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Electron Affinity, Electronegativity, and Electrophilicity of Atoms and Ions†

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The electron affinity, electronegativity, and electrophilicity of several neutral atoms and their positive and negative ions are calculated at various levels of theory using different basis sets in the gas phase as well as in the presence of solvent and counterions. The electron affinity and electronegativity of all of the anions and dianions are negative in gas phase, and accordingly the electrophilicity is unexpectedly large vis-a-vis its quadratic definition. Many of these trends get altered in case the effects of solvent and counterions are taken into account.

1. Introduction

Electron affinity, electronegativity, and electrophilicity are three related chemical concepts.[1−3] Although electron affinity is a physically observable and experimentally measurable quantity, electronegativity and electrophilicity are arbitrarily defined quantities. The difference in energy of a neutral atom and its anion in gas phase is the electron affinity (A) which may be equated with the electron-gain enthalpy with a minus sign, at $T = 0$ K. Therefore, the electron affinity of an N-electron system is given by

$$A = \mathrm{E(N)} - \mathrm{E(N+1)} \tag{1}$$

The electronegativity of an atom in a molecule is the power with which it attracts electrons to itself.[4] To provide an absolute definition of electronegativity (χ) of an isolated species like an atom, ion, molecule or solid, Mulliken[5] defined it as

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

where I is the ionization potential given by

$$I = \mathrm{E(N-1)} - \mathrm{E(N)} \tag{3}$$

It implies that a system with larger I and A values would prefer to accept an electron rather than losing it. Unlike Pauling electronegativity[4] (atoms-in-a-molecule definition), Mulliken electronegativity is absolute, as it is defined for the whole molecule. The energy of a system may be approximately expressed as a quadratic function of the charge, and it attains its minimum value for the majority of the atoms and ions around the mononegative charge.[1−3] This fact is to be verified in the present work. Considering the slope of this parabola to be the electronegativity (χ), it is easy to show that the χ of a system also changes with the charges on it,[6] which may become negative for the negatively charged species as the hardness (η, see below) is always positive because of the convexity of the E versus N plot.[7−10] The electrophilicity of a system is the measure of its reactivity toward attracting electrons from a nucleophile so that they form a bond. Inspired by the work of Maynard et al.,[11] a definition of an electrophilicity index (ω) is proposed by Parr et al.[12−14] as,

$$\omega = \frac{\mu^2}{2\eta} = \frac{\chi^2}{2\eta} \tag{4}$$

where μ is the chemical potential[15] (the negative of the electronegativity) and η is the chemical hardness.[16] This definition is based on the energy lowering due to the maximum amount of electron flow, which may be more or less than one as opposed to exactly one in the definition of A (eq 1), to a system from a free electron gas at 0 K with $\mu = 0$. Although Maynard et al.[11] provided the empirical definition based on kinetic data, the same definition (eq 4) is obtained by Parr et al.[12−14] from an energy viewpoint. The concept of net electrophilicity (electroaccepting power of a system relative to its own electrodonating power) is also introduced, and an electrophilicity equalization principle is proved.[17]

These conceptual density functional theory based reactivity descriptors may be considered[7] to be the zero temperature limits (where the equilibrium state becomes the associated ground state) of the corresponding finite temperature quantities in canonical/grand canonical ensembles. Although these descriptors are useful[7−25] in analyzing structure, properties, reactivity, dynamics, toxicity, aromaticity, and so forth, these definitions are not strictly valid[26] due to the discontinuity in the E versus N curve.[27] This problem may, however, be avoided by considering these quantities in the zero temperature limit of a grand canonical ensemble or the isolated system under study as a part of a larger system.[26] The application of these descriptors in analyzing the chemical reactivity is generally made through some related electronic structure principles. The chemical potential (electronegativity) equalization principle[28] is akin to a similar principle in thermodynamics. For a stable state of a system or the favorable direction of a physicochemical process, hardness often gets maximized,[21] and electrophilicity gets minimized.[23,24]

Most of the neutral atoms possess positive A values, and the halogen atoms have typically high A values as they attain a noble gas (with very small or negative A values) configuration after accepting an electron. Anions possess negative A values since in these systems electron−electron repulsion outweighs the electron−nuclear attraction. The formation of stable metal oxides or sulphides is generally explained in terms of the role played by the lattice energy and solvation energy.[1,2] Pearson[29−31] has shown that the electronegativity values are more or less

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Table 1. Ionization Potential (*I*), Electron Affinity (*A*), Electronegativity (*χ*), Chemical Hardness (*η*), Electrophilicity (*ω*), and the Values of μ^+, μ^-, ω^+, and ω^- for Electroaccepting and Electrodonating Processes of Atoms and Ions Using Koopmans' Theorem at the B3LYP/6-311+G(d) Level of Theory

	I	A	χ	η	ω	μ^+	μ^-	ω^+	ω^-
	eV	eV	eV	eV	eV	eV	eV	eV	eV
(a) Atoms									
Li	29.308	1.172	15.240	28.136	4.128	−1.172	−29.308	0.024	15.265
Be	6.318	1.430	3.874	4.889	1.535	−1.430	−6.318	0.209	4.083
B	7.386	2.571	4.978	4.814	2.574	−2.571	−7.386	0.687	5.665
C	6.017	4.324	5.171	1.693	7.897	−4.324	−6.017	5.523	10.693
N	7.886	5.944	6.915	1.943	12.307	−5.944	−7.886	9.092	16.007
O	10.385	8.192	9.288	2.193	19.670	−8.192	−10.385	15.300	24.588
F	12.727	2.302	7.514	10.425	2.708	−2.302	−12.727	0.254	7.768
Ne	15.693	−3.964	5.864	19.656	0.875	3.964	−15.693	0.400	6.264
(b) Ions									
Li^+	63.914	6.942	35.428	56.971	11.015	−6.942	−63.914	0.423	35.851
Be^+	68.764	10.518	39.641	58.246	13.489	−10.518	−68.764	0.950	40.591
B^+	20.576	12.378	16.477	8.197	16.560	−12.378	−20.576	9.346	25.823
C^+	68.764	10.518	39.641	58.246	13.489	−10.518	−68.764	0.950	40.591
N^+	21.619	19.357	20.488	2.262	92.770	−19.357	−21.619	82.809	103.297
O^+	25.517	23.039	24.278	2.478	118.914	−23.039	−25.517	107.085	131.363
F^+	30.017	27.331	28.674	2.686	153.049	−27.331	−30.017	139.048	167.722
Ne^+	34.383	16.930	25.656	17.453	18.857	−16.930	−34.383	8.211	33.867
(c) Ions									
Li^{2+}	60.721	45.921	53.321	14.800	96.048	−45.921	−60.721	71.238	124.559
Be^{2+}	137.136	21.395	79.265	115.741	27.143	−21.395	−137.136	1.977	81.243
B^{2+}	125.330	26.798	76.064	98.532	29.360	−26.798	−125.330	3.644	79.708
C^{2+}	41.782	30.441	36.112	11.341	57.492	−30.441	−41.782	40.854	76.966
N^{2+}	45.182	35.684	40.433	9.498	86.063	−35.684	−45.182	67.034	107.467
O^{2+}	44.333	41.511	42.922	2.821	326.499	−41.511	−44.333	305.391	348.313
F^{2+}	50.268	47.268	48.768	2.999	396.487	−47.268	−50.268	372.478	421.246
Ne^{2+}	56.792	53.623	55.207	3.169	480.918	−53.623	−56.792	453.710	508.917
(d) Ions									
Li^-	−0.580	−1.744	−1.162	1.165	0.580	1.744	0.580	1.306	0.144
Be^-	−0.245	−2.538	−1.392	2.293	0.422	2.538	0.245	1.405	0.013
B^-	−1.946	−3.044	−2.495	1.098	2.835	3.044	1.946	4.220	1.724
C^-	−2.029	−3.402	−2.716	1.373	2.686	3.402	2.029	4.216	1.500
N^-	−1.609	−3.283	−2.446	1.674	1.788	3.283	1.609	3.220	0.774
O^-	−1.296	−7.078	−4.187	5.782	1.516	7.078	1.296	4.332	0.145
F^-	−0.353	−11.062	−5.708	10.709	1.521	11.062	0.353	5.713	0.006
Ne^-	−1.515	−12.124	−6.820	10.608	2.192	12.124	1.515	6.927	0.108
(e) Ions									
Li^{2-}	−2.398	−3.101	−2.750	0.703	5.376	3.101	2.398	6.839	4.089
Be^{2-}	−0.835	−1.383	−1.109	0.547	1.123	1.383	0.835	1.746	0.637
B^{2-}	6.802	5.754	6.278	1.048	18.801	−5.754	−6.802	15.793	22.071
C^{2-}	−6.972	−8.129	−7.551	1.158	24.626	8.129	6.972	28.546	20.995
N^{2-}	−8.402	−11.733	−10.067	3.331	15.213	11.733	8.402	20.663	10.596
O^{2-}	−9.289	−15.326	−12.307	6.037	12.546	15.326	9.289	19.455	7.147
F^{2-}	−11.781	−18.026	−14.903	6.245	17.782	18.026	11.781	26.014	11.111
Ne^{2-}	−17.234	−19.898	−18.566	2.665	64.681	19.898	17.234	74.297	4.089

same in the gas and the solution phases. However, the corresponding hardness values decrease on solvation.

In the present work we calculate the energy, electron affinity, ionization potential, electronegativity, hardness, and electrophilicity of some selected atoms and their cations, dications, anions, and dianions to analyze the electron-accepting characteristics of those systems. Section 2 provides the numerical details, while results and discussion are presented in Section 3. Finally Section 4 contains some concluding remarks.

2. Numerical Details

All of the calculations are done at the HF/6-311+G(d), B3LYP/6-311+G(d), and MP2/6-311+G(d) levels of theory. The *I* and *A* values are calculated using eqs 3 and 1, respectively, χ using eq 2, η as[32] $(I-A)$, and ω using eq 4. We also use Koopmans' theorem to approximate *I* and *A* in terms of the appropriate frontier orbital energies. Calculations are also performed in the solution phase,[33] in the presence of counterions as well as with different basis sets. Electrodonating (ω^-) and electroaccepting (ω^+) powers[34] are also calculated in terms of $\mu^- = -I$, $\mu^+ = -A$, and $\eta^+ = \eta^- = \eta^\pm = (\mu^+ - \mu^-)$.

3. Results and Discussion

Tables 1 and 2 present the values of the ionization potential, electron affinity, electronegativity, chemical hardness, and electrophilicity of selected atoms and ions in the gas phase and in aqueous phase, respectively. The calculations are done by using the Koopmans' theorem through the energies of the associated frontier orbitals, at the B3LYP/6-311+G(d) level of theory, and Tables I to III (Supporting Information) present the energy, ionization potential, electron affinity, electronegativity, chemical hardness, and electrophilicity of the selected atoms and ions in the gas phase calculated from the ΔSCF (self-consistent field) using the HF, MP2, and B3LYP levels of theory, respectively. Koopmans' theorem can reproduce the expected trends in most cases but for Li and F. In case of Li, the *I* value is overestimated, while it is underestimated in case of F. Both cations and dications are highly electronegative and

Table 2. Ionization Potential (I), Electron Affinity (A), Electronegativity (χ), Chemical Hardness (η), Electrophilicity (ω), and the Values of μ^+, μ^-, ω^+, and ω^- for Electroaccepting and Electrodonating Processes of Atoms and Ions Using Koopmans' Theorem in Aqueous Solution at the B3LYP/6-311+G(d) Level of Theory

	I	A	χ	η	ω	μ^+	μ^-	ω^+	ω^-
	eV	eV	eV	eV	eV	eV	eV	eV	eV
(a) Atoms									
Li	29.310	1.173	15.241	28.137	4.129	−1.173	−29.310	0.024	15.266
Be	6.319	1.430	3.874	4.889	1.535	−1.430	−6.319	0.209	4.083
B	7.458	2.519	4.988	4.939	2.519	−2.519	−7.458	0.642	5.630
C	6.244	4.307	5.275	1.937	7.183	−4.307	−6.244	4.787	10.063
N	7.981	5.916	6.948	2.065	11.687	−5.916	−7.981	8.471	15.420
O	10.454	8.153	9.303	2.300	18.812	−8.153	−10.454	14.448	23.751
F	12.746	2.291	7.519	10.455	2.703	−2.291	−12.746	0.251	7.770
Ne	15.693	−3.963	5.865	19.656	0.875	3.963	−15.693	0.400	6.264
(b) Ions									
Li^+	55.273	0.150	27.711	55.123	6.965	−0.150	−55.273	0.000	27.711
Be^+	60.951	2.865	31.908	58.086	8.764	−2.865	−60.951	0.071	31.979
B^+	12.541	4.440	8.491	8.101	4.450	−4.440	−12.541	1.217	9.708
C^+	14.959	7.737	11.348	7.222	8.916	−7.737	−14.959	4.145	15.493
N^+	14.464	12.126	13.295	2.338	37.801	−12.126	−14.464	31.445	44.740
O^+	16.156	13.526	14.841	2.630	41.881	−13.526	−16.156	34.789	49.631
F^+	22.151	19.419	20.785	2.731	79.089	−19.419	−22.151	69.038	89.823
Ne^+	25.296	8.128	16.712	17.167	8.134	−8.128	−25.296	1.924	18.636
(c) Ions									
Li^{2+}	90.156	29.442	59.799	60.713	29.449	−29.442	−90.156	7.139	66.938
Be^{2+}	120.797	5.259	63.028	115.538	17.192	−5.259	−120.797	0.120	63.1480
B^{2+}	109.065	10.560	59.813	98.505	18.159	−10.560	−109.065	0.566	60.379
C^{2+}	26.009	14.682	20.346	11.327	18.272	−14.682	−26.009	9.515	29.861
N^{2+}	30.703	21.190	25.947	9.513	35.385	−21.190	−30.703	23.601	49.547
O^{2+}	20.757	17.662	19.210	3.095	59.609	−17.662	−20.757	50.391	69.601
F^{2+}	34.493	31.462	32.978	3.031	179.372	−31.462	−34.493	163.262	196.24
Ne^{2+}	38.591	35.380	36.985	3.211	212.990	−35.380	−38.591	194.899	231.884
(d) Ions									
Li^-	4.417	1.435	2.926	2.982	1.436	−1.435	−4.417	0.345	3.272
Be^-	5.010	1.850	3.430	3.160	1.862	−1.850	−5.010	0.542	3.972
B^-	4.058	2.526	3.292	1.532	3.536	−2.526	−4.058	2.082	5.374
C^-	4.549	2.841	3.695	1.708	3.998	−2.841	−4.549	2.364	6.059
N^-	5.738	3.797	4.767	1.940	5.856	−3.797	−5.738	3.715	8.482
O^-	7.423	0.769	4.096	6.654	1.261	−0.769	−7.423	0.044	4.141
F^-	8.736	−3.010	2.863	11.746	0.349	3.010	−8.736	0.386	3.248
Ne^-	7.144	−3.998	1.573	11.143	0.111	3.998	−7.144	0.717	2.290
(e) Ions									
Li^{2-}	4.379	2.198	3.289	2.181	2.480	−2.198	−4.379	1.108	4.397
Be^{2-}	3.686	2.546	3.116	1.141	4.256	−2.546	−3.686	2.840	5.956
B^{2-}	4.554	2.041	3.298	2.513	2.164	−2.041	−4.554	0.829	4.127
C^{2-}	4.425	2.866	3.645	1.559	4.261	−2.866	−4.425	2.634	6.279
N^{2-}	5.702	1.023	3.362	4.679	1.208	−1.023	−5.702	0.112	3.474
O^{2-}	8.726	−1.589	3.569	10.315	0.617	1.589	−8.726	0.122	3.691
F^{2-}	7.263	−2.191	2.536	9.455	0.340	2.191	−7.263	0.254	2.789
Ne^{2-}	−0.530	−4.215	−2.372	3.685	0.764	4.215	0.530	2.411	0.038

electrophilic, as expected. For anions and dianions both I and A and hence χ values are negative. It implies that they will not like to accept electrons. It may be noted that their ω values are very high, which is counterintuitive and definitely a drawback of the quadratic appearance of χ in eq 4. Tables IV to VI (Supporting Information) report all of these quantities in the aqueous phase. For the neutral atoms and their cations and dications the numerical values differ, but the trends remain more or less the same as that obtained in the gas phase. However, for the anions and the dianions, the situation changes drastically. Calculations do not converge for N^{2-} in the aqueous phase for the cases of HF and MP2 levels of theory. The χ values become positive in several systems, and the ω values are no longer large. Tables I to VI (Supporting Information) also present the two-parabola model results for electrodonating and electroaccepting processes in the gas and aqueous phases, respectively. At a constant external potential the energy change due to electron transfer may be approximated through a quadratic expression.[7] Taking a cue from the Perdew−Parr−Levy−Balduz[27] prescription of the discontinuity in the E versus N curve, Gázquez et al.[34] suggested the definitions of electrodonating and electroaccepting powers through two different parabolic expressions for the addition and the removal of electrons, respectively. It may be noted that,[34] while larger ω^+ implies better accepting power, smaller ω^- implies better donating power. In general ω^+ follows the trend (for an element X) $X < X^+ < X^{2+}$ (also $X < X^- < X^{2-}$), and ω^- follows the trend $X^- < X < X^{2-}$ (also $X < X^+ < X^{2+}$). The anomaly in these trends may be rationalized in the cases with positive $\mu^\pm$ values (negative $\chi^\pm$ values) and by considering the quadratic appearance in the formula:[34] $\omega^\pm = (\mu^\pm)^2/2\eta$.

To check the inadequacy of the Koopmans' approximation we calculate the I and A values using eqs 1 and 3. Most of the important calculated quantities are provided in Tables I to VI (Supporting Information). We use the HF/6-311+G(d), MP2/6-311+G(d), and B3LYP/6-311+G(d) levels and also other basis sets like 6-31+G(d) and 6-311++G(d) for both in the gas-phase and also in the aqueous-phase calculations. A good agreement is found in the gas-phase calculation for atoms and their corresponding positive ions with experimental values. The

Table 3. Comparison of the Calculated B3LYP/6-311+G(d) Values with the Experimental Values

	I/eV			*A*/eV			χ/eV			η/eV		
atoms/ ions	calcd	exptl	ref	calcd	exptl	ref	calcd	exptl	ref	calcd	exptl	ref
Li	5.62	5.39	32	0.56	0.62	32	3.09	3.00	32	2.52	2.38	32
Be	9.12	9.30		−0.23	0.40	32	4.45	4.90	32	4.67	4.50	32
B	8.73	8.30	32	−0.35	0.28	32	4.19	4.29	32	4.06	4.01	32
C	9.77	11.26	32	1.64	1.27	32	5.76	6.27	32	5.46	5.00	32
N	14.60	14.53	32	1.06	0.07	32	7.83	7.30	32	6.72	7.23	32
O	15.29	13.61	32	4.36	1.46	32	9.82	7.54	32	5.97	6.08	32
F	21.40	17.42	32	3.48	3.40	32	12.44	10.41	32	8.96	7.01	32
Li^+	76.05	75.64	30	5.62	5.39	30	40.93	40.52	30	35.22	35.12	30
Be^{2+}	154.26	153.89	30	18.59	18.21	30	86.42	86.05	30	67.83	67.84	30

use of the B3LYP/6-311+G(d) level of theory to calculate the ionization potential and electron affinity for the atoms and their cations and dications provides the best correlation with the experimental values. Table 3 presents the comparison between the calculated and the experimental values wherever available.

For any system (except Be and Ne), energy becomes a minimum for the mononegative ion (Figure 1). However, its absolute μ value is not zero presumably because the external potential is not constant due to the change in the effective nuclear charge on electron addition or removal. Moreover, a smooth quadratic interpolation between the reference system and its corresponding cation and anion (cf. eq 2) leads to a minimum which is slightly displaced from the reference point. The *A* value of the N-electron system is same as the *I* value of the corresponding (N + 1) electron system (see eqs 1 and 3), which is not obeyed when Koopmans' approximation is used. It may be noted that this approximation should strictly be applied within the HF theory. As electrons are taken out, the *I*, *A*, χ, and ω values increase, implying that it is difficult to eject electrons further and the system would rather prefer to accept electrons. For the anions the *A* and χ values are negative, implying that they do not prefer to accept electrons any more as the electron−electron repulsion becomes stronger than the electron−nuclear attraction. However, large ω values for the dianions are surely counterintuitive and are arising out of the quadratic appearance of χ in the expression for ω (eq 4). This problem persists in the (ω^+, ω^-) values apart from their problems mentioned above.

The ω^+ values of dianions are very large and are larger than the related ω^- values. The dianions are unstable in the gaseous phase, which can be stabilized by considering the presence of suitable counterions.[35−38] There are other ways to tackle the anions and dianions problem, for example, the potential well approach used by Geerlings et al. and De Proft and Tozer.[39,40] Since aromatic trigonal clusters are expected to be important traps[41] for noble gas atoms and hydrogen and the related cluster anions and dianions are known to possess negative electronegativity values,[42] the sensitivity of results to the position of the counterions is checked. As reported in Tables VII to IX of the Supporting Information, we notice that the results are not very sensitive to the exact location of the counterion. We calculate the ionization potential and the electron affinity for $M^{2-}(Z^+)_2$: M = Li to Ne, molecules where Z contains one unit of point positive charge. Tables X to XII (Supporting Information) present the values of the ionization potential, electron affinity, electronegativity, hardness, electrophilicity, and also that of μ^+, μ^-, ω^+, and ω^- for the electroaccepting and electrodonating processes of the dianions in the presence of counterions, calculated at the HF, MP2, and B3LYP levels of theory, respectively, with the 6-311+G(d) basis set. Because of the presence of positive counterions, the otherwise negative values of the ionization potential and the electron affinity of all of the dianions become positive.

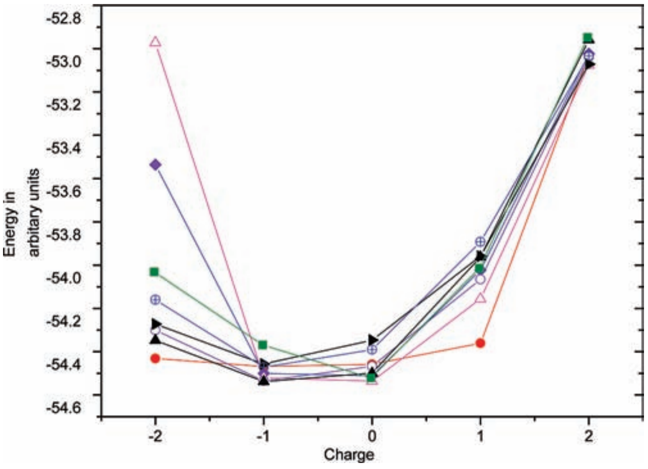

Figure 1. Change in energy values of Li through Ni with charges of (−2 to +2). Red ●, Li; green ■, Be; blue ⊕, B; black right-pointing triangle, C; ▲, N; purple ○, O; pink △, F; ◆, Ne.

4. Concluding Remarks

It has been demonstrated through the calculation of ionization potential and electron affinity of several neutral atoms and their cations, dications, anions, and dianions at the gas and solution phases at various levels of theory using different basis sets that the mononegative ion is the most stable species of any element (except Be and Ne). Calculated values of electron affinity, electronegativity, and electrophilicity of dianions often provide some counterintuitive trends. The presence of counterions and/or solvent often remedies these problems.

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Supporting Information Available:

Tables of different reactivity descriptors for atoms and ions calculated at different levels of theory and the energy values of dianions in the presence of counterions placed at different locations and calculated at the HF/6-311+G(d) level of theory. This material is available free of charge via the Internet at http://pubs.acs.org.

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