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Effective Shell Charge of Electrons on a Sphere

A Discussion of Hund's Rules, Negative Ions and the Chemical Bond

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By ignoring the radial motions of the electrons in the valence shell of an atom one formally obtains the problem of electrons constrained to move on a sphere. This sphere will be attracted by the core as if it had an effective charge equal to the number of electrons on it minus a certain quantity resulting from the mutual repulsion of the electrons. This "effective shell charge" is a very simple, but still precise and quantitative concept which provides a good understanding of many empirical facts about atoms and ions, most notably Hund's rules. Implications for negative ions are discussed and chemical bonding is touched briefly. A qualitative difference in physical behavior for small and large sphere radii is pointed out.

Key words: Electrons on a sphere – Screening – Effective charge – Hund's rules – Negative ions – Chemical bonding.

1. Introduction

The basic assumption in most treatments of atoms is that the electrons move in a spherically symmetric field and this has proved to be an excellent approximation for most purposes. The ground state of the majority of free atoms is, however, not spherically symmetric. On the contrary Hund's rules [1] tell us that open shell atoms maximize first spin, then orbital angular momentum. In modern theoretical jargon [2], this phenomenon is referred to as "spontaneous symmetry breaking"; the ground state solution has a lower symmetry than the equations of motion. In this article I will try to explain the physical origin of Hund's rules

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and a few other empirical facts about atoms and ions using the simple model system of electrons on a sphere. This is an idealized model of the real situation of a type often studied by theoreticians since it is usually the only way to isolate and pin down certain aspects of reality that are otherwise hopelessly entangled. It is known that the radial one-electron functions for a given n, l-shell peak at a relatively narrow range of r-values. Thus it is a physically reasonable idea that the angular interactions of these electrons can be studied as if they were moving on a sphere of appropriate radius. The sphere as a whole can then be thought of as being attracted by the (spherically symmetric) core as if it had a certain effective charge which will depend on the distribution of electrons on it according to a precise formula given below. By doing so, one arrives at Hund's rules since those shells which have the maximum effective shell charge turn out to be precisely those which maximize spin and then orbital angular momentum for that spin.

The literature contains many theoretical and computational studies of Hund's rules. The most exhaustive one is a review article by Katriel and Pauncz [3]. Their main result is that zeroth order wave-functions which reproduce the correct energy ordering of the multiplet levels but violate the virial theorem because the energy differences all sit in V_{ee} (electron–electron repulsion) can be subjected to a radial scaling that make them obey the virial theorem without having their energy ordering changed. Many other studies have stressed the importance of anisotropy or angular correlation (the word here taken in its broadest sense i.e. including Fermi correlation) in explaining the energy ordering. Kutzelnigg et al. [4] were probably the first. More recently Shim and Dahl [5], Warner et al. [6] and Thakkar and Smith [7] have discussed this point of view further. The present study is in agreement with and to some extent unifies the two above mentioned approaches.

The electrostatics of electrons on a sphere has previously been discussed in terms of single configuration wavefunction peak probabilities by Linnett and Poe [8] and later, more pertinently by Dahl [9]. These studies as well as classical multiplet theory, however, do not in themselves explain Hund's rules unless combined with ideas of radial scaling, since, as has been rather slowly realized [3], multiplet energy differences simply do not sit in the electron–electron repulsion part of the energy. In the present approach the radius of the valence shell appears explicitly in the formulae and, as discussed at the end of Sect. 3, one must not think of it as having the same value for different levels in real atoms.

Ezra and Berry [10] have recently presented accurate solutions for two particles on a sphere as a model for doubly excited states of atoms. The solutions presented in this article only become "exact" in the two extreme limits of zero and infinite sphere radius. It is one of the main points of the present study that the nature of the solution is different in the small and large radius (atomic units) limits. Thus the model casts some light on the qualitative differences between positive and negative ions which may be regarded as physical representatives of these two limits.

2. Effective Shell Charge

The interactions of a set of electrons with the radial part of their (one-particle) wave-functions peaked at roughly the same distance r from the nucleus will here be treated approximately by assuming that the electrons are constrained to move on a sphere of radius r. Consider the electrostatic potential energy of N negative unit charges on a sphere of radius r attracted by a positive charge $N+q$ at its center:

$$\phi = -\sum_1^N \frac{N+q}{r} + \sum_{i<j}^N \frac{1}{|\boldsymbol{r}_i - \boldsymbol{r}_j|} \tag{1}$$

where

$$|\boldsymbol{r}_i| = r; \qquad i = 1, 2, \ldots, N. \tag{2}$$

We introduce the notation

$$\boldsymbol{r}_i \cdot \boldsymbol{r}_j = r^2 \cos\theta_{ij} \tag{3}$$

and

$$v(\theta_{ij}) = \sum_{l=0}^{\infty} P_l(\cos\theta_{ij}) \tag{4}$$

where P_l are Legendre polynomials (see e.g. [21] formula B99, p. 497), so that (1) can be written

$$\phi = -\frac{(N+q)N}{r} + \frac{1}{r}\sum_{i<j}^N v(\theta_{ij}). \tag{5}$$

The number of terms in the sum over $i<j$ is $N(N-1)/2$ so that the operator $\hat{\delta}$ defined as:

$$\hat{\delta} \equiv \frac{2}{N(N-1)} \sum_{i<j}^N v(\theta_{ij}) \tag{6}$$

will have expectation values (which we denote δ) corresponding to the arithmetic average of the terms in the sum i.e. inverse electron–electron distances on the unit sphere. Using (6) we can write (5) as follows

$$\phi = -(N+q)\hat{Q}(N,q)/r \tag{7}$$

where $\hat{Q}$ is the "effective shell charge" operator:

$$\hat{Q}(N,q) \equiv N\left[1 - \frac{1}{2}\frac{(N-1)}{(N+q)}\hat{\delta}\right]. \tag{8}$$

Effective shell charge so defined, is a direct measure of how strongly the shell is pulled by the charge inside. If the particles on the sphere were non-interacting it would simply reduce to N, the total charge on the sphere. The fact that the particles repel each other makes $Q = \langle\hat{Q}\rangle < N$, the precise value depending on the angular distribution through δ and on the charge inside: $N+q$. One notes that the smaller the charge inside the more sensitive is Q to the angular distribution. Note that q is defined so that it is zero for the outermost shell in neutral atoms, positive for inner shells (d and f electrons) and positive ions, negative for negative ions. This implies neglect of penetration into the core, an obvious limitation of the present model.

3. Electrons on a Sphere of Small Radius; Hund's Rules

So far we have only discussed the potential energy operator for the electrons on the sphere. The kinetic energy operator is obtained from the usual expression in spherical polar coordinates by removing the derivatives with respect to r and is thus, in atomic units

$$\hat{T} = \frac{-1}{2r^2} \sum_{i=1}^{N} \left(\frac{1}{\sin^2 \theta_i} \frac{\partial^2}{\partial \varphi_i^2} + \frac{1}{\sin \theta_i} \frac{\partial}{\partial \theta_i} \sin \theta_i \frac{\partial}{\partial \theta_i} \right) = \frac{1}{2r^2} \sum_{1}^{N} \hat{l}_i^2 \tag{9}$$

where $\hat{l}_i$ is the orbital angular momentum operator for electron i. To solve the complete Schrödinger equation

$$\left[\frac{1}{2r^2} \sum_{i=1}^{N} \hat{l}_i^2 \left(\frac{\partial}{\partial \theta_i}, \frac{\partial}{\partial \varphi_i} \right) + \frac{1}{r} \sum_{i<j}^{N} \upsilon(\theta_{ij}) \right] \Psi = \left(E + \frac{(N+q)N}{r} \right) \Psi \tag{10}$$

($\cos \theta_{ij} = \cos \theta_i \cos \theta_j + \sin \theta_i \sin \theta_j \cos (\varphi_i - \varphi_j)$) for our model problem, exactly (analytically) is unfortunately not possible. The nature of the solutions is discussed further in the next section. (For the case of two particles see Ref. [10].) Here we make the usual assumption that the electron–electron repulsion can be treated as a first order perturbation and that therefore the eigen-states can be constructed as products of spherical harmonics, $Y_{lm}(\theta, \varphi)$, eigen-states of $\hat{l}^2$. Eigen-states of $\hat{S}_z$ (z-component of total spin) and $\hat{L}_z$ (z-component of total orbital angular momentum) with the correct permutational symmetry is then obtained as usual by multiplying each Y_{lm} with a spin-function (taken to be eigen-function of $\hat{s}_z$) and anti-symmetrizing over all electron coordinates. Expectation values of the operator $\hat{\delta}$ as defined in Eq. (6) over these Slater determinants can be obtained in exact algebraic form using well-known formulas and techniques from atomic multiplet theory as given by Condon and Shortley [11] or Slater [12]. In order to illustrate the connection between effective shell charge and the nodal structure of the angular wave-functions Tables 1 and 2 and Fig. 3 display such single determinant expectation values. The δ-values are calculated from the usual expression for the determinantal matrix-element of the two-particle operator $\hat{\delta}$, in terms of coulomb and exchange integrals. (For these one can then use the formulas (13–20) and (13–22) in Slater [12] with F^k and G^k equal to one.) The states of real atoms are, however, normally also eigen-states of $\hat{L}^2$ and $\hat{S}^2$ so linear combinations of such determinants that diagonalize these operators are physically more relevant. The relative δ-values for all such multiplets arising from shells containing only p or only d electrons are displayed in Figs. 1 and 2. (For energy level ordering only relative δ-values are of interest; these are easily generated using Slater [12] Appendix 21a putting $F^2 = F^4 = 1$.)

Since δ appears with negative sign in the effective shell charge formula (8) the smaller δ is the larger is the effective shell charge (this applies to real atoms only if q can be thought of as essentially constant). Therefore the relative ordering of the δ-values is the predicted ordering of the energy levels in the present scheme (this is further discussed below). As one sees in Figs. 1 and 2 Hund's rules correctly give the lowest levels in each of the six different cases and also a rough idea of the ordering in general. Note especially the rising trend with decreasing orbital angular momentum (to the right in the figures).

Table 1. δ-values for maximum spin single determinants corresponding to configurations l^n with $l = p, d, f$ and $S_z = n/2$ (symmetric spin function). All different determinants given except those that differ only in the sign of L_z. They are specified through the magnetic quantum numbers m of the included Y_{lm} except for d^3, f^5, and f^4 for which those of the $2l+1$ m-values not included are specified. Note that minimum δ always corresponds to maximum L_z for these completely antisymmetric angular functions (maximal number of Fermi-nodes)

$L_z = \sum m$	δ-values		m-values of spherical harmonics
	p^2		
1,0	0.80000		
	d^2	d^3	
3,2	0.81633	0.84354	1,2; 0,2
0	0.84354	0.85261	−1,1
1	0.87075	0.86168	−1,2
1	0.89796	0.87075	0,1
0	0.92517	0.87982	−2,2
	d^4		
2,1,0	0.85714		
	f^2	f^5	
5,4	0.84029	0.88179	2,3; 1,3
3,2	0.85566	0.88333	0,3; 0,2
3,2,0	0.87103	0.88487	1,2; −1,3; −1,1
1,1,0	0.91714	0.88948	−1,2; −2,3; −2,2
1	0.94788	0.89255	0,1
0	0.99400	0.89716	−3,3
	f^3	f^4	
6,5	0.85054	0.86847	1,2,3; 0,2,3
3	0.86079	0.87359	−1,1,3
4,1,0	0.87616	0.88128	−1,2,3; −2,0,3; −2,0,2
4	0.88128	0.88384	0,1,3
2,0	0.88640	0.88640	−1,1,2; −3,1,2
3,3,2,2	0.89153	0.88896	−2,2,3; −2,1,3; −1, 0,3; 0,1,2
1,1,0	0.90178	0.89409	−3,1,3; −2,1,2; −3,0,3
1	0.90690	0.89665	−1,0,2
2	0.91714	0.90177	−3,2,3
0	0.92227	0.90433	−1,0,1
	f^6		
3,2,1,0	0.88640		

Table 2. δ-values for $S_z = 0$ single determinants corresponding to configurations l^2 with $l = p, d, f$. All possible combinations of m quantum numbers listed. For notation see Table 1. Comparing with Table 1 one notes how the absence of the Fermi-nodes in the wave-functions given here increases the coulomb-repulsion significantly thereby decreasing the effective shell charge

$L_z = \sum m$	δ-values	m-values of spherical harmonics
	p^2	
1	0.92000	0,1
0	1.04000	−1,1
	d^2	
2	0.93197	0,2
3,1	0.95011	1,2; −1,2
1	0,98639	0,1
0	1.05669	−1,1
0	1.08390	−2,2
	f^2	
3	0.92492	0,3
4,2	0.93813	1,3; −1,3
2	0.97773	0,2
5,1	0.97990	2,3; −2,3
3,1	0.98135	1,2; −1,2
1	1.01809	0,1
0	1.04989	−2,2
0	1.07148	−1,1
0	1.11951	−3,3

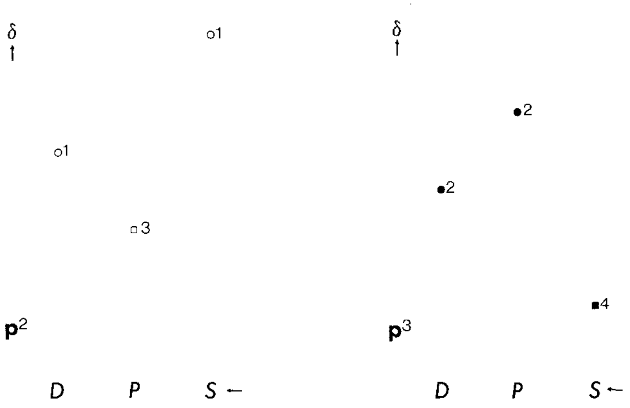

Fig. 1a,b. Energy ordering for multiplet levels of p-electrons as given by the effective shell charge concept. Shown are the relative δ-values for the states; the orbital angular momentum is indicated on the horizontal axis and increases to the left, the spin multiplicities, $2S+1$, are given explicitly at each state and are also distinguished by different symbols. Note that the pattern of levels for p^4 is the same as that for p^2 (this corresponds to two holes in the spherically symmetric shell p^6)

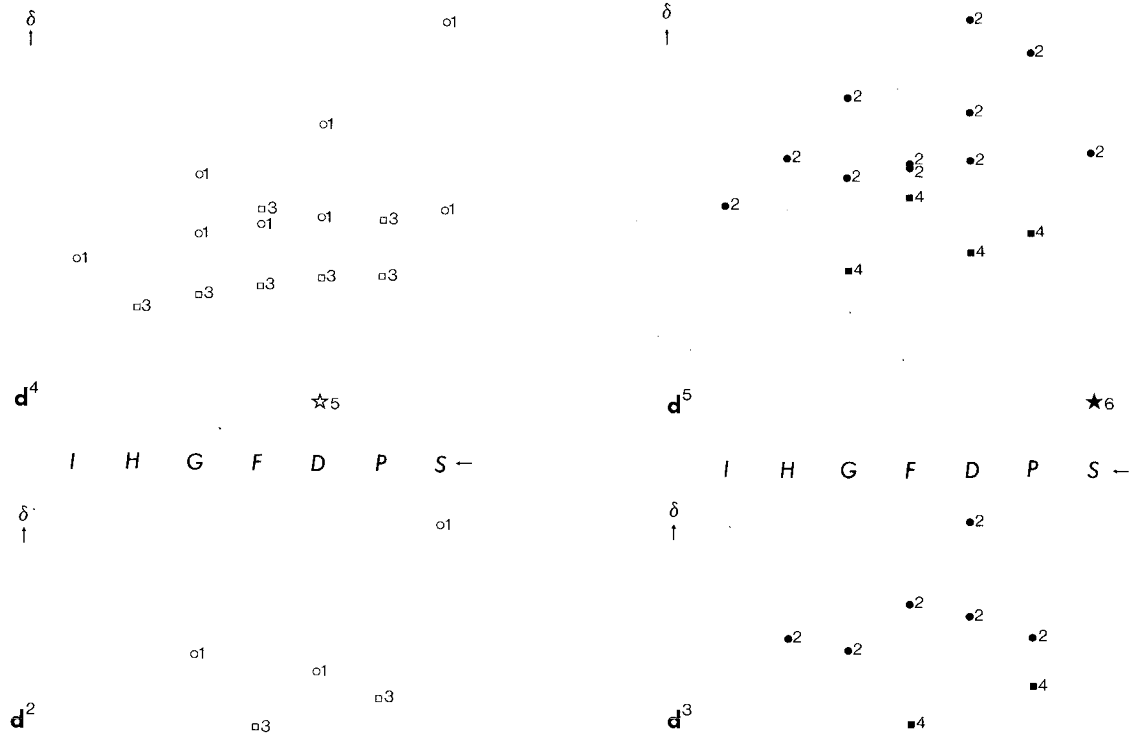

Fig. 2a–d. Same as Fig. 1 but for d-electrons. Recall that d^8, d^7 and d^6 have the same level patterns as d^2, d^3 and d^4 respectively. Note the general tendency of energy to increase with decreasing spin multiplicity and, for fixed spin, with decreasing angular momentum (i.e. to the right in the figure) though there are numerous exceptions. The values have been calculated from reference [12] Table A21a-1

It is important that one does not think of the radius r of the valence shell as the same for all levels in the multiplet. The valence shell is prevented from collapsing into the core region by the Pauli-principle (and/or centrifugal forces). When the shell charge increases the shell contracts against these forces and the kinetic energy goes up but the virial theorem ensures that the potential energy goes down twice as much. The net result is a contracted atom with lower energy. This point of view leads to a physical understanding of the radial scaling of Ref. [3].

4. Electrons on a Sphere of Large Radius; Negative Ions

As one can see in Eq. (8) the smaller q, the more important δ will be in determining the effective shell charge. I.e. neutral atoms and negative ions will be much more sensitive to the angular behavior of the wave-functions than positive ions. This conclusion can be made without any consideration of the radius of the valence shell sphere (it does not appear in the formula). However, this is not all.

As Eq. (10) shows, the radius r appears as a parameter in the Schrödinger equation for the shell electrons in such a way, that in the limit when r goes to zero the kinetic energy operator dominates completely. In this limit the solutions discussed in section 3 become exact. On the other hand, when r goes to infinity the potential energy operator becomes dominating and it is no longer meaningful to treat the two-particle operator as a perturbation as in the previous section. In this limit it is more consistent with standard quantum mechanical approximation methods to consider eigen-states of the potential energy operator as approximate energy eigen-states.[1]

It is a well known experimental fact that negative ions are big. One can therefore predict that uncorrelated wave-functions (Slater determinants of spherical harmonics) do not describe the angular motion in the outer shell of negative ions or large radius atoms particularly well. Eq. (10) leads one to believe that eigen-states of the $\hat{\delta}$-operator might be better zeroth order approximations to the energy eigen-states in these situations, the one-electron operators now acting as perturbations. The eigen-states of $\hat{\delta}$ are states corresponding to definite geometric arrangements of the particles (or to be more precise, of the centers of charge of non-overlapping spherical particle distributions) on the sphere and there will be a continuum of such states (depending on $2N-3$ parameters). Among these the only ones of special interest are those that minimize δ. The bottom curve in Fig. 3 shows δ-values for such states; they correspond to the well known geometries: two antipodal particles, equilateral triangle, tetrahedron etc. Note that it is not necessary for the particles to be localized to points (this would correspond to infinite kinetic energy) to make δ minimum. As already

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[1] In this case the wave-function (probability amplitude) will depend mainly on the relative coordinates, θ_{ij}, of the particles; the dependence of the positions, θ_i, φ_i, themselves will be a second order effect. In Ref. [10] results are presented for two different sphere radii and the increase in angular correlation with sphere radius is clearly visible

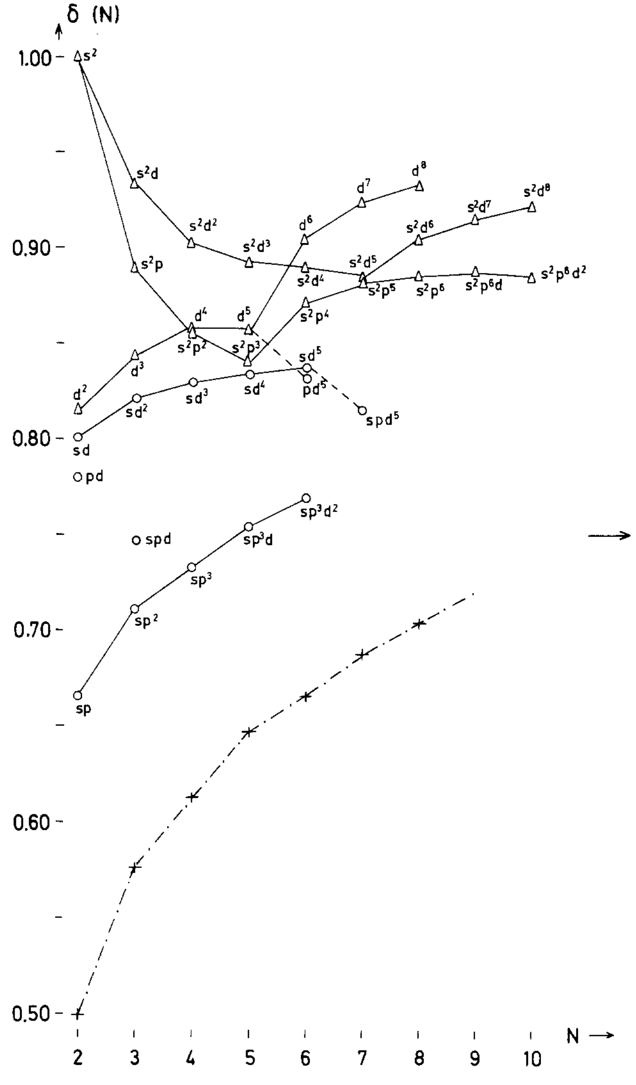

Fig. 3. δ-values for single determinants that maximize S_z and then L_z (thus estimating the lowest multiplet without diagonalization). The number of electrons, N, is given on the horizontal axis. The curves indicate successive addition of electrons to a shell. Crosses on the lowest (dot–dash) curve correspond to minimum δ-values for fixed geometry eigen-states of $\hat{\delta}$; these are: an antipodal pair, and equilateral triangle, a tetrahedron, a trigonal bi-pyramid, an octahedron, a pentagonal bi-pyramid, and an anti-prism. The large N limit of this curve is 3/4. Note the minimum in the s^2p^n-curve at s^2p^3 which coincides with a maximum in the ionization-potentials at the corresponding atoms. Note also the considerable reduction in going from the gound state, s^2p^2, of Carbon to the sp^3 "tetrahedral" valence state and the even more dramatic reduction in going from s^2 to sp, the configuration of the outer shell of the negative Helium ion [22] ($1s2s2p$, ^4P)

mentioned, particles having spherical non-overlapping probability distributions will make up eigen-states of $\hat{\delta}$.

I will now consider the question: how negative can an atomic ion get? The discussion will be purely electrostatic and will reveal some rather fundamental mathematical properties of the Coulomb interaction. It is possible that they are of small practical significance but the fact that they have hitherto been largely ignored in literature is by no means a guarantee that this is the case. It is probably safe to say that ions of charge less than -1 will never be stable with respect to the emission of an electron to infinity but, as the argument below indicates, shortlived species of multiple negative charge should exist. Assume a core of net charge $+1$ $(=N+q)$ and thus insert in Eq. (8)

$$q = 1 - N. \tag{11}$$

If one now increases N (the number of particles in the shell outside the core), the effective shell charge must eventually change sign. This means that there is no longer a net attraction of the shell to the unit charge at the center; the electron–electron repulsions dominate and such a system would dissociate. At what N-value does this happen? If one successively inserts $N = 1, 2, \ldots$ and the corresponding minimum δ-value (corresponding to the most favorable geometric arrangement of the electrons on the sphere) from the bottom curve in Fig. 3 in the effective shell charge formula

$$Q = N[1-(N-1)\delta/2] \tag{12}$$

one finds that the limit N is four. I.e. for $N > 4$ Q will always be negative but a single proton (for example) can attract four electrons to make a triply charged negative ion as long as the geometry is favorable. What happens if one inserts some large core charge $C = N + q$ in (8)? The limiting minimum δ-value for large N is (Fig. 3) 0.75 so one finds that now the sign change in Q comes when

$$N = (8/3)C \tag{13}$$

which means that e.g. a core of charge $C = 10$ can attract a sphere with $N = 26$ electrons. These numbers may be of some relevance in plasma physics but give, as already mentioned, only crude estimates since the kinetic energy has been completely ignored. They also illustrate how dramatic correlation effects can get, albeit under rather unlikely circumstances.

5. A General Mechanism for Energy Reduction in Many Electron Systems; the Chemical Bond

There is a fair amount of literature on the precise physical mechanism behind the energy reduction in chemical bonding. Here I only wish to briefly point out how the concepts and points of view of this paper have some relevance also to this problem. Of central importance is the virial theorem $2\langle T\rangle = -\langle V\rangle$ which is valid for the electronic energy in the separated atoms as well as at the equilibrium geometry in the molecule. As a consequence any net energy reduction must come in the form of potenital energy and the kinetic energy must increase by half the same amount. The following view of the mechanism behind the energy reduction in (covalent) bonds between open shell atoms is consistent with these facts: the tendency, summarized by Hund's rules, of open shell atoms to maximally break the approximate spherical symmetry is strongly enhanced by the fact that the effective field for the valence electrons ceases to be spherically symmetric when bonding takes place. This presumably leads to a further increase in effective shell charge which, in turn, enables the atom to contract and shift charge density nearer the nucleus as discussed at the end of section 3. The absolute value of the electron-nuclear attraction energy thus increases and the total energy goes down. The detailed behavior of the charge density in bonding can be rather complicated (see Bader [13] for a review) but on the whole it seems to be consistent with this point of view.

It is also tempting to see part of the explanation for the success of the valence shell electron pair repulsion theory (VSEPR) in Fig. 3. This theory predicts equilibrium geometries of molecules (see Gillespie [14]) and, in this context, it is significant that it is always the electrostatically favorable arrangements that maximize the effective shell charge of the valence shell.

6. Discussion and Conclusions

Though the specific model problem of electrons on a sphere only has been treated before, as far as I am aware, in Ref. [10], many others have studied atoms along similar lines. The effective shell charge concept is distinct from but, of course, related to concepts that go under names such as screening, shielding or effective (core) charge and that have been useful tools since the beginning of atomic physics. In recent times there has been an increased interest in this type of ideas in connection with the HAM-method of Åsbrink et al. [15] and with the work of Kregar [16] and Kregar and Weisskopf [17]. A very complete collection of atomic shielding efficiencies have recently been compiled by Åsbrink [18]. The main objective in these studies is to solve the radial problem i.e. to find the optimal exponents in Slater type one electron functions, and in this they differ fundamentally from the present study.

For the radial behavior of atoms there have long existed various simple models, especially the celebrated Thomas–Fermi approximation which, properly handled, can reproduce the trends of increasing radii and decreasing ionization potentials through the periodic table quite well [19] (in this connection see also Rau et al. [20]). The weakness of all such models is that they are usually quite unable to take account of the pronounced shell structure of atoms. This article attempts to remedy this by presenting a model which has the shell structure as its starting point and basic assumption. *Ab initio* calculations are today capable of reproducing most experimental facts about atoms but this does not mean that one can do away with the profound understanding of the underlying physics that always comes from the simplest models and approximations.

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