Calculating average values for many-electron atoms under the central field approximation

When the Hamiltonian for a many-electron atom can be written, in the ***central field approximation***, as

$$\mathcal{H} \approx - (\hbar^2/2\mu)\{\nabla_1^2 + \nabla_2^2 + \nabla_3^2 + \nabla_4^2 + ...\} + V(r_1) + V(r_2) + V(r_3) + V(r_4) + ...$$

then the problem is exactly separable, no matter how complicated the $V(r_i)$ expressions may be, as long as each one is a function only of the distance of the ith electron from the nucleus, not of θ_i or ϕ_i.

In this case then the problem

$\mathcal{H}\,\Psi(1, 2, 3, 4,...) = E\,\Psi(1, 2, 3, 4,...)$ can be solved by solving individual *one-electron problems*:

$$\{- (\hbar^2/2\mu)\nabla_i^2 + V(r_i)\}\Psi(r_i , \theta_i , \phi_i) = E_i\,\Psi(r_i , \theta_i , \phi_i .)$$

Since the only θ_i , ϕ_i dependence is in ∇_i^2 then each *one-electron problem* to be solved can be solved by separation of the variables θ_i , ϕ_i leading to the same solutions as for the hydrogen atom itself, namely the same quantum numbers ℓ and m and the same functions $Y_{\ell m}(\theta_i , \phi_i)$ arise in precisely the same way as for the hydrogen atom. The only difference is that the remaining differential equation in r to be solved :

$$\{ (\hbar^2/2\mu)[\partial^2/\partial r_i^2 + (2/r_i)\,\partial/\partial r_i + \ell(\ell+1)/ r_i^{\,2}] + V(r_i)\}\, F(r_i) = E_i\, F(r_i)$$

is different from that in the hydrogen atom in that here, $V(r_i) \neq -Ze^2/r_i$

This means that the functions $F(r_i) \neq R_{n\ell}(r_i)$.

Nevertheless, a simple product function $\Psi(r_i , \theta_i , \phi_i) = F(r_i) \cdot Y_{\ell m}(\theta_i , \phi_i)$ is associated with the one-electron energy E_i. This also means that the many electron functions can be written as simple products (to be antisymmetrized later)

$$\Psi(1, 2, 3, 4, ...) = \Psi(r_1, \theta_1 , \phi_1)\cdot\Psi(r_2, \theta_2 , \phi_2)\cdot\Psi(r_3, \theta_3 , \phi_3)\cdot\Psi(r_4, \theta_4 , \phi_4)\cdot\, ...$$

which is represented by an "***electronic configuration***" such as $1s^2 2s^1 2p^3 3d^2$.

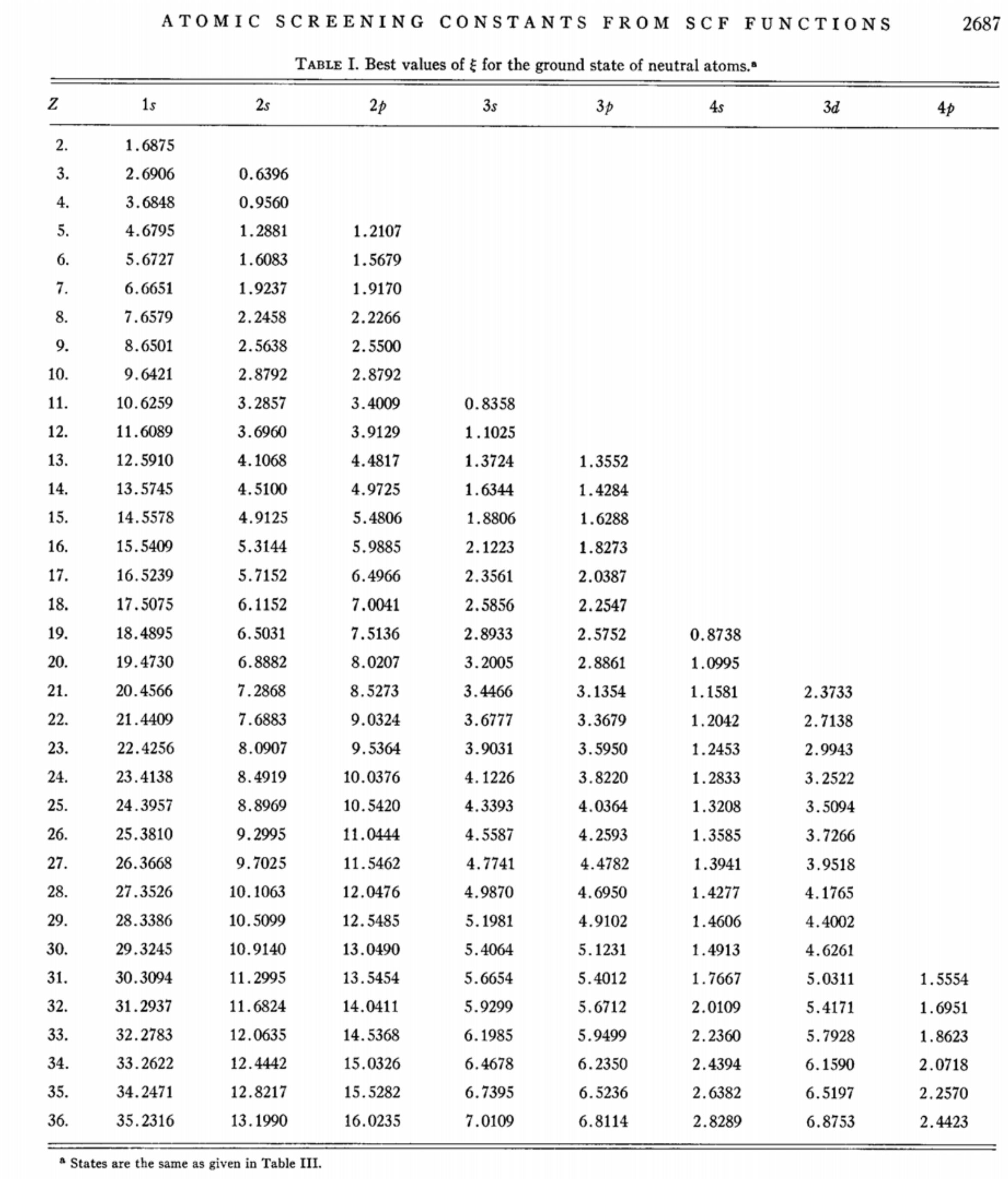
If the effect of all the other electrons were to reduce the nuclear charge seen by the ith electron, from the full charge Z down to $Z_{\text{eff}}^{(i)}$ then, the many-electron problem separates into

$$\{ (\hbar^2/2\mu)[\partial^2/\partial r_i^2 + (2/r_i)\,\partial/\partial r_i + \ell(\ell+1)/ r_i^{\,2}] - Z_{\text{eff}}^{(i)} e^2/r_i \}\, F(r_i) = E_i\, F(r_i)$$

each one of which is a hydrogen atom with $Z_{\text{eff}}^{(i)}$ appearing everywhere Z used to be. This means that $F(r_i) = R_{n\ell}(r_i)$, just as for the hydrogen atom, and all the wavefunctions that we found for the hydrogen atom are the same ones as for each electron in the many-electron atom. Because of this, the one-electron energies are $E_i = -(Z_{\text{eff}}^{(i)}/n_i)^2\,(e^2/2a_0)$ and all the one-electron operators *Op* which can be expressed in terms of r_i can be obtained from the integrals derived for the hydrogen atom, for example the average value:

$$\langle (r/a_0)^2 \rangle = (n^2/2Z^2)[5n^2 + 1 - 3\,\ell(\ell+1)]$$

Clementi and Raimondi, for example, provide tables of $[Z_{\mathrm{eff}}^{(i)}/n]$ for each electron in the ground configuration of atoms He up to Kr. [E. Clementi and D. L. Raimondi, J. Chem. Phys. 38, 2686 (1963)] Of course, these only apply to that particular configuration. Clearly the amount of effective screening by the other electrons depends on which types of functions describe their probability distribution in space.



ATOMIC SCREENING CONSTANTS FROM SCF FUNCTIONS 2687

TABLE I. Best values of ξ for the ground state of neutral atoms.[a]

Z	1s	2s	2p	3s	3p	4s	3d	4p
2.	1.6875							
3.	2.6906	0.6396						
4.	3.6848	0.9560						
5.	4.6795	1.2881	1.2107					
6.	5.6727	1.6083	1.5679					
7.	6.6651	1.9237	1.9170					
8.	7.6579	2.2458	2.2266					
9.	8.6501	2.5638	2.5500					
10.	9.6421	2.8792	2.8792					
11.	10.6259	3.2857	3.4009	0.8358				
12.	11.6089	3.6960	3.9129	1.1025				
13.	12.5910	4.1068	4.4817	1.3724	1.3552			
14.	13.5745	4.5100	4.9725	1.6344	1.4284			
15.	14.5578	4.9125	5.4806	1.8806	1.6288			
16.	15.5409	5.3144	5.9885	2.1223	1.8273			
17.	16.5239	5.7152	6.4966	2.3561	2.0387			
18.	17.5075	6.1152	7.0041	2.5856	2.2547			
19.	18.4895	6.5031	7.5136	2.8933	2.5752	0.8738		
20.	19.4730	6.8882	8.0207	3.2005	2.8861	1.0995		
21.	20.4566	7.2868	8.5273	3.4466	3.1354	1.1581	2.3733	
22.	21.4409	7.6883	9.0324	3.6777	3.3679	1.2042	2.7138	
23.	22.4256	8.0907	9.5364	3.9031	3.5950	1.2453	2.9943	
24.	23.4138	8.4919	10.0376	4.1226	3.8220	1.2833	3.2522	
25.	24.3957	8.8969	10.5420	4.3393	4.0364	1.3208	3.5094	
26.	25.3810	9.2995	11.0444	4.5587	4.2593	1.3585	3.7266	
27.	26.3668	9.7025	11.5462	4.7741	4.4782	1.3941	3.9518	
28.	27.3526	10.1063	12.0476	4.9870	4.6950	1.4277	4.1765	
29.	28.3386	10.5099	12.5485	5.1981	4.9102	1.4606	4.4002	
30.	29.3245	10.9140	13.0490	5.4064	5.1231	1.4913	4.6261	
31.	30.3094	11.2995	13.5454	5.6654	5.4012	1.7667	5.0311	1.5554
32.	31.2937	11.6824	14.0411	5.9299	5.6712	2.0109	5.4171	1.6951
33.	32.2783	12.0635	14.5368	6.1985	5.9499	2.2360	5.7928	1.8623
34.	33.2622	12.4442	15.0326	6.4678	6.2350	2.4394	6.1590	2.0718
35.	34.2471	12.8217	15.5282	6.7395	6.5236	2.6382	6.5197	2.2570
36.	35.2316	13.1990	16.0235	7.0109	6.8114	2.8289	6.8753	2.4423

[a] States are the same as given in Table III.

In the Slater approximation, the Hamiltonian is taken to be of the form

$$\mathcal{H} \approx - (\hbar^2/2\mu)\{\nabla_1^2 + \nabla_2^2 + \nabla_3^2 + \nabla_4^2 +\ldots\} -Z_{\mathrm{eff}}^{(1)}e^2/r_1 -Z_{\mathrm{eff}}^{(2)}e^2/r_2 -Z_{\mathrm{eff}}^{(3)}e^2/r_3 -Z_{\mathrm{eff}}^{(4)}e^2/r_4 -\ldots$$

Since the $Z_{\mathrm{eff}}^{(i)}$ are constants, although each is different from Z itself, the many-electron problem separates into

$$\{ (\hbar^2/2\mu)[\partial^2/\partial r_i^2 + (2/r_i)\,\partial/\partial r_i + \ell(\ell+1)/ r_i^{\,2}] -Z_{\mathrm{eff}}^{(i)}e^2/r_i \}\, F(r_i) = E_i\, F(r_i)$$

each one of which is a hydrogen atom with $Z_{\mathrm{eff}}^{(i)}$ appearing everywhere Z used to be. This means that $F(r_i) = R_{n\ell}(r_i)$, just as for the hydrogen atom, and all the wavefunctions that we found for the hydrogen atom are the same ones as for each electron in the many-electron atom under the Slater approximation. Because of this, the one-electron energies are $E_i = -(Z_{\mathrm{eff}}^{(i)}/n_i)^2\,(e^2/2a_0)$ and all the one-electron operators $\mathcal{O}p$ which can be expressed in terms of r_i can be obtained from the integrals derived for the hydrogen atom, for example, given

$\int\psi_{n,\ell,m}{}^*r^2\,\psi_{n,\ell,m}\,d\tau = [n^2/2Z^2]\cdot\{ 5n^2 +1- 3\ell(\ell+1)\}$ for H-like atom.

the average value:

$$\langle(r/a_0)^2\rangle = (n^2/2Z^2)[5n^2 +1 -3\,\ell(\ell+1)]$$

Slater's rules:

1. $s_{1s} = 0.30$

2. For electrons with $n > 1$ and $\ell = 0, 1$

$$s_{n\ell} = 0.35k_{\mathrm{same}} + 0.85k_{\mathrm{in}} + 1.00k_{\mathrm{inner}}$$

where

k_{same} = number of other electrons in the same shell as the screened electron of interest

k_{in} = number of electrons in the shell with principal quantum number n-1

k_{inner} = number of electrons in the shell with principal quantum number n-2

3. For 3d electrons

$$s_{3d} = 0.35k_{3d} + 1.00k_{\mathrm{in}}$$

where

k_{3d} = number of 3d electrons

k_{in} = number of electrons with $n \leq 3$ and $\ell < 2$

<u>Example:</u> Energy Calculations

Problem: The electron transfer that occurs when a Li^+ and a H^- ion are formed from a Li atom and a H atom leads to the formation of LiH. Using Slater's rules, ***derive an expression for the calculation of the energy change*** that is involved when this occurs. Is the energy evolved or absorbed in this chemical reaction? ***Do the calculations***, giving your answer in eV.

Using Slater's rules,

Li Z = 3, electronic configuration: $1s^22s$

electron	n	ℓ	screening from others			$s_{n\ell}$	Z-$s_{n\ell}$
			1	2	3		
1	1	0	self	0.30	0	0.30	2.70
2	1	0	0.30	self	0	0.30	2.70
3	2	0	0.85	0.85	self	1.70	1.30

Li^+ Z = 3, electronic configuration: $1s^2$

electron	n	ℓ	screening from others			$s_{n\ell}$	Z-$s_{n\ell}$
			1	2			
1	1	0	self	0.30		0.30	2.70
2	1	0	0.30	self		0.30	2.70

H^- Z = 1, electronic configuration: $1s^2$

electron	n	ℓ	screening from others			$s_{n\ell}$	Z-$s_{n\ell}$
			1	2			
1	1	0	self	0.30		0.30	0.70
2	1	0	0.30	self		0.30	0.70

Energy = $-\{Z_{eff}(i)/n_i\}^2 (e^2/2a_0)$ for each electron

Before: Li + H

Energy for Li = $-13.6\ \text{eV}\cdot\{2\cdot[2.70/1]^2 + [1.30/2]^2\}$

Energy for H = $-13.6\ \text{eV}\cdot\{[1/1]^2\}$

Total energy = $-13.6\ \text{eV}\cdot\{15.00 + 1\}$

After: $Li^+ + H^-$

Energy for Li^+ = $-13.6\ \text{eV}\cdot\{2\cdot [2.70/1]^2\}$

Energy for H^- = -13.6 eV·{2· $[0.70/1]^2$}
Total energy = -13.6 eV·{14.58 + 0.98}
Energy difference = E_{after} - E_{before} = -13.6 eV{ 15.56 - 16 } = +5.98 eV
Although E_{after} is higher than E_{before}, the reaction produces charged particles which have Coulomb interaction energy equal to $\{- e^2/r_{LiH}\}$ at the separation r_{LiH}.

<u>Example:</u> Diamagnetic susceptibility of a many-electron atom:
Problem: When an atom is placed in a magnetic field, the magnetic field induces a magnetic moment in the atom. The energy term in this case is proportional to the square of the applied magnetic field and the proportionality constant is called the magnetic susceptibility. The magnetic susceptibility, χ, is diamagnetic unless the atom has unpaired electrons.The diamagnetic susceptibility contributes to the susceptibility of all molecules. χ^d has the following <u>operator</u> (for an atom having N electrons):

$$Op = -(e^2/3mc^2)\ ½\sum_{i=1}^{N} r_i^{\,2}\ .$$

Derive the method by which it will be possible to calculate the diamagnetic susceptibility χ^d (in units of cm^3 per atom or molecule) of a single Be atom in its ground state, using Slater's rules. ***Carry out the numerical computations.*** The answer should be very small; to get the observed <u>molar</u> magnetic susceptibility one has to multiply this by Avogadro's number. The quantity $(e^2/3mc^2)$ is 9.393×10^{-14} cm and $a_0 = 0.529167 \times 10^{-8}$ cm .

Solution:
χ^d has the following <u>operator</u> (for an atom having N electrons):

$$Op = -(e^2/3mc^2)\ ½\sum_{i=1}^{N} r_i^{\,2}\ .$$

Calculate $\langle\chi^d\rangle$ for the ground state of the Be atom Z=4.

How to do it:
(1) First determine the electronic configuration for the ground state.
(2) Then determine for each electron the screening contributions due to all the other electrons $s_{n\ell}$. Then $Z_{eff} = Z - s_{n\ell}$ for that electron.
(3) Once you have Z_{eff} you also have the wavefunctions:
$\Psi(r_i, \theta_i, \phi_i) = F(r_i)\cdot Y_{\ell m}(\theta_i, \phi_i)$ for each electron,
and for the Be atom the wavefunction is a product of four such functions.
(4) Having this, it is trivial to evaluate the desired average value by using Postulate 3:

$$\langle \chi^d \rangle = \iint \Psi(1, 2, 3, 4)^* \{-(e^2/3mc^2)\, ½ \sum_{i=1}^{N} r_i^{\,2}\}\, \Psi(1, 2, 3, 4)\, d\tau_1 d\tau_2\, d\tau_3\, d\tau_4$$

This works out into

$-(e^2/3mc^2)\ ½\ \{$

$\iint\Psi(1)^*r_1^{\,2}\ \Psi(1)d\tau_1\cdot\iint\Psi(2)^*\Psi(2)d\tau_2\cdot\iint\Psi(3)^*\Psi(3)d\tau_3\cdot\iint\Psi(4)^*\Psi(4)d\tau_4 +$

$\iint\Psi(1)^*\Psi(1)d\tau_1\cdot\iint\Psi(2)^*\ r_2^{\,2}\ \Psi(2)d\tau_2\cdot\iint\Psi(3)^*\Psi(3)d\tau_3\cdot\iint\Psi(4)^*\Psi(4)d\tau_4 +$

$\iint\Psi(1)^*\Psi(1)d\tau_1\cdot\iint\Psi(2)^*\Psi(2)d\tau_2\cdot\iint\Psi(3)^*\ r_3^{\,2}\ \Psi(3)d\tau_3\cdot\iint\Psi(4)^*\Psi(4)d\tau_4 +$

$\iint\Psi(1)^*\ \Psi(1)d\tau_1\cdot\iint\Psi(2)^*\Psi(2)d\tau_2\cdot\iint\Psi(3)^*\Psi(3)d\tau_3\cdot\iint\Psi(4)^*\ r_4^{\,2}\ \Psi(4)d\tau_4\ \}$

$=\ -(e^2/3mc^2)\ ½\ \{$

$\iint\Psi(1)^*r_1^{\,2}\ \Psi(1)d\tau_1 + \iint\Psi(2)^*\ r_2^{\,2}\ \Psi(2)d\tau_2 + \iint\Psi(3)^*\ r_3^{\,2}\ \Psi(3)d\tau_3 \iint\Psi(4)^*\ r_4^{\,2}\ \Psi(4)d\tau_4\}$

Given $\int\psi_{n,\ell,m}{}^*r^2\ \psi_{\,n,\ell,m}\ d\tau = [n^2/2Z^2]\cdot\{\ 5n^2\ +1-\ 3\ell(\ell+1)\}a_0^{\,2}$ for H atom, we can evaluate all the integrals because the functions Ψ(1) etc. are hydrogen atom functions.

Given Be atom with 4 electrons in the ground configuration $1s^22s^2$.
Applying Slater's rules

electron	n	ℓ	screening from others				$s_{n\ell}$	$Z_{eff} = Z\text{-}s_{n\ell}$
			1	2	3	4		
1	1	0	self	0.30	0	0	0.30	3.70
2	1	0	0.30	self	0	0	0.30	3.70
3	2	0	0.85	0.85	self	0.35	2.05	1.95
4	2	0	0.85	0.85	0.35	self	2.05	1.95

given $\int\psi_{n,\ell,m}{}^*r^2\ \psi_{\,n,\ell,m}\ d\tau = [n^2/2Z^2]\cdot\{\ 5n^2\ +1-\ 3\ell(\ell+1)\}a_0^{\,2}$ for H atom.

electron	n	ℓ	$5n^2+1$ $-3\ell(\ell+1)$	$Z_{eff}^{\,2}$	$\dfrac{n^2}{2Z_{eff}^{\,2}}$	$\langle r^2\rangle$
1	1	0	6	13.69	0.0365	$0.219a_0^{\,2}$
2	1	0	6	13.69	0.0365	$0.219a_0^{\,2}$
3	2	0	21	3.8025	0.526	$11.045a_0^{\,2}$
4	2	0	21	3.8025	0.526	$11.045a_0^{\,2}$

Then, summing up,

$\langle\chi^d\rangle = 9.393\times10^{-14}\cdot ½\cdot[0.219+0.219+11.045+11.045]a_0^{\,2}\ = 2.63\times10^{-30}\ \cdot$ $(0.219+11.045) = 29.624\times10^{-30}\ \text{cm}^3$ per atom $= 17.84\times10^{-6}\ \text{cm}^3$ per mole

A note about units of the B^2 term in energy: $\text{gauss}^2 = \text{erg cm}^{-3}$