SUPPORTING INFORMATION: Electronegativity Seen as the Ground State Average Valence Electron Binding Energy

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Calculation of $\bar{\chi}$ exemplified on Gadolinium (Gd):

Calculation of $\bar{\chi}$ proceeds through Eq. 1,

$$\bar{\chi} = \sum_{i=1}^{n} n_i \varepsilon_i / n, \qquad (1)$$

where ε_i is the energy of the ith shell, e.g., 4f shell, 5d shell, etc., n_i is the occupation the ith level and n is the total number of electrons. In this work the average is limited to the valence levels.

Gd example: Gd has 10 valence electrons and its electronic ground state configuration is $[Xe]6s^2 5d^1 4f^7$. We first calculated the energy of the atom's $^9D_2$ ground state. We then calculate the energies of the $^{10}D_{5/2}$, $^8S_{7/2}$, and $^8H_{3/2}$ states of the Gd^+ cation, which are the lowest $^{2S+1}L_J$ states of the $[Xe]6s^1 5d^1 4f^7$, $[Xe]6s^2 5d^0 4f^7$, and $[Xe]6s^2 5d^1 4f^6$ configurations. Subtracting the atomic $^9D_2$ energy from those cationic energies, we calculated the 6s, 5d and 4f binding energies of Gd to be 6.1, 6.8 and 17.0 eV, respectively (Table S1), which translates into the $\bar{\chi}$-value as follows:

$$\bar{\chi} = \sum_{i=1}^{n} n_i \varepsilon_i / n = \frac{2(6.1)+1(6.8)+7(17.0)}{2+1+7} = 13.8 \text{ eV e}^{-1}$$

Table S1. Valence ionization potentials for elements 1-96. All data is compiled from the NIST Atomic Spectra database, except for those energies shown in bold. Energies in bold have been calculated at the GMC-QDPT level of theory, as described in the methodology section.

Atom	level	Binding energy, eV
1 H	1s	13,598
2 He	1s	24,587
3 Li	2s	5,392
4 Be	2s	9,323
5 B	2p	8,298
	2s	12,927
6 C	2p	11,260
	2s	16,592
7 N	2p	14,534
	2s	20,335
8 O	2p	13,618
	2s	28,476
9 F	2p	17,423
	2s	37,855
10 Ne	2p	21,565
	2s	48,475
11 Na	3s	5,139
12 Mg	3s	7,646
13 Al	3p	5,986
	3s	10,622
14 Si	3p	8,152
	3s	13,461

Atom		level	Binding energy, eV
15	P	3p	10,487
		3s	16,152
16	S	3p	10,360
		3s	20,204
17	Cl	3p	12,968
20		3s	24,544
18	Ar	3p	15,760
		3s	29,239
19	K	4s	4,341
20	Ca	4s	6,113
21	Sc	3d	8,017
		4s	6,561
22	Ti	3d	9,923
		4s	6,828
23	V	3d	11,450
		4s	7,069
		1^{st} IP: $3d^3 4s^2$ --> $3d^4$	6,746
24	Cr	3d	8,250
		4s	6,767
25	Mn	3d	14,234
		4s	7,434
26	Fe	3d	10,793
		4s	7,902
27	Co	3d	12,927
		4s	8,296
		1^{st} IP: $3d^7 4s^2$ --> $3d^8$	7,881
28	Ni	3d	13,969
		4s	8,681
		1^{st} IP: $3d^8 4s^2$ --> $3d^9$	7,640
29	Cu	3d	10,445
		4s	7,726
30	Zn	3d	17,171
		4s	9,394
		4p	3,383
31	Ga	4p	5,999
		4s	11,872
32	Ge	4p	7,899
		4s	14,294
33	As	4p	9,789
		4s	16,585

Atom		level	Binding energy, eV
34	Se	4p	9,752
		4s	20,152
35	Br	4p	11,814
		4s	23,770
36	Kr	4p	14,000
		4s	27,514
37	Rb	5s	4,177
38	Sr	5s	5,695
39	Y	4d	6,217
		5s	6,321
40	Zr	4d	8,407
		5s	6,634
41	Nb	4d	7,051
		5s	6,759
42	Mo	4d	8,553
		5s	7,092
43	Tc	4d	7,438
		5s	7,119
44	Ru	4d	8,495
		5s	7,361
45	Rh	4d	9,552
		5s	7,459
46	Pd	4d	8,337
47	Ag	4d	12,432
		5s	7,576
48	Cd	4d	17,581
		5s	8,994
49	In	5p	5,786
		5s	11,028
50	Sn	5p	7,344
		5s	13,105
51	Sb	5p	8,608
		5s	15,021
52	Te	5p	9,010
		5s	17,836
53	I	5p	10,451
		5s	20,607
54	Xe	5p	12,130
		5s	23,397
55	Cs	6s	3,894

Atom		level	Binding energy, eV
56	Ba	6s	5,212
57	La	5d	**6,49**
		6s	**5,81**
		1^{st} IP $5d^6 s^2$ --> $5d^2$	5,577
58	Ce	4f	**11,13**
		5d	**6,75**
		6s	**5,74**
59	Pr	4f	**7,51**
		6s	**5,37**
60	Nd	4f	**8,04**
		6s	**5,41**
61	Pm	4f	**8,21**
		6s	**5,44**
62	Sm	4f	**9,25**
		6s	**5,50**
63	Eu	4f	**10,49**
		6s	**5,53**
64	Gd	4f	**17,03**
		5d	**6,82**
		6s	**6,06**
65	Tb	4f	**8,11**
		6s	**5,86**
66	Dy	4f	**8,84**
		6s	**5,94**
67	Ho	4f	**8,73**
		6s	**6,02**
68	Er	4f	**7,85**
		6s	**6,09**
69	Tm	4f	**9,44**
		6s	**6,17**
70	Yb	4f	**10,75**
		6s	**6,25**
71	Lu	5d	5,426
		6s	6,888
72	Hf	5d	6,825
		6s	7,277
73	Ta	5d	7,944
		6s	7,550
74	W	5d	8,944
		6s	7,864

Atom		level	Binding energy, eV
75	Re	5d	9,542
		6s	7,834
76	Os	5d	**9,44**
		6s	8,438
77	Ir	5d	11,357
		6s	8,967
78	Pt	5d	9,552
		6s	8,959
79	Au	5d	11,090
		6s	9,226
80	Hg	5d	14,841
		6s	10,438
81	Tl	6p	6,108
		6s	12,239
82	Pb	6p	7,417
		6s	14,597
83	Bi	6p	7,286
		6s	15,857
84	Po	6p	8,414
		6s	**19,83**
85	At	6p	9,318
		6s	**20,90**
86	Rn	6p	10,749
		6s	**26,17**
87	Fr	7s	4,073
88	Ra	7s	5,278
89	Ac	6d	5,380
		7s	5,968
90	Th	6d	6,307
		7s	6,495
91	Pa	5f	**6,72**
		6d	**6,13**
		7s	**6,02**
92	U	5f	**8,78**
		6d	**6,33**
		7s	**6,12**
93	Np	5f	**9,60**
		6d	**6,38**
		7s	**6,17**

Atom		level	Binding energy, eV
94	Pu	5f	**7,69**
		7s	**5,96**
95	Am	5f	**8,96**
		7s	**6,04**
96	Cm	5f	**12,79**
		6d	**6,32**
		7s	**6,49**

Table S2. Electronegativity of Atoms 1-96[a]

#	Atom	$\overline{\chi}$	#	Atom	$\overline{\chi}$	#	Atom	$\overline{\chi}$
1	H	-13,60	33	As	-12,51	65	Tb	-7,70
2	He	-24,59	34	Se	-13,22	66	Dy	-8,36
3	Li	-5,39	35	Br	-15,23	67	Ho	-8,31
4	Be	-9,32	36	Kr	-17,38	68	Er	-7,60
5	B	-11,38	37	Rb	-4,18	69	Tm	-9,00
6	C	-13,93	38	Sr	-5,69	70	Yb	-10,19
7	N	-16,85	39	Y	-6,29	71	Lu	-6,40
8	O	-18,57	40	Zr	-7,52	72	Hf	-7,05
9	F	-23,26	41	Nb	-6,99	73	Ta	-7,79
10	Ne	-28,29	42	Mo	-8,31	74	W	-8,58
11	Na	-5,14	43	Tc	-10,93	75	Re	-9,05
12	Mg	-7,65	44	Ru	-8,35	76	Os	-9,19
13	Al	-9,08	45	Rh	-9,32	77	Ir	-10,83
14	Si	-10,81	46	Pd	-8,34	78	Pt	-9,49
15	P	-12,75	47	Ag	-11,99	79	Au	-10,92
16	S	-13,64	48	Cd	-16,15	80	Hg	-14,11
17	Cl	-16,28	49	In	-9,28	81	Tl	-10,20
18	Ar	-19,13	50	Sn	-10,22	82	Pb	-11,01
19	K	-4,34	51	Sb	-11,17	83	Bi	-10,71
20	Ca	-6,11	52	Te	-11,95	84	Po	-12,22
21	Sc	-7,05	53	I	-13,35	85	At	-12,63
22	Ti	-8,38	54	Xe	-14,95	86	Rn	-14,60
23	V	-9,70	55	Cs	-3,89	87	Fr	-4,07
24	Cr	-8,00	56	Ba	-5,21	88	Ra	-5,28
25	Mn	-12,29	57	La	-6,04	89	Ac	-5,77
26	Fe	-10,07	58	Ce	-7,34	90	Th	-6,40
27	Co	-11,90	59	Pr	-6,65	91	Pa	-6,32
28	Ni	-12,91	60	Nd	-7,16	92	U	-7,49
29	Cu	-10,20	61	Pm	-7,42	93	Np	-8,16
30	Zn	-15,87	62	Sm	-8,31	94	Pu	-7,26
31	Ga	-9,91	63	Eu	-9,39	95	Am	-8,31
32	Ge	-11,10	64	Gd	-13,82	96	Cm	-10,88

[a] $\overline{\chi}$ values are compiled from data shown in Table S1. Energies are negative as $\overline{\chi}$ denotes the average electron energy relative to vacuum.

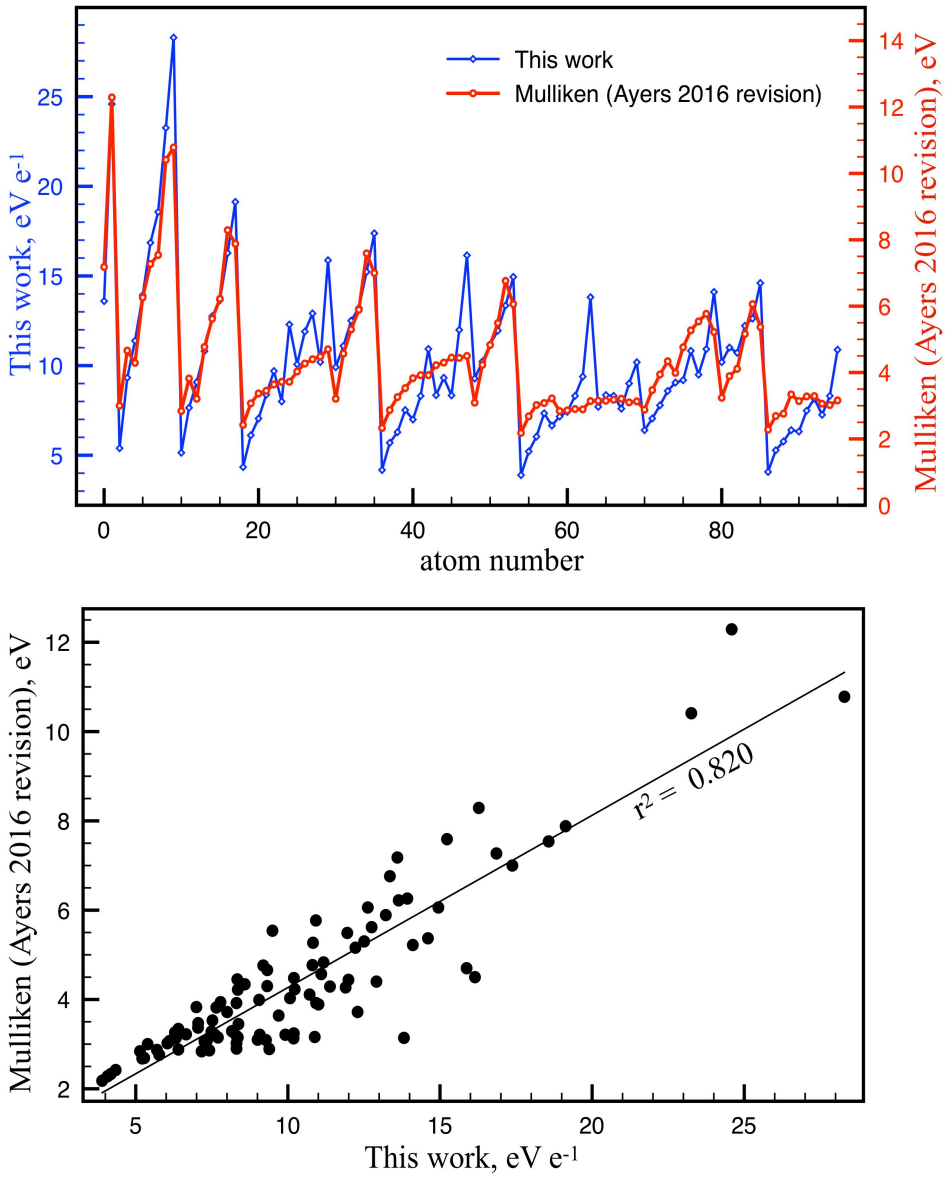

Figure S1. Comparison between electronegativities calculated in this work and the Mulliken electronegativities revised by Cárdenas, Heidar-Zadeh and Ayers. [1]

(1) Cárdenas, C.; Heidar-Zadeh, F.; Ayers, P. W. Benchmark values of chemical potential and chemical hardness for atoms and atomic ions (including unstable anions) from the energies of isoelectronic series. *Phys. Chem. Chem. Phys.* **2016**, *18*, 25721-25734.