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Derivation of ionization energy and electron affinity equations using chemical hardness and absolute electronegativity in isoelectronic series

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ABSTRACT

Chemical hardness (η) and absolute electronegativity (χ) have important applications in chemistry. In the conceptual Density Functional theory (DFT), these concepts has been associated with electronic energy and the relationship with ionization energy (I) and electron affinity (A) of these concepts has been given. In this study, graphical method was used in order to see the relationship with the atomic number (Z) of chemical hardness and absolute electronegativity in isoelectronic series. These series was considered because all members of an isoelectronic series have the same shielding constant. Chemical hardness and electronegativity equations depending on atomic number were obtained from graphs of $\chi=f(Z)$ and $\eta=f(Z)$ for isoelectronic series that contain electron from 1 to 20. Ionization energy and electron affinity equations were obtained making use from the chemical hardness and electronegativity equations. In the last stage, the relationship with the number of electron of coefficients in the ionization energy and electron affinity equations was examined. As a result, new equations consistent with experimental results that depending on atomic number and number of electron were obtained.

Keywords: Theoretical chemistry; ionization energy; electron affinity; chemical hardness; absolute electronegativity; DFT.

INTRODUCTION

Chemical hardness and absolute electronegativity are two of important properties of atoms, ions or molecules. Several issues of chemistry have been made more understandable using these concepts and qualitative and quantitative solutions for various issues are proposed through these concepts. Chemical hardness is defined as the resistance towards the deformation or polarization of electron cloud of atoms, ions or molecules [1,2]. Chemical hardness concept was revealed by Pearson within the framework of the classification of Lewis acids and bases [3,4]. Chemical principles such as Pearson's hard and soft acids and bases (HSAB) [5-9] and maximum hardness principle (MHP) [10] offer theoretical description opportunity in many issues related with chemistry.

Electronegativity is an important concept such as chemical hardness in chemistry. Pauling's definition [11,12] is most suitable for theoretical explanations although many definitions is recommended for electronegativity.

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The pauling who suggested for the first time a scientific definition of electronegativity as "the power of an atom in a molecule to attract electrons toward itself."

In density functional theory, some chemical properties are identified as response functions of the electronic energy (E) with respect to number of electrons [13,14]. Thus, mathematical definitions were obtained for chemical concepts such as electronegativity, chemical hardness. Absolute electronegativity and hardness are defined respectively from the first and second derivate of the energy E with respect to the number N of the electrons [15, 16]. Electronegativity and hardness are given as follows

$$\chi = -\frac{\partial E}{\partial N} \quad (1)$$

$$\eta = \frac{1}{2}\frac{\partial^2 E}{\partial N^2} \quad (2)$$

The equation depending on ionization energy and electron affinity of chemical hardness and electronegativity was obtained with method of finite differences of Pearson. As a result of this method, chemical hardness and absolute electronegativity can be approximately calculated directly from ionization potential and electron affinity.

In this study, ionization energy and electron affinity equations are obtained using chemical hardness and absolute electronegativity. As is known, all members of an isoelectronic series have the same number of electrons. The most important feature of these series is the same screening constants of members of series. Relation with atomic number of chemical hardness and absolute electronegativity was determined by graphical method. Equations of ionization energy and electron affinity obtained from equations of chemical hardness and absolute electronegativity. Ionization energy and electron affinity values are usually calculated as experimental. In this study, derivation of equations depending on the atomic number and number of electron for ionization energy and electron affinity in isoelectronic series containing electron from 1 to 20 was aimed.

METHODS

Graphical method was used in order to obtain chemical hardness and absolute electronegativity equations depending on atomic number in isoelectronic series containing electron from 1 to 20. For example, performed operations in isoelectronic series containing one electron are given below. The same procedure was repeated for all isoelectronic series containing electron from 1 to 20.

Table 1. η values for systems that contains one electron (eV)

Ion	Z	η
He^{+}	2	14.91
Li^{2+}	3	23.40
Be^{3+}	4	31.91
B^{4+}	5	40.26
C^{5+}	6	48.95
N^{6+}	7	57.48
O^{7+}	8	66.04
F^{8+}	9	74.60
Ne^{9+}	10	83.18

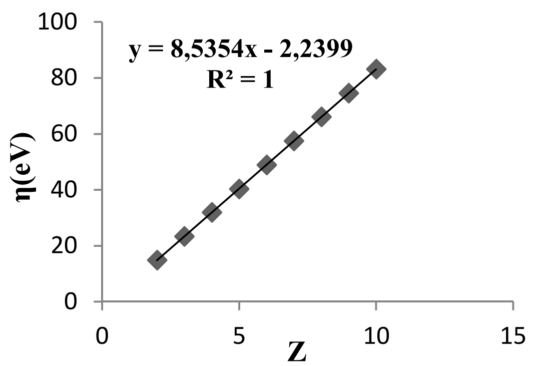

Fig. 1. η =f(Z) graph for systems that contains one electron.

Same graph were drawn for all isoelectronic series containing electron from 1 to 20. As a result, equations depending on atomic number for chemical hardness and electronegativity were obtained and obtained these equations are provided in Table 3 and Table 4.

Table 2. χ Values for systems that contains one electron (eV)

Ion	Z	η
He^{+}	2	39.50
Li^{2+}	3	99.03
Be^{3+}	4	185.80
B^{4+}	5	299.79
C^{5+}	6	441.02
N^{6+}	7	609.53
O^{7+}	8	805.34
F^{8+}	9	1028.48
Ne^{9+}	10	1278.97

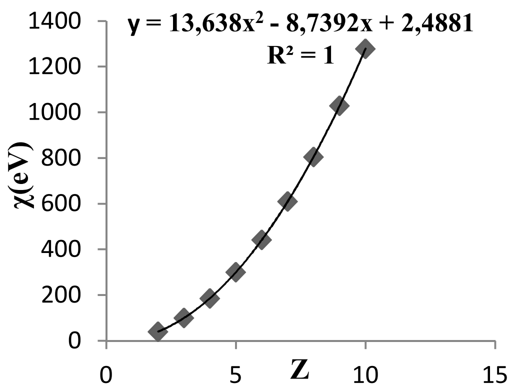

Fig. 1. χ =f(Z) graph for systems that contains one electron.

As given in the introduction, chemical hardness and electronegativity are given as follows,

$$\eta = \frac{I-A}{2} \tag{3}$$

and

$$\chi = \frac{I+A}{2} \tag{4}$$

Therefore, we can obtain ionization energy and electron affinity equations taking difference and sum of absolute electronegativity and chemical hardness.

$$\chi + \eta = \left(\frac{I+A}{2}\right) + \left(\frac{I-A}{2}\right) = I \tag{5}$$

$$\chi - \eta = \left(\frac{I+A}{2}\right) - \left(\frac{I-A}{2}\right) = A \tag{6}$$

Their sums and differences can be taken because both absolute electronegativity and chemical hardness equations depend on atomic number. As a result of this, we can obtain ionization energy and electron affinity equations depending on atomic number.

Obtained ionization energy and electron affinity equations are given in Table 5 and Table 6.

It is seen that that both ionization energy equations and electron affinity equations are quadratic equations. İonization energy and electron affinity equations can be represented as follows,

$$I = aZ^2 - bZ + c \tag{7}$$

$$A = a^{I}Z^2 - b^{I}Z + c^{I} \tag{8}$$

In Table 5 it is seen that a values are almost the same as numerical in ionization energy equations. (e.g. systems that contains electron 2 to 10). In the equations that have approximately the same a values, the relationship with the number of electron (N) of b and c values using graphical was examined. Same procedures were repeated for electron affinity equations. In the electron affinity equations that have approximately the same a', the relationship with the number of electron of b' and c' values using graphical method was examined. Obtained results are given in Table 7 and Table 8.

Table 3. Chemical hardness equations for systems that contain electron in different numbers

Number of electron	Chemical Hardness equation	Number of electron	Chemical Hardness equation
1	η= 8.5354Z-2.2399	11	η =0.9489Z-7.535
2	η=5.1116Z^2-3.132Z-1.4612	12	η=2.0203Z-19.732
3	η=1.9125Z-3.1886	13	η=0.9Z-8.2665
4	η=3.2156Z-7.5381	14	η=0.9394Z-9.2878
5	η=2.3194Z-7.3331	15	η=1.3406Z-14.862
6	η=2.3505Z-8.9432	16	η=0.9832Z-11.091
7	η=2.8931Z-12.187	17	η=0.9413Z-10.77
8	η=2.3718Z-12.489	18	η=3.5794Z-51.133
9	η=2.2922Z-13.04	19	η=1.3778Z-22.603
10	η=0.9212Z^2-9.804Z+17.503	20	η=1.3666Z-22.813

Table 4. Absolute electronegativity equations for systems that contain electron in different numbers

Number of electron	Absolute electronegativity equation	Number of electron	Absolute electronegativity equation
1	χ=13.638Z^2-8.7392Z+2.4881	11	χ=1.5801Z^2-26.965Z+107.24
2	χ=8.5329Z^2-14.225Z+6.4174	12	χ=1.5777Z^2-29.8352Z+133.47
3	χ=3.4217Z^2-13Z+11.012	13	χ=1.5832Z^2-32.934Z+162.88
4	χ=3.4286Z^2-18.253Z+22.251	14	χ=1.5857Z^2-34.846Z+180.85
5	χ=3.4359Z^2-23.909Z+37.561	15	χ=1.5835Z^2-37.079Z+204.63
6	χ=3.4262Z^2-28.365Z+52.699	16	χ=1.5859Z^2-39.496Z+231.37
7	χ=3.4285Z^2-33.677Z+74.271	17	χ=1.6149Z^2-42.669Z+266.45
8	χ=3.4327Z^2-39.025Z+99.27	18	χ=1.6569Z^2-49.24Z+352.93
9	χ=3.4379Z^2-43.828Z+125.65	19	χ=1.6642Z^2-54.37Z+426.35
10	χ=2.5125Z^2-36.17Z+119.93	20	χ=1.6728Z^2-57.459Z+474.86

Table 5. Ionization energy equations for systems that contain electron in different numbers

Number of electron	Ionization energy equation	Number of electron	Ionization energy equation
1	I=13.638Z^2-0.2038Z+0.2482	11	I=1.5801Z^2-26.016Z+99.705
2	I=13.6446Z^2-17.357Z+4.956	12	I=1.5777Z^2-27.815Z+113.74
3	I=3.4217Z^2-11.087Z+7.8234	13	I=1.5832Z^2-32.034Z+154.61
4	I=3.4286Z^2-15.037Z+14.712	14	I=1.5857Z^2-33.906Z+171.56
5	I=3.4359Z^2-21.589Z+30.228	15	I=1.5835Z^2-35.738Z+189.77
6	I=3.4262Z^2-26.016Z+43.756	16	I=1.5859Z^2-38.512Z+220.27
7	I=3.4285Z^2-30.784Z+62.084	17	I=1.6149Z^2-41.727Z+255.68
8	I=3.4327Z^2-36.653Z+86.781	18	I=1.6569Z^2-45.660Z+301.79
9	I=3.4379Z^2-41.536Z+112.61	19	I=1.6642Z^2-52.992Z+403.75
10	I=3.4337Z^2-45.974Z+137.43	20	I=1.6728Z^2-56.092Z+452.05

Table 6. Electron affinity equations for systems that contain electron in different numbers

Number of electron	Electron affinity equation	Number of electron	Electron affinity equation
1	A=13.38Z^2-17.274Z+4.728	11	A=1.5801Z^2-27.914Z+114.8
2	A=3.4213Z^2 -11.093Z+7.878	12	A=1.5777Z^2-31.855Z+153.2
3	A=3.4217Z^2-14.912Z+14.20	13	A=1.5832Z^2-33.831Z+171.1
4	A=3.4286Z^2-21.450Z+29.79	14	A=1.5857Z^2-35.785Z+190.1
5	A=3.4359Z^2-26.228Z+44.89	15	A=1.5835Z^2-38.419Z+219.5
6	A=3.4262Z^2-30.715Z+61.64	16	A=1.5859Z^2-40.479Z+242.4
7	A=3.4258Z^2-36.570Z+86.46	17	A=1.6149Z^2-43.610Z+277.2
8	A=3.4327Z^2-41.397Z+111.8	18	A=1.6569Z^2-52.819Z+404
9	A=3.4379Z^2-46.120Z+138.7	19	A=1.6642Z^2-55.748Z+448.9
10	A=1.5913Z^2-26.366Z+102.4	20	A=1.6728Z^2-58.825Z+497.6

RESULTS AND DISCUSSION

As a result, ionization energy and electron affinity equations can be expressed as follows and ionization energy and electron affinity can be calculated with these equations.

$$I = aZ^2 - bZ + c \quad (9)$$

$$A = a^{\prime}Z^2 - b^{\prime}Z + c^{\prime} \quad (10)$$

In These equations, relationship with the number of electron of coefficients are given in Table 7 and Table 8. As is known, ionization energy and electron affinity values are usually calculated as experimental. Moreover, there are fewer equations related with ionization energy and electron affinity in the current literature. Ionization energy and electron affinity values of atoms and ions can be easily calculated. Knowledge of the atomic number and number of electron of the atom or ion is sufficient to make calculations with these equations. Comparison of experimental ionization energy and electron affinity values with calculated from obtained equations ionization energy and electron affinity values are given Table 9 and Table 10. Results in tables show that calculated values are compatible with experimental data. Moreover, relative error values are very low. Calculated values are close to experimental values in all systems that contain electron from 1 to 20.

Table 7. Relationship between number of electron with b and c values in ionization energy equations

N	a	b	c
1-2	13.64	17.153N - 16.949	4.7078N – 4.4596
3-10	3.43	5.0793N - 4.4312	$1.5706N^2$-1.5527N- 2.5854
11-14	1.58	$0.0679N^2$ + 0.7486N + 9.6854	$1.4797N^2$-15.061N+87.896
15-16	1.59		
17	1.61		
18	1.65		
19-20	1.67	3.1N – 5.908	48.3N-513.95

Table 8. Relationship between number of electron with b’ and c’ values in electron affinity equations

N	$a^{\prime}$	$b^{\prime}$	$c^{\prime}$
1	13.38	17.274	4.728
2-9	3.43	5.0888N+0.5721	$1.611N^2$+1.2138N-6.6946
10-11	1.59	2.4426N+1.8072	$0.5375N^2$+10.243N-55.23
12	1.57		
13	1.58		
14-16	1.59		
17	1.61		
18	1.66	3.003N-1.2597	$1.9N^2$-25.4N+245.6
19-20	1.67		

Table 9. Calculated and experimental ionization energy values for some selected ions

Ion	Experimental I (I_E)	Calculated I (I_C)	I_E - I_C	% Relative error
He^{+}	54.41	54.39	0.02	0.036
Li^{2+}	122.44	122.37	0.07	0.057
C^{+}	24.38	24.38	0.00	0.000
N^{2+}	47.44	47.45	0.01	0.021
Mg^{7+}	265.89	265.91	0.02	0.007
Al^{8+}	330.22	330.21	0.01	0.003
Si^{9+}	401.42	401.39	0.03	0.007
F^{2+}	62.70	62.51	0.19	0.303
Ne^{3+}	97.11	96.82	0.29	0.298
Na^{4+}	138.39	137.98	0.41	0.296
Mg^{5+}	186.50	185.99	0.51	0.273
S^{7+}	328.22	328.13	0.09	0.027
CI^{8+}	400.02	400.05	0.03	0.007
Ar^{9+}	478.68	478.84	0.16	0.033
Ca^{7+}	147.24	147.20	0.04	0.027
Sc^{8+}	180.02	180.07	0.05	0.027
Ti^{9+}	215.91	216.11	0.20	0.092
Sc^{5+}	111.10	110.89	0.21	0.189
Ti^{6+}	140.84	140.57	0.27	0.191
V^{7+}	173.70	173.42	0.28	0.161
Cr^{8+}	209.24	209.45	0.21	0.100
Mn^{9+}	248.32	248.64	0.32	0.128
Co^{7+}	156.49	157.02	0.53	0.338
Ni^{8+}	192.77	192.93	0.16	0.083

Table 10. Calculated and experimental electron affinity values for some selected ions

Ion	Experimental A (A_E)	Calculated A (A_C)	A_E - A_C	% Relative error
Be^{3+}	153.89	153.83	0.06	0.038
B^{4+}	259.36	259.30	0.06	0.023
C^{+}	11.25	11.21	0.04	0.355
N^{2+}	29.60	29.65	0.05	0.168
O^{3+}	54.93	54.96	0.03	0.054
O^{+}	13.61	13.32	0.29	2.130
F^{2+}	34.97	35.03	0.06	0.171
Ne^{3+}	63.44	63.60	0.16	0.252
Si^{6+}	205.05	205.01	0.04	0.019
P^{7+}	263.21	263.16	0.05	0.018
Ar^{8+}	143.45	143.42	0.03	0.020
K^{9+}	175.81	175.93	0.12	0.068
P^{+}	10.48	10.13	0.35	3.339
S^{2+}	23.32	23.51	0.19	0.814
Cl^{3+}	39.61	40.05	0.44	1.110
Ar^{+}	15.75	15.46	0.29	1.841
K^{2+}	31.62	31.60	0.02	0.063
Cr^{7+}	161.05	160.75	0.30	0.186
Mn^{8+}	196.46	196.27	0.19	0.096
Fe^{9+}	235.03	235.02	0.01	0.004
Co^{8+}	156.49	156.96	0.47	0.300
Ni^{9+}	192.77	192.74	0.03	0.015
Ti^{2+}	13.57	13.80	0.23	1.694
V^{3+}	29.30	30.28	0.98	3.344

CONCLUSION

Ionization energies and electron affinities of atoms and atomic ions are generally determined experimentally. Moreover, ionization energies of atoms and ions can be calculated taking advantage Slater's rules. In the present report, ionization energy and electron affinity equations are presented using chemical hardness and absolute electronegativity concepts. Obtained results have quick and easy calculation ability ionization energies and electron affinities. Additionally, obtained results from the equations are compatible with experimental data.

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