

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

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Abstract:

We revisit the Maximum Hardness Principle (MHP), formulated by Pearson in 1987, and an equivalent Minimum Polarizability Principle (MPP) from Chattaraj and Parr, with particular emphasis on the cases where nuclear potential acting on electrons does not remain constant, and where substantial modifications of the nuclear geometry take place (Generalized MHP, GMHP). As an introduction to the forthcoming discussion of applicability of the GMHP for extended solids (Part 2) we introduce here basic concepts related to electronic hardness. We also present overview of important manifestations of the GMHP for molecular systems such as (i) a tendency of two free radicals to couple, (ii) a reduced reactivity of noble gases, (iii) symmetry-breaking distortions related to Jahn-Teller effect, and/or these connected with (anti)aromatic character of certain organic molecules, (iv) enhanced reactivity of excited states, (v) high-low spin transitions, etc. GMHP is an important qualitative indicator in studies of molecular isomerism and reactivity. Quantitative aspects, traditionally measured by changes of electronic + nuclear energy, are equally readily explained by changes of hardness (or polarizability) of a molecular system. Several important exceptions from (G)MHP are discussed.

Keywords: molecular systems • electronic structure • electronic hardness • isomerism • free radicals

Introduction

Since its introduction by Pearson half a century ago,^[1] the theory of Hard and Soft Acids and Bases (HSAB) has become an immensely useful tool for classification of chemical molecules and ionic fragments, in particular transition metal complexes.^[2,3] However, the absolute (electronic) hardness, η , property central to the HSAB theory, has become a quantitative descriptor of stability and reactivity only twenty years later, when Pearson and Parr have proposed how absolute value of hardness, η , could either be derived from experimental data or from theoretical calculations.^[4] Hardness is linked to the first derivative of a chemical potential, μ ,^[5] or to the second derivative of electronic energy, E , with respect to the number of electrons, N , at a constant external potential, v , of an N -electron system^[4]:

$$\eta = \frac{1}{2} [\delta\mu/\delta N]_v = \frac{1}{2} [\delta^2 E/\delta N^2]_v \quad (\text{Eq.1})$$

It has been further showed^[4] that hardness can be linked to the first ionization potential, I_p , and the first electron affinity of the system, E_A , via the approximated relationship:

$$\eta \approx \frac{1}{2} (I_p - E_A) \quad (\text{Eq.2})$$

which – assuming applicability of the Koopman's theorem – yields the relationship between hardness and the energies of the frontier orbitals, ϵ_{HOMO} and ϵ_{LUMO} (Figure 1):

$$\eta \approx \frac{1}{2} (\epsilon_{\text{LUMO}} - \epsilon_{\text{HOMO}}) \quad (\text{Eq.3})$$

In this way, hardness constitutes one half of the electronic band gap at the Fermi level of a chemical system:

$$\eta \approx \frac{1}{2} \Delta E_F \quad (\text{Eq.4})$$

It is worthwhile to notice that Eq.2 links hardness to another important quantitative descriptor *i.e.* Mulliken electronegativity, χ , which in turn can be approximated as:

$$\chi \approx \frac{1}{2} (I_p + E_A) \quad (\text{Eq.5})$$

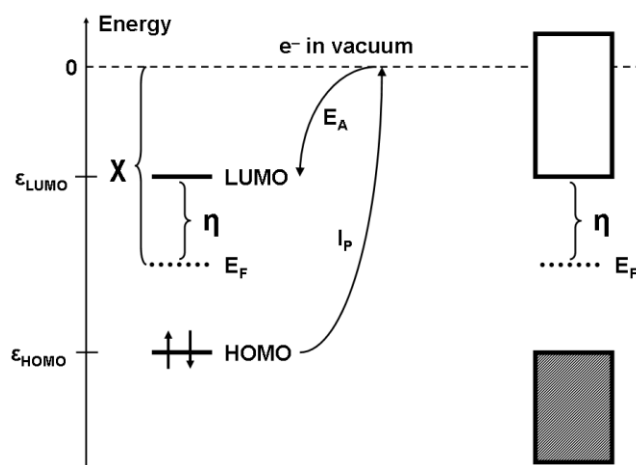


Figure 1. Left: graph depicting the frontier orbitals, HOMO and LUMO, with their respective orbital energies, ϵ_{HOMO} and ϵ_{LUMO} , the associated first ionization potential, I_p , and the first electron affinity, E_A , position of the Fermi level of a molecule, E_F , and the values of the Mulliken electronegativity, χ , and Pearson hardness, η . Right: analogous graph for a solid, with the top of the valence band and the bottom of the conduction band playing the role of molecule's frontier orbitals.

The ten properties expressed in equations (1-5): η , χ , μ , E , N , I_p , E_A , ϵ_{HOMO} , ϵ_{LUMO} , and ΔE_F indeed constitute a set of elementary descriptors of a chemical system, which – especially when linked to the Molecular Orbital (MO) theory and combined with detailed analysis of electron density in the frontier orbitals – can be used to qualitatively understand a system's stability and recognize major scenarios of its chemical reactivity. It is not the purpose of this concept paper to provide a detailed overview of problems which have been tackled with the use of HSAB – this is left for a comprehensive review. It is probably fair to say that the most frequent applications of the HSAB theory were in the description of mechanisms and kinetics of elemental chemical reactions, with theoretical support coming from studies using the gas phase models.

The Maximum Hardness Principle (MHP), which is in focus of this concept paper, has been first formulated a quarter century ago by Pearson, who noticed that “*There seems to be a rule of nature that molecules arrange themselves so as to be as hard as possible*”.^[6] Geometry distortions of the $\text{Pd}[\text{P}(\text{CH}_3)_3]_2$ molecule were provided as one important illustration of this statement, the linear isomer being *more stable* and also *electronically harder* in

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This work is dedicated to Prof. Ralph G. Pearson at his 97th birthday.

comparison to the bent isomer. Thus, since Pearson has suggested the ‘arrangement’ of molecules (which implies modification of nuclear positions, not just of the electronic structure) so to fulfil the MHP; thus more stable isomer should also exhibit larger hardness. This is very important and will be explored in the current work.

Subsequent studies have showed that the MHP is a valid principle provided that temperature and chemical potential are constant.^[7] Indeed, the proof of the MHP which was presented in 1991 by Parr and Chattaraj^[8] have used statistical mechanics and they extended the principle to finite temperatures but the requirement of the constant chemical potential has been preserved in the proof.^[9] Accordingly, IUPAC officially defines the MHP as follows: “**A chemical system at a given temperature will evolve to a configuration of maximum absolute hardness, provided that the potential due to the nuclei, plus any external potential and the electronic chemical potential, remain constant.**”^[10] Thus, the IUPAC definition of the MHP follows the mathematical proof^[8] and it does not consider the original Pearson’s suggestion which should be phrased as: “*the most stable isomer form also has the largest hardness*”. The latter version of the MHP which does not require the constancy of the chemical and external potentials during molecular distortion is sometimes referred to as the Generalized MHP (GMHP).^[11] Although GMHP has not been proven, yet numerous cases have been discussed when it still holds even though the chemical and external potentials vary during the molecular rotation or along the reaction coordinate.^[12]

A chemical bond is a subtle compromise between internuclear repulsions and attractive interactions, where electrons – despite their mutual repulsion – try to condense more effectively in the internuclear region to screen the internuclear repulsion. Interestingly, Parr and Gazquez have showed in 1993 that for a state with maximum hardness, electronic energy and nuclear repulsion energy *each* reach their respective extremum values.^[13] This is fascinating since this suggests that the internuclear repulsion is, weirdly, maximized, when a chemical bond forms, while the electronic structure adopted is such as to maximize hardness (*i.e.* - to some approximation - to maximize the HOMO/LUMO gap). Regretfully, this does not imply that one could algorithmically search for the optimum geometry of a system (*i.e.* molecule or solid) by imposing the condition of reaching maximum hardness or maximum of internuclear repulsion (in a similar fashion as the condition of minimum of total energy is imposed in modern quantum chemistry programs). Clearly, such procedure applied *in silico* would lead to ‘nuclear fusion’. This characteristics of the GMHP has been discussed in the past from the viewpoint of molecular vibrations;^[11,14] it has been noticed that the GMHP does apply to totally symmetric molecular vibrations, such as concomitant bond compression of all chemical bonds present in the molecule. For example, there is *no* ‘hardness barrier’ preventing the nuclear fusion of two D atoms into a less polarizable He atom (while there is a total energy barrier for this process) - hardness monotonically grows during fusion. In view of these considerations it is even more striking why GMHP does hold so effectively for all *realistic* internuclear separations. This even permits a *restrictive* theoretical search for broad band gap (*i.e.* electrically insulating) polymorphic forms using “learning algorithms”, as exemplified by a recent study of novel forms of carbon and SiO₂.^[15]

Hardness and Electronegativity of Atoms

For most elements, the first E_A takes on rather small values as compared to the corresponding first I_p . The largest E_A value is that for Cl atom (3.62 eV), but this is still only < 28% of the I_p value for this element (12.97 eV). Metals - which constitute vast majority (82%) of elements in the Periodic Table - typically have I_p values < 10 eV (except for Hg, 10.44 eV) and E_A not exceeding 1 eV (here, only a few late, particularly noble transition metals exceed this threshold). This means that the I_p is a major contributor both to η as well as to χ ; hence one expects that:

$$\eta \approx \chi \quad (\text{Eq.6})$$

The relationship (Eq.6) between η and χ holds quite nicely as exemplified by Group 1 elements from H to element 119 (Figure 2). The span of electronegativity and hardness values for Group 1 is large; the values of η and χ tend to cluster for all alkalis, but the corresponding values for nonmetallic H are very much off. Nevertheless, $\eta \approx \chi$ for all these elements.

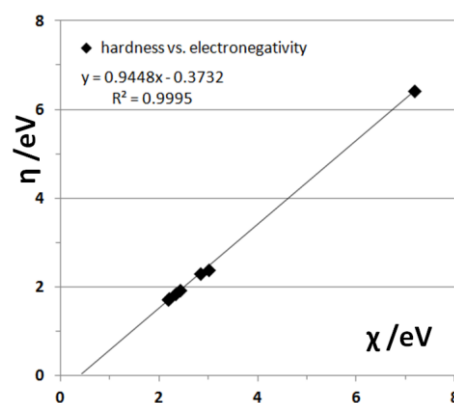


Figure 2. Comparison of Pearson hardness and Mulliken electronegativity for Group 1 elements, together with a linear fit to the data, which passes through point (0.4, 0.0). Correlation including additionally noble gases (SI) yields a similar fit with curve passing through point (0.6, 0.0).

He is the hardest and most electronegative atom in the Periodic Table ($\eta = \chi = 12.3$ eV as based on null E_A), Cs is the softest and least electronegative one ($\eta = 1.71$ eV, $\chi = 2.18$ eV). Relativistic effects render Fr - as well as predicted element 119 from period VIII - less electropositive than cesium.^[16] As we will see in Part 2 of this paper, the span of η and χ values slightly increases when one moves from isolated atoms and molecules in the gas phase to extended matter (solids, liquids). Here, $\eta_{\min} = \chi_{\min} \approx 0$ eV (for metals) while $\eta_{\max} = \chi_{\max} \approx 12.3$ eV (liquid He at 4.2 K).

The fact that for most atoms values of Pearson hardness are similar to those of absolute (Mulliken) electronegativity does not imply that hardness is a redundant descriptor and could be discarded. The differences between η and χ turn out to be much larger for certain molecules; and they tend to differ a lot for cations, anions or excited states of a given atom or molecule, as well as for various isomers of the same species. Moreover, as we will see, certain drawback of hardness which proven from its simplified definition given by Eq.2, may be eliminated when a definition based on electronic polarizability is used instead.

Minimum Polarizability Principle

The HOMO-LUMO gap is a major factor which governs the electronic polarizability (*i.e.* a static electric dipole polarizability, α) for most systems.^[17] Thus, the MHP can be rephrased as a "Minimum Softness Principle" or its alternative, a "Minimum Polarizability Principle" (MPP).^[18] The qualitative relationship between hardness and polarizability (*i.e.* static electric dipole polarizability) has been initially simplified as a direct proportionality:

$$\alpha \sim \eta^{-1} \quad (\text{Eq.7})$$

Let us now examine how polarizability changes for Group 1 elements and then whether the proportionality expressed in Eq.6 really holds. The first dependence is illustrated in Figure 3, the latter one in Figure 4.

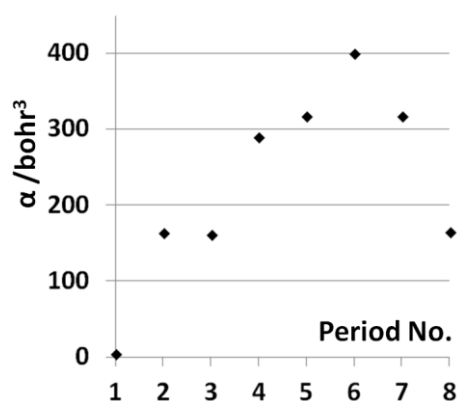


Figure 3. The plot of absolute polarizability vs. number of period of the Periodic Table for Group 1 elements.

It turns out that α changes much more dramatically than η as one goes down the Group 1. Notably, α is very small for H (only 3.26-times larger than the record small polarizability of He), rises dramatically from H to Li, surprisingly is nearly identical for Li and Na, then rises again from Na via K to Rb, reaches maximum for Cs and then drops sharply for Fr and as-yet unknown element 119 (eka-francium). The most accurate theoretical value for Fr is nearly identical to that for Na(I) and less than half of that for Cs,^[16] this is due to relativistic effects which greatly stabilize the ns shell (for $n=7, 8$) and consistent with the observed and calculated trends for I_p and E_A values of these heavy elements. Clearly, the electric dipole polarizability, α , reveals important chemical trends more pronouncedly than I_p , E_A , χ or η , and as such is an extremely valuable descriptor. Moreover, α can be very precisely determined using measurements of dielectric constant or refractive index or calculated from the first methods.^[19] But does α indeed correlate inversely with hardness as postulated in Eq.7? The relationship between the two for Group 1 elements is illustrated in Figure 4.

It turns out that for Group 1 elements α is inversely proportional to η , but the exponent of the power dependence is close to -3.3 . This explains why α is more sensitive descriptor than η . On the other hand, when the analogous fit is done only for the noble gas atoms, one obtains exponent of -3.5 . The more

accurate correlation which covers a broader span of parameters by including both Group 1 elements and He atom (*cf.* SI) yields:

$$\alpha \sim \eta^{-3.3} \quad (\text{or alternatively } \eta \sim \alpha^{-1/3.3}) \quad (\text{Eq.8})$$

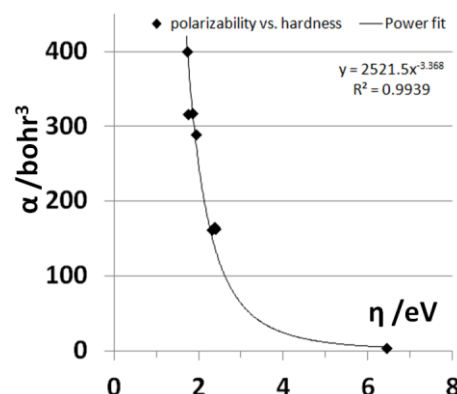


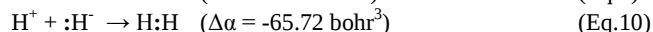
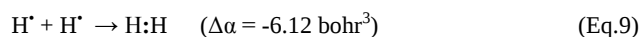
Figure 4. The plot of absolute polarizability vs. hardness for Group 1 elements, together with a power fit to the data.

Note, the Bohr model of H atom yields $I_p \sim R_n^{-1}$ where R_n is a radius of a given orbit for principal quantum number n . In other words, $I_p \sim V_n^{-1/3}$ where V_n is volume of atom limited by its Bohr radius (for a given shell, n). Since $\eta \sim I_p$ and α is expressed in the units of volume, it is not striking to see that $\alpha \sim \eta^{-3}$.

Indeed, several authors have noticed that proportionality expressed by (Eq.8) is well fulfilled.^[20] Hati and Datta^[20b] have combined the expressions for energy required to charge a conducting sphere with an empirical equation of polarizability for such a sphere and they found out that proportionality described by Eq.8 should indeed hold. However, it would be interesting to derive the expected exponent directly from the density functional theory.

Polarizability as an descriptor: coupling of free radicals

The practical use of the MPP *i.e.* of the values of α will be illustrated here for the formation of smallest chemical molecule, H_2 , via two distinct chemical reactions:



If one tries to analyze Eq.9 within the framework of the MHP and using two simplistic MO descriptors (ϵ_{LUMO} and ϵ_{HOMO}), one immediately bumps into a problem since η of $H^\bullet$ would be evaluated as null (due to $\epsilon_{LUMO} = \epsilon_{HOMO}$). This is certainly not the case, $H^\bullet$ must possess a non-zero hardness. This formal problem obviously arises due to severe inapplicability off the Koopman's theorem for free radicals. If one then chooses to switch to a more reasonably defined values of I_p and E_A , the problem will be largely (but still not completely) solved. The I_p and E_A values for $H^\bullet$ are 13.6 eV and 0.75 eV, respectively, while those for H_2 are 15.42 eV and 0 eV. Using Eq.2 one obtains that: $\eta(H^\bullet)=7.18$ eV, and $\eta(H_2)=7.71$ eV. Thus, hardness formally increases upon formation of H_2 molecule from two hydrogen radicals, but the increase is not

spectacular, as could be expected for formation of a very strong chemical bond. The problem here is with the formally null value of E_A for H_2 . Indeed, E_A is ill defined for the species which prefer not to attach electron, for it is set as zero for such systems. This approach does not differentiate between, say, a hard He atom and a much softer Xe atom, and it tends to lead to underestimated values of hardness, in particular for hard species, for which virtual orbitals are placed well above the zero energy level (for free electron in vacuum). A more fair description would render E_A negative (and in principle different!) for various systems of this kind, but the precise negative values of E_A are difficult to be evaluated from experiment. Fortunately, theoretical estimates of negative E_A values may be achieved from the *ab initio* calculations. We will come back to this important problem in Part 2.

A still different type of problem (aside from those discussed above) arises when analyzing MHP for reaction described by Eq.10. While $\eta(H^-)$ could be evaluated from the I_p and E_A values as 0.38 eV, the hardness of electron-free H^+ could be described as infinite. Of course, infinite value of any physicochemical property is not a very useful quantitative descriptor.

One elegant way to avoid all the above-mentioned problems is to use the values of electronic polarizability instead. *E.g.*, a clear picture evolves when analyzing the formation of H_2 molecule using the MPP. The combined electronic polarizability of 2 $H^\bullet$ atoms equals 9 bohr³, that of H^- is 68.6 bohr³, that of H^+ is 0 bohr³, and the one of H_2 molecule is 2.88 bohr³. The reactions described by Eq.9 and 10 may now be associated with the corresponding values of $\Delta\alpha$: $\Delta\alpha(\text{Eq.9}) = -6.12 \text{ bohr}^3$, $\Delta\alpha(\text{Eq.10}) = -65.72 \text{ bohr}^3$.

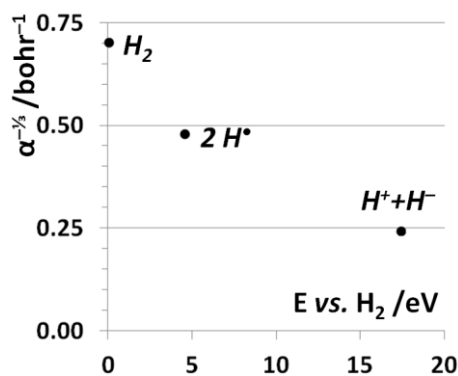


Figure 5. The plot of inverse cubic root of the absolute polarizability vs. relative energy with respect to H_2 molecule for three sets of species corresponding to the stoichiometry of "2H".

The magnitude of 'electronic stiffening' which takes place during the chemical reactions (as measured by $\Delta\alpha$) is qualitatively correlated with the very different exoenergeticities of these reactions (-4.52 eV and -17.37 eV, respectively, per $H_2^{[21]}$). In other words, the dissociated ($H^- + H^+$) system constitutes the softest and the least stable arrangement of nuclei and electrons, the ($H^\bullet + H^\bullet$) representation is already harder and more energetically stable while the H_2 molecule is the hardest and the most stable form. This is illustrated in Figure 5 where we have chosen to plot $\alpha^{-1/3}$ with respect to relative energy with respect to H_2 molecule, for three sets of species corresponding to the stoichiometry of "2H". One important quantitative result here is that homolytically

dissociated H_2 (*i.e.* $H^\bullet + H^\bullet$) is about 1.5-times softer than H_2 while the heterolytically dissociated H_2 (*i.e.* $H^+ + H^-$) is about 3-times softer than H_2 . Note, this semi-quantitative comparison was possible based on $\alpha^{-1/3}$ values, since (i) the η value cannot be derived for H^+ based on simplistic definition from Eq.2 because proton cannot be further ionized, while (ii) the η value for H^- would be in large error since E_A of this soft anionic species is null. Clearly, α , with its large span of values for diverse chemical species, provides a direct and sensitive quantitative perspective on chemical reactions as if one was looking at the problem through a magnifying glass. Use of α has proved very prolific also for theory of metallization of solid state systems (*cf.* Part 2 of this series).

Analyzing the case of "2H" stoichiometry one may also realize that the MHP does not forbid the existence of very soft species which are composed of hard atoms; one just expects them to be very reactive and prone to electron loss. This is indeed the case of anions, such as H^- , which is vastly more polarizable than a neutral and very hard H atom from which it originates (by the factor of 15); recall, H^- is a powerful reducing agent, one of the best ones available in chemistry. Soft excited states of hard atoms or molecules constitute another example; we will return to this problem in another section.

Polarizability change as a measure of energetic propensity for chemical reaction

To get more intuition about how much polarizability may change during a chemical reaction we will now systematically explore two generalized reaction types similar to these from Eqns.9-10:



for a broader set of free radicals, $R^\bullet$, radical-cations, R^+ , and radical-anions, R^- . The results are collected in Table 1 for R being a Group 1 element. *Cf.* SI for similar analysis for R_1R_2 connections where $R_1 \neq R_2$ and R_1 and R_2 are Group 1 elements. Properties of Group 1 elements vary from nonmetallic, electronegative H to most electropositive Cs; simultaneously, all alkali metals have measurable E_A values and they form stable anions in the gas phase. Again, one may consider both homolytic and heterolytic bond breaking reactions. Indeed, Group 1 elements provide us with a broad spectrum of reaction energies (from 0.46 to 17.37 eV) and polarizability changes (from 6.12 to 3023.8 bohr³), and these all are connected with formation of a single chemical bond *i.e.* pairing of two free radicals.

As data listed in Table 1 show, process of σ bond formation for Group 1 elements is always connected with substantial decrease of α . The smallest relative value of $\Delta\alpha/\alpha$ of 15.6% is observed for the homolytic bond formation of the diatomic molecule for the least electronegative element, Cs.^[34] The largest $\Delta\alpha/\alpha$ value of 68% for the homolytic bond formation is seen for H with the largest bond dissociation energy in this set (as described in the previous section). Again, qualitative relationship between polarizability and energy factors seem to apply.

The heterolytic coupling of R^+ and R^- , which is much more exoenergetic than the homolytic one, is usually connected with much larger absolute changes of α and of $\Delta\alpha/\alpha$. This is natural

considering that ionic description of these homonuclear systems is rather unrealistic. For example, α decreases by *ca.* 16% upon formation of Cs_2 from two Cs atoms, but by as much as *ca.* 80% for an analogous process involving cesium ions. Another way to phrase the MPP is that the ionic R^+R^- , "electromer" must have small contribution to the ground state of the R_2 molecule in the valence bond theory - which we know is indeed the case. Further simple trends of this kind for α and of $\Delta\alpha/\alpha$ may be noticed for heteronuclear systems R_1R_2 , where R_1^+R_2^- and R_1^-R_2^+ isomers obviously differ in energy and in polarizability (**SI**). Another general observation is large differences of hardness (or its equivalent, polarizability) of reactants usually lead to spontaneous redox (*i.e.* electron-transfer) or vigorous acid-base (*i.e.* electron pair sharing) reactions. These are meant to increase hardness of the softest specie in the system by decreasing its number of electrons - or forcing it to share them with the harder counterpart.

Table 1. Negative absolute ($-\Delta\alpha$) and relative ($-\Delta\alpha/\alpha_R$) polarizability change as well as negative energy change ($-\Delta E$) for reactions described by Eqns.11-12. Data for homonuclear molecules R_2 where R is a Group 1 element.

Reactants	$-\Delta\alpha$ /bohr ^{3[a]}	$-\Delta\alpha/\alpha_R$ /%	$-\Delta E$ /eV ^[b]	Ref(s).
2H	6.12	68.0	4.52	[23]
2Li	114	34.8	1.14	[24]
2Na	63.4	19.5	0.76	[24]
2K	104.2	17.9	0.57	[24]
2Rb	104.1	16.3	0.51	[25]
2Cs	125.3	15.6	0.46	[25]
2Fr	162.6-196.7-	25.5-30.9	0.30-0.44	[25,26,27]
H^+/H^-	65.72	95.8	17.37	[28]
Li^+/Li^-	871.5	72.7	5.92	[29,30]
Na^+/Na^-	1123.6	77.5	5.33	[29,30]
K^+/K^-	1989.7	77.4	3.84	[29,30]
Rb^+/Rb^-	2350.6	78.7	4.20	[29,30]
Cs^+/Cs^-	3023.8	79.0	3.88	[29,30]
Fr^+/Fr^-	2989.8	82.5	3.78-3.92	[29,30,31,32]

[a] Ref.[22] used for all neutral atoms. [b] Ref.[33].

The final conclusion is that since when reaction goes downhill in energy, chemical systems usually progressively 'harden', thus it should be difficult to find a very soft polyatomic molecule *in its ground state* which is composed exclusively of very hard atoms. Take benzene molecule with a seemingly soft π electron system. According to the I_p and E_A values, benzene has rather large hardness of 4.62 eV, not much smaller than that of the softer of the constituting atoms (C: 4.84 eV). But if one takes a more

correct *negative* value of the electron affinity of benzene (-1.53 eV) into calculations, one finds out that benzene is actually *harder* (5.60 eV) than C atom but *softer* than H atom (6.42 eV).^[35]

A few important failures of the GMHP for simple molecular systems

The GMHP is an appealing and strong rule of Nature - as explained using a number of examples above and well-documented through a large number of excellent theoretical contributions in the literature. For example, theoretical studies for 130 heteroaromatic molecules have showed that the most stable isomer is also the least polarizable.^[36] And yet GMHP has some exceptions. In 2000 Hohm author has studied 108 inorganic and organic molecules and found only 5 exceptions (or 4.6%) from the GMHP.^[37] More recently, Blair and Thakkar have recently scrutinized a more representative set of 2386 experimental and theoretical polarizabilities relevant to diverse chemical reactions. Their study reveals 86 exceptions which suggests that the MPP is violated approximately 3.6% per cent of the cases.^[38]

One marked exception of violation of the GMHP is provided by the F_2 molecule, as first noticed by Hohm.^[37] Electronic polarizability of F^* atom is 3.70-3.76 bohr³,^[34] that of F_2 is 8.38-8.64 bohr³.^[35] Thus, combined polarizability of two F^* atoms is *smaller* than that of the F_2 molecule. And yet, formation of F_2 from two F^* radicals is energetically downhill by *ca.* 1.65 eV (Table 2). While the failure of the GMHP in this case is not fully understood, one is tempted to link it with the well-known effect of the lone-pair lone-pair π - π repulsion which greatly affects the F-F chemical bond (*i.e.* weakens it substantially with respect to what could be expected based on bond energies trend for the entire dihalogen series). Concomitantly, the strong σ bond cannot form and the split of the π^* states from the σ^* ones (and thus hardness) is smaller than expected. However, this explanation is not valid; 'normal' Cl_2 molecule also violates the GMHP: Cl_2 is slightly softer than two separate Cl^* atoms ($\alpha(\text{Cl}_2) = 30.98$ bohr³^[36] while $\alpha(\text{Cl}^*) = 14.57$ -14.73 bohr³),^[34] despite the fact that Cl_2 is strongly bound with respect to radicals (by *ca.* 2.5 eV). Br_2 and I_2 behave similarly to Cl_2 but the effect seems to diminish with the atomic number (Table 2). Regrettably, α value for At_2 is not known from experiment or calculations to further confirm or refute this trend.

Table 2. Absolute ($-\Delta\alpha$) and relative ($-\Delta\alpha/\alpha_R$) of polarizability change (with minus sign) as well as energy change (with minus sign) for reactions described by Eqn.11. Data for homonuclear molecules R_2 where R is a Group 17 element. Cf. **SI** for similar analysis for R_1R_2 connections where $\text{R}_1 \neq \text{R}_2$. ND = not determined.

Reactants	$-\Delta\alpha$ /bohr ^{3[a]}	$-\Delta\alpha/\alpha_R$ /%	$-\Delta E$ /eV ^[b]	Ref(s).
2F	-1.12/-1.24	-14.9/-16.8	1.65	[39]
2Cl	-1.52/-1.84	-5.2/-6.3	2.52	[39]
2Br	-0.30/-2.04	-0.7/-4.5	1.99	[39]
2I	-0.51/-1.05	-0.7/-1.5	1.56	[40]
2At	ND	ND	0.87±0.13	[41]

[a] Ref.[22] used for all neutral atoms. [b] Ref.[33].

Clearly, the three lightest dihalogen molecules constitute exceptions from the GMHP.^[42] Two interhalogen molecules (BrCl, ICl), three organic molecules (C₂H₂, C₂H₄, and C₂F₆ but not C₂H₆) behave similarly (SI). More such examples have been pointed out (O₂, O₃). However, it is clear that the number of exceptions from GMHP for molecules is rather small which renders GMHP a quite strong and useful predicative rule.

Now, having discussed applicability (and failures^[3]) of GMHP for reactivity of atoms and for isomerism of molecules in the gas phase, let us focus on hardness of noble gas (NG) atoms.

The lightest noble gases: too hard to react

The Group 18 elements^[43] which adopt a stable doublet (He) or octet (heavier NGs) electronic configuration have long resisted all attempts to push them into chemical bonding in neutral molecules. The breakthrough came with the synthesis of 'XePtF₆' by Bartlett in 1962;^[44] and to this day chemistry of NGs is predominated by their connections with F.^[45] The high *I_p* values of NGs - especially the two lightest ones - have been traditionally blamed for these elements' inertness. Indeed, the *I_p* values for He and Ne are by far and away larger than that of F while the one for Ar is slightly smaller and those for Kr and Xe are substantially smaller than that of F (Figure 6).^[46] This qualitatively explains the ranking of stabilities of NG difluorides: (i) XeF₂ is both an energetically and thermodynamically stable system at ambient (p,T) conditions, (ii) stability of KrF₂ is purely due to a small negative enthalpic term while entropic contribution tends to dissociate this molecule apart to Kr and F₂, while (iii) ArF₂ has not yet been prepared - its ground state corresponds to a weakly bound van der Waals complex, Ar...F₂.^[47]

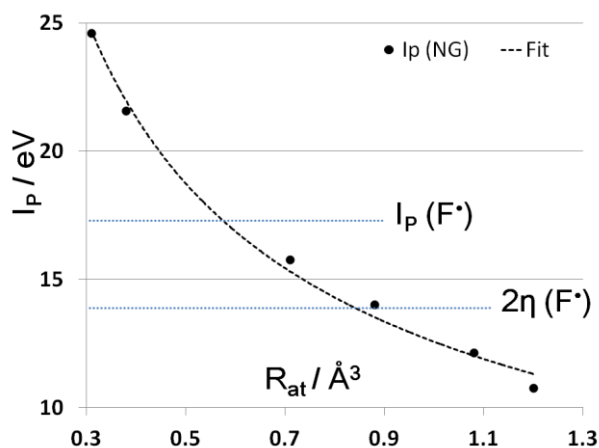


Figure 6. The first ionization potential (*I_p*) vs. atomic radius (*R_{at}*) for noble gases. The monotonic correlation between the two is emphasized by the fit to exponential equation. The *I_p* and 2η values for F• atom have been shown for comparison.

An alternative view on this problem is that from the GMHP perspective. Due to *E_A* values being formally 0 eV for all NGs (except for element 118, which is predicted to have a tiny *E_A* of 0.06 eV),^[48] $\chi = \eta = \frac{1}{2} I_p$. On the other hand, 2 η of F• atom is smaller than its *I_p*, and nearly equal to 2 η of Kr atom (Figure 6). The values of electronic polarizability even more acutely emphasize the inertness of He and Ne (Figure 7). Thus, note that F₂ molecule is substantially softer than He atom, thus the reaction

system (He+F₂) could obey the GMHP *only* if electron transfer took place from F₂ to He thus leading to F₂⁺...He⁻. While this is prevented by both the null value of *E_A* of He and the large value of *I_p* for F₂. The same situation applies to Ne. Thus, GMHP offers an alternative explanation of inertness of two lightest noble gases to the commonly used energy arguments.

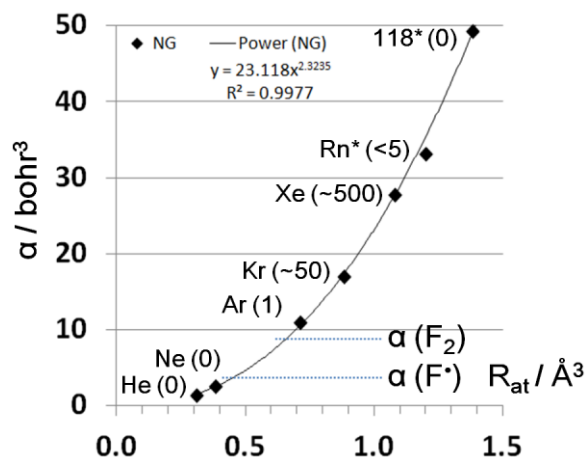


Figure 7. The electronic polarizability (α) vs. atomic radius (*R_{at}*) for noble gases (including radioactive ones: radon and element 118). The theoretical polarizability of element 118 was shown in this plot while the atomic radius of this element has been calculated from the power fit to be 1.38 Å. At each atomic symbol a number is specified in brackets showing the number of known neutral compounds which contain a given NG element^[21]. The α values for F• atom and F₂ molecule have been shown for comparison.

He: from Pearson to Pauli hardness

He atom, which is the least polarizable atom in the Periodic Table, concomitantly has a huge HOMO/LUMO gap of over 40 eV,^[42] a null electron affinity,^[49] and the first excited state at energy as high as 21.218 eV with respect to the ground state.^[50] Spectacular inertness and the record large Pearson hardness of a helium atom render it an excellent tool to probe interactions with diverse chemical compounds. Specifically, Stone and Tong as well as Piel *et al.* proposed that helium atom may probe the valence repulsion energy that is related to the Pauli exclusion principle.^[51] The theoretical experiment in question involves pushing of a He atom into a molecule from various directions, and calculating the valence repulsion energy and its first derivative. This allows to define the molecular surface ("shape") *i.e.* an isosurface of valence repulsion energy of a given (arbitrarily selected) threshold. The Pauli hardness (PH, which is expressed in units of force) of a point on the isosurface is defined as the first derivative of the valence repulsion energy in the direction normal to the isosurface. Analysis performed for a series of four related molecules, CH₄, NH₃, H₂O and HF, has revealed several interesting features. First, the small values of the PH were associated with the presence of free electron pairs in the molecules, and accordingly CH₄ exhibits anomalously large PH in the series. This is similar to what is expected for Pearson hardness: Lewis bases usually exhibit small η. Secondly, the molecular surfaces exhibit unexpected complexity, with a large number of minima and maxima of PH. Last but not the least, it turns out that the minima of energy for such closed-shell molecule - van der Waals He complexes usually adopt geometries which correspond to He atom pointing to a maximum PH of the molecule which is probed by He.^[52] So there is clear analogy between this behaviour and the GMHP.

Similarly, Chałasiński *et al.*^[52] was able to show that He or Ar atoms may serve as a reliable probe to analyse the anisotropy of "molecular ability" to participate in exchange, induction, SCF-deformation and dispersion interactions. These authors draw "contours of exchange" for several simple molecules (Figure 8) which point out to various important features of these chemical species such as large repulsive lone pair on C atom of the CO molecule, the small concave regions for the Cl₂ molecule along the molecular axis, and an even more pronounced concave on Cl atom of the ClF molecule, which we interpret as a "σ hole" (these days related to propensity for so called "halogen bonding"). Indeed, the "σ hole" on halogen calculated for the HF, HCl and HBr series^[53] increases in order F (no hole) < Cl (small hole) < Br (pronounced hole), as typical for halogen bonding acceptors.^[54]

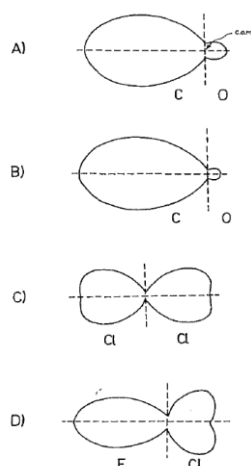


Figure 7. "Contours of exchange" for A) Ar-CO, B) He-CO, C) Ar-Cl₂, and D) Ar-FCI complexes (see text). Reproduced from Ref.[52] with permission from the authors.

Clearly, substantial *Pearson hardness* of helium atom is of value for theoretical chemistry considerations of the *Pauli hardness*, definition of molecular shape, localizing of the lone pairs, and more. Argon has been used for the same purpose. But it should be remembered that argon is a much softer probe than helium. Indeed, since year 2000 argon is not noble anymore.

NG atoms in the electric field: getting softer

HArF is the only case documented by experiment, when Ar has been forced to chemical bonding at the low-temperature conditions.^[55] A stable HArF molecule may be formed via a photochemically-assisted insertion of Ar atom into the H-F bond:



Importantly, $\alpha(\text{Ar})=11.1 \text{ bohr}^3$ while $\alpha(\text{HF})=5.6 \text{ bohr}^3$, hence now it is the NG atom which is the softer one of two reactants. This is a different situation, qualitatively, from what we saw before for helium and neon. The relative softness of Ar is pray to the harder species, HF, especially its positively charged, hard H⁺ site; indeed, an ionic resonance structure (HAr⁺)F⁻ is a reasonable description of the so-formed HArF molecule and this valence bond form has a substantial share in the ground state.^[55] However, the calculations of $\alpha(\text{HArF})$ from the first methods point yield the

value of 30.20 bohr^3 ^[56] which suggests that, interestingly, HArF softens as reaction described by Eq.12 takes place. Formation of HArF (energetically facile at low temperatures) is thus one more exception from the GMHP.

As stated above, MHP applies to cases when the external potential is constant. But what happens to hardness when, say, the external electric field is turned on? A NG atom which interacts with an increasing electric field becomes polarized and loses its spherical symmetry while its energy decreases. Simultaneously, it becomes *softer* since diffuse virtual orbitals have been mixed with the more contracted occupied orbitals in order to generate the dipole moment (as a response to external field). According to the GMHP, an increased softness implies enhanced reactivity. Thus, facile formation of HArF might be viewed as arising from polarization of an Ar atom inside of the H⁺...F⁻ dipole (aside from fractional charge transfer). A similar line of thinking may be applied while trying to design a neutral molecule, which contains the smallest NG atom, helium. Specifically, a system composed of He and O atom develops a minimum on the Potential Energy Surface (PES) of the singlet state when embedded in a strong electric field (Figure 8).^[43b] The equilibrium He-O separation for the field of 0.1 au is $\sim 1.0 \text{ \AA}$, corresponding to real chemical bond.

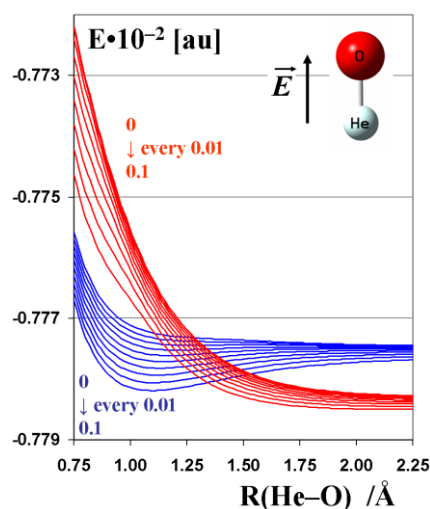


Figure 8. Impact of the strength of the external electric field, *E* (atomic units), on the lowest singlet (blue, ¹S) and triplet (red, ³P) potential energy surfaces of HeO molecule. Graphs show energy, *E* · 10⁻² (hartree) vs. the interatomic separation, (Å) for ten different values of electric field from 0.0 up to 0.1 au. Reproduced from Ref.[43b] with permission from the author.

CsFHeO and (HeO)(LiF)₂^[43] are two examples of the theoretically predicted neutral metastable systems, which now await preparation. In these molecules the strong ionic CsF dipole or two parallel LiF dipoles simply mimic the action of the electric field on HeO moiety. It must be bore in mind that since He atom has the smallest electronic polarizability of all chemical systems, it is unlikely that these neutral molecules which contains chemically bound helium atom, could be energetically stable with respect to He and by-products. Indeed, the two systems mentioned in Ref.[43] are high-energy metastable systems and as such they do not bend the GMHP.

It seems that the fascinating line of failures and successes of NG chemistry^[45,57] could make headlines as a 'story of chemists fighting against the GMHP'.

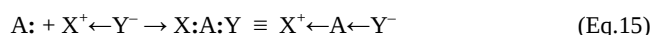
Still a different approach to soften He atom has been taken by Frenking *et al.* a quarter century ago.^[58] These authors have predicted that He atom would readily attach to the Be site of the BeO dipole:



The He...BeO bond dissociation energy is quite small, *ca.* 0.18 eV according to the most accurate recent estimates; this suggests that covalent chemical bond does not form - rather, dispersive interactions are anomalously strong.^[59] Yet having in mind resistance of He against any bonding, the effect of "σ hole" on Be site is impressive and reminiscent of so called "beryllium bond". Similar approach has led Boggs *et al.* to investigate complexes of He with coinage metal fluoride molecules, MF (M=Cu, Ag, Au).^[60] These authors have found that the most strongly bound complex in this series is He...CuF, with the He dissociation energy of 0.20 eV and thus the bonding strength is similar to that for He...BeO. Since these weakly stable ground states have very different character than the previously mentioned covalently-bound local minima (CsFHeO and (HeO)(LiF)), it is worth investigating whether polarizability might increase upon formation of the weakly bound He...BeO and He...CuF adducts. Actually, such calculations were performed for He...BeO by Kłos *et al.* upon request of this author.^[61] The calculations point out to substantial electronic stiffening of (He + BeO) reactants upon formation of the He...BeO adduct. Specifically, polarizability decreases from 34.2027 bohr³ to 27.0350 bohr³ *i.e.* by as much as -21%. This is huge percent effect, similar for example to what we have seen for formation of a sigma bond between two Na atoms (Table 1). Recalling the approximate dependence between polarizability and hardness (Eq.8) we may estimate that the electronic hardness of reactants increased during reaction by *ca.* 7.5%.

Push-pull molecules

The concept of inserting of an atom or entire molecular fragment between two polarizing functional groups in order to soften it (as we have seen for HArF, Eq.13) and red-shift its electronic transitions is in fact well known for decades in organic chemistry:



The resulting so called "push-pull" molecules^[62] X:A:Y exhibit interesting optical properties due to enhanced polarizability and especially higher-order polarizabilities (first hyperpolarizability etc.). The concept of a "push-pull" molecule will be discussed here in relationship to GMHP based on an asymmetrically-substituted acetylene, LiC≡CF. This highly polar molecule (for demonstration purposes restricted in our calculations to linear geometry)^[63] can be viewed either as a product of insertion of the C₂ molecule into the Li-F bond, or as a product of a complex reaction:



Energies of selected molecular orbitals of HC≡CH and LiC≡CF are compared in Figure 9. It can be seen that a simultaneous substitution of 2 H atoms for Li and F dramatically affects the MOs of acetylene. First, the bonding σ and π orbitals

are substantially destabilized as compared to those of unsubstituted acetylene. Secondly, the antibonding σ* and π* states are substantially stabilized. This can be easily understood while assuming an ionic formulation of the substituted molecule as Li⁺C≡CF⁻ (*cf.* Eq.15). Such formulation is not unrealistic; population analysis indicates the following sequence of Mulliken charges on atoms: Li^{+0.83}C^{-0.59}≡C^{+0.14}F^{-0.39} which suggests both the substantial ionic character of both terminals and very strong polarization of the CC interior.

Destabilization of the filled orbitals for example of π HOMO can be traced back to the lone-pair lone-pair repulsion between C₂ unit and 2p orbitals of F⁻. On the other hand, stabilization of the σ* LUMO (as well as π* manifold) is due to beneficial effect of the empty 2p orbitals and 2s-p hybrids of Li⁺. Both effects lead to decrease of an energy gap and hence increase of polarizability. Indeed, linear LiC≡CF is computed to be polarizable with α=30.83 bohr³. Were polarizability an additive property, one would expect, based on the calculated values of α for C₂H₂, LiF and H₂ (Eq.16) that α(LiC≡CF)=24.73 bohr³. However, the value computed for this molecule is larger by 25% than the expected value.^[64] This increase is mostly due to increase of the α_{zz} component of the polarizability tensor, where z is direction of molecular axis. Hyperpolarizability experiences dramatic changes, as well, but this will not be further dwelled upon here.

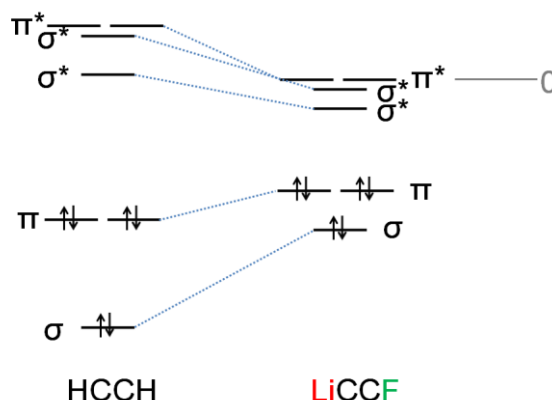


Figure 9. Selected electronic energy levels HC≡CH and LiC≡CF.^[63] Gray "0" line represents energy of an electron in vacuum. Note that Mulliken electronegativity does not change substantially, but hardness does.

Having learned how to make a molecular system soft, let us now turn again to some interesting cases of nobility and inertness.

Lessons from diatomics: hard and "noble" Group 2 (s²), Group 12 (d¹⁰s²) and Yb & No (f¹⁴s²) atoms

Large hardness and nobility of Group 18 elements with their closed-shell (s²p⁶) configuration manifests itself in relative large ionization potentials and null electron affinity but also in unusually low melting and boiling points of atomic solids which they form. Thus, at ambient (p,T) conditions only element 118 is predicted to be a liquid^[65], the remaining NGs are gases. The boiling point of He is as low as 4.2 K and He cannot be crystallized at 1 atm unless pressure is increased, further testifying to its remarkable inability to bind to other atoms of the same type. The He...He dimer is not bound; a tiny minimum appears on the

PES due to ultimately weak van der Waals interactions but the potential well cannot host even one vibrational level. One particularly interesting case of a similar inertness is that of a beryllium atom. Be atom has hardness of 4.66 eV which is approaching that of nonmetallic C (4.84 eV) and a null electron affinity. The electronic configuration of Be atom in its ground state is $1s^2 2s^2 2p^0$ with the closed 2s shell, in analogy to He ($1s^2$). Concomitantly, Be atom has a small electronic polarizability of ca. 37.7 bohr^3 ^[22] which is markedly smaller than that of preceding Li (164.0 bohr^3)^[22] and nearly identical to that of Si (37.3 bohr^3)^[22]. Clearly, Be atom is a hard and small atom and it resembles He to come extent.^[43] Therefore, it is not surprising that Be_2 dimer is very weakly bound; the Be...Be separation is ca. $2.45 \text{ \AA}$, i.e. 36 % larger than twice the covalent radius of Be. The dissociation energy of Be_2 is a mere 0.12 eV (Figure 10).^[66]

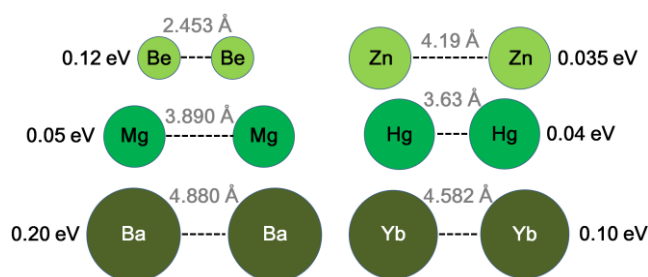


Figure 10. The molecular geometries, and dissociation energies of homonuclear dimers, M_2 , of six selected metallic elements, M, discussed in text. The values of covalent radii of these elements are reflected in the size of atomic spheres.^[66,67,68] All presented dimers are held by very weak attractive interactions which work against the closed-shell/closed-shell Pauli repulsion.

Dimers of the heavier Group 2 metals share the same characteristics with Be_2 : long metal-metal separations and very small dissociation energies (Figure 10). Moreover, dimers of Group 12 ($d^{10}s^2$) elements, Zn, Cd and Hg, as well as that of late lanthanide, Yb ($f^{14}s^2$), also behave in a similar fashion (Figure 10). No calculations are available for the dimer of an isoelectronic late actinide, Nobelium (No, element 102)^[69] but it may be supposed that it will be similar to Yb_2 .

Case of Hg is particularly appealing among those analyzed. Mercury is the only metallic element for which I_p exceeds 10 eV while its remarkable hardness (5.22 eV) exceeds that of nonmetallic Cl (4.68) and approaches that of noble gas, Rn (5.38 eV) (!). Polarizability of a Hg atom equals as little as 33.9 bohr^3 ^[22] which is remarkably small, given its large number of electrons. These are obviously manifestations of very strong relativistic effects, which affect greatly properties of Hg as well as Pt and Au. Recall, Hg is the only liquid metal at ambient conditions (which again testifies to weak interatomic interactions), and its specific resistivity is $9.6 \text{ } \Omega\text{m}$, which is one of the largest among metals and similar to that for semimetallic Bi ($13 \text{ } \Omega\text{m}$). All these anomalous properties may be traced back to the closed-shell/closed-shell (Pauli) repulsion of hard Hg atoms, overlapped with very weak attractive van der Waals interaction. These 'noble' features of Hg combined with the alchemical or homeopathic prescription "*Similia similibus curentur*" (i.e. "Like cures like") urged this author to propose that amalgam of Xe might form at appropriate conditions.^[45] This supposition has been confirmed by DFT calculations: metallic HgXe alloy adopting CsCl structure should form at pressure of ca. 75 GPa .^[45]

Closer inspection of a larger set of physicochemical properties of Group 2, Group 12 elements, Yb and No, and their comparison to these from Group 18 (shortly "M"), reveals additional similarities between them, especially when one contrasts them with the elements preceding ("M-1") and following them ("M+1") in the Periodic Table (Figure 11).

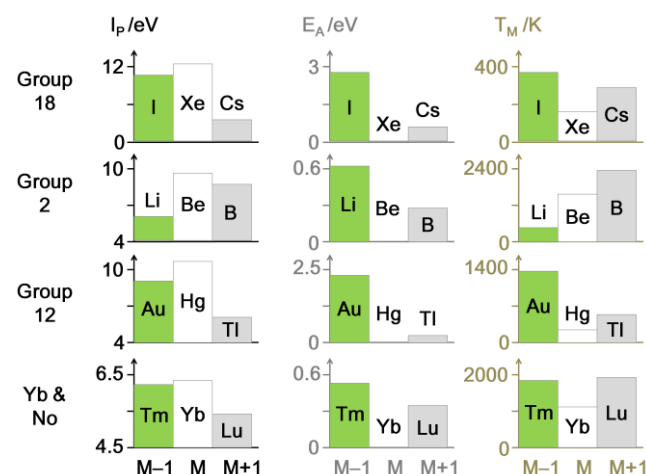


Figure 11. Selected examples of physicochemical parameters for an element M, element preceding it (M-1) and the one following it (M+1) in the Periodic Table, where M is a selected Group 18, Group 2 or Group 12 element, or Yb. I_p - ionization potential, E_A - electron affinity, T_M - melting point. The only exceptions from the trends described in text are Be's TM (which is higher than that of the preceding Li)^[70] and Li's I_p which is smaller than that of B.

Specifically, elements M exhibit larger I_p than its neighbours, the smallest (null) E_A (these together imply the largest hardness), and the lowest melting point suggesting weaker interatomic interactions. The elements M-1 usually show the largest E_A value while the elements M+1 the smallest I_p (there are 2 exceptions from these trends as described in caption to Figure 11). Similar trends usually hold for other elements in the same group of the Periodic Table. Thus, elements M are 'noble gas-like' in a given set and the elements M-1 are electronegative 'halogen-like' species. Some of M+1 elements are electropositive 'alkali metal-like' and some indeed readily form monovalent state (e.g. Tl, more seldom B). Indeed, similarity of Au to halogens ($\text{Au}\sim\text{I}$) has been long discussed in the literature. Au forms aurides. Cu and Ag do not, but their E_A values are surprisingly large. H obviously forms hydrides and it has been compared to either iodine or fluorine as based on various physicochemical features ($\text{H}\sim\text{I}$ or $\text{H}\sim\text{F}$). In addition, all alkali metals may act as halogens and all form anionic species stable in the gas phase.

Based on the picture drawn here, one may attempt to reshape the Periodic Table so that it reflects the observed trends.^[71] One possible form of the Periodic Table nicely incorporating these trends ("Periodic Table as viewed from Pearson hardness") is showed in Figure 12.

The hardest elements which are similar to each other in many aspects are "noble" elements from Groups 2, 18, 12 as well as Yb and No. Elements from Groups 1, 17, 11 as well as Tm and Md serve as $1e^-$ deficient "halogens"; Group 1 elements (H and alkalis) are "halogens" but they may also be mono-positive, thus similar to nonmetals from Group 17 (except F), and Group 11 metals; note, monovalent state of Tm is yet to be showed.

s	H	He																		
	Li	Be																		
	Na	Mg																		
	K	Ca																		
	Rb	Sr																		
p	Cs	Ba																		
	Fr	Ra																		
	119	120																		
	B	C	N	O	F	Ne														
	Al	Si	P	S	Cl	Ar														
d	Ga	Ge	As	Se	Br	Kr														
	In	Sn	Sb	Te	I	Xe														
	Tl	Pb	Bi	Po	At	Rn														
	113	114	115	116	117	118														
	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn										
f	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd										
	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg										
	Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn										
	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb						
	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No						

Figure 12. One possible arrangement of the chemical elements in a Periodic Table emphasizing the closed shell "noble" character of elements from current Groups 2, 18, 12, Yb and No, as well as "halogen" character of elements from current Groups 1, 17, 11, Tm and Md. Note that He is placed in Group 2, above Be.

Excited states: (usually) soft and reactive

So far we have been dealing with atoms or molecules in their ground electronic state. It could be expected, based on the GMHP, that the excited states of an atom or molecule will be softer than the ground state. Exciting electrons to virtual levels - usually more diffuse and less bound than the occupied ones - increases electronic softness (as in the Bohr model of a H atom). The excitations are typically realized by breaking of the existing electron pairs (either lone pair or bonding pairs); this always comes at energy price. For obvious reasons, a singly- or a multiply-excited state - is usually more polarizable than the ground state. But how large this effect may be?

Experimental estimates of polarizability of the excited states is only seldom performed due to technical difficulties. Theoretical estimates are also rarely available. Fortunately, data can be found in the literature on polarizability of two excited states of the smallest neutral molecule, H_2 .^[72] $\alpha(H_2)$ in its $^1\Sigma_g$ ground state is 2.88 bohr³. The first bound excited state is $^1\Sigma_u^+$ which lies close to 11.4 eV above the ground state. The minimum of the PES is at 1.2928 Å and this state exhibits substantial ionic character. It turns out that the calculated $\alpha(H_2)$ in this state equals *ca.* 111.8 bohr³ and thus it is nearly 40 times larger than that of the ground state (!). This translates to a 3.4-fold softening of a molecule in terms of hardness. Polarizability of $^1\Sigma_u^+$ - albeit large - is still half of that for the extremely soft 'naked' H^- anion (216.1 bohr³).

The second electronic state for which polarizability was calculated is an unbound $^3\Sigma_u^+$. Interestingly, at $H...H$ internuclear separation of 1 bohr (corresponding to a vertical excitation) the diagonal components of the polarizability tensor which are perpendicular to molecular axis are virtually identical in the excited state than in the ground state. It is the parallel component which differs greatly for both electronic states. Although the authors^[71] do not provide any specific value, yet it may be

estimated from their figure 9.4. that $\alpha(^3\Sigma_u^+)$ is probably of the order of 1000 bohr³ since it diverges to infinity for $R(H...H)=0.8$ bohr due to the level crossing with the state $^3\Sigma_g^+$ at this distance. Clearly, excited states are by order(s) of magnitude more polarizable than the ground state. It would be interesting to study this effect quantitatively for a much broader set of atoms and molecules, and their excited states (including very soft Rydberg states).^[73]

Excited state polarizabilities have also been calculated for water molecule.^[74] It turns out that for the lowest-lying triplet state $\alpha(^3B_1)$ is close to 80.9 bohr³ while for the lowest lying excited singlet state $\alpha(^1B_1)$ is close to 99.2 bohr³ (CCSD/ ORHF_e results). These values may be compared to the experimental value for the ground state of 9.63 bohr³ (which is very close to the best theoretical value^[74]). Thus, polarizability increases upon excitation by *ca.* 1 order of magnitude (thus similarly as for H_2). Interestingly, the excited singlet state is considerably harder than the excited triplet state; it pays off to keep all electrons paired up to exhibit smaller softness. We will come back to this important feature in Part 2 of this series when analyzing high-pressure phenomena for solids.

Van Wijngaarden provides a valuable set of calculated polarizabilities for over 50 lowest-lying electronic states of a Rb atom and the measured values for over a dozen of them.^[75] The calculated values of α turn out to vary by as much as 5 orders of magnitude; moreover, for the several low-lying excited states α scales up approximately with n^7 where n is an effective principal quantum number (Figure 13). This is qualitatively similar to what have been found for H atom where α scales up approximately with n^{5-6} where n is a effective principal quantum number.^[76] Clearly, some very highly-excited electronic states will tend to be very soft. We will return to polarizability of excited states while analyzing the progress of a chemical reaction in one of forthcoming sections.

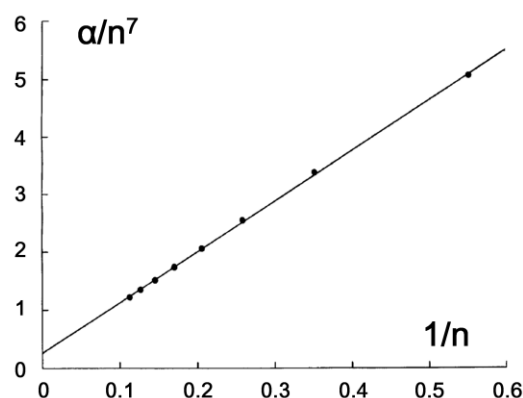


Figure 13. The dependence of α/n^7 on $1/n$ for excited states of Rb atom where n is the effective principal quantum number. The curve best fitting the data is given by: $\alpha/n^7 = 0.267 + 8.69 / n$. Redrawn after Ref.^[75]

In view of the examples presented above it is interesting to point out an excited state of a molecule which exhibits a smaller polarizability than the ground state. Not surprisingly, one such case is provided by the system for which the ground state is not a singlet but rather a triplet (diradical), and the excited state in question - namely molecular dioxygen - has all electrons paired up. 3O_2 shows an equilibrium bond length of 1.20752 Å which slightly elongates to 1.2156 Å upon excitation by nearly 1 eV to 1O_2 .^[42]

Despite that, $\alpha(^3\text{O}^2) > \alpha(^1\text{O}^2)$ since $\alpha(^3\text{O}^2) = 9.95 \text{ bohr}^3$ and $\alpha(^1\text{O}^2) = 9.41 \text{ bohr}^3$ ^[77]. It is of interest whether this effect would hold for other lowest lying singlet states of molecules which adopt triplet configuration in their ground state.

Hybridization as viewed from polarizability perspective

The Be atom, which we have discussed in length in one of preceding sections, has a rather low-lying stan excited state at *ca.* 2.7 eV, which corresponds to transfer of one electron from 2s to 2p subshell:



A double excitation from the 2s to the 2p shell:



costs 4.7 eV more than the first one, 7.4 eV altogether.

Be atoms are not closed shell in the same way as helium atom, with its closed electron doublet $1s^2$ valence shell and the first excitation energy of over 21 eV. The $2s^2$ shell of Be is quasi-closed *i.e.* relatively easy to open, as judged from the first excitation energy of 2.7 eV. Hybridization of the 2s set with the low-lying virtual 2p orbitals contributes covalent character to the bonding in the compounds of beryllium. The energy expended in promoting the 2s electrons into the 2p orbital can be compensated for by the formation of additional sigma bonds, as in well-researched linear beryllium dihalide molecules.

Interestingly, the calculated polarizability of Be in the excited state $\text{Be}^* (^3\text{P}_0)$ is surprisingly low, 39.33 bohr^3 (as compared to the ground state ^1S , 37.62 bohr^3).^[78] This implies that s-p mixing is not only facile but also it does not lead to significant loss of hardness of a Be atom. Another spectacular result is that the doubly-excited Be^{**} state (^3P) is also pretty hard - its calculated polarizability is 43.30 bohr^3 .^[79] These unusual features of Be atom are related directly to the MHP and they offer an alternative explanation of why the s-p mixing (*i.e.* forming of an s-p hybrid) is so facile for Be.

MHP: the Molecular Orbital picture

In one of the preceding sections we have analyzed the applicability of the GMHP for single bond formation in diatomics. The further examples of the GMHP may now be provided for more complex molecular systems, and illustrated using the Molecular Orbital (MO) perspective. The MO picture is of value here since it may easily be extended to extended solids using the ramifications of the band theory. Here it will be exemplified for a molecule exhibiting a polarized dative bond within a strongly bound Lewis acid - Lewis base complex.^[80]

When a Lewis acid, A, *i.e.* a species with a low-lying empty LUMO, interacts with a Lewis base, B, *i.e.* a species with a high-lying doubly-filled HOMO, the predominant MO interaction is that of the HOMO_B with LUMO_A (Figure 14). Simultaneously, the interaction between HOMO_A and LUMO_B is weaker than the one

described above, since the separation of HOMO_A and LUMO_B in the energy scale is larger, and we will omit it from further considerations. Four new MOs evolve from formation of the AB adduct:

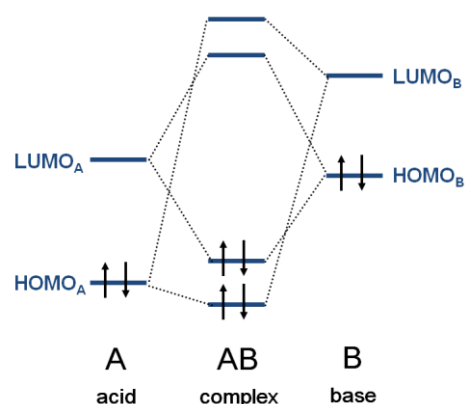


Figure 14. The MO interactions upon formation of a Lewis acid (A) - Lewis base (B) complex. The predominant MO/MO interaction is that between low-lying LUMO_A and high-lying HOMO_B , and it leads - via substantial mixing of the two - to two new MOs of the AB complex, which are separated by a gap.

two of which (those originating from HOMO_B and LUMO_A) are of particular importance. The occupied one is stabilized with respect to HOMO_B while the upper one is destabilized with respect to LUMO_A . The gap opens up between frontier orbitals of the AB adduct; most often this *new gap* is larger than the smaller one of the two individual MO gaps of the interacting components (for mathematic considerations related to HSAB principle and minimization of the chemical potential *cf.* Ref.[18]). Importantly, energy of the AB complex is lower than that of the (acid + base components) at a large separation, which is a manifestation of the GMHP: the (A+B) system *adopts such geometry* which permits formation of a new dative bond between B and A in order to (i) decrease electronic energy *and* (ii) to increase hardness.

The acid-base reactions of the Brønsted-Lowry type - *i.e.* these involving a proton transfer - also nicely corroborate the GMHP. One prototypical example is provided by the reaction of ammonia molecule and H_3O^+ in the gas phase (the case considered here assumes full separation of the product molecules from each other):



Proton-affinity of H_2O equals 691 kJ mol^{-1} while that of NH_3 is amounts to $853.6 \text{ kJ mol}^{-1}$.^[81] Simultaneously, NH_3 is electronically softer, as measured by its (static) electric dipole polarizability of 14.810 bohr^3 , as compared to that of water, 9.816 bohr^3 .^[82] Thus, when the energetically-preferred reaction (Eq.21) takes place, the H^+ transfer occurs in such a way that the electronically softest element of the reaction system disappears, *i.e.* it becomes protonated (and thus much harder in electronic sense). In fact, the reaction products (NH_4^+ , H_2O) tend to interact further when they aggregate (Eq.11), via formation of an asymmetric hydrogen bond:



The decrease of the electronic energy of the system (Eq.22) is now much smaller as compared to the first step of reaction (Eq.21) but the (now) softest element (H_2O molecule) is again slightly 'hardened' due to interaction of the 'soft' lone pair at O atom with a proton which is chemically bound to NH_3 . This is how a chemical system economically utilizes positions of its nuclei to increase electronic hardness.

The considerations presented here may, of course, be modified in such a way that to illustrate the fate of the redox (electron-transfer) reactions. The strongest reducing agents typically originate from electron-rich neutral species (such as metals: Li, Ba etc.) or negatively charged ones (such as certain anions: H^- , Li^- , N_3^- , solvated electrons in ammonia e^-_{solv} , etc.), more seldom from cations at unusual low oxidation states (Tm^{2+} , Sm^{2+} etc.). All these systems bind electron(s) weakly, they tend to have rather diffuse valence orbitals and hence exhibit substantial electronic softness. In the course of chemical reactions the strong reducing agents are 'scavanged' even by weak or moderately strong oxidizers and the corresponding oxidized systems are much harder (Li^+ , Ba^{2+} , H_2 or H^+ , N_2 , NH_3 , Tm^{3+} , Sm^{3+} , respectively). Again, this is the core of the MHP and GMHP.

Summarizing this section one might say that the chemical reactions - be these acid-base or redox ones - clearly occur at the expense of the electronically softest reagents, usually by depopulating (or just hardening) of their occupied MOs; this is done by utilizing of the virtual orbitals of the hardest elements of the system. Of course, since the acid-base and redox reactions are two most fundamental types of reactions in chemistry; then any complex chemical reaction can be described using the combined language of acid-base and electron-transfer processes.

Having analyzed simple and more complex chemical reactions we now turn to a few prototypical distortions of small or more complex molecular entities linked to their isomerism, which may be analyzed from the view point of the GMHP.

Redox reactions

Above we have discussed the formation of the acid-base adduct and thus the validity of the GMHP in terms of Lewis acidity and basicity. The acid-base reactions constitute, together with the redox reactions, two central types of chemical processes. The conceptual link between the electron pair-sharing and electron-transfer phenomena is straightforward and it may be expressed using the ramifications of the MO theory, regardless whether the redox process involves two or only one electron. The relationship between both key classes of chemical processes is well known since the early work of Usanovich, who introduced more general approach than the Lewis^[83]. Usanovich's unifying classification of chemical species (oxidizers & acids vs. reducers & bases) is quite intuitive for chemists and especially electrochemists, who have long known that reactions involving strong oxidizers usually lead to acidification of the reaction environment, while reactions involving strong reducing agents facilitate the formation of bases, e.g.:

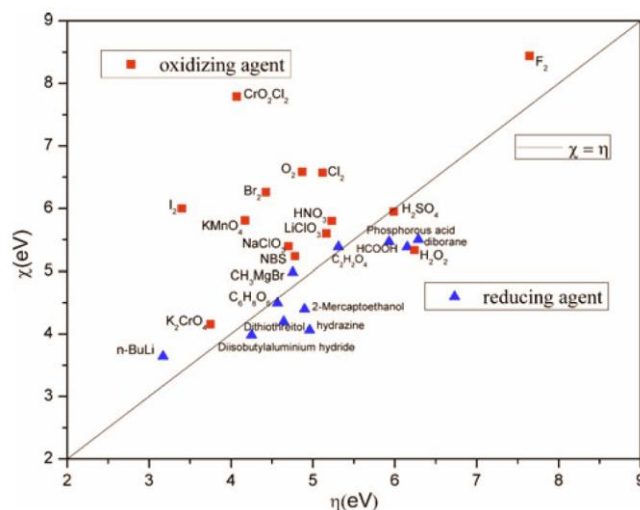


Figure 15. Illustration of the dependence between η and χ for a number of strong oxidizing and reducing agents. Reproduced with permission from Ref.[80].

Chattaraj *et al.*^[80] were the first to realize that the simplified equality $\eta \approx \chi$ (Eq.6) illustrated in Figure 2 does not hold for most of strong reducing and oxidizing agents. Specifically, for most of strong oxidizers $\chi > \eta$ while for strong reductants the opposite is found (Figure 15). This is obviously an exemplification of the strong influence of the E_A for these species: most electron-poor species (oxidizers) have appreciable positive E_A values while most electron-rich species (reducing agents) exhibit *formally negative* E_A values. Given what was said above about the Usanovich classification, it is expected that analogous inequalities hold also for superacids and superbases, respectively.

And it is now interesting to search for marked exceptions from those rules of thumb.

Jahn-Teller effect: transition metal complex meets GMHP

As it is well known, non-linear molecules which have degenerate MOs are, at certain d electron counts, subject to the first order Jahn-Teller (JT) effect.^[84] An octahedral $[\text{Cu}^{2+}\text{L}_6]$ complex nicely exemplifies this behaviour (Figure 16). Undistorted system has two degenerate MOs which are filled with 3 electrons thus leading to large polarizability and hence small hardness. Either a normal or an inverse JT effect both lead to appearance of a band gap between these orbitals, thus increasing η . This is further enhanced by the action of the 2nd order JT effect, which increases η even more.

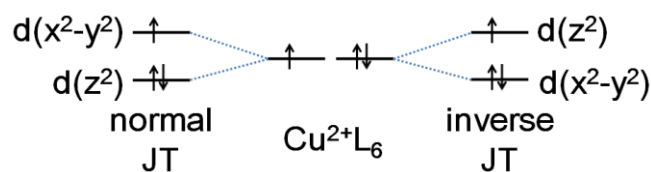


Figure 16. Illustration of energy changes of MOs for an octahedral Cu^{2+} complex with 6 L ligands: an undistorted complex (center), a distorted D_{4h} complex with a 4+2 coordination of Cu^{2+} (left), and a distorted D_{4h} complex with a 2+4 coordination of Cu^{2+} (right).

The symmetry-breaking distortions clearly decrease polarizability of the $[\text{Cu}^{2+}\text{L}_6]$ complex; extension of such analysis to solid state compounds containing isolated JT-active cations, is straightforward. Similar, but less strict scenario is found in the systems which exhibit the second order JT effect. Moreover, it is expected that the Jahn-Teller effect cannot be fully annihilated in the chemical systems unless the odd-electron at the JT center is somehow made delocalized (which is in principle possible in the solid state rather than isolated molecules). We will further discuss it in Part 2 of this series.

Undistorted or distorted? GMHP has its say for aromatic and antiaromatic systems

Also the aromatic (for $2+4n$ π electrons) or antiaromatic (for $4n$ π electrons) character of cyclic – and the associated distortions of the CC skeleton – of cyclic unsaturated compounds may be linked to the GMHP. This is exemplified by aromatic cyclobutadiene (CBDE) dication and a related antiaromatic neutral system (Figure 17).^[7]

Neutral CBDE prefers to take a rectangular configuration of the carbon framework, since this leads both to decrease of energy *and* to increase of hardness; CBDE is antiaromatic in light of the Hückel rules.^[85] The π bonds become nearly localized in the process of distortion. On the other hand, aromatic CBDE^{2+} is known to be stable in its squared configuration of the carbon skeleton. Notice, however, that a hypothetical rectangular distortion for CBDE^{2+} should not lead to appreciable change of energy since such distortion affects mostly the degenerate empty LUMO. This is because changes of the π overlap between 2p atomic orbitals of the neighbouring C atoms largely cancel out during distortion. Hence, it is impossible to judge based exclusively on orbital energy criterion whether CBDE^{2+} should or should not distort. However, one may notice that a rectangular distortion would greatly decrease hardness since the HOMO/LUMO gap would decrease. Thus, CBDE^{2+} chooses to stay undistorted and this is again in agreement with the Hückel rules. Clearly, as in the case of the JT effect, both cyclic hydrocarbon species analyzed here try to maximize η , which is an appealing manifestation of the GMHP.^[86]

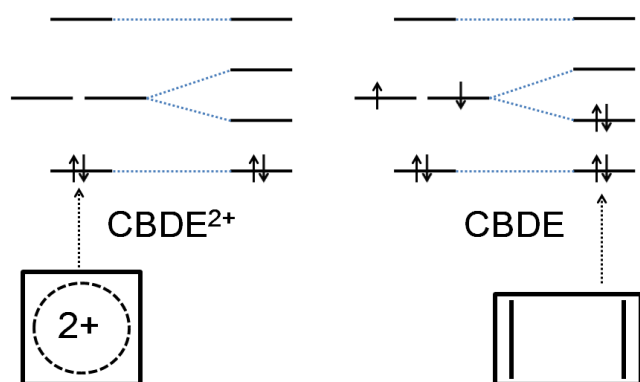


Figure 17. Illustration of the applicability of GMHP for a prototypical aromatic system, cyclobutadiene dication (left), and a prototypical antiaromatic system, cyclobutadiene. A molecule with a square carbon skeleton (left set of MOs for a given molecule) is distorted to a rectangular one (right set of MOs in each case). This leads to decrease of η for CBDE^{2+} but to the increase of η for CBDE; correspondingly, CBDE^{2+} remains squared, while CBDE distorts to form a rectangle.

Cyclic form of ozone, ${}^1\text{O}_3$

Ozone (O_3), a high-energy allotrope of oxygen, will again serve us to discuss applicability of the GMHP. According to VSEPR theory, this molecule should adopt an undistorted trigonal-planar geometry (D_{3h}) with three O-O-O bond angles of 60° (since there are 2 bonds + one lone pair = 3 electron density groups on each carbon atom). The corresponding Lewis dot formula is a perfectly reasonable valence bond representation of the O_3 molecule (Figure 18). However, this so-called cyclic ozone has never been prepared in the free form;^[87] the actual singlet ground state of ozone corresponds to a severely distorted triangle (C_{2v}) with two O-O bonds at 1.278 Å and O-O-O bond angle of 116.8° , which leads to a secondary (essentially non-bonding) third O...O distance of 2.177 Å. The global minimum (which is often thought of as a hybrid of two resonance structures) is at energy of about 1.3 eV more negative than that of the triangular ring form.^[88]

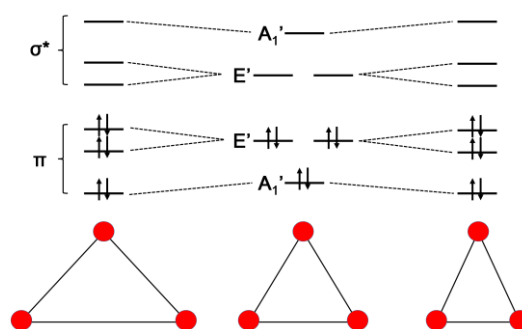


Figure 18. Illustration of the applicability of GMHP for cyclic isomer of ozone. Deformation of one O-O-O angle – either decrease or increase – would lead to softening of a molecule; thus, cyclic ozone is a local minimum.

But could the exotic cyclic ozone (D_{3h}) be prepared? The calculations suggest that the D_{3h} form of O_3 is a local minimum on the potential energy surface, which is protected by an appreciable well with the barrier height of over 1 eV.^[87,88] The GMHP fully supports this computational result. It turns out that deformation of one O-O-O angle – either decrease or increase – would lead to softening of a molecule (Figure 16); thus, cyclic ozone is a hard local minimum and could be sought for in experiment.^[89]

Transition States: an inevitable compromise during a chemical reaction

The usefulness of the GMHP for studies of chemical reactions may also be illustrated using a conceptual construct of a transition state (TS) of a chemical reaction. This is illustrated in Figure 19.

Progress of a chemical reaction along the reaction coordinate may be visualized in a classical picture using the potential energy curves of the reactants (R) and products (P) which mix up as reaction progresses and passes through a transition state (TS). The TS is immediately identified as a state of such geometry which has the *smallest* electronic hardness along q . The TS is much softer than both the reactants and the products but it is not infinitely soft. A chemical reaction may occur only if excited states – which are usually much softer than the ground state – are temporarily admixed to the ground state by partial occupation of virtual orbitals. Moreover, it turns out that the reaction progresses along

such q that the TS along this q is the hardest among all possible TSs.^[90] Thus, Nature "protects" from excessive reactivity not only the minima on the potential energy surface, but also the TSs for chemical reactions. Actually, TS is the softest state along the reaction pathway only for the symmetric reactions, *e.g.*:



or for isomerisation of CBDE from one rectangular minimum to another via a squared transition state. Some deviations from this rule have been found for non-symmetric reactions,^[87] for example:



the most typical one being that the softest point along q is not precisely at the TS but rather in its close vicinity. On the other hand, the reactions which proceed without breaking of a chemical bond but consist exclusively of a bond formation, *e.g.*:



usually do not exhibit any energy barrier and they take place with the progressive hardening of a chemical system *i.e.* without any TS.

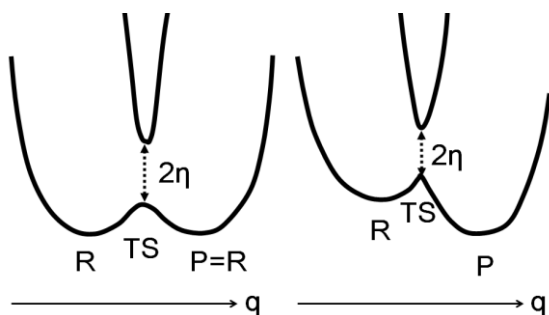


Figure 19. Illustration of the progress of a chemical reaction as expressed by the potential energy curves of the reactants (R) and products (P) which mix up as reaction progresses along the reaction coordinate, q , and passes through a transition state (TS). The electronic hardness is the smallest for the TS along q . A symmetric (identity) reaction (left) and a spontaneous non symmetric reaction (right) are illustrated.

The link between the GMHP and the general mechanism of chemical reactions^[91] is crucial not only for our control of industrial catalytical reactions, but also for understanding of these which occur in the living matter. It is not without a cause that the best catalysts which efficiently decrease reaction barriers and electronically soften the substrates rank from the heavy and polarizable 4d and 5d metals (Ru, Rh, Pd, Ag, Os, Ir, Pt, Au) - either in their elemental form but also bound in coordination complexes; their lighter less polarizable 3d homologues do not enjoy much success in industrial catalysis. On the other hand, Nature has devised smart methods to make use of the light abundant metallic elements (*e.g.* Cu, Fe, Zn, Mg) to facilitate important chemical reactions so that they proceed with low barriers; this has been achieved by careful design of the electric field from ligands around the active site of enzymes;^[92] and the purpose of such design is likely to bring down in energy one particular excited state which has polarizability tensor fitting to the electric field of the reaction cavity. Similar GMHP-related

arguments might apply to excited states which are active for solar energy harvesting during photosynthesis.^[93]

Spin Transitions

The majority of systems which we have discussed so far involved either formation of systems exhibiting an electron pair from two substrates (free radical ones, closed shell cationic and anionic, or closed-shell neutral acid and base), and systems showing geometry distortions due to the degenerate or quasi-degenerate ground state (the JT effect, the 2nd order JT effect, and antiaromatic systems, ozone etc.). One peculiar example – which disobeys the GMHP – involved the molecular dioxygen, which has a diradical ground state, and which is electronically softer than the first excited singlet state. Let us now look more closely at the molecular systems which contain Transition Metals (TMs) and may exhibit a richness of spin states (multiplicities). Let us focus on the classical even-electron case of the low-spin (LS) and high-spin (HS) Ni(II) systems with the electronic configuration of $3d^8$ (Figure 20).

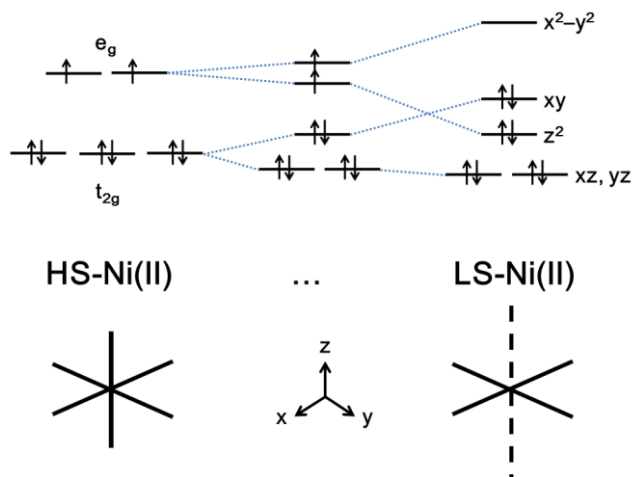


Figure 20. Illustration of the HS, intermediate, and LS scenarios for an $\text{Ni(II)}\text{L}_6$ system in the weak, medium and strong-ligand field, respectively.

The crystal field theory predicts for the d^8 system in an octahedral (O_h) environment of six point charges that the d orbitals would split as $3 t_{2g} + 2 e_g$. If this was the case, all Ni(II)-containing molecules would be high-spin ($S=1$) paramagnetic species. However, the situation gets more complex with real ligands. Indeed, the weak-field ligands, such as F-, O-, S- or N-donor ones, usually lead to the HS ground state. However, the strong-field ligands, particularly those having the low-lying π orbitals (CO , CN^- , NO_2^- , etc.), tend to stabilize the square-planar LS (diamagnetic, $S=0$) ground state (Figure 20). The latter scenario obviously opens the HOMO-LUMO gap; the larger is the destabilization of the x^2-y^2 orbital with strong σ -donor ligands, the concomitant stabilization of the z^2 lone pair, and the stabilization of the xy orbital via ligand acceptor orbitals, the larger is the HOMO-LUMO gap. However, the HS scenario is also related to gap opening, this time via the spin-polarization of the MOs (this is not apparent from Fig.20 but appears in any unrestricted Hartree-Fock or DFT calculations). Thus, the gap opens between the highest occupied α spinorbital and the lowest unoccupied β spinorbital.

The situation for the medium-field ligands (intermediate between the two in Fig.20) or for the set of two different kinds of ligands ($4L_1+2L_2$) is the most complex. Depending on the placement of ligands in the spectrochemical series a given system will either adopt a HS or a LS ground state, whichever gap leads to an electronically harder state.^[94] Again, the GMHP seems to be at play. For cases at the verge of equilibrium between the two, a subtle influence of temperature or external pressure may lead to the spin-crossover phenomenon, as exemplified by thousands of examples described in the literature. We will further dwell on that in the Part 2.

From an atom or a molecule, via a cluster or an oligomer, towards a solid

One natural link between an isolated atom – or a molecule (discussed here in Part 1) – and the corresponding solids (Part 2), is provided by atomic or molecular crystals. Such species are held by weak van der Waals forces, and many properties of the extended crystal are governed mostly by the properties of isolated building blocks (atom or molecule). Crystals of noble gases, or of saturated hydrocarbons, exemplify this feature very well. Obviously, high chemical inertness of the isolated building blocks (as described by the (G)MHP) results in a similarly high inertness of the solid. Moreover, it may be noticed that solids may even slightly stiffen up (electronically) as compared to the isolated building blocks, as exemplified by methane (Figure 21).

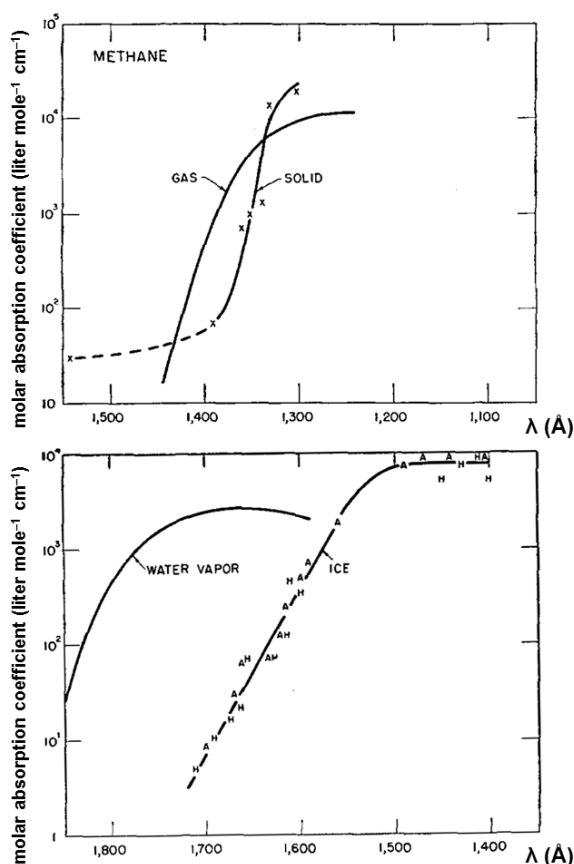


Figure 21. Molar absorption coefficient of solid and gas-phase methane (top) and water/ice (bottom) as a function of wavelength. Notice the blue-shift of the absorption edge in the UV range upon gas $\rightarrow$ solid transition. Reproduced with permission from Ref.[95]

The cases of molecular systems containing the unsaturated bonds, with few exceptions, are also straightforward –they oligo- or polymerize; thus (from energy viewpoint only), HCN will readily yield 1,3,5-triazine, C_2H_2 would either trimerize (giving benzene) or infinite-chain polyacetylene, C_2H_4 will give broad band gap (colourless) polyethylene, while the analogous C_2F_4 will form poly-perfluoroethylene (Teflon[®]) explosively. In all these processes part of – or all – π electrons are turned into less polarizable σ ones. Numerous confirmations of the (G)MHP of this kind may be suggested.

However, the most interesting cases of solidification processes correspond to formation of bulk metals (*i.e.* infinitely polarizable bodies) from isolated atoms (an isolated atom always has some kind of energy gap, *i.e.* it is a nanoscopic semiconductor); recall that the solidification process is certainly downhill in energy (sublimation enthalpy is positive for all elemental metals). Let us thus examine the formation of elemental lithium from Li atoms, via cluster stages (Figure 22).^[96]

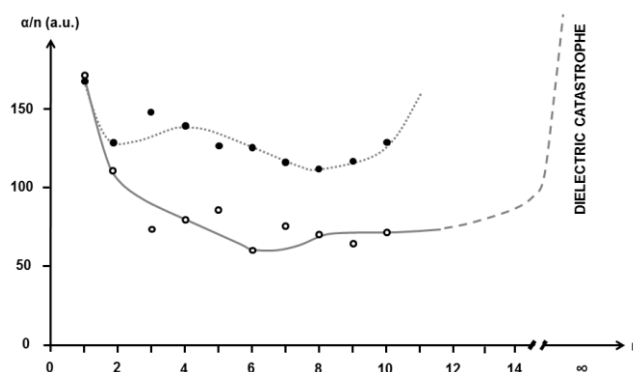


Figure 22. The static electronic dipole polarizability per one atom (a/n) in function of a cluster size, n , for lithium (open circles) and sodium (filled circles). Lines were drawn to guide an eye for points corresponding to $n=1, 2, 4, 6, 8$ and 10 . Numerical experimental data taken from Ref.[96a].

As discussed above, formation of Li_2 molecule from two Li atoms follows the GMHP. However, it is clear from Fig.22 that the process of forming of a bulk solid from lithium atoms, is quite complex, and it also shows well-known odd-even effects.^[97] Let us thus focus on even clusters only. The experimental polarizability per atom first decreases (up to $n=6$) but then slightly increases (for $n=8, 10$). Larger clusters have been studied computationally^[98] but, regrettably, polarizability has not been calculated. However, a “dielectric catastrophe” (*i.e.* polarizability divergence) is known to occur for metal clusters of a certain finite size (typically for $n \sim 20$);^[99] this phenomenon corresponds to band structure formation when a semiconducting cluster becomes a chunk of metallic matter. Very similar phenomena, which are related to strong nonadditivity of polarizability (and thus necessitate departure from two-body effects towards higher-order terms), have been observed for sodium, mercury, beryllium, copper, and many other metallic elements.^[100] Occasionally, band gap may open again for large “magic”-size clusters, but closes for $n \rightarrow \infty$.

Formation of metallic moiety from semiconducting atoms seems to be at the first sight a strong case against the GMHP. Consequently, part 2 of this duology has been devoted largely to metals, and solids in general.

Summary and Outlook

In 2013, 95 y.o. Prof. Ralph G. Pearson wrote in his letter to the author: "I hope you are right that the MHP is a universal law. I have not thought about it in such terms. I just saw that it usually seemed to be true."^[101,102]

Here we have revisited the MHP and GMHP formulated by Pearson and its reformulation by Chattaraj as the Minimum Polarizability Principle. We have showed that GMHP may be used to rationalize a large diversity of important chemical and physical phenomena occurring for atoms and isolated molecules and to predict the progress and the fate of a chemical reaction in the gas phase. GMHP does not have many exceptions and it is very useful for understanding of, *inter alia*, inertness of light noble gases (and that of Be and related quasi-closed shell elements), the phenomenon of hybridization of atomic orbitals, the first- and second-order Jahn-Teller effect, the nature of distortions occurring for antiaromatic hydrocarbons, appearance of magic numbers in the stability charts for polyatomic clusters,^[103] spin crossover phenomena, progress of chemical reactions, enhanced polarizability of the excited states, and more. The (electronically) softest species are usually eliminated (or substantially hardened) in the course of chemical reactions, be these of acid-base or redox type.^[104] Electric polarizability turns out to be a valuable descriptor of atoms, molecules and chemical reactions, especially that it is an observable which can be quite precisely determined, while the values of η reported in the literature - calculated according to various simplified definitions of hardness - tend to differ not only for larger molecules but even for atoms.^[105]

The considerations presented in this work set ground for associated discussion of applicability of the omnipresent (G)MHP for solids in Part 2 of this series.^[106]

Acknowledgements

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Entry for the Table of Contents

Layout 2:

Hardness rules

*Wojciech Grochala**

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



Part 1 of this duology is devoted to isolated atoms and molecules, and to chemical reactions between them; we introduce here basic concepts beyond the Generalized Maximum Hardness Principle,

and the corresponding Minimum Polarizability Principle, and we illustrate applicability of both Principles to a broad range of chemical phenomena and distinct systems in the gas phase.