Ca, Sr and Ba atoms [52] have inner-shell  $I$  values some 5 to 7 eV higher than the metallic elements. Electronegativity equalization cannot be universally valid for all compounds, at least because of the two following problems. The equalization does not take place over long distances, but need "conducting contacts" across short chemical bonds (e.g. it would be highly surprising if adding iodoform or iodide anions would decrease  $x$  of  $Cr(OH_2)_6^{3+}$  in a solution). A more serious dilemma occurs in systems having a much higher ionization energy than electron affinity, as is eminently the case for lanthanide compounds [20,53] where it is not possible to change the oxidation state of gadolinium (III) and erbium (III), though they are  $4f^7$  and  $4f^{11}$  systems, and not closed-shell cases like aluminium (III). Besides the quite large influence of spin-pairing energy (of order 5 eV) making the oxidation (ionization) about as easy in  $4f^{7+q}$  as in  $4f^q$ , the  $I(z)$  treatment would render the compounds highly covalent with  $z$  close to 2, in disagreement with a large amount of spectroscopic information.

When speaking about "one-electron energies", the model assumed is eqs. (2) and (3) with a suitably chosen  $U(x,y,z)$ . One might ask for ionization energies  $I$  (to be compared with photo-electron spectra) but it is not perfectly certain that the semi-empirical parametrizations like the Extended Hückel Model [11] do not rather provide the average value of  $I$  and the electron affinity for a given M.O. The same problem is prominent for the energy band model [41] for crystalline solids. This model seems satisfactory for the strongly conducting alkali — and coinage-metals, and for adamantoid semiconductors (Si, Ge, GaAs, InSb, .)

but is not evidently appropriate for most compounds. Actually, even the atoms scandium, titanium, chromium, manganese and iron lose one 4s electron rather than a 3d electron by ionization; and vanadium, cobalt and nickel lose two 4s electrons (one of which is transferred to the 3d shell) with the groundstate of  $M^+$  belonging to  $3d^{q+1}$  (besides the closed-shell  $K = 18$ ). All the neutral atoms mentioned (except chromium) have groundstates belonging to  $3d^q 4s^2$ , and all the  $M^{+2}$  to  $3d^q$ . Hence, the question of whether 3d or 4s electrons are the most stable, does not have a straightforward answer; as far as occupation goes, 4s is served as first priority in the neutral atoms from calcium to nickel, but the 4s are removed at first by ionization, providing an argument for greater stability of 3d. This situation (which is particularly paradoxical in the four  $M^+$  retaining one 4s electron in their groundstate classified as  $3d^q 4s$ ) can be rationalized [54] by the much larger parameter  $J(3d,3d)$  of interelectronic repulsion than the (rather comparable)  $J(3d,4s)$  and  $J(4s,4s)$ .

Ferreira [55] wrote a very profound review on paradoxical violations of the proposition by Koopmans. There is overwhelming evidence from photo-electron spectra [54, 56,57] that many iron (III) and copper (II) compounds have higher  $I$  values for their (partly occupied) d-like orbitals than for the highest filled M.O. concentrated on the ligands. In a way, it is even more enigmatic that many (if not most) lanthanide (III) compounds have higher  $I$  for their partly filled 4f shell (ionizing to several J-levels of  $4f^{q-1}$ ) than of the filled M.O., since it exemplifies higher  $I$  of anti-bonding than of bonding M.O. having the same symmetry type. Textbooks expect strong effects of covalent delocalization (in the L.C.A.O. model) when the  $I$  values almost coincide. Spectroscopic evidence is strongly against extensive delocalization of the seven 4f orbitals, even in ionized states having lost a photo-electron. The plausible conclusion is that the very weak anti-bonding effects [2,17–20] on 4f orbitals are determined by the  $I$  values of ligand orbitals, but by the (much smaller) electron affinity of the 4f shell. This is another way of saying that the treatment of differential ionization energies is not applicable to 4f group compounds, since the strong stabilization of  $4f^q$  obtained by the intra-shell interelectronic repulsion being proportional to  $q(q-1)$  only, rather than to  $q^2$ , discourages involvement in L.C.A.O. formation.

Recent reviews [58–60] discuss electronegativities and their equalization, with special attention paid to "group electronegativities" of organic substituents (such as  $CH_3$ ,  $CH_2F$ ,  $CHF_2$  and  $CF_3$ ). Attempts are made to base electronegativities on the density functional theory of Kohn and Sham, and several tables give calculated properties of monatomic entities rather than considering the observed barycentre energies of eq. (8). Since the Schrödinger equation (and other quantum-mechanical expressions) agrees (if valid) with experimental results, calculation of approximate energies is necessarily more indeterminate, though they allow discussion of the (negative) electron affinities of noble gases and of  $O^-$ . These reviews [59,60] consider the Mulliken  $x_M = (I_0 + I_1)/2$  (of appropriate valence-states) the fundamental concept of electronegativity. Though the Pauling values  $x_p$  by no means have a well-defined linear relation to  $x_M$ , they still tend to show up in rather unexpected contexts. Thus, electron transfer

spectra [23,61] of transition-group complexes can be rationalized by optical electronegativities  $x_{opt}$  showing the  $x_p = 2.5; 2.8; 3.0$  and  $3.9$  for  $X = I, Br, Cl$  and  $F$ . For a given d-group element,  $x_{opt}$  increases rather smoothly with the oxidation state (and is closely related to the refined spin-pairing energy treatment [20,53] of 4f group compounds). When this concept was introduced 1961 for absorption bands, where one or more reducing ligands (collectively) transfer one electron to an empty or partly filled shell of an oxidizing atom, it was not realized that the lowest  $I$  of a filled M.O. of gaseous halide molecules generally is  $(3.7 \text{ eV})x_{opt}$  (the same numerical constant as for the electron transfer bands) or until 1.5 eV higher; and usually 1 eV below this expression (because of interatomic relaxation effects) in solid halides [4].

## SOFTNESS ACCORDING TO PEARSON

The differential quotient  $I(z)$  in eq. (8) normally jumps discontinuously at any  $z$  value passing a closed shell (such as sodium for  $z = +1$  or noble gases at  $z$  zero). Hence, it does not seem appropriate to define the electronegativity as  $dE/dz$  at these singularities. There is an excessive emphasis on evaluating electronegativities of neutral atoms [58–60] as a main indicator of chemical behaviour of a given element; such parameters would seem only marginally relevant for the chemistry of manganese, iron, ruthenium, cerium, gadolinium, ytterbium, thorium or uranium. However, there is an interesting riddle behind this approach. In what sense are the s electrons which are so strongly needed for stabilizing neutral atoms of the 3d, 5d, 4f and 5f groups replaced by the electronic density of the surrounding atoms in condensed matter [20,34] ?

Pearson [62] introduced the concepts of softness and of hardness, pointing out that soft bases react preferentially with soft (Lewis) acids (called anti-bases by Jannik Bjerrum), and that hard bases react preferentially with hard anti-bases. This idea has a certain ensemble of precursors among complex chemists, though Pearson added that all metallic surfaces are intrinsically "soft". Though the concepts were sharply criticized by several mathematically minded physical chemists, it seems possible [35] to connect them with measurable quantities, and in particular (as proposed by Ahrland) to the ionization energy of a gaseous  $M$  atom, when losing  $z$  electrons (to vacuo) and forming  $M^{z+}$  in aqueous solution. Parr and Pearson [63] defined  $\eta = (I_1 - I_0)/2$  as the "absolute hardness" of an atom [such as  $(17.42 - 3.40)/2 = 7.01$  eV for fluorine, but only  $(10.45 - 3.06)/2 = 3.70$  eV for iodine] and the huge values  $(I_2 - I_1)/2 = 35.12$  eV for  $Li^+$  and  $(I_4 - I_3)/2 = 45.77$  eV for  $Al^{3+}$ . If the polynomial  $E$  in eq. (8) has the same coefficients for negative and positive  $z$  (i.e. the neutral atom is not a closed-shell system)  $\eta$  is  $1/2 (d^2 E/dz^2)$ , and this result has been introduced [60,63] as a definition of hardness. Physically, it is very appealing that a vanishing difference between ionization energy and electron affinity (as occurring in graphite and typical metals) corresponds to vanishing hardness. However, the writer has his doubts whether it would have any consequences for the chemistry of lithium (I) or aluminium (III) if the huge  $I_2$  (or  $I_4$ ) were twice as big, and may suggest

to introduce a function  $\eta/(1 + \eta)$  reaching the extreme values 1 for maximal hardness and 0 for absence of hardness. Such a function needs the choice of an energy unit for  $\eta$ , much like the tacit choice 1 eV of Pauling for his "thermochemical" electronegativity  $x_p$ . Alternatively, one may use  $1/(1 + \eta)$  for softness.

## TOTAL ENERGIES AND RELATIVISTIC EFFECTS

In compounds, one might extend eq (5) to  $E = T + W + Q + C$ , where  $W$  is the Coulomb electrostatic interaction between (point-like) nuclei. However, this is, by itself, an argument for the need of introducing a local potential  $U(x, y, z)$  in eq. (2). In large volumes of a stable compound [11] the (negative)  $Q$ , and the (positive)  $W$  and  $C$  are all proportional to the fifth power of the linear extension (say, the length of the side of a cube) of samples having the same geometric shape, and hence each proportional to the number of moles of the compound to the power  $5/3$ . It needs a rather miraculous kind of fine tuning to have  $-E = T$  simply proportional to the number of moles (and to the third power of the linear extension). In a single neutral atom, Politzer and Parr [64] pointed out the interesting (approximately valid) result that  $E = 3Q/7$ , that is one-seventh of the nuclear attraction is cancelled by the interelectronic repulsion  $C$ . These authors also expressed  $E$  (in hartree) as being close to one of the two expressions (the second is the best for  $Z$  above 7):

$$\begin{aligned} & -0.84 Z^{7/3} + 0.80 Z^2 - 0.59 Z^{5/3} \\ & -0.7754 Z^{7/3} + 0.536 Z^2 - 0.309 Z^{5/3} \end{aligned} \quad (9)$$

Two important problems for  $E$  values of monatomic entities (and strongly influencing the calculation of stationary states of polyatomic molecules and ions) have not yet been touched upon in this paper. One is relativistic effects [65–68] being roughly proportional to  $Z^4$  and hence occurring to the extent 0.13 : 0.41 : 1 : 2.52 for  $Z = 60, 80, 100$  and 126. Among the general trends are a strong radial contraction and stabilization of  $1s$  and (to a smaller extent) subsequent  $ns$  orbitals; a comparable effect (for the same  $n$ ) on the  $j = 1/2$  component of  $np$  orbitals; and expansion and destabilization of  $nd$  and  $nf$  orbitals. Already in uranyl salts [69] and other uranium compounds, the optical and photo-electron spectra show quite spectacular effects. There is little doubt [5,11] that the chemical stability of thallium(I), lead(II) and bismuth(III) is related to relativistic effects. Spin-orbit coupling is a first-order relativistic effect, and already in  $5p$  of iodine and its compounds, it has the size 1 eV. The actual groundstates (to which present-day relativistic calculations are quite good approximations) have  $E$  considerably more negative than non-relativistic Hartree-Fock functions for high  $Z$ . When it is said in the beginning of this paper that the ratio between  $-E$  and the Gombas-Gaspar formula  $-E_{GG} = Z^{2.4}$  ry at first decreases from 1.03 (for  $Z = 6$ ) to 1.01 (around  $Z = 50$ ) and smoothly moves back to 1.04 (for  $Z = 80$ ), it may be added that the ratio between the non-relativistic Hartree-

Fock result [64] and  $-E_{GG}$  gets below 1.01 at  $Z$  about 40, must cross 1 around 70, and is 0.996 for  $Z = 84$ . Hence,  $E_{GG}$  remains a much better approximation to non-relativistic calculations for high  $Z$ . It may also be noted that this pragmatic formula is nearly as successful as eq. (9) though it lacks the connection with  $Z^{7/3}$  derived from the Thomas-Fermi model [64]. The Dirack-Fock function for  $Z = 126$  evaluated by Joseph B. Mann [11,70] has this ratio 1.208, increasing dramatically to 1.78 for  $Z = 164$  (assuming standard nuclear density; the Dirac treatment is divergent above  $Z = 137$  for a positively charged point).

## CORRELATION ENERGY

The other outstanding problem is correlation energy  $E_{\text{corr}}$  defined by Löwdin as the (negative) difference between  $E$  of the non-relativistic total wave-function (in practice obtained from  $E$  as sum of observed  $I_n$  values, corrected for relativistic effects) and  $E$  of the Hartree-Fock treatment. This is not a large percentage of  $E$  (and is actually smaller than the relativistic stabilization already for  $Z$  above 15) but from the point of view of a chemist, it is far more pernicious. For instance, all neutral atoms starting with sodium ( $Z = 11$ ) have  $-E_{\text{corr}}$  larger than their first ionization energy  $I_1$ . Hence, the calculated Hartree-Fock groundstate is not situated above only one factual  $E$  of a state with the same symmetry type, but above an infinite number of such states, taking the backbone out of the variational principle. The most striking expression of this effect is the squared amplitude of the Hartree-Fock function in the total wave-function. Textbooks joyfully note that this squared amplitude is 0.99 for helium. It oscillates between 0.88 and 0.93 for beryllium ( $Z = 4$ ) to neon ( $Z = 10$ ) though it must be admitted in all fairness that the intermixing of  $1s^2 2s^2$  and  $1s^2 2p^2$  produces exceptional conditions in the beryllium atom (on the other hand Russell-Saunders coupling including the quantum number  $S$  is a far better description of states in this atom than the electron configurations). For two-digit  $Z$  values, it seems a good approximation [7] that  $-E_{\text{corr}}$  is proportional to the square-root of the total binding energy (taken as  $E_{GG}$ ) and specifically (0.7 eV)  $Z^{1.2}$ . This expression is 38 eV for  $Z = 30$  (zinc), 90 eV for  $Z = 60$  (neodymium) and 133 eV for  $Z = 80$  (mercury). With an (admittedly quite crude second-order perturbation) argument [20] the squared amplitude of the Hartree-Fock function should have the order of magnitude 0.7 in zinc and 0.4 in neodymium. The most important admixed configurations providing  $E_{\text{corr}}$  are two-electron substitutions [23] in the Hartree-Fock configuration, and it is quite conceivable that the eventual 4-, 6-, 8-... electron substitutions become divergent above  $Z = 80$ . For the purpose of the chemist, the important question is not whether the squared amplitude of the Hartree-Fock function ducks below 0.5 at  $Z = 40$  or 50, but the inevitable further aggravation of the correlation problem in all compounds, compared to the gaseous atoms.

There is a strong motivation to obtain reliable thumb rules for correlation effects (like the quaint fact [3,4] that the observed one-shot ionization energies of inner shells are decreased by intra-atomic relaxation, compared with the predicted Hartree-Fock  $I$  values, to an extent close to



0.8 eV times the square-root of  $I$  in eV). Thus, Robles and Kemister [71] compiled correlation energies for the 17 atoms having  $Z$  below 19, and for 15 gaseous molecules having one-digit  $Z$  nuclei. To a good approximation, the correlation energy is 0.025 times the exchange energy in atoms, and 0.04 times the exchange energy in the molecules studied. Here, the words "exchange energy" do not mean K-integrals in the SCS treatment [1,10] but comprise a substantial part of the interelectronic repulsion. Thus, the helium groundstate [involving no K-integral, and hence having identical Hartree and Hartree-Fock function] is said to have the exchange energy close to the hydrogenic J-integral 135/128 hartree. This heuristic approach has a certain similarity to an earlier suggestion [72] that the  $F^0$  integrals [10] for the same  $n$  value behave as if  $Z$  were 0.075 smaller, and the  $F^k$  integrals (with positive  $k$ ) for a given  $n\ell$  shell behave as if  $Z$  were one unit smaller. The latter quantities determine the distance of individual (S,L) terms from the configuration barycentre, and include parameters such as  $D$  in eq. (4). Correspondingly the observed term distances for gaseous  $M^{+z}$  containing  $3d^q$  (with  $q$  from 2 to 8) are roughly  $(z+2)/(z+3)$  times the Hartree-Fock results [23]. This discrepancy is larger [26] for  $4f^q$ , about 0.75 (and not 0.83) for  $z=3$ .

## IS QUANTUM CHEMISTRY FEASIBLE FOR TWO-DIGIT $Z$ VALUES?

Compared with  $E_{GG}$  for two-digit  $Z$  values, chemical bonding is a very weak effect, and for  $Z$  above 50 comparable to a clerk in a post office weighing a parcel before and after putting on stamps, in order to check whether enough postage has been paid. In the strict sense of finding paths of reaction, and absolute or relative minima of energy we are probably restricted (for a long time reaching into the next millennium) to systems containing a low number of nuclei, all with one-digit  $Z$  values. A typical prospective field is helium chemistry. Two neutral molecules, HeLiH [73] and HeBeO [74] have been computed not to dissociate in the gaseous state (though they readily precipitate LiH and BeO). Many cations such as  $HeH^+$ ,  $He_2^+$ ,  $HeNe^+$ ,  $HeW^{+2}$  and  $HePt^{+2}$  are known from mass spectrometry, and  $HeO^+$ ,  $HeBe^{+2}$  and  $HeTi^{+2}$  [75] from calculations, as well as several carbon-containing cations [76,77] such as  $HeC^{+2}$  (dissociating at large  $R$  to He and  $C^{+2}$  rather than to the repelling  $He^+$  and  $C^+$ ),  $HeCCH^+$ ,  $He_2C_2^{+2}$ , etc. Because of the relative size of  $I_3$  of the lanthanide atom and  $I_1$  of helium it is easily seen [20] that gaseous  $HeM^{+3}$  dissociate to He and  $M^{+3}$  except  $HeEu^{+3}$  and  $HeYb^{+3}$  (where the coordinated base helium is too reducing) dissociating to

TABLE I

Internuclear distances  $R$  (in Å), ionicities  $\rho$  and fractional charges  $z_M$  (of the central atom in binary molecules and complex anions) obtained by minimizing the sum of atomic  $E$  of equation (8) and the Madelung energy. Hypothetical compounds are marked (hyp.).  $R$  values in parentheses are estimated. Ionicities and fractional charges in rectangular brackets correspond to minimum energy for fully ionic forms.

	$R$	$\xi$	$z_M$		$R$	$\xi$	$z_M$
$SF_6$	1.58	0.555	3.33	$ZrF_6^{-2}$	2.04	[1]	[4]
$ClO_4^-$	1.43	1.265	4.06	$ZrCl_6^{-2}$	2.45	0.907	3.44
$TiF_6^{-3}$	(1.99)	[1]	[3]	$MoCl_6^{-3}$	(2.50)	0.928	2.57
$TiCl_6^{-3}$	(2.43)	0.962	2.77	$MoCl_6^{-2}$	(2.42)	0.775	2.65
$TiCl_4$	2.18	0.66	2.64	$MoCl_6^-$	(2.34)	0.595	2.57
$TiBr_4$	2.31	0.605	2.42	$MoCl_6$	(2.26)	0.42	2.52
$TiF_6^{-2}$	1.91	0.90	3.40	$MoF_6$	(1.82)	0.592	3.55
$TiCl_6^{-2}$	2.35	0.793	2.76	$RuF_6$	(1.80)	0.50	3.0
$CrF_6$	(1.68)	0.50	3.0	$RuCl_6$ (hyp.)	(2.24)	0.33	2.0
$CrCl_6$ (hyp.)	(2.12)	0.383	2.3	$RuO_4^{-2}$	(1.85)	1.29	3.16
$CrO_4^{-2}$	1.65	1.365	3.46	$RuO_4^-$	1.79	1.023	3.09
$FeCl_4^-$	2.19	0.767	2.07	$RuO_4$	1.70	0.785	3.14
$FeBr_4^-$	(2.32)	0.705	1.81	$PdF_6^{-2}$	1.89	0.745	2.47
$FeF_6^{-3}$	2.03	0.887	2.32	$PdCl_6^{-2}$	(2.31)	0.63	1.78
$FeF_6$ (hyp.)	(1.66)	0.45	2.7	$TeF_6$	1.84	0.66	3.96
$FeCl_6$ (hyp.)	(2.10)	0.33	2.0	$XeF_2$	1.99	0.28	0.56
$FeO_4^{-2}$	(1.60)	1.275	3.1	$XeF_4$	1.95	0.23	0.92
$FeO_4$ (hyp.)	(1.55)	0.715	2.86	$XeO_4$	(1.75)	0.225	0.90
$NiF_6^{-4}$	2.01	[1]	[2]	$PtF_6^{-2}$	1.91	0.808	2.85
$NiCl_6^{-4}$	2.50	0.935	1.61	$PtCl_6^{-2}$	2.33	0.675	2.05
$NiF_6^{-2}$	1.70	0.727	2.36	$PtF_6$	(1.80)	0.467	2.8

He<sup>+</sup> and Eu<sup>+2</sup> or Yb<sup>+2</sup>

In this paper, quantum chemistry has been turned slowly around in the limelight of the last 30 years of experience, so that one can admire some of the facets. At this occasion, some facets have been neglected; radiative and non-radiative transition probabilities [2,69]; Stokes shift of luminescence, chemical reactions, overtone combinations of vibrational spectra [9] and other phenomena

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