Modified Hartree-Fock Relationship to Calculate the Effective Energy of Atomic Sub-shells in Transition Elements

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Abstract

In this study, the part in question of the total energy is that due to the mutual interactions between the electrons themselves, the fact that this is the total effective energy of sample electrons in shells and sub-shells. The result was that only 0.2564 of the total energy of the atom is divided between the individual electrons and the effective energy of each of them is proportional to the reciprocal of their occupation numbers i.e. $1/(n+2l+1)^2$, the proportionality constant was fortunately equivalent to the effective nuclear charge (Z_{eff}) of the sub-shell type according to the studies done by both Slater and Clementi and Raimondi. The amazing news was that the algebraic sum of the effective energy for each electron was again very close to 0.2564 E_T.

Keywords: Hartree-Fock, Effective Energy of Atomic, Transition Elements

Introduction

In chemistry and physics the traditional distribution of electrons among the shells and sub-shells based on experimental results in treating both chemical reactions and X-ray spectroscopy. In these, the obeyed rules are those committed to the energy needed to isolate the electrons in question with the other electrons in the same atom, keeping in mind, the net mutual-repulsive energy is part of the total energy of the atom.

Hartree [1] and co-works tried to formulate this phenomenon with the other models built by Bohr, Rutherford, Thomson, and Dirac. But the idea stayed unchanged until the birth of quantum mechanics.

In 1943, Hartree and Fock [2] extended their model through what is called the central field method for the total energy of the atom. They depended on N-dimensional Schrodinger equation and separating the different parts of atomic total energy (E_T) as:

1. The kinetic energy of the electrons which was a positive quantity and contributed to (0.9999 E_T).
2. The mutual repulsive interaction contributed to (+0.3335E_T).
3. The Coulomb interaction between the nucleus and the electrons contributed to (-1.7936E_T).
4. The net exchange energy due to the instability of the atom contributed to (-0.04907E_T).

From this, it is found that the net-effective energy for the electrons participating in atomic activities is a measure of the net repulsive energy between the electrons divided in the sub-shells of the atom [3].

Theory and Results

Let us first calculate the occupation number $f(n,l)$ through what is called the effective nuclear charge of electrons in the shells and sub-shells. In quantum mechanics the following phrases are replacing the traditional names used in the shell model of the atom [4].

1. Fundamental quantum number: $L=n+k+1$, where (k) is the order of dimensions used to solve the Schrodinger equation, (n) is the principal quantum number.

2. The orbital quantum number (l) which is a measure for the angular statue of the electrons.

3. The orientation quantum number (m) connected to both spinning and orbiting processes of the electron.

4. The spin quantum number |s|=1/2.

5. Orbital angular momentum quantum number (m_l) which have *2l*+1 values [*-l, ….,0, ….,+l*].

6. Spin magnetic quantum number (m_s) which have *2s*+1 = 2 values always [±1/2].

Also the following modification in atomic structure is taken into consideration:

Shell → Quantum Enclosure; Sub-shell → Quantum State; Orbital → Quantum Box

The occupation number found via an exact solution for the N-dimensional radial part of Schrodinger equation preformed by Gang-Chen [5] in 2004 and Schwinger [6] in 2006. Both models depend on the famous second-order radial part of Schrodinger differential time dependent equation using lower order Laplace transform. Swanson [7] proposed that the motion of an electron in N-dimensional Euclidian space is part of radial parts of the Schrodinger equation:

$$\left[\frac{d^2}{dr^2}+\frac{2}{r}\frac{d}{dr}-\frac{l(l+1)}{r^2}+\frac{2m}{\hbar^2}(E-V)\right]R=0 \qquad (1)$$

Here putting L=*l,* and N for three dimensional shape of the atom, Eq.(1) is modified to:

$$\left[\frac{d^2}{dr^2}+\frac{N-1}{r}\frac{d}{dr}-\frac{LL+N-2}{r^2}+\frac{2m}{\hbar^2}(E-V)\right]R_L(r)=0 \qquad (2)$$

The model is depending on the general form of the transform and the multivalue wave function required:

$$\frac{\alpha-(2L+N-1)\beta}{2\beta}=l \quad , \qquad l=0,1,2,3,\dots,(n-1)$$

Bender and Boettcher solved eq. 2, depending on the bound-state electron and defining *D*=*l*+*k*+1, then

$$E_{D,L}=-\frac{mZ^2e^4}{2\hbar^2}\frac{1}{\left[D+\frac{N-3}{2}\right]^2} \qquad (3)$$

Keeping in mind, that the lowest term including *N=3*, the second term of the dominator of eq.3 is vanished [8]. The atomic units have been used throughout the paper, $m=e=\hbar=1$, thus eq.3 is reduced to:

$$E_{n,l}=-\frac{1}{2}\frac{Z^2}{[n+l]^2} \qquad (4)$$

Equation 4 is a simplified form for the general cases treated including the orbital and the effective energies of the electron in a quantum state (n, *l*).

Schwinger [9] tried to stick with the net force exerted on electron in any state (n, *l*) relative to other electrons in question. Firstly they formulated the Clementi and Raimond [10] model of the effective nuclear charge on an electron in question by expanding Slater rules for inner shells and sub-shells. Their attempt was successful up to (*5p*) state, since the X-ray spectroscopy couldn't intervene with energies higher than this.

After a series of experiments, [11] they found that the occupation number of Eq.4 is not a powerful tool for this purpose, instead of (*l*) they tried to replace it with (m_l) or (2*l*+1) for any quantum state. This attempt was working for atoms with no (*f*) electrons, where other researcher tried to generalize the case for another model which was $[n+2m_l]^2$ or $[n+4l+2]^2$ which was successful for all other sub-states. The results with this model is shown in Table (1);

Table (1): The quantum state series of atomic sub-shells and their corresponded occupation number from equation 6.

Quantum State	*N*	*l*	$f_{n,l}[n(n+2l+1)]$
1*s*	1	0	2
2*s*	2	0	6
2*p*	2	1	10
3*s*	3	0	12
3*p*	3	1	18
4*s*	4	0	20
3*d*	3	2	24
4*p*	4	1	28
5*s*	5	0	30
4*d*	4	2	36
5*p*	5	1	40
6*s*	6	0	42
4*f*	4	3	44
5*d*	5	2	50
6*p*	6	1	54
7*s*	7	0	56
↓	↓	↓	↓

Thus, the final result is:

$$E_{eff}(n,l)=\frac{Z_{eff}^{2}}{[n(n+2l+1)]}=\frac{Z_{eff}^{2}}{n^{2}+2nl+n} \tag{5}$$

In equation 5, the quantity (n+2l+1) is called the occupation number $f_{n,l}$ and it defined in the self-consisted method [10].

Finally, and after a lengthy attempt Rudzikas [12] have noted the limitation of Eq.5 for an atom with (*d*) or (*f*) electrons. The approach was through what is called the density matrix approximation, in which each electron was considered to be in quantum box. Eq. (3) was solved for an N=Z dimension and the modification was successful where the quantum box was related to both m_l and m_s, the orientation and spin quantum numbers. Finally the denominator of Eq. (5) was replaced with n (n+4l+2) for the two values of $m_s[\pm 1/2]$ for heavy atoms [Z>20]and the attempt was in good agreement with experiments done by Evans [13], i.e. :

$$E_{eff}=\frac{Z_{eff}^{2}}{n[n+4l+2]} \tag{6}$$

The data for each quantum state of transition elements are shown in Table (2). The values of E_{eff} in atomic unit (Hartrees) for three regions are shown in Fig(1).

Table (2): The quantum states of transition elements with their corresponded effective energies from Eq.(6)

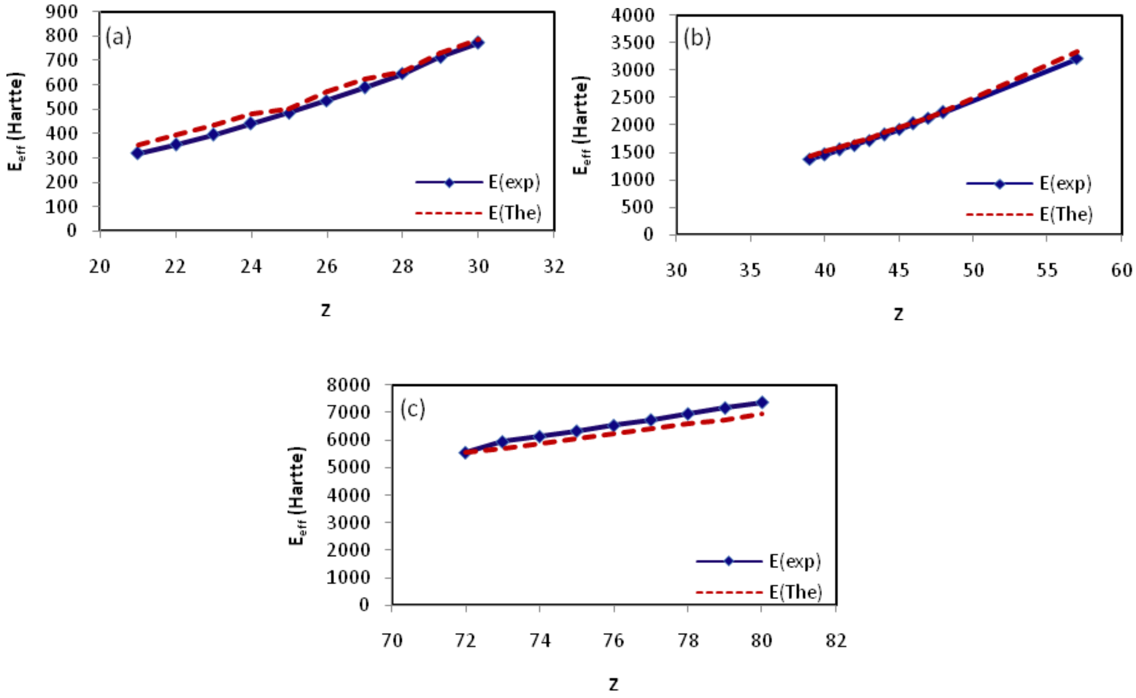
		E_{eff} (Hartrre)						
Z	*Element*	*1s*	*2s*	*2p*	*3s*	*3p*	*4s*	*3d*
21	Sc	104.62	23.22	11.63	6.68	2.45	0.85	0.3
22	Ti	114.90	26.27	13.053	7.6	2.83	0.92	0.39
23	V	125.23	29.09	14.55	8.56	3.23	0.99	0.422
24	Cr	137.05	32.05	16.11	9.98	3.65	1.05	0.56
25	Mn	148.79	35.18	17.78	10.59	4.07	1.11	0.65
26	Fe	161.05	38.43	19.51	11.69	4.54	1.18	0.74
27	Co	173.8	41.84	21.33	12.82	5.01	1.24	0.83
28	Ni	187.04	45.4	23.22	13.99	5.51	1.3	0.93
29	Cu	200.77	49.09	25.19	15.2	6.02	1.36	1.03
30	Zn	214.98	52.94	27.24	16.44	6.58	1.42	1.14
39	Y	364.35	91.02	49.00	34.66	14.81	8.13	3.81
40	Zr	383.35	95.87	51.82	37.09	15.8	8.88	3.87
41	Nb	402.84	100.83	54.7	39.6	16.83	9.34	4.07
42	Mo	422.83	106.00	57.67	42.19	18.02	10.36	4.38
43	Tc	443.29	111.14	60.65	45.46	19.33	11.83	4.75
44	Ru	462.23	116.5	63.84	47.61	20.58	12.47	5.1
45	Rh	485.67	122.14	67.04	50.54	22.01	13.81	5.41
46	Pd	507.57	127.56	70.32	53.36	24.00	14.42	5.85
47	Ag	539.00	133.28	73.68	56.36	24.68	15.78	6.26
48	Cd	552.86	139.13	77.12	59.44	26.16	17.42	6.68
57	La	807.69	195.53	111.51	89.97	40.40	33.17	9.64
72	Hf	1246.09	314.35	182.12		72.19	60.77	20.20
73	Ta	1280.92	320.18	188.39	163.13	74.53	63.23	20.90
74	W	1316.60	332.09	193.60	168.15	77.15	65.80	21.62
75	Re	1355.40	341.14	199.14	173.25	78.30	65.15	22.34
76	Os	1388.00	350.31	204.77	178.42	81.75	70.9	23.09
77	Ir	1425.40	359.60	210.48	183.60	84.24	73.44	23.85
78	Pt	1462.68	369.02	217.09	188.19	86.77	76.17	24.81
79	Au	1500.78	378.56	222.60	194.32	89.30	78.90	25.09
80	Hg	1539.00	388.22	228.01	199.80	91.90	81.66	26.18

Table (2): Continue.

		E_{eff} *(Hartrre)*						
Z	*Element*	*4p*	*5s*	*4d*	*5p*	*6s*	*4f*	*5d*
21	Sc							
22	Ti							
23	V							
24	Cr							
25	Mn							
26	Fe							
27	Co							
28	Ni							
29	Cu							
30	Zn							
39	Y	1.62	1.07	0.56				
40	Zr	1.81	1.15	0.67				
41	Nb	1.98	1.26	0.641				
42	Mo	2.24	1.35	0.76				
43	Tc	2.50	1.45	0.79				
44	Ru	2.70	1.56	0.83				
45	Rh	2.93	1.62	0.90				
46	Pd	3.14	---	0.94				
47	Ag	3.44	1.71	0.93				
48	Cd	3.77	1.79	1.28				
57	La	7.67	2.08	1.35	2.09	1.76	1.15	
72	Hf	14.38	13.23	6.34	3.21	3.17	1.31	1.18
73	Ta	15.00	14.30	6.73	3.46	3.45	1.85	1.22
74	W	15.64	15.39	7.05	3.26	3.26	1.98	1.24
75	Re	16.30	16.48	7.38	4.05	3.82	2.09	1.34
76	Os	16.92	17.50	7.70	4.33	4.25	2.17	1.48
77	Ir	17.56	18.56	8.05	4.62	4.53	2.28	1.55
78	Pt	18.25	18.96	8.42	4.92	4.89	2.35	1.67
79	Au	19.72	20.16	8.80	5.23	5.17	2.44	1.80
80	Hg	20.74	21.94	9.11	5.57	5.38	2.53	1.93

Conclusions

Throughout the whole work, it is clear that the effective energy useful in an electron is that part which concerns the mutual repulsion interactions between the individual electrons. The fact that other parts of the total energy of an atom contributes in Coulomb and kinetic interactions of the electrons is really true, since the real distribution of electrons in quantum box was investigated. The following observations are necessary to be taken into consideration from the data calculations and graphs.



Fig(1): Comparison of Calculated and experimental E_{eff} in three atomic mass region (a) firs region (21-30), (b) second region (39-57), (c) third region (72-80).

1. The transition elements are called so, because they transfer the *p*-type atoms to those of *f*-types and all of them own active *d*-subshells.
   (a) The first region ($Z=21 \longrightarrow 30$) has regularly increased in ionization energies and outmost (*3d*) electrons sub-sequently.
   (b) The second region has that of (*4d*) progressions.
   (c) The third region has that of (*5d*) progressions.
   The result is that (Nb, Z=41, Mo, Z=42 and Rh, Z=45) in the second region have irregularity because of their super active chemical property. Also (Pt, Z=78) own this irregularity, finally (Cr, Z=24, and Cu, Z=29) contributes to the same property.
2. The coincidence between experimental (Solidline) and theoretical (dots) decrease for the second region ($Z=39 \longrightarrow Z=48$) compared with those of the first and third regions. The reason for this is quite clear, since those have more irregularities (5 elements) rather than the other two regions.
3. There is a little difference between the total value theoretical and experimental effective energies for the whole elements and especially in transition elements, the difference increase with increasing atomic number (Z). Relativistic quantum theory interprets this by adding a new factor which called Quantum-Correction Energy (Q_{cor}) to each experimental value resulted from the non-filled quantum box of the atoms and the results will agree with each other fairly.

References

1- Hartree, D.R., Proc. Cambridge phil. Soc., 24, 89,111,426 (1928).

2- Hartree, D.R., Fock V. "On the numerical solutions of generalized equation of Schrodinger equation for N electron", Physics, E, 368(1934).

3- Schwinger J., "Thomas-Fermi model: The second correction", Phys. Rev. A24(5), 2353-2361 (1981).

4- J. Pillar, "Quantum Chemistry", Pergamon Press, 2nd edition (2003).

5- Chang, C., "Density functional approximation for occupation number of sub-shells", Phys. Let. A426, 55 (2006).

6- Schwinger J., "Quantum Electrodynamics and Relationships", Dover, New York (2006).

7- Swanson R.A., and Drake W.F., "Transposed matrix method for semi-classical atoms", J. Phys. A24, 79 (2001).

8- Romeo A., "Fourier transform of N dimensional Schrodinger equation", J. of Math. Phys., 36, 4005 (2005).

9- Schwinger J., "Physics of Atoms, Molecules and Quanta", Springer Verlag. 3rd edition (2007).

10- Clementi E., and Raimondi, "Calculation of effective quantum numbers of sub-shells in atoms", J. Chem. Phys., 38, 2686 (1963).

11- Drake G. W. F., "Density matrix $-\gamma$ - approach to enhance accumulation number for sub-states", Phys. Rev. A203 (1997).

12- Rudzikas Z. B., "Theoretical Atomic Spectroscopy", Cambridge Univ. Press, Cambridge (1997).

13- Evans R. G. "Local density approximation for the effective electron energy in actinides", Spectro-Comp. Science, Plenum Press, New York (1990).