Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

The Generalized Maximum Hardness Principle revisited and applied to atoms and molecules (Part 1)

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Contents.

Consider reactions:

$R_1^{\bullet} + R_2^{\bullet} \rightarrow R_1{:}R_2$ (Eq.S1)

$R_1^{+} + R_2^{-} \rightarrow R_1{:}R_2$ (Eq.S2)

$R_1^{-} + R_2^{+} \rightarrow R_1{:}R_2$ (Eq.S3)

We will refer to these in sections S1-S4.

Table S1. Negative absolute ($-\Delta\alpha$) and relative ($-\Delta\alpha/\alpha_R$) polarizability change as well as negative energy change ($-\Delta E$) for reactions described by Eqn.S1-S3. Data for heteronuclear molecules ($R_1 \neq R_2$) where R_1, R_2 are Group 1 elements.

Reactants	$-\Delta\alpha$ /bohr^3	$-\Delta\alpha/\alpha_R$ /%	$-\Delta E$ /eV
H/Li	139.1	82.6	2.47-2.52
H^+/Li^-	1173.1	97.8	15.46-15.51
H^-/Li^+	190.1	87.9	7.11-7.16
H/Na	121.4	72.6	1.95-2.08
H^+/Na^-	1402.2	96.8	15.01-15.14
H^-/Na^+	171.3	78.9	6.34-6.47
H/K	233.0	79.0	1.80-1.90
H^+/K^-	2503.4	97.6	14.90-15.00
H^-/K^+	159.5	72.0	5.39-5.49
H/Rb	257.2	79.6	1.73-1.77
H^+/Rb^-	2913.0	97.8	14.85-14.89
H^-/Rb^+	159.0	70.6	5.15-5.19
H/Cs	351.8	86.8	1.85-1.86
H^+/Cs^-	3756.3	98.6	14.98-14.99
H^-/Cs^+	178.0	76.8	4.99-5.00
Li/Na	56.8	17.4	0.91
Li^+/Na^-	1408.2	97.2	5.76
Li^-/Na^+	1160.3	96.7	5.43
Li/Cs	-33.0	-5.5	0.73
Li^+/Cs^-	3212.2	84.3	5.65
Li^-/Cs^+	616.9	50.8	4.01
Na/K	344.2	75.9	0.68
Na^+/K^-	2515.5	98.0	5.53
Na^-/K^+	1402.5	96.5	4.48
K/Cs	91.0	13.2	0.50
K^+/Cs^-	3214.9	84.3	4.37
K^-/Cs^+	1980.5	76.7	3.89

Table S2. Negative absolute (-Δα) and relative (-Δα/α_R) polarizability change as well as negative energy change (-ΔE) for reactions described by Eqn.S1. Data for two heteronuclear molecules ($R_1 \neq R_2$) where R_1, R_2 are Group 17 elements.

Reactants	*-Δα /bohr^3*	*-Δα/α_R /%*	*-ΔE /eV*
Br/Cl	-1.2/-2.3	-3.4/-6.5	2.26
I/Cl	-33.3/-33.8/	-67.0/-68.7	2.19

Table S3. Negative absolute (-Δα) and relative (-Δα/α_R) polarizability change as well as negative energy change (-ΔE) for reactions described by Eqn.S1-S3. Data for two selected heteronuclear molecules ($R_1 \neq R_2$) where R_1, R_2 are combinations of Group 1 and 17 elements.

Reactants	*-Δα /bohr^3*	*-Δα/α_R /%*	*-ΔE /eV*
H/F	2.8	34.1	5.91
H^+/F^-	5.1[c]	48.6[c]	16.11
H^-/F^+	212.4	97.5	22.59
Li/F	138.5	82.6	5.98±0.22
Li^+/F^-	-18.5[c]	-181.4[c]	7.97±0.22
Li^-F^+	1170.3	97.6	22.79±0.22

Note, calculations of polarizability for halide anions are not reliable, as they tend to produce values which differ by a factor of 2. See a) Ø. Sørensen, L. Veseth, Physica Scripta. Vol. 52, 299-308, 1995; b) C. Hättig, B. A. Heß, The Journal of Chemical Physics 108, 3863 (1998), and references therein. Therefore, the tabularized data are for the smallest calculated polarizability of halide anions found in the literature. This certainly leads to qualitatively wrong tabularized -Δα and - $\Delta\alpha/\alpha_R$ values for $Li^+/F^-$and to quantitatively wrong values for H^+/F^-.

Table S4. Negative absolute (-Δα) and relative (-Δα/α_R) polarizability change as well as negative energy change (-ΔE) for reactions described by Eqn.S1. Data for systems where $R_1=R_2$ and R_1, R_2 are selected organic and inorganic radicals, diradicals or triradicals.

Reactants	*-Δα /bohr^3*	*-Δα/α_R /%*	*-ΔE /eV*
$2CH_3$	3.59	11.2	3.82
$2CH_2$	-1.23	-4.2	7.07
2CH	-1.33	-6.0	9.98
$2CF_3$	-17.5	-61.3	4.21
2CN	15.24	34.2	6.25
2N	3.31	22.3	9.81
$2NO_2$	2.44	6.2	0.59
$2NH_2$	-0.03	-0.1	2.56-3.08
2OH	-1.81	-18.6	2.15
2O	-0.06/+1.54	-0.6/+12.7	5.12