Quantum Mechanical Study of Some Atomic Properties

Prabhat Ranjan, Tanmoy Chakraborty
Manipal University Jaipur,
India

E-mail: prabhat.ranjan@jaipur.manipal.edu

tanmoy.chakraborty@jaipur.manipal.edu

Abstract:-

Invoking the atomic radius as size descriptor, we can easily predict and model so many physico chemical properties of atoms and molecules. Since it has not been possible to isolate an atom and to determine its size, the atomic size is not an observable. The theoretical paradigm to study the electronic structure and properties of atoms, molecules and crystalline bodies is quantum mechanics or wave mechanics. But, radius is not a quantum mechanical observable and cannot be evaluated easily. As we know that atomic radius is periodic in nature, we can compute the absolute size of atom invoking its periodic correlation with other periodic properties. Recently Chakraborty et al. published a new set of theoretical atomic radii on basis of other periodic properties namely effective nuclear charge and ionization energy. In this venture , we have used that particular atomic size to calculate another important periodic parameter namely global hardness (η). Using the inverse relationship between atomic size and global hardness, we have computed a set of atomic hardness for 103 elements of the periodic table. The express periodicity of periods and groups exhibited by the computed atomic hardness and the manifest relativistic effect of the lanthanoids and actinoids, etc. speak volumes for the efficacy of the present method. We have also applied our computed atomic hardness to evaluate another important periodic parameter, electrophilicity index (ω).The absolute electronegativity value evaluated by Chakraborty et al. is the necessary input to compute the electrophilicity index .A comparative study has been done with our computed electrophilicity index values with other reported results. A nice correlation supports the validity of this work.

Introduction:-

The atomic radius is an important parameter to correlate many physico chemical properties of atoms and molecules. The proper idea about the atomic size helps to demonstrate so many biochemical processes. A study of proper size descriptor is still active field of research. Since it has not been possible to isolate an atom and to determine its size, the atomic size is not an observable. The theoretical paradigm to study the electronic structure and properties of atoms, molecules and crystalline bodies is quantum mechanics or wave mechanics. But, radius is not a quantum mechanical observable and cannot be evaluated easily. As we know that atomic radius is periodic in nature, we can compute the absolute size of atom invoking its periodic correlation with other periodic properties. Recently Chakraborty et al. [1] published a new set of atomic radii of 103 elements of the periodic table .The set of radius is already applied into the real world for calculating the internuclear distance of some hetero nuclear diatomic molecules. In this venture we have applied the same set of atomic radii to calculate the another fundamental periodic property-atomic hardness.

The hardness is also an important chemical parameter. From the early days of chemistry, a lot of scientific research is being carried out to define the atomic hardness. Muliken [2] first time pointed out the term –hardness, for explaining the deformation of atoms, molecules or ions in the presence of small perturbation. Later, Pearson and Klopman [3] tried to rationalize this intrinsic atomic property. Pearson introduced the famous HSAB principle which qualitatively has explained the hard and soft nature of atoms in the particular chemical reaction.
Parr and Pearson [4] using conceptual Density Functional Theory proposed an equation through which we can quantitatively calculate the atomic hardness (η). The ansatz is –

$$\eta = (I-A)/2 \qquad (1)$$

Where I and A represent the ionization energy and electron affinity of the atoms respectively.
On basis of their concept, finally a computation friendly ansatz was established and that is

$$\eta = 1/(2r) \qquad (2)$$

Where r is the absolute radii of the atoms.
Although, recently Ghosh et al. [5] reported a new ansatz to evaluate the atomic hardness with proper dimension, the concept of Parr and Pearson is still active and important to evaluate the atomic hardness.
In this study, we have used the equation (2) to compute the atomic hardness of 103 elements of the periodic table and the new set of atomic radii of Chakraborty et al.[1] is used as input of size descriptor.
Our computed global hardness exhibits the periodic behavior. A comparative study of our computed atomic hardness with the other existing data validates our effort.

Using our evaluated atomic hardness, we have calculated another atomic parameter-electrophilicity index (ω). Parr et al. [6] introduced the global electrophilicity index as

$\omega = (\mu)^2/ (2\eta) = (\chi)^2/ (2\eta)$.

The electronegativity (χ) used of the above ansatz has been collected from the reference [7].

Method of Computation:

In this venture we have first calculated the global hardness of 103 atoms of the periodic table. The computed hardness is reported in atomic unit. The following ansatz has been used to compute the atomic hardness.

$$\eta = 1/(2r) \qquad (2)$$

Where r is the absolute radii of the atoms. The atomic radii have been taken from the reference [1]. The evaluated set of hardness is presented in the Table -1.

Using this reported hardness, we have calculated the electrophilicity index (ω). To compute electrophilicity index, we have used the proposed ansatz of Parr et al. The ansatz is –

$\omega = (\chi)^2/ (2\eta)$

where, χ represents the electronegativity of the atoms. In this calculation we have taken the electronegativity from the reference [7].The electrophilicity index has been reported in atomic unit.

Results and Discussions:-

We have presented our computed atomic hardness in the Table -1. The atomic hardness of 103 elements of the periodic table are plotted as a function of atomic number in the Figure -1.As the atomic hardness is neither quantum mechanical observable nor it can be evaluated experimentally. In absence of any benchmark, we have made a comparative study of our computed data with the recently published atomic hardness of Ghosh and Islam[5]. The nice correlation between our results with the other existing data supports our effort.

To perform a validity test of our evaluated atomic hardness, we have computed the electrophilicity index for a series of 103 elements of the periodic table.

The computed electrophilicity index of 103 elements is plotted as a function of atomic number in the Figure -2. The electrophilicity index of the present calculation exhibits a nice periodic behavior.

Conclusions:

In the present venture, we have computed a fundamental periodic property-atomic hardness. As we know that all periodic properties are interrelated, we have used our recently published radii to compute the set of hardness. To perform validity test, we have compared our computed hardness with the other existing data. A nice correlation is observed that supports our effort. Secondly, we have computed the another periodic property, electrophilicity index of 103 elements, invoking our evaluated global hardness. The computed electrophilicity index exhibits a nice periodic behavior that validate our model.

References:

[1] T.Chakraborty, K.Gazi, D. C.Ghosh , Mol. Phys. 108 (2010) 2081.
[2] R. S Mulliken, J. Am. Chem. Soc. 74 (1952) 811.
[3] R. G. Pearson, J. Am. Chem. Soc. 85 (1963) 3533 ; G. Klopman, J. Am. Chem. Soc. 86 (1964) 1463
[4] R. G. Parr, R. G. Pearson, J. Am. Chem. Soc.105 (1983) 7512
[5] D. C. Ghosh, N.Islam, Int. J.Quant. Chem. 110 (2010) 1206
[6] R.G.Parr, L.V. Szentpaly, S. Liu, J. Am. Chem. Soc. 121 (1999) 1922
[7] D.C.Ghosh, T. Chakraborty, B.Mandal, Theo. Chem. Acc. 124 (2009) 295

Table 1: Computed atomic hardness of present calculation and a comparative table with Ghosh and Islam's computed hardness.

Atomic No.	Elements	Atomic Hardness (a.u)	Atomic Hardness(eV)	GI Hardness (eV)
1	H	0.425675676	11.58306081	6.429954
2	He	0.909903714	24.75938996	12.54491
3	Li	0.12677271	3.449612208	2.374587
4	be	0.233559891	6.355398182	3.496763
5	be	0.200211864	5.447965042	4.619009
6	c	0.280832095	7.64172214	5.740979
7	N	0.376279863	10.23895137	6.862467
8	O	0.344845562	9.383592597	7.985436
9	F	0.46145797	12.55673282	9.106475
10	Ne	0.601500341	16.36742578	10.23034
11	Na	0.118697291	3.229871972	2.444141
12	Mg	0.181693332	4.944057268	3.014651
13	Al	0.13787713	3.751774582	3.584907
14	Si	0.192380398	5.234863022	4.155131
15	P	0.25388601	6.908492228	4.725803
16	S	0.249340369	6.784800792	5.295972
17	Cl	0.321194465	8.740022578	5.866186
18	Ar	0.402801035	10.96061897	6.436619
19	K	0.09895658	2.692707506	2.327318
20	Ca	0.14197564	3.863299136	2.758724
21	Sc	0.152630365	4.15322485	2.858192
22	Ti	0.159532136	4.34102894	2.95783
23	V	0.157228593	4.278347258	3.057341
24	Cr	0.157603193	4.288540473	3.156725
25	Mn	0.174641938	4.75218177	3.256383
26	Fe	0.185658153	5.051944008	3.355931
27	Co	0.185580025	5.049818067	3.455609
28	Ni	0.179098416	4.873447001	3.555013

29	Cu	0.181220464	4.931190055	3.654418
30	Zn	0.225019134	6.122995663	3.75416
31	Ga	0.137070037	3.729812785	4.18552
32	Ge	0.184223352	5.012901622	4.616627
33	As	0.233621755	6.357081582	5.066215
34	Se	0.231374607	6.295934418	5.479496
35	Br	0.286580743	7.798148597	5.9111
36	Kr	0.347609038	9.458789543	6.341847
37	Rb	0.094985102	2.584639624	2.120458
38	Sr	0.131497863	3.578188351	2.53737
39	Y	0.148551538	4.042235908	2.633547
40	Zr	0.16005323	4.355208444	2.729753
41	Nb	0.160811961	4.37585426	2.825974
42	Mo	0.166185153	4.522064188	2.92213
43	Tc	0.170610613	4.642485396	3.018371
44	Ru	0.17269286	4.699145412	3.114598
45	Rh	0.174791914	4.756262782	3.210756
46	Pd	0.197492163	5.373959248	3.306947
47	Ag	0.177381511	4.826728297	3.403195
48	Cd	0.214268362	5.830456393	3.499376
49	In	0.131884564	3.588710861	3.916369
50	Sn	0.170160772	4.630244759	4.333233
51	Sb	0.202820788	5.518956462	4.750079
52	Te	0.211900376	5.766021142	5.166979
53	I	0.249481426	6.788639072	5.583887
54	Xe	0.294687604	8.018744404	6.000897
55	Cs	0.088144175	2.398491156	0.682915
56	Ba	0.119463633	3.250724909	0.920095
57	La	0.127782875	3.477099821	1.157089
58	Ce	0.124558678	3.389366191	1.394276
59	Pr	0.123104122	3.349786266	1.631473
60	Nd	0.124482499	3.387293282	1.868439
61	Pm	0.125832224	3.424020639	2.105658
62	Sm	0.127505783	3.46955985	2.342665
63	Eu	0.128197674	3.488386919	2.579815
64	Gd	0.139498102	3.795882855	2.817026

65	Tb	0.132399299	3.602717338	3.054037
66	Dy	0.134124088	3.649650547	3.291169
67	Ho	0.136223229	3.706770284	3.528297
68	Er	0.138143469	3.759021928	3.765525
69	Tm	0.140066698	3.811354931	4.002555
70	Yb	0.141686747	3.855438072	4.239478
71	Lu	0.121823204	3.314931215	4.476583
72	Hf	0.151139544	4.112658137	4.706522
73	Ta	0.181506379	4.938970092	4.950847
74	W	0.183673469	4.997938776	5.187931
75	Re	0.181121227	4.928489698	5.425608
76	Os	0.20181527	5.491595302	5.661914
77	Ir	0.212121212	5.772030303	5.900043
78	Pt	0.209501188	5.700736817	6.136715
79	Au	0.214511552	5.837073855	6.37413
80	Hg	0.245819398	6.688991639	6.610266
81	Ti	0.1397486	3.802699166	1.704349
82	Pb	0.171952171	4.678990512	1.941353
83	Bi	0.168406314	4.582504201	2.178492
84	Po	0.196728625	5.353182602	2.415812
85	At	0.227985525	6.203714113	2.652778
86	Rn	0.257042938	6.994395376	2.889955
87	Fr	0.094331551	2.566855829	0.988253
88	Ra	0.121120571	3.295811865	1.28195
89	Ac	0.118278128	3.218466139	1.349725
90	Th	0.140722225	3.829192469	1.417526
91	Pa	0.134841767	3.66917933	1.936857
92	U	0.141815843	3.858950906	2.230558
93	Np	0.143445733	3.903301854	2.52412
94	Pu	0.137884315	3.751970089	3.043613
95	Am	0.136013159	3.701054076	3.416868
96	Cm	0.136701798	3.719792622	3.404984
97	Bk	0.141550313	3.851725566	3.92442
98	Cf	0.143135346	3.894855891	4.218081
99	Es	0.145937896	3.971116099	4.511593
100	Fm	0.147788204	4.021464812	4.805093

101	Md	0.149643705	4.071954869	5.098982
102	No	0.151269152	4.116184885	5.392605
103	Lr	0.102470761	2.788331888	5.460699

Table 2: Computed Electrophilicity Index in atomic Unit as a function of atomic number.

Atomic No.	Element	Electrophilicity Index
1	H	0.081750308
2	He	0.107743395
3	Li	0.055311965
4	be	0.041625082
5	be	0.071221816
6	c	0.076076315
7	N	0.085037005
8	O	0.137205123
9	F	0.148856233
10	Ne	0.162529063
11	Na	0.036642652
12	Mg	0.032885305
13	Al	0.060816096
14	Si	0.061487174
15	P	0.065415382
16	Si	0.092556778
17	Cl	0.098501085
18	Ar	0.106102239
19	K	0.05305375
20	Ca	0.04317573
21	Sc	0.041777319
22	Ti	0.041628346
23	V	0.044040392
24	Cr	0.045855207
25	Mn	0.04323336
26	Fe	0.042520376
27	Co	0.044516598
28	Ni	0.048302415
29	Cu	0.050020208
30	Zn	0.042238003
31	Ga	0.085557696
32	Ge	0.078943525

33	As	0.07732442
34	Se	0.09687082
35	Br	0.096760336
36	Kr	0.098285815
37	Rb	0.072286552
38	Sr	0.057937869
39	Y	0.052685538
40	Zr	0.050282309
41	Nb	0.051511152
42	Mo	0.051351253
43	Tc	0.051573313
44	Ru	0.05257908
45	Rh	0.05364434
46	Pd	0.049066264
47	Ag	0.056496589
48	Cd	0.04839928
49	In	0.091782338
50	Sn	0.083708723
51	Sb	0.083085188
52	Te	0.094377038
53	I	0.095249421
54	Xe	0.095818489
55	Cs	0.150534618
56	Ba	0.112946511
57	La	0.10782066
58	Ce	0.11340111
59	Pr	0.118081724
60	Nd	0.120615983
61	Pm	0.123683592
62	Sm	0.126933761
63	Eu	0.131701328
64	Gd	0.126619338
65	Tb	0.139945269
66	Dy	0.145271737
67	Ho	0.150744866
68	Er	0.156990605

69	Tm	0.163825326
70	Yb	0.171639196
71	Lu	0.211883483
72	Hf	0.181329397
73	Ta	0.160788136
74	W	0.16921972
75	Re	0.182909324
76	Os	0.175087794
77	Ir	0.175967455
78	Pt	0.192154711
79	Au	0.20043338
80	Hg	0.1868436
81	Ti	0.105020173
82	Pb	0.088254171
83	Bi	0.093504602
84	Po	0.0833216
85	At	0.075070028
86	Rn	0.06971736
87	Fr	0.053183901
88	Ra	0.044475072
89	Ac	0.046399309
90	Th	0.039760562
91	Pa	0.049253896
92	U	0.052387387
93	Np	0.058431976
94	Pu	0.076417398
95	Am	0.0886897
96	Cm	0.091084095
97	Bk	0.112487893
98	Cf	0.127994517
99	Es	0.144424207
100	Fm	0.163961278
101	Md	0.185947018
102	No	0.210914184
103	Lr	0.321253424

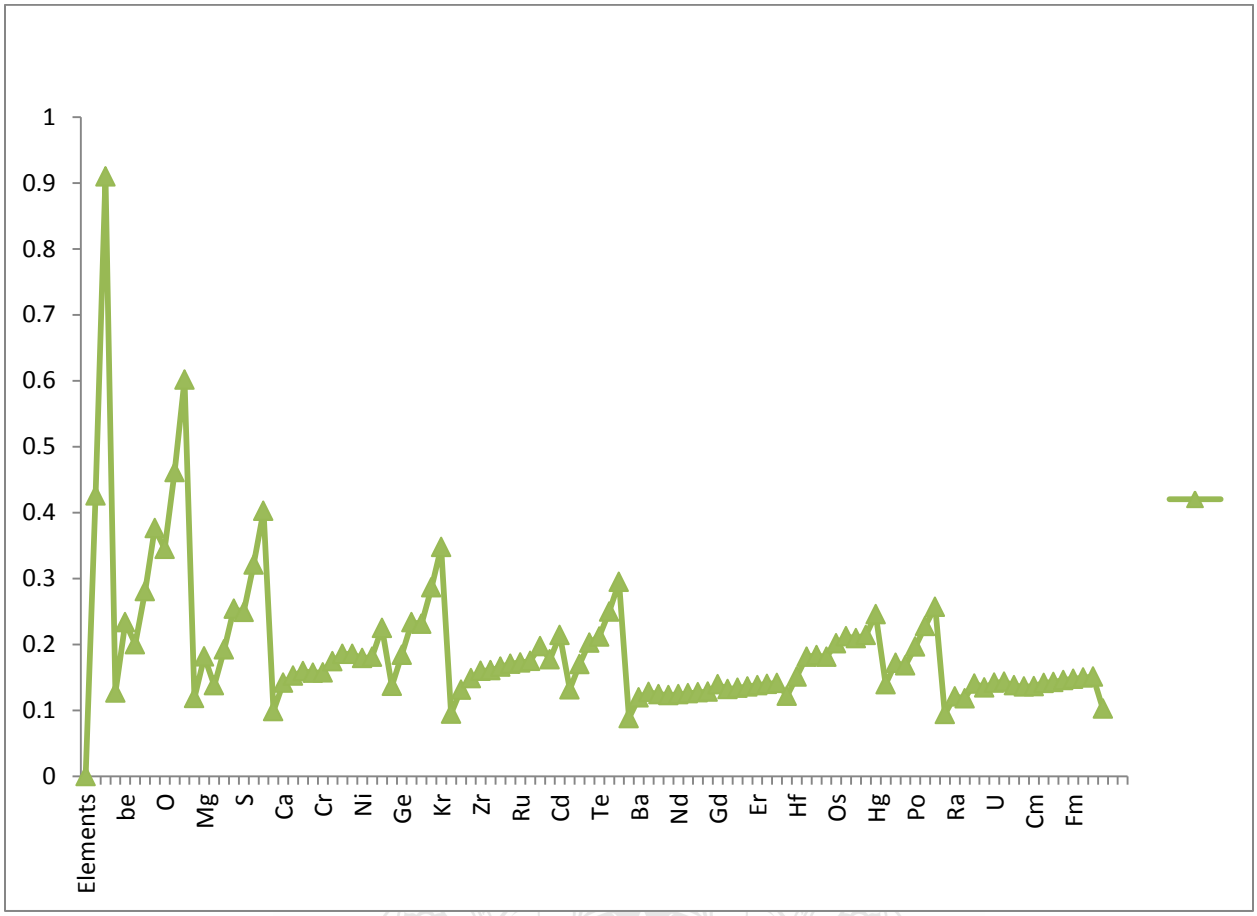

Figure 1: A plot of Computed atomic hardness in Y-axis as a function of Elements (X-axis)

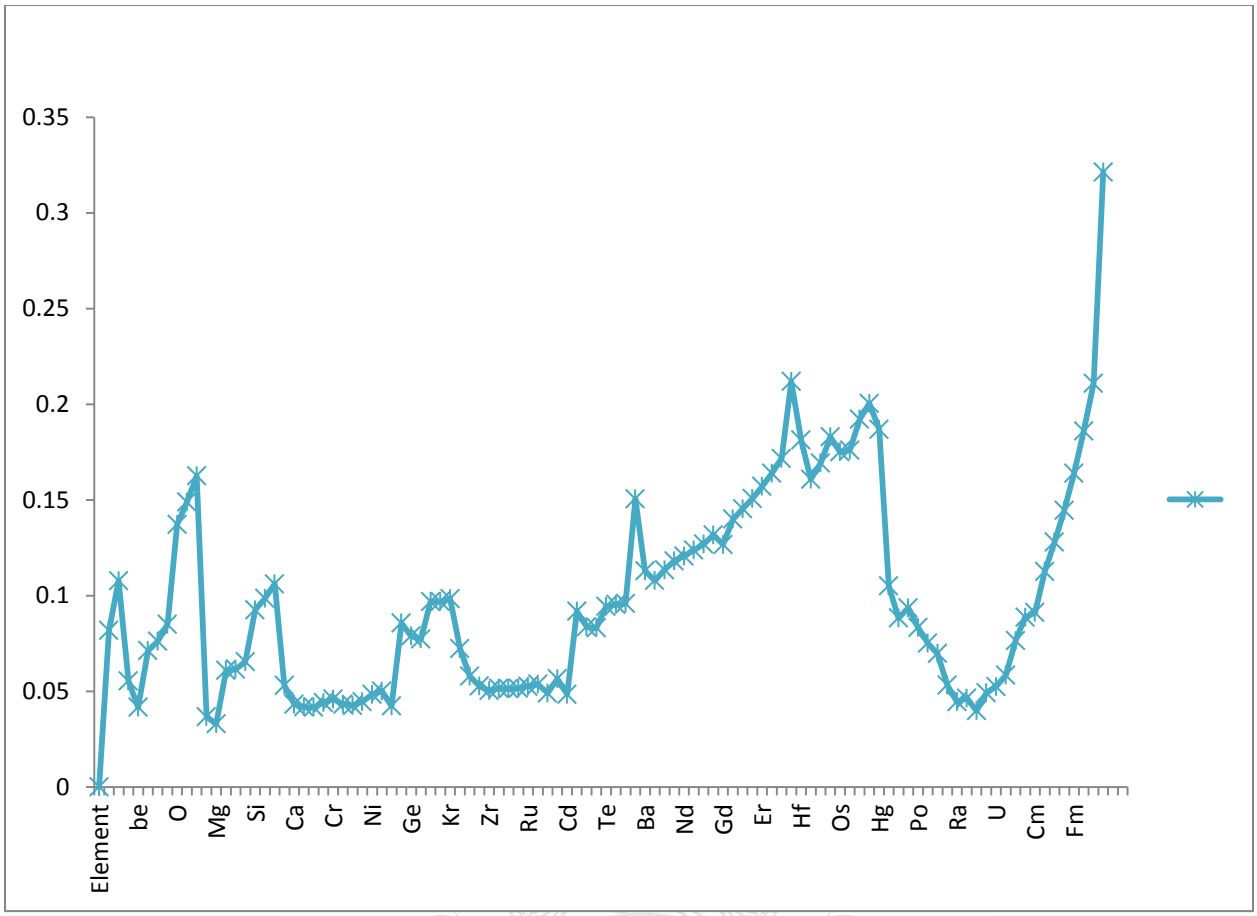

Figure 2: A plot of Electophilicity Index in Y-axis and as a function of Elements in X-axis