CHAPTER 1

PROBABILITY DISTRIBUTIONS AND VALENCE SHELLS IN ATOMS

Andreas Savin
Laboratoire de Chimie Théorique
CNRS et Université Pierre et Marie Curie
4, place Jussieu, F–75252 Paris
E-mail: savin@lct.jussieu.fr

Formulas for the probabilities of finding ν electrons in an arbitrarily chosen volume, Ω are presented, and computed for Hartree–Fock atoms. Maximizing the difference between the Hartree–Fock and independent particle model probabilities (originating in the Pauli principle), provides a good indicator for a spatial separation of the valence shell in atoms, from Li to Xe.

Contents

1. Introduction

In order to recover chemical information, the molecular space is often divided into significant regions. Politzer and Parr [1] considered the use of the minima of the radial density, $4\pi r^2\rho(r)$, to define a meaningful boundary surface separating the core and valence regions of atoms. Of course, this choice is not unique. It is possible to define boundaries differently using the same function [2], or using the different functions. Examples are the loges of Daudel and co-workers (see, e.g., [3] and references therein), the atomic basins of Bader and co-workers, the basins of the laplacian of the electron density (see, e.g., [4] and references therein), or basins of the electron localization function (ELF) [5,6]. The population of a spatial region is given by the integral of the electron density over it. (see, e.g., [4]. This can be written also as the expectation value of the operator:

$$\hat{\mathbf{N}}_\Omega = \sum_{i=1,N} \hat{N}_\Omega(\mathbf{r_i}) \tag{1}$$

where N is the total number of electrons in the system, Ω the considered spatial region, and $\hat{N}_\Omega(\mathbf{r}_i)$ is 1 when electron i is in Ω and 0 otherwise(see, e.g., [7]). Of course, the population is only an average number, as $\hat{\mathbf{N}}_\Omega$, does not commute with the hamiltonian. In fact, the variance (or fluctuation in the average population of the region Ω)[7,8],

$$\sigma^2 = \langle \hat{\mathbf{N}}_\Omega^2 \rangle - \langle \hat{\mathbf{N}}_\Omega \rangle^2$$

turns out to be quite large with respect to $\langle \hat{\mathbf{N}}_\Omega \rangle$. For example, in the hydrogen molecule, at equilibrium distance, the atomic basins (the regions left and right of the median plane) have each a population of 1, while σ is close to 2/3. This is due to the fact that in any of the two regions there is a finite probability to find 0 or 2 electrons.

It may thus be of interest to get the underlying information, namely the probability of finding ν electrons in a region of space Ω, $p(\nu, \Omega)$. (In order to simplify notation, the variable Ω will be omitted below: $p(\nu, \Omega) = p(\nu)$.) Consider, e.g., two hydrogen atoms at infinite inter-nuclear separation. The average number of electrons, on each atom, is equal to 1, both for the ground state (two H atoms), and for the ionic state (one H^+ and one H^-). The probabilities are however different: in the first case, $p(0) = p(2) = 0, p(1) = 1$, while in the second case, $p(0) = p(2) = 1/2, p(1) = 0$.

The present paper will show in its first part that it is often not difficult to obtain the probabilities $p(\nu)$. Next, these will be used to produce a division of space, by underlying the 'specificity' of the system, in the sense that $p(\nu)$ maximally differs one which could be obtained by considering that the particles were independent, but yielding the same $\langle \hat{\mathbf{N}}_\Omega \rangle$.

As an application, the valence shell of the atoms, from Li to Xe will be considered, in the Hartree–Fock approximation. This is not a trivial task, as for heavier atoms, some of the spatial indicators like the laplacian of the density, do not yield shell separators [9,10,11], while others, like the electron localization function may sometimes yield an average number of valence shell electrons which significantly differs from the one expected from the orbital occupation [12]. (The radial density itself can be produce either of these cases, depending on the criterion used (see, e.g., [13], or [2].)

2. The probabilities of having ν electrons in the spatial region Ω

The probability of finding electrons $1, 2, \ldots, \nu$ in the spatial region Ω, and electrons $\nu+1, \ldots, N$ outside it (in $\bar{\Omega}$), is given by:

$$\int_{\Omega} d1d2\ldots d\nu \int_{\bar{\Omega}} d\nu+1\ldots dN \mid \Psi \mid^2$$

where $\int_{\Omega}$ means that the integration is performed only within Ω, the 'integration' over all spins is implicitly assumed, and Ψ is the N-electron wave function. As the electrons are indistinguishable, the probability $p(\nu)$ of having ν electrons in the spatial region Ω is given by:

$$p(\nu) = \binom{N}{\nu} \int_{\Omega} d1d2\ldots d\nu \int_{\bar{\Omega}} d\nu+1\ldots dN \mid \Psi \mid^2 \tag{2}$$

The probabilities $p(\nu)$ can be also expressed in terms of the m-th order reduced density matrices, $\Gamma^{(m)}$ (see, e.g., [15], and references therein):

$$p(\nu) = \frac{1}{\nu!} \sum_{i=0,N-\nu} \frac{(-1)^i}{i!} \int_{\Omega} \Gamma^{(\nu+i)} \tag{3}$$

The integral on the r.h.s. is over all variables appearing in Γ. The reduced density matrices used in this paper are defined using the McWeeny normalization (see, e.g., [14]):

$$\Gamma^{(m)} = \frac{N!}{(N-m)!} \int |\Psi|^2 d\mathbf{r}_{m+1} \cdots d\mathbf{r}_N \tag{4}$$

($0 \le m < N$; for $m = N$, no integration is performed). $\int_{\Omega} \Gamma^{(m)}$ gives - up to the normalization prefactor - the probability of finding m electrons in Ω, no matter where the other $N-m$ are. It thus has contributions from the situations where $m' > m$ electrons are in Ω. In order to obtain the probability of having exactly m electrons in Ω, one has to eliminate the contributions coming from having more than m electrons in Ω, which is done by linearly combining $\Gamma^{(m)}$ with $\Gamma^{(m')}$, $m' > m$ yielding Eq. 3. An example is given in the appendix.

A third formula for the $p(\nu)$ can be obtained by considering $\langle \hat{\mathbf{N}}_\Omega^m \rangle$ with $0 \leq m \leq N$. If these are known, the following system of equations can be solved for the $p(\nu)$ (cf., e.g., [16,17]):

$$\langle \hat{\mathbf{N}}_\Omega^m \rangle = \sum_{\nu=0,N} p(\nu)\nu^m \tag{5}$$

An example will be again given in the appendix.

3. The probabilities for single determinant wave functions

When the wave function is approximated by a single Slater determinant one can of course use Eq 2. One can also generate the probabilities by using the integrals

$$\omega_{ij} = \int_\Omega \phi_i \phi_j \tag{6}$$

where $0 \leq i, j \leq N$ and ϕ_i are spin-orbitals. One way to see it, is to realize that the product of two determinants, is equal to the determinant of the product matrix, which has, in our case (of the square of the Slater determinant), the elements:

$$\sum_{k=1}^{N} \phi_i(k)\phi_j(k)$$

(The normalization factor $1/N!$ has been intentionally left out here for the sake of clarity.) The determinant can be now expanded into a sum of determinants:

$$\begin{vmatrix} \phi_1(k_1)\phi_1(k_1) & \phi_1(k_2)\phi_2(k_2) & \dots \\ \phi_2(k_1)\phi_1(k_1) & \phi_2(k_2)\phi_2(k_2) & \dots \\ \dots & \dots & \dots \end{vmatrix}$$

in which $k_1, k_2, \dots$ take any values between 1 and N. Notice, however, that if any two of the k_i are identical, the determinant vanishes:

$$\begin{vmatrix} \phi_1(k)\phi_1(k) & \phi_1(k)\phi_2(k) & \dots \\ \phi_2(k)\phi_1(k) & \phi_2(k)\phi_2(k) & \dots \\ \phi_3(k)\phi_1(k) & \phi_3(k)\phi_2(k) & \dots \\ \dots & \dots & \dots \end{vmatrix} = \phi_1(k)\phi_2(k) \begin{vmatrix} \phi_1(k) & \phi_1(k) & \dots \\ \phi_2(k) & \phi_2(k) & \dots \\ \phi_3(k) & \phi_3(k) & \dots \\ \dots & \dots & \dots \end{vmatrix} = 0$$

Thus, only the $N!$ determinants will be left, in which the $k_1, \ldots k_N$ are different. The integration over each of the variables in Eq. 2 can now be performed over each of the $\phi_i(k)\phi_j(k)$ which appear when expanding the determinant. Remember that two types of integrals are present, over Ω, when $k \leq \nu$, and over $\bar{\Omega}$, when $k > \nu$. The former yields ω_{ij}, of Eq. 6, while the latter is given by $\delta_{ij} - \omega_{ij}$, due to the orthonormalization of the spin-orbitals. In order to condensate the information, we can write again the determinants, in which each product $\phi_i(k)\phi_j(k)$ has been replaced by ω_{ij}, for $1 \leq k \leq \nu$, and by $\delta_{ij} - \omega_{ij}$ for $\nu \leq k \leq N$. In short, in order to obtain $p(\nu)$, one sums up all the determinants of the matrices having ν columns (or lines) ω_{ij}, and $N - \nu$ columns (lines) $\delta_{ij} - \omega_{ij}$. This method may be convenient to use when $p(\nu)$ is needed when ν is small or close to N.

Another way to obtain the $p(\nu)$ is to use Eq. 3. As it contains higher-order reduced density matrices, this evaluation of the $p(\nu)$ seems tedious. In fact, it reduces to an expression in which the matrix S_Ω (having elements ω_{ij}) is taken to some power ($\leq m$):

$$\int_\Omega \Gamma^{(m)} = \sum_\alpha c_\alpha (TrS_\Omega^{m_1})(TrS_\Omega^{m_2})\ldots \quad (single\ determinant\ \Psi) \tag{7}$$

where Tr means the trace of a matrix, and α is any set of numbers, $m_1, m_2, \ldots$, which sum up to m, $m_1 + m_2 + \ldots = m$ (the partitions of m). The coefficients c_α can be determined from combinatorial considerations. For a given partition $\alpha = (m; m_1, m_2, \ldots, m_\tau)$, they are given by:

$$c_\alpha = (-1)^{\sum_{j,even} t_j} \frac{m!}{m_1 m_2 \ldots m_\tau} \frac{1}{t_1! t_2! \ldots t_N!} \tag{8}$$

where t_j is the number of times the integer j appears in the list $\{m_1, m_2, \ldots, m_\tau\}$. All terms c_α can be generated with a few lines of Mathematica code[18].

Eq. 7 appears in the following way: For a single determinant wave function, $\Gamma^{(m)} = \det G$, where the matrix G has elements (see, e.g., [14]):

$$G_{pq} = \sum_{i=1,N} \phi_i(x_p)\phi_i(x_q) \tag{9}$$

When expanding the determinant into a sum of products, each product shows terms of the type $\phi_i(x_q)\phi_j(x_q)$, each x_q appearing twice. Integration over all x_q yields sums of products of terms ω_{ij}. (For more details, see the example given in the appendix.)

A reduction of the size of the matrices S_Ω is achieved by taking care of spin or spatial degeneracy, which gives a factor equal to the degree of degeneracy in front of each Tr.

The number presented in this paper were produced using Eqs. 3 and 7. For numerical convenience, two limits were imposed in the present calculation:

- A grid was constructed to explore the inner/outer region in the atoms: the step size was uniformly taken as 0.02 bohr, and it was considered that $r = 10$ bohr is sufficiently large to consider that there are practically no electrons beyond it.
- All $p(\nu > 24)$ were set to zero. Of course, this approximation was made due to the rapidly increasing number of partitions with N. Using the approximation allows to use the formula for $N \leq 24$, cf. Eq. 3. The approximation can be justified, however, by the nature of the $p(\nu)$ which show vanishingly small values except in the regions around the maxima (see below). As our interest lies in detecting the valence shell ($0 \leq \nu \leq 8$), tests have shown that taking 24 as an upper limit seems quite safe.

Figure 1 shows a typical plot of the $p(\nu)$, as obtained for the Mg atom. (This kind of plots can be found in literature, e.g., in [4].) It shows the probability of finding ν electrons beyond the radius, r, given as the abscissa. The curve approaching 1, as r gets large, is of course, that of $p(0)$; as r gets larger, the probability to find an electron beyond r goes to zero. Near to the origin, another curve tends to 1; this is that corresponding to $p(N)$: Ω becomes the whole space, and we become sure to find all N electrons in it. In between, the curves of $p(\nu)$, $(0 < \nu < N)$ raise and then fall with increasing r. It is conspicuous that two maxima are more pronounced in our example of Mg: they correspond of $\nu = 2$, and of $\nu = 10$. Of course, this can be related to the shell structure of Mg: $\nu = 2$ corresponds to the valence shell, and $\nu = 10$ corresponds to the two outermost shells.

For the sake of clarity, the plots given in Fig. 1 can be simplified, by showing just the positions of the maxima of $p(\nu)$, r_p, and the values of $p(\nu)$ at these positions (cf. Fig. 2).

Plots were performed for all atoms, from Li to Xe, using the atomic near Hartree–Fock wave functions (using Slater type function basis sets) of Bunge et al. [19]. All plots are available on the web site.[20] They essentially

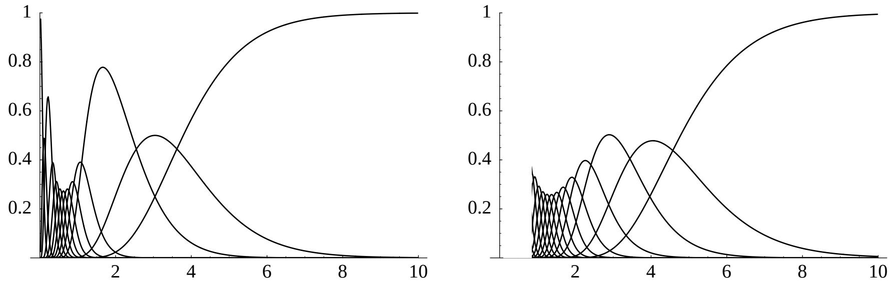

Fig. 1. Probabilities $p(\nu)$ of having ν electrons in a spherical shell, beyond r, as a function of r, for $\nu = 0, 1, \ldots$, in Mg (left), and Zr(right). In each of the plots, the maxima of the curves can be used to attribute the curves to ν, the one having the outermost maximum, at 1, corresponding to $\nu = 0$. From right to left, the curves pertain to $\nu = 1, 2, \ldots$. The numerically unsafe region (at small r) is not shown for Zr.

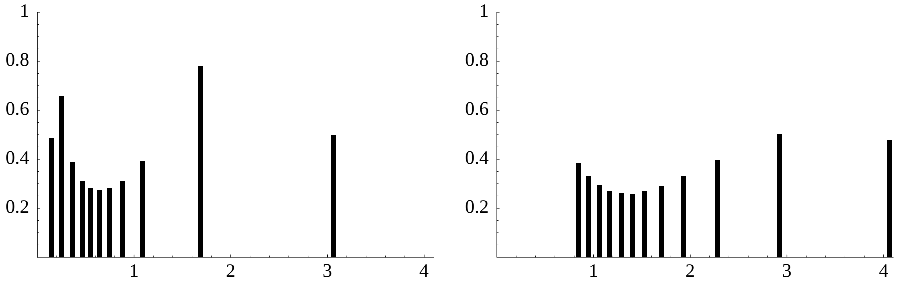

Fig. 2. The positions of the bars show the radius r_p of the spherical shell for which the probabilities of having ν electrons is maximal, for Mg(left) and Zr (right). The height of the bars indicate the values of $p(\nu)$ at these points. The last bar on the right corresponds to $\nu = 1$. The values for larger ν follow from right to left.

show the same features as the ones discussed for the Mg atom. For heavier atoms, however, the maxima of $p(N_{val})$, N_{val} being the number of valence shell electrons, are less pronounced (see Figs. 1, 2). In particular, $p(1) \approx p(2)$, for Zr, but also for other elements, like Cd.

It may be worth mentioning the relationship between $p(\nu)$ and and the radial density, mentioned in the introduction. To this end, we will not consider Ω as the region outside a sphere of radius r, but a spherical shells of radius r and of infinitesimal thickness, δr. For such an Ω, $\Gamma^{(m)}$ (Eq. 3) can be expanded in a Taylor series around the reference position. When considering only the leading terms to order ν, all integrals involving $\Gamma^{(m)}$, with $m > \nu$ will become negligible, because an m-fold integration is required, and each integration introduces a term proportional to δr. From Eq. 3 it follows that all $p(m > \nu)$ will become negligible, too. For example, to first order in the thickness of the spherical shell, δr: $p(0) = 1 - p(1) + \ldots$, $p(1) = 4\pi r^2 \rho(r)\delta r + \ldots$, $p(\nu > 1) = 0 + \ldots$. One thus recovers the expected connection between the radial density and the probabilities of finding electrons on spherical sheets.

One can extend this picture to molecules: one may look at surfaces of constant density ρ. The formula is similar to that of the one above, where $4\pi r^2 \rho(r)$ has been generalized to the product of the density on this surface (ρ) multiplied by the area of the surface $A(\rho)$. Searching the maxima of $A(\rho)\rho$ (by changing ρ) is analogous to the search of the maximum of the radial density in atoms (which gives, e.g., the Bohr radius for the hydrogen).

It may be worth mentioning that such considerations can be applied in order to define ELF (by considering the probabilities of having two pair of electrons in the same small region of space).

4. Detection of the valence shell in atoms

A simple way to define the valence region of the atom is to simply find the radius, $r(N_{val})$, beyond which the electron density, ρ, integrates to the number of electrons which is attributed to the outer shell, N_{val}: (see, e.g., [2], cf. Table 1):

$$N_{val} = \int_{r(N_{val})}^{\infty} \rho \tag{10}$$

The maximum of $p(\nu = N_{val})$ is at r_p which normally is not at $r(N_{val})$. The values of r_p are given in Table 1, while those for $\langle \hat{\mathbf{N}}_\Omega \rangle$, with Ω being the spherical shell beyond r_p, are given in Table 2. One notices that r_p lies at a value which is higher than r_N (by a few per cent). Correspondingly, the average number of electrons outside the sphere with radius r_p is lower than N_{val}.

One would like, however, to be able to define the valence shell without a preliminary knowledge of N_{val}. It is tempting to choose the separating surface in such a way that the relative fluctuation (see, e.g., [8,21])

$$\lambda = \frac{\langle \hat{\mathbf{N}}_\Omega^2 \rangle - \langle \hat{\mathbf{N}}_\Omega \rangle^2}{\langle \hat{\mathbf{N}}_\Omega \rangle} \tag{11}$$

is minimal. With this definition, only the reduced density matrices up to second order would be needed. Two plots, for Mg and Zr, are shown in Fig. 3. This criterion works nicely for light elements, but for transition metals the results are not always good. (cf. Table 1, 2). The integral over the density beyond the outer radius minimizing the relative fluctuation, r_λ, does not yield a good value for, e.g., Zr (2.6 instead of 2); λ only shows a shoulder, and thus does not produce a separation for the valence shell of Nb or Mo.

Table 1: Radius of the sphere defining the separation between valence and core, from $\int_r \rho = N_{val}$, $r(N_{val})$; the position of the maxima of the probabilities $p(N_{val})$, r_p; that of the minima of the relative fluctuations λ, r_λ; and the maximal deviation of $p(\nu)$ from the binomial distribution, r_Δ.

	$r(N_{val})$	r_p	r_λ	r_Δ
Li	1.53	1.57	1.56	1.57
Be	0.99	1.00	0.99	1.00
B	0.70	0.72	0.71	0.72
C	0.54	0.55	0.54	0.55
N	0.43	0.44	0.43	0.44
O	0.36	0.37	0.35	0.37
F	0.31	0.31	0.30	0.31
Ne	0.27	0.27	0.25	0.27
Na	2.13	2.20	2.19	2.21
Mg	1.63	1.66	1.65	1.66
Al	1.35	1.38	1.37	1.38
Si	1.16	1.17	1.16	1.17
P	1.01	1.02	1.01	1.02
S	0.89	0.90	0.89	0.90
Cl	0.80	0.80	0.79	0.80
Ar	0.72	0.73	0.72	0.73
K	3.06	3.16	3.15	3.18

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	$r(N_{val})$	r_p	r_λ	r_Δ
Ca	2.45	2.49	2.47	2.50
Sc	2.46	2.47	2.32	2.47
Ti	2.40	2.40	2.24	2.40
V	2.33	2.33	2.17	2.33
Cr	2.80	2.81	2.35	2.81
Mn	2.18	2.20	2.06	2.20
Fe	2.13	2.14	2.00	2.15
Co	2.08	2.09	1.95	2.09
Ni	2.02	2.04	1.90	2.04
Cu	2.45	2.49	2.27	2.51
Zn	1.92	1.94	1.82	1.94
Ga	1.66	1.67	1.62	1.67
Ge	1.47	1.48	1.44	1.48
As	1.33	1.33	1.30	1.33
Se	1.21	1.22	1.19	1.22
Br	1.12	1.12	1.09	1.12
Kr	1.04	1.04	1.01	1.04
Rb	3.46	3.57	3.55	3.58
Sr	2.83	2.88	2.85	2.89
Y	2.94	2.94	2.58	2.94
Zr	2.89	2.89	2.46	2.89
Nb	3.42	3.42	∞	3.43
Mo	3.26	3.28	∞	3.30
Tc	2.65	2.66	2.36	2.67
Ru	3.08	3.12	2.44	3.15
Rh	2.99	3.04	2.61	3.08
Pd	∞	∞	∞	∞
Ag	2.83	2.90	2.71	2.94
Cd	2.32	2.35	2.20	2.36
In	2.06	2.08	2.02	2.08
Sn	1.87	1.88	1.82	1.88
Sb	1.71	1.72	1.67	1.72
Te	1.59	1.59	1.54	1.59
I	1.48	1.49	1.44	1.49

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	$r(N_{val})$	r_p	r_λ	r_Δ
Xe	1.39	1.40	1.34	1.40

Table 2: Valence electron numbers, as given by the occupation of Hartree–Fock valence orbitals,N_{val}, and by $\int_r \rho$, where r is given by the maxima of the probabilities $p(N_{val})$, $N(r_p)$; the minima of the relative fluctuations λ, $N(r_\lambda)$; and the maximal deviation of $p(\nu)$ from the binomial distribution, $N(r_\Delta)$.

	N_{val}	$N(r_p)$	$N(r_\lambda)$	$N(r_\Delta)$
Li	1	0.99	0.99	0.99
Be	2	1.99	2.00	1.99
B	3	2.98	3.00	2.98
C	4	3.98	4.00	3.98
N	5	4.98	5.01	4.97
O	6	5.97	6.03	5.97
F	7	6.97	7.05	6.97
Ne	8	7.98	8.08	7.97
Na	1	0.97	0.98	0.97
Mg	2	1.97	1.98	1.97
Al	3	2.97	2.98	2.97
Si	4	3.97	3.99	3.97
P	5	4.97	5.00	4.97
S	6	5.98	6.01	5.97
Cl	7	6.98	7.01	6.98
Ar	8	7.98	8.02	7.98
K	1	0.96	0.97	0.96
Ca	2	1.96	1.98	1.96
Sc	2	2.00	2.15	1.99
Ti	2	2.00	2.19	2.00
V	2	1.99	2.20	1.99
Cr	1	0.99	1.40	0.99
Mn	2	1.98	2.18	1.98
Fe	2	1.99	2.20	1.98
Co	2	1.98	2.21	1.98

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	N_{val}	$N(r_p)$	$N(r_\lambda)$	$N(r_\Delta)$
Ni	2	1.98	2.21	1.98
Cu	1	0.97	1.17	0.96
Zn	2	1.98	2.19	1.97
Ga	3	2.98	3.09	2.97
Ge	4	3.98	4.09	3.98
As	5	4.98	5.10	4.98
Se	6	5.98	6.12	5.98
Br	7	6.99	7.14	6.99
Kr	8	7.99	8.16	7.99
Rb	1	0.96	0.96	0.95
Sr	2	1.95	1.99	1.95
Y	2	2.00	2.41	2.00
Zr	2	2.00	2.60	2.00
Nb	1	1.00	0	0.99
Mo	1	0.98	0	0.97
Tc	2	1.97	2.49	1.96
Ru	1	0.97	1.83	0.94
Rh	1	0.96	1.42	0.93
Pd	0	0	0	0
Ag	1	0.95	1.13	0.91
Cd	2	1.95	2.24	1.93
In	3	2.96	3.11	2.95
Sn	4	3.96	4.14	3.96
Sb	5	4.97	5.20	4.97
Te	6	5.98	6.24	5.97
I	7	6.98	7.29	6.98
Xe	8	7.98	8.34	7.98

The results obtained from finding the minima of the variance σ^2 are not encouraging either: although the numbers are good for the light elements, they do not yield the valence shell for Cr-Zn and Zr-In. The numbers are not shown in the tables for this reason.

Let us now consider using the all the $p(\nu)$. One can try to use the loges, defined by finding the minimum of the 'missing information function' (see,

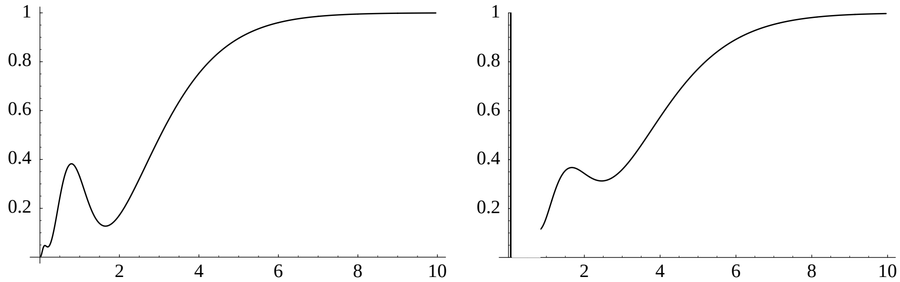

Fig. 3. The relative fluctuation, λ, for a spherical region beyond r, as a function of r, in Mg (left), and Zr(right). The numerically unsafe region (at small r) is not shown for Zr.

e.g., ^{3}):

$$-\sum_{\nu=0,N} p(\nu)\log_2 p(\nu)$$

It turns out, however, that for some heavier elements, the minimum transforms into a shoulder, as it did in some cases for the fluctuation λ.

We will now show that a comparison with a model of independent particles provides a useful criterion to generate the spatial separation of the valence shells in the atoms Li to Xe. First, notice that the main features of the $p(\nu)$ (cf. Figure 1, from left to right: decrease in $p(N)$ and increase in $p(0)$; $p(\nu)$, for $0 < \nu < N$ vanishes at both at zero and infinity, and is positive in-between) are independent of the specificity of the probability distribution. Let us imagine for a moment, that electrons were independent. Let us denote p_{bin} the probability of finding such an independent particle in Ω. The probability to find the independent, indistinguishable particles $1, 2, \ldots, \nu$ in Ω and $\nu+1, \nu+2, \ldots N$ outside it is given by:

$$p_{bin}^{\nu}(1-p_{bin})^{N-\nu}$$

The probability to find ν independent, indistinguishable particles in Ω, and $N-\nu$ outside it is thus:

$$p_{indep}(\nu) = \frac{N!}{(N-\nu)!\nu!}p_{bin}^{\nu}(1-p_{bin})^{N-\nu}$$

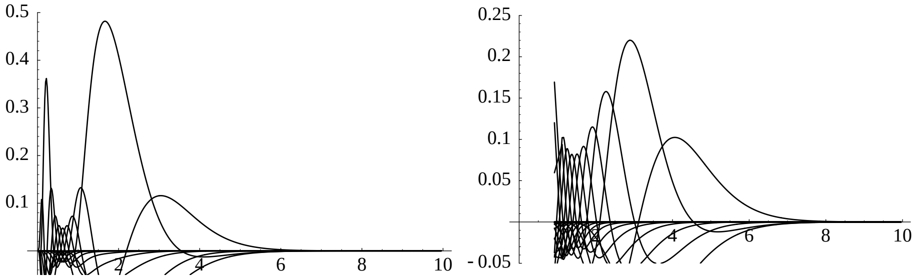

Fig. 4. Difference between the probabilities $p(\nu)$ of having ν electrons in a spherical shell, beyond r, and those obtained from a binomial distribution, as a function of r, in Mg (left), and Zr(right). The numerically unsafe region (at small r) is not shown for Zr.

This is nothing but the binomial distribution (cf., e.g., [22]). For it, p_{bin} is related to the average number of particles in Ω:

$$\sum \nu p_{indep}(\nu) = N p_{bin}$$

In order to emphasize the valence shell structure using the $p(\nu)$, it seems convenient to consider the difference between the real probabilities, $p(\nu)$, and the probabilities obtained assuming that the electrons were independent, $p_{indep}(\nu)$:

$$\Delta(\nu) = p(\nu) - p_{indep}(\nu)$$

The parameter p_{bin} can be fixed by the requirement that the average number of particles in Ω is the same in the real and in the fictitious system:

$$\langle \hat{\mathbf{N}}_\Omega \rangle = N p_{bin}$$

Of course, the difference between $p(\nu)$ and $p_{indep}(\nu)$ arises at Hartree–Fock level, due to the Pauli principle. In Fig. 4, $\Delta(\nu)$ is plotted as a function r. As before, we simplify the figure by showing, for each ν, a bar, having the height of the function (now $\Delta(\nu)$), at point r (now r_Δ) where its maximum is reached (Fig. 5). In order to choose a ν, we will take those which correspond to local maxima in ν. For Mg, two maxima are present: one at $\nu = 2$, corresponding to its valence shell, and the other at $\nu = 10$, corresponding to the two outermost shells of the atom. Please notice in Zr, given as another example in Fig. 4, how Δ accentuates the difference between the peek at $\nu = 2$ and $\nu = 1$ (cf. Fig. 2).

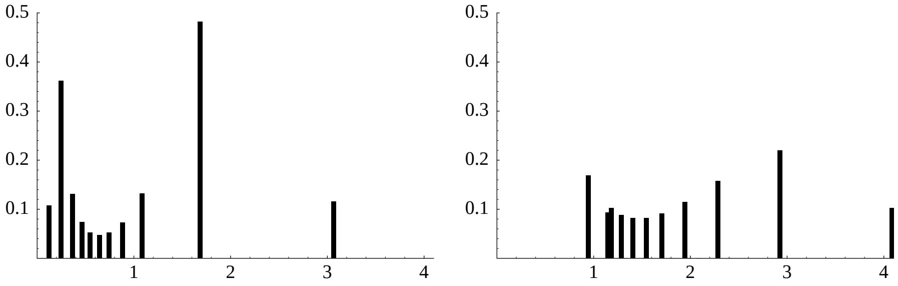

Fig. 5. The positions of the bars show the radius r_Δ of the spherical shell for which the difference $\Delta(\nu)$ between the probabilities $p(\nu)$ of having ν electrons and the probabilities of having ν fictitious independent particles, $p_{indep}(\nu)$ is maximal, for Mg(left) and Zr (right). The height of the bars indicate the values of $\Delta(\nu)$ at these points. The last bar on the right corresponds to $\nu = 1$. The values for larger ν follow from right to left.

In fact, comparing the maxima of $p(\nu) - p_{bin}(\nu)$, for different ν, the first outermost maximum corresponds in all studied cases to $\nu = N_{val}$. Its position is very close to that of the maximum of $p(N_{val})$ (Table 1). (In fact the differences between this position, r_Δ, and r_p seem close to the limits of the numerical accuracy of the calculation.) $\Delta(\nu)$ thus seems to yield a quite reasonable criterion for spatially defining the valence shell in atoms. One can now either use $\Delta(\nu) = p(\nu) - p_{indep}(\nu)$ in order to determine N_{val} and choose as a shell separator the maximum of $p(N_{val})$, or directly take r_Δ as the radius of the separating sphere.

5. Conclusions and outlook

The probabilities $p(\nu)$ of having ν electrons in a volume Ω can be written in a closed form, and easily obtained for single determinant wave functions, as long as the number of electrons in Ω does not become excessively high (which is commonly the case). It is the hope behind this paper, that these probabilities can be useful for chemical interpretations. An example is given, by studying the shell structure of atoms.

In order to select a given number of electrons, it was useful to analyze the difference between $p(\nu)$ and the probabilities of independent particles. (This difference is due to the Pauli principle, and present at Hartree–Fock level).

A first question which can be raised is that of obtaining $p(\nu)$ for more elaborate wave functions. Of course, Eq. 2 is quite general, and can be even used for complicated wave functions in Quantum Monte Carlo calculations. In fact, work using variational Quantum Monte Carlo wave functions is in progress [23]. Furthermore, multi-determinant wave functions yield formulas related (via transition density matrices) to Eqs. 4 and 7. (For closely related work, see [24,25] where no sharp boundaries were used.) In general, one expects correlation to reduce the variance (see, e.g., [26], where results for the uniform electron gas are presented).

The second question is the definition of the volumes Ω. This paper suggests to emphasize the difference between the real probabilities and those of a hypothetical one of independent particles. This requires, however, to explore different volumes, until the optimal criterion (i.e., the maximal difference) is achieved. To investigate it concretely, algorithms are needed, which are different from the currently used for defining spatial regions. The latter define the volumes by following the gradients of some function of the three spatial coordinates). Algorithms for varying surfaces until an optimal criterion is reached are used nowadays (level set methods [27]) and seem applicable to the present approach [28].

Finally, we would like to point out a feature noticed in many cases. In Refs. [16,17], the $p(\nu)$ were assumed to lie on a curve $C\exp[-a(\nu-\nu_0)^2]$, where the parameters C, a, ν_0 were determined from the Eqs. 5, $m = 0, 1, 2$. From the data obtained in the present work, it turns out that very often the $p(\nu)$ lie very close to a normalized Gaussian curve. Furthermore, the two free parameters can be quite well approximated by simply taking $\langle \hat{\mathbf{N}}_\Omega \rangle$, and σ^2. (The present numerical material typically produces errors in $p(\nu)$ of the order of 0.01.) As only two parameters are required, one may further ask, under which conditions all $p(\nu)$, (and thus even all $\int_\Omega \Gamma^{(m')}$, with $m' > 1$), can be obtained from $\sum p(\nu) = 1$ and $\langle \hat{\mathbf{N}}_\Omega \rangle$, i.e., using only the electron density, like in density functional theory (cf. Eq. 5).

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Appendix

This appendix exemplifies several formulas for the number of electrons, $N = 3$. We start with Eq. 5. As $\hat{\mathbf{N}}_\Omega^m = [\sum_{i=1,N} \hat{N}_\Omega(\mathbf{r}_i)]^m$ and $\hat{N}_\Omega(\mathbf{r}_i)^m = \hat{N}(\mathbf{r}_i)$, we get:

$$\begin{aligned}
\hat{\mathbf{N}}_\Omega &= \sum_{i=1,3} \hat{N}_\Omega(\mathbf{r}_i)\\
\hat{\mathbf{N}}_\Omega^2 &= \sum_{i=1,3} \hat{N}_\Omega(\mathbf{r}_i) + 2\sum_{i<j} \hat{N}_\Omega(\mathbf{r}_i)\hat{N}_\Omega(\mathbf{r}_j)\\
\hat{\mathbf{N}}_\Omega^3 &= \sum_{i=1,3} \hat{N}_\Omega(\mathbf{r}_i) + 6\sum_{i<j} \hat{N}_\Omega(\mathbf{r}_i)\hat{N}_\Omega(\mathbf{r}_j) + 6\hat{N}_\Omega(\mathbf{r}_1)\hat{N}_\Omega(\mathbf{r}_2)\hat{N}_\Omega(\mathbf{r}_3)
\end{aligned}$$

We observe one-, two-, and three-body operators. The expectation values are thus, by using the rules for m-body operators (see, e.g., [14]):

$$\begin{aligned}
\langle\hat{\mathbf{N}}_\Omega^0\rangle &= 1\\
\langle\hat{\mathbf{N}}_\Omega^1\rangle &= \int_\Omega \Gamma^{(1)}\\
\langle\hat{\mathbf{N}}_\Omega^2\rangle &= \int_\Omega \Gamma^{(1)} + \int_\Omega \Gamma^{(2)}\\
\langle\hat{\mathbf{N}}_\Omega^3\rangle &= \int_\Omega \Gamma^{(1)} + 3\int_\Omega \Gamma^{(2)} + \int_\Omega \Gamma^{(3)}
\end{aligned}$$

By introducing these expression in the system of equations 5, and solving for $p(\nu)$, we obtain the expressions given in Eq. 3, for the special case $N = 3$:

$$\begin{aligned}
p(0) &= 1 - \int_\Omega \Gamma^{(1)} + \frac{1}{2}\int_\Omega \Gamma^{(2)} - \frac{1}{6}\int_\Omega \Gamma^{(3)}\\
p(1) &= \int_\Omega \Gamma^{(1)} - \int_\Omega \Gamma^{(2)} + \frac{1}{2}\int_\Omega \Gamma^{(3)}\\
p(2) &= \frac{1}{2}\int_\Omega \Gamma^{(2)} - \frac{1}{2}\int_\Omega \Gamma^{(3)}\\
p(3) &= \frac{1}{6}\int_\Omega \Gamma^{(3)}
\end{aligned}$$

We will now directly obtain these equations, starting with Eqs. 2 and 4. Of course,

$$p(3) = \binom{3}{3}\int_\Omega d1d2d3 \mid \Psi \mid^2 = \binom{3}{3}\int_\Omega d1d2d3 \frac{(3-3)!}{3!}\Gamma^{(3)}$$

Furthermore, using $\int_{\bar{\Omega}} = \int - \int_{\Omega}$, we have:

$$\begin{aligned}
p(2) &= \binom{3}{2} \int_{\Omega} d1d2 \int_{\bar{\Omega}} d3 \mid \Psi \mid^2 \\
&= \binom{3}{2} \int_{\Omega} d1d2 \int d3 \mid \Psi \mid^2 - \binom{3}{2} \int_{\Omega} d1d2 \int_{\Omega} d3 \mid \Psi \mid^2 \\
&= \binom{3}{2} \int_{\Omega} d1d2 \frac{(3-2)!}{3!} \Gamma^{(2)} - \binom{3}{2} \int_{\Omega} d1d2d3 \frac{(3-3)!}{3!} \Gamma^{(3)}
\end{aligned}$$

and

$$\begin{aligned}
p(1) &= \binom{3}{1} \int_{\Omega} d1 \int_{\bar{\Omega}} d2d3 \mid \Psi \mid^2 \\
&= \binom{3}{1} \int_{\Omega} d1 \int d2d3 \mid \Psi \mid^2 \\
&\quad - \binom{3}{1} \int_{\Omega} d1 \int_{\Omega} d2 \int d3 \mid \Psi \mid^2 - \binom{3}{1} \int_{\Omega} d1 \int d2 \int_{\Omega} d3 \mid \Psi \mid^2 \\
&\quad + \binom{3}{1} \int_{\Omega} d1d2d3 \mid \Psi \mid^2 \\
&= \binom{3}{1} \int_{\Omega} d1 \frac{(3-1)!}{3!} \Gamma^{(1)} - 2 \binom{3}{1} \int_{\Omega} d1d2 \frac{(3-2)!}{3!} \Gamma^{(2)} \\
&\quad + \binom{3}{1} \int_{\Omega} d1d2d3 \frac{(3-3)!}{3!} \Gamma^{(3)}
\end{aligned}$$

Let us now consider the case when the wave function is approximated by a single Slater determinant. The reduced density matrix Γ^m, is the determinant of the matrix with elements G_{pq} (Eq. 9). For example, for $m = 3$, one has

$$\begin{aligned}
\Gamma^{(3)} = \sum_{i,j,k}^{N} & \phi_i(x_1)\phi_i(x_1)\phi_j(x_2)\phi_j(x_2)\phi_k(x_3)\phi_k(x_3) \\
& -\phi_i(x_1)\phi_i(x_1)\phi_j(x_3)\phi_j(x_2)\phi_k(x_2)\phi_k(x_3) \\
& -\phi_i(x_3)\phi_i(x_1)\phi_j(x_2)\phi_j(x_2)\phi_k(x_1)\phi_k(x_3) \\
& -\phi_i(x_2)\phi_i(x_1)\phi_j(x_1)\phi_j(x_2)\phi_k(x_3)\phi_k(x_3) \\
& +\phi_i(x_3)\phi_i(x_1)\phi_j(x_1)\phi_j(x_2)\phi_k(x_2)\phi_k(x_3) \\
& +\phi_i(x_2)\phi_i(x_1)\phi_j(x_3)\phi_j(x_2)\phi_k(x_1)\phi_k(x_3)
\end{aligned}$$

To obtain Eq. 7, $\int_\Omega$ is performed, and one obtains (cf. Eq. 6):

$$\begin{aligned}\int_\Omega \Gamma^{(3)} = &\sum_{i,j,k}^{N} \omega_{ii}\omega_{jj}\omega_{kk} \\ &-\omega_{ii}\omega_{jk}\omega_{kj} \\ &-\omega_{ik}\omega_{jj}\omega_{ki} \\ &-\omega_{ij}\omega_{ji}\omega_{kk} \\ &+\omega_{ij}\omega_{jk}\omega_{ki} \\ &+\omega_{ik}\omega_{kj}\omega_{ji} \\ = &\sum_{i}^{N}\omega_{ii}\sum_{j}^{N}\omega_{jj}\sum_{k}^{N}\omega_{kk} \\ &-\sum_{i}^{N}\omega_{ii}\sum_{j,k}^{N}\omega_{jk}\omega_{kj} \\ &-\sum_{i,k}^{N}\omega_{ik}\omega_{ki}\sum_{j}\omega_{jj} \\ &-\sum_{i,j}\omega_{ij}\omega_{ji}\sum_{k}\omega_{kk} \\ &+\sum_{i,j,k}\omega_{ij}\omega_{jk}\omega_{ki} \\ &+\sum_{i,j,k}\omega_{ik}\omega_{kj}\omega_{ji}\end{aligned}$$

which is, in a more compact notation:

$$\Gamma^{(3)} = (TrS_\Omega)^3 - 3TrS_\Omega TrS_\Omega^2 + 2TrS_\Omega^3$$

Of course, the coefficients can be directly obtained from Eq. 8, the partitions of 3 being $\{1, 1, 1\}$, $\{1, 2\}$ and $\{3\}$.

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