

REVIEW ARTICLE

THE MAXIMUM HARDNESS PRINCIPLE: AN OVERVIEW

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It has been known for a long time that the stability of a chemical species is intimately connected with the corresponding gap between the highest occupied and lowest unoccupied molecular orbitals. It also helps in understanding whether a chemical reaction is favourable. Implications of a principle of maximum hardness in the context of various physico-chemical processes have been reviewed. Formal proofs and numerical calculations pertaining to this principle have been highlighted. In general, hardness implies stability.

Key Words: Maximum Hardness Principle (MHP); Molecular Orbitals; Density Functional Theory; Aromaticity

Introduction

Density functional theory (dft)¹ has been found to be useful in providing theoretical basis for popular qualitative chemical concepts² like electronegativity³ and hardness⁴. Idea of electronegativity was first introduced by Pauling⁵ and that of hardness was given by Pearson⁶ in the context of hard-soft-acid-base (HSAB) principle which states that "hard likes hard and soft likes soft". For the ground state of an N-electron system the electronegativity (χ) is defined as⁷

$$\chi = -\mu = -\left(\frac{\partial E}{\partial N}\right)_{\nu(\mathbf{r})}, \quad \dots (1)$$

where μ is the chemical potential (the Lagrange multiplier associated with the normalisation constraint of dft¹), E is the total electronic energy and $\nu(\mathbf{r})$ is the external potential. Hardness (η) has been defined as⁸ the corresponding second derivative,

$$\eta = \frac{1}{2} \left(\frac{\partial^2 E}{\partial N^2}\right)_{\nu(\mathbf{r})}, \quad \dots (2)$$

Operational definitions of μ and η can be obtained⁸ by making use of a finite difference approximation of eqs. (1) and (2) as

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$$\mu = -\frac{I+A}{2}, \quad \dots (3)$$

and

$$\eta = \frac{I-A}{2}, \quad \dots (4)$$

where I and A are ionisation potential and electron affinity of the system respectively. Assuming the validity of Koopmans' theorem eqs. (3) and (4) can be written as⁹

$$\mu = \frac{1}{2} (\epsilon_{\text{LUMO}} + \epsilon_{\text{HOMO}}), \quad \dots (5)$$

and

$$\eta = \frac{1}{2} (\epsilon_{\text{LUMO}} - \epsilon_{\text{HOMO}}), \quad \dots (6)$$

where ϵ_{HOMO} and ϵ_{LUMO} are the highest occupied- and the lowest unoccupied molecular orbital energies respectively. Therefore, hardness is just half of the HOMO-LUMO gap.

"The presence of a good HOMO- and LUMO gap in molecules has long been associated with structural and kinetic stability. Bartell's use of the second-order Jahn-Teller theorem highlighted this viewpoint when he showed how molecules with small gaps could distort to give more stable structures with larger gaps¹⁰. An example is the opening up of the gap on pyramidalisation of ammonia. In studying the most stable substitution pattern of cyclobutadienes, Hoffman identified the more stable (trans) $A_2B_2C_4$ isomer as the one with the larger HOMO-LUMO gap¹¹. In organometallic chemistry as well, similar ideas apply, whether the cis or trans form of $ML_4(CO)_2$ and ML_4O_2 species is more stable depends upon electron count. However, in each case for a given electron configuration the more stable structure is found to be the one with the larger gap. In fact, the concept that a small HOMO-LUMO gap signals a geometric distortion is well recognised in almost all areas of molecular chemistry"¹². Bader¹³ also pointed out in the similar spirit that "The bonds in a transition-state molecule are longer and weaker than usual, and hence the top-most orbitals will be higher in energy and the antibonding combinations will be correspondingly lower in energy, i.e., the separation between the bonding and antibonding combinations in general decreases as the bonding decreases." Since a hard molecule has a large gap and a soft one a small gap Pearson¹⁴ forwarded the principle of maximum hardness (PMH) which states: "There seems to be a rule of nature that molecule arrange themselves so as to be as hard as possible. A large HOMO-LUMO gap increases stability."

In the present paper, we delineate the present status of this principle and review its implications in various physico-chemical processes. First we present

different approaches to obtain a formal proof of the principle. Implications of the maximum hardness principle in connection with the stability of the closed-shell species, the stability of the isomers, molecular vibrations, molecular internal rotations, aromaticity, chemical reactions, HSAB principle and statistical distributions are reviewed in subsequent sections. A summary is given in the last section.

Towards a Formal Proof of the Principle of Maximum Hardness

Statement 1: *Relative to its positive and negative ions, a species is more stable the larger is its absolute hardness*^{15,16}

Proof: Consider the disproportionation reaction



Associated change in energy is

$$\Delta E = A_s - I_s = -2 \eta_s, \quad \dots (8)$$

where I_s and A_s are ionisation potential and electron affinity of S respectively. Therefore, relative to $S^+ + S^-$, S is more stable the greater is η_s .

Statement 2: *Under the constraint of constant chemical potential, a species is more stable the greater is its absolute hardness*¹⁷.

Proof: In Hückel molecular orbital theory the total energy of a conjugated organic molecule is given by

$$E = N\mu + G\beta, \quad \dots (9)$$

and the hardness is

$$\eta = A\beta \quad \dots (10)$$

where N is the number of carbon atoms in the conjugated system, β is resonance integral and $G > 0$, $A < 0$ are numbers dependent on external potential. For a given μ , a small $|\beta|$ implies E less negative and η less positive.

Statement 3: *For given temperature, external potential and chemical potential, in a grand canonical ensemble, the softness of the equilibrium state is minimum in comparison to the softnesses of the nearby nonequilibrium states*¹⁸.

Proof: The finite temperature definition of softness is¹⁹ (inverse of hardness)

$$\langle S \rangle = \left(\frac{\partial N}{\partial \mu} \right)_{\nu(\nu), T} = \frac{1}{kT} \langle (N - \bar{N})^2 \rangle \quad \dots (11)$$

k is the Boltzmann constant.

Considering the chemical system as a member of a grand canonical ensemble characterised by bath parameters μ , $v(\mathbf{r})$ and T we can write eq. (11) as

$$\langle S \rangle = \frac{1}{kT} \sum_{N,i} P_{N,i}^0 (N - \langle N \rangle)^2, \quad \dots (12)$$

where $P_{N,i}^0$ is the equilibrium distribution given by

$$P_{N,i}^0 = \frac{1}{\Xi} \exp \left[-\frac{1}{kT} (E_{Ni} - N\mu) \right] \quad \dots (13)$$

and the grand partition function is

$$\Xi = \sum_{N,i} \exp \left[-\frac{1}{kT} (E_{Ni} - N\mu) \right]. \quad \dots (14)$$

Let $P_{N,i}$ be the probabilities defining the nonequilibrium distributions of the same system at the same temperature, generated through small perturbation of the bath parameters. The non-equilibrium average softness may be written as

$$\bar{S} = \frac{1}{kT} \sum_{N,i} P_{N,i} (N - \langle N \rangle)^2. \quad \dots (15)$$

Making use of the classical statistical mechanics the equilibrium state can be characterised by the grand potential $\Omega(r^N, p^N) = H(r^N, p^N) - N\mu$ and the respective probability distribution $f(r^N, p^N)$ (corresponding to $P_{N,i}^0$). Let $F(r^N, p^N)$ (corresponding to $P_{N,i}$) are the probabilities for the nearby nonequilibrium distributions generated through a small physical perturbation $\Delta \Omega(r^N, p^N)$. We consider²⁰ only those nearby nonequilibrium states which are generated by the following form of the perturbation,

$$\Delta \Omega = -kT \ln [CB(r^N, p^N)], \quad \dots (16)$$

where $B(r^N, p^N)$ is a physical observable of the system and C is a positive constant acting as a component of the perturbing field that couples with B . At $t=0$ we have

$$F(r^N, p^N) = \frac{\exp \left(-\frac{\Delta \Omega}{kT} \right)}{\left\langle \exp \left(-\frac{\Delta \Omega}{kT} \right) \right\rangle} f(r^N, p^N) \quad \dots (17)$$

$$= \langle B \rangle^{-1} B(r^N, p^N) f(r^N, p^N). \quad \dots (18)$$

Following Chandler²¹, we get

$$\bar{B}(0) - \langle B \rangle = \langle B \rangle^{-1} \langle (B(0) - \langle B \rangle)^2 \rangle. \quad \dots (19)$$

If we take B as the softness eq. (19) gives

$$\bar{S}(0) - \langle S \rangle \geq 0. \quad \dots (20)$$

Note that B can be any positive semidefinite physical observable to have a proof of this kind. Pearson²² obtained a principle of maximum physical hardness in this manner.

Statement 4: *When the energy is decreasing, the HOMO-LUMO gap increases; when the energy is increasing, the gap decreases. When the energy is at a minimum for the system, the gap will be at maximum²³.*

Proof: Consider the interaction of two frontier orbitals. The HOMO energy decreases but the LUMO goes up in energy, more than the HOMO goes down. The net energy lowering goes with an increase in the HOMO-LUMO gap. If the HOMO interacts with another filled orbital of similar energy, HOMO goes up in energy and LUMO being empty has no energy change upto first order. The net increase in energy goes with lowering of the gap. Reversing the reaction coordinates we get opposite results but with same conclusion.

For ionic interactions the HOMO is associated with the anion and the LUMO is associated with the cation. When the ions approach, the orbital energy of the anion is lowered by the potential due to cation and the orbital energy of the cation is increased by the potential due to anion. Energy lowers and the HOMO-LUMO gap increases.

Statement 5: *For any process for which $N\mu$ does not change, as E increases H must decrease, and as E decreases H must increase where E is the total electronic energy and H is a hardness functional²⁴.*

In dft¹ we have (for the ground state)

$$E[\rho] = \int d\mathbf{r} v(\mathbf{r}) \rho(\mathbf{r}) + F[\rho] \quad \dots (21)$$

and

$$\mu = v(\mathbf{r}) + \frac{\delta F[\rho]}{\delta \rho(\mathbf{r})}, \quad \dots (22)$$

where $F[\rho]$ is the sum of kinetic and electron-electron repulsion energy functionals. Combine eqs. (21) and (22) to obtain

$$E[\rho] = N\mu - H[\rho], \quad \dots (23)$$

where $H[\rho]$ is a hardness functional defined by²⁴

$$H[\rho] = \int d\mathbf{r} \rho(\mathbf{r}) \frac{\delta F[\rho]}{\delta \rho(\mathbf{r})} - F[\rho]. \quad \dots (24)$$

Therefore, for any ground state to ground state process, eq. (23) gives

$$\Delta\Omega = \Delta(E - N\mu) = -\Delta H \quad \dots (25)$$

Thus, for a constant $N\mu$ a maximum (minimum) of E corresponds to a minimum (maximum) in H . If we consider the total energy including V_{nn} (nuclear repulsion energy), any state that is an extremal for both E and V_{nn} (for constant $N\mu$) is also an extremal for H .

Statement 6: *Within a three level model at constant temperature, \bar{S} is always greater than or equal to $\langle S \rangle$ if the nonequilibrium state is either generated by changing μ alone or by changing μ and also changing $v(\mathbf{r})$ by a constant such that there is a constant shift in all energy levels. In case the average electronic energy in the equilibrium state is less than that of the nonequilibrium state and the average number of particles is kept fixed, $\bar{S} \geq \langle S \rangle$ is valid for the nonequilibrium states generated by changing μ and $v(\mathbf{r})$ ²⁵.*

Proof: Consider a three-level model for an atom/molecule and its positive and negative ions with energy values E_0 , $E_0 + I_0$ and $E_0 - A_0$ respectively.

Bath parameters for the equilibrium state in a grand canonical ensemble of this species are T , μ , E_0 , I_0 and A_0 . Corresponding nonequilibrium states are characterised by T , $\mu + \Delta\mu$, $E_0 + \Delta E_0$, $I_0 + \Delta I_0$ and $A_0 + \Delta A_0$. Excess of a non-equilibrium property over an equilibrium one can be written as follows²⁵:

$$\begin{aligned} \delta E = \bar{E} - \langle E \rangle &= \frac{\exp\left(\frac{\eta_0}{kT}\right)}{2 + \exp\left(\frac{\eta_0}{kT}\right)} \\ &\times \frac{I_0 \exp\left[-\frac{(\Delta I + \Delta\mu)}{kT}\right] - A_0 \exp\left[\frac{(\Delta A + \Delta\mu)}{kT}\right] - (I_0 - A_0)}{\exp\left[-\frac{(\Delta I + \Delta\mu)}{kT}\right] + \exp\left[\frac{(\Delta A + \Delta\mu)}{kT}\right] + \exp\left(\frac{\eta_0}{kT}\right)} \\ &\quad - \frac{2\mu_0}{2 + \exp\left(\frac{\eta_0}{kT}\right)} \\ &\times \frac{\exp\left[-\frac{(\Delta I + \Delta\mu)}{kT}\right] - \exp\left[\frac{(\Delta A + \Delta\mu)}{kT}\right]}{\exp\left[-\frac{(\Delta I + \Delta\mu)}{kT}\right] + \exp\left[\frac{(\Delta A + \Delta\mu)}{kT}\right] + \exp\left(\frac{\eta_0}{kT}\right)} \quad \dots (26) \end{aligned}$$

and

$$\delta S = \bar{S} - \langle S \rangle = \frac{\exp\left(\frac{\eta_0}{kT}\right)}{kT \left[2 + \exp\left(\frac{\eta_0}{kT}\right) \right]} \times \frac{\exp\left[-\frac{(\Delta I + \Delta \mu)}{kT}\right] + \exp\left[\frac{(\Delta A + \Delta \mu)}{kT}\right] - 2}{\exp\left[-\frac{(\Delta I + \Delta \mu)}{kT}\right] + \exp\left[\frac{(\Delta A + \Delta \mu)}{kT}\right] + \exp\left(\frac{\eta_0}{kT}\right)} \dots (27)$$

where η_0 is the absolute hardness of the system and $\langle N \rangle = N_0$, the particle number of the neutral species. Condition for S being greater than or equal to $\langle S \rangle$ becomes [eq. (27)]

$$\exp\left[-\frac{(\Delta I + \Delta \mu)}{kT}\right] + \exp\left[\frac{(\Delta A + \Delta \mu)}{kT}\right] \geq 2. \dots (28)$$

In case $\Delta I = 0, \Delta A = 0, \Delta E_0 = 0$ or $\Delta I = 0, \Delta A = 0, \Delta E_0 \neq 0$, the above condition reduces to

$$\cosh(\Delta \mu / kT) \geq 1 \dots (29)$$

which is true for all possible $\Delta \mu$ values.

However, if $\Delta I \neq 0, \Delta A \neq 0, \Delta E_0 \neq 0$ and $\bar{N} = \langle N \rangle = N_0 (\bar{\mu} = -\frac{1}{2}(\bar{I} + \bar{A}))$ inequality (28) becomes

$$\exp\left[\frac{(\Delta I - \Delta A)}{2kT}\right] \leq 1, \text{ i.e., } \Delta I \leq \Delta A \dots (30)$$

which alongwith convexity of energy, in eq. (26) gives

$$\delta E \geq 0. \dots (31)$$

Statement 7: At constant μ , increase (decrease) in η means increase (decrease) in stability^{26,27}

Proof: Consider the reaction



takes place in two steps and the interaction energy can be written as

$$\Delta E_{\text{int}} = \Delta E_v + \Delta E_\mu. \dots (33)$$

In eq. (33), ΔE_v is the energy change associated with charge transfer at constant external potential so that chemical potentials of A and B get equalised while ΔE_μ is the change in energy when $v(\mathbf{r})$ changes to take the system towards equilibrium at constant chemical potential. It has been shown^{26,27} that

$$\Delta E_\mu \approx -C(N) \Delta \eta, \quad \dots (34)$$

where $C(N)$ is a positive constant for a given N . Thus, a positive $\Delta \eta$ implies a negative ΔE_μ and *vice versa*. The system AB evolves towards a state of maximum hardness, under conditions of constant chemical potential. It has been generalised²⁶ that if μ is an extremal for a given reaction coordinate at a specific point, an extremum in E implies an extremum in η . Gazquez *et al.*²⁶ wrote

$$\left(\frac{\partial E}{\partial Q}\right)_N = N \left(\frac{\partial \mu}{\partial Q}\right)_N - \frac{1}{2} N^2 \left(\frac{\partial \eta}{\partial Q}\right)_N. \quad \dots (35)$$

For any point along the reaction coordinate Q where μ is a constant or an extremum, extremum in E implies that in η . The minus sign in eq. (35) ensures opposite signs in curvatures of E and η . Similar analysis was first provided by Pearson and Palke²⁸ and also by Pearson²⁹. Pal *et al.*³⁰ have shown that constant μ condition is important and $\Delta \eta$ during molecule formation not only depends on the binding energy of the molecule being formed but also on the binding energies of corresponding cations and anions.

Statement 8: *Hardness is an extremum for the symmetric nuclear configuration when symmetry breaking variations around this configuration is considered*^{30a}.

Proof: Consider a nuclear configuration of a molecule possessing symmetry elements of the point group G . Global quantities like E , μ and η will be invariant with respect to all symmetry operations of G and functional derivatives of these quantities (P , say) with respect to external potential $v(\mathbf{r})$ will belong to the totally symmetric irreducible representation of G . Writing variation in P due to change in $v(\mathbf{r})$ as

$$\delta P = \int \frac{\delta P}{\delta v(\mathbf{r})} \delta v(\mathbf{r}) d\mathbf{r}, \quad \dots (35a)$$

it can be shown^{30a} that for any symmetry breaking variation $\delta v(\mathbf{r})$, the integral vanishes and P attains its extremum value with respect to this variation.

Various statements and respective proofs of the maximum hardness principle presented in this section are valid only for certain model systems representing many physically realistic situations. A general and complete proof of this principle is still awaited. Several numerical calculations supported this principle. Those are reviewed in next few sections.

Stability of Closed-shell Species

Statement: *Any species with closed shell structure is associated with extra stability and higher hardness value in comparison to its open shell neighbours.*

Parr and Zhou³¹ have demonstrated this principle for nuclei, atoms, molecules and metallic clusters. For nuclei³² it is known that the gap between the highest occupied nuclear energy level and the lowest unoccupied one is larger for the closed shells in comparison to the nearby open shells. When atomic hardnesses³³ are plotted³¹ against atomic numbers both shell structures and sub-shell structures are prominent. Local maxima are conspicuous for atoms with completely filled *s*-shells and half-filled *p*-shells. Therefore, the octet principle^{34,35} or Sidgwick's 18-electron rule³⁶ can be understood in terms of hardness maxima for closed-shell and closed-subshell species. For molecules, the shell structure may be considered in terms of Hückel ($4n+2$) rule or Wade-Mingos ($2n+2$) rule³⁷. It is also known³⁸ that the neutral molecules with all bonding MOs occupied and all antibonding MOs vacant are thermodynamically stable.

Shell structure in metallic clusters are associated with pronounced intensity in mass spectra^{39,40}. Harbola⁴¹ has calculated the hardness for lithium clusters using a spherical jellium background model. Local maxima in hardness are observed for clusters with magic number of atoms, having extra stability. A non-local density functional calculation⁴² has verified the similar result for carbon fullerenes. Especially large HOMO-LUMO gaps are observed for C_{60} , C_{70} , C_{100} , C_{90} and C_{32} and they are expected to be less reactive. To quote Kurita *et al.*⁴² "Therefore, it is not the size of the binding energy, but the HOMO-LUMO gap which can explain the experimental results that C_{60} and C_{70} are especially stable. Furthermore, from the viewpoint of HOMO-LUMO gaps, C_{100} , C_{90} and C_{32} can be stable fullerenes."

Stability of Isomers

Statement: *The most stable isomer of a species is the hardest.*

Through *ab initio* SCF level calculation on geometrical isomers of HCN, Chattaraj *et al.*⁴³ have shown that HCN is energetically more stable and harder than HNC. Unless otherwise specified hardness is always calculated as the HOMO-LUMO gap. Calculation of HCN-HNC pair has been repeated⁴⁴ along with *ab initio* SCF calculations on isomers of several HAB and HAB⁺ molecules (AB = SiN, BO, AlO, BS, AIS, BeF, CO, SiO, CS, N₂) in the context of 1,2-hydrogen shift reactions. It has been observed in most cases that the more stable isomer is harder.

Extended Hückel^{29,45}, *ab initio* SCF^{43,44,46-50} coupled cluster⁵¹ (with eqs. (3) and (4)), INDO/2⁵², dft⁵³ (using $\eta = \frac{1}{2} (\partial\mu/\partial N)_{\text{ref}}$) etc. calculations have been performed and the above statement has been found to be valid in general. For closo-borane anions^{29,45}, $B_6H_6^{2-}$ and $B_7H_7^-$, the hardness is much larger for the stable structure than the unstable ones in both cases. On the other hand three possible isomers of $B_8H_8^-$ have comparable hardness values and the ion is known to be fluxional. For structural isomers of Si_2H_2 , corresponding to extrema in the potential energy surface, the stability order has been found to be same⁴³ as the hardness order for the isomers having comparable μ -values. Cations of carbonyl, isocarbonyls and dicarbonyls of lithium and sodium have been studied⁴³. In both the cases carbonyl cations are more stable and harder than the corresponding isocarbonyl cations and dicarbonyl cations are more stable and harder than the corresponding monocarbonyl cations. For the three

isomers of FHCl^- the stability and hardness decrease⁴⁶ in the order $[\text{F}-\text{H}\dots\text{Cl}]^- > [\text{F}\dots\text{H}-\text{Cl}]^- > [\text{F}\dots\text{H}\dots\text{Cl}]^-$. It has been shown⁴⁷⁻⁵³ that the more stable isomer of HCP⁴⁷, silicon hydrides⁴⁸, P_6^{49} , As_6^{49a} , SiC_2^{50} , H_2O^{51} , $\text{C}_{60}\text{NH}_2^{+52}$ and Si_4^{53} are generally associated with the higher hardness values. Where there are more than two isomers, increasing stability goes with increasing hardness in most cases.

Different colorings of the arrangement of the cation or the anion in a solid is analogous to *cis-trans* isomerization in molecules. It has been shown¹² *via* computation of band gaps for different anion ordering patterns in rocksalt and sphalerite that the more stable pattern is associated with larger band gap in both the cases.

Molecular Vibrations

Statement: *For the non-totally symmetric distortions the hardness is maximum at the equilibrium geometry.*

Pearson and Palke²⁸ have carried out Hartree-Fock level calculations on ammonia and ethane. Starting from the respective equilibrium geometries the molecular geometry is distorted along vibrational symmetry coordinates. It has been observed²⁸ that for asymmetric distortions μ and $\nu(\mathbf{r})$ remain constant for small displacements in the sense that positive and negative deviations are equivalent and hardness is maximum at the equilibrium geometry. However, for totally symmetric distortions neither μ nor ν is constant and η is maximum when all nuclei coalesced. They have argued²⁸ that “*the existence of symmetry in a molecule depends on the hardness. If the hardness decreases upon any distortion that destroys an element of symmetry, that element is stable. If the hardness increases, the molecule distorts and the element vanishes.*” Similar symmetry arguments have been given also by Gazquez *et al.*²⁶ and Makov^{30a}. As a corollary, it has been highlighted²⁸ that for the planar form ($\theta = 120^\circ$) of NH_3 the hardness is minimum a fact having a bearing in the understanding of transition states (TS) in terms of η profiles^{13,23}. Hardness determines²⁸ the molecular point group but not its equilibrium geometry (bond lengths and bond angles) which is obtained from the electrostatic Hellmann-Feynman theorem.

Ab initio SCF level calculations have been performed⁴³ on HCN , HNC , Li_2F^+ , LiF_2^- , PH_3 and H_2S molecules. Like the work of Pearson and Palke²⁸, here also it has been shown that the hardness is maximum at the united atom limit for symmetric distortions and for zero deformation around equilibrium geometry in the cases of asymmetric distortions. See last paragraph in Section 3 of Ref. 43 where it was noted that softness is a local minimum²⁰ at the equilibrium configuration of HNC . Warren and Gimarc⁵⁴ carried out similar *ab initio* calculations on five isomers of P_6 which is valence isoelectronic with benzene. The most probable structures of P_6 are five valence isomers of benzene, viz., benzene (planar hexagonal form), prismane, Dewar benzene, benzvalene and bicyclopentenyl. All of these isomers have been found⁵⁴ to be associated with real minima on the PES. The maximum hardness principle is obeyed⁵⁴ only for the asymmetric vibrations (μ and ν are roughly constants) around equilibrium geometries of all five isomers. Pal *et al.*⁵¹ have studied the vibrations of H_2O

molecule around the equilibrium geometry as well as around a nonstable linear symmetric geometry with O–H bond lengths fixed at their equilibrium value. This calculation was within coupled cluster theory and includes extensive correlation and relaxation effects in the calculation of I and A . Only for the asymmetric modes μ remains more or less constant and PMH is shown to be valid in both cases.

For diatomic molecules only possible vibrational mode is a symmetric stretching and consequently PMH is not supposed to be valid. Pal *et al.*³⁰ have given an explanation within a simple three level model why hardness is not a good index for the stability of a diatomic molecule. They have shown that $\Delta\eta$ during molecule formation depends on binding energy of the molecule being formed and also its cation and anion. Through Hartree-Fock level calculation on H_2 , Li_2 and N_2 and their monopositive and mononegative ions Gazquez *et al.*²⁶ have shown that at constant μ , change in electronic energy is proportional to $\Delta\eta$ with a negative slope.

Umbrella inversions in ammonia and phosphine have been studied at the MNDO⁵⁵ and *ab initio* SCF⁴³ levels respectively. It has been observed in both the cases that at the transition state of the inversion barrier the relative energy is maximum and hardness is minimum. This fact may be considered to be a corollary^{13,23} of PMH.

Molecular Internal Rotation

Statement: *The most stable rotational conformer is associated with the maximum hardness value and the least stable one with the minimum hardness value.*

Hardness profile have been calculated⁴⁷ at the *ab initio* SCF level for C_2H_4 under rotation around the C=C double bond, rotation of H_3X-YH_3 ($X, Y=C, Si$) around $X-Y$ single bond, HCP to HPC conversion through the rotation of H around the midpoint of CP and rotation of the BHBH plane in diborane. It has been observed⁴⁷ in all the cases that the less stable structure is associated with a lower hardness value. It has also been shown⁴⁷ that in general a larger barrier to internal rotation goes with larger difference in hardnesses of two pertinent conformers. *Ab initio* calculations⁴⁴ have revealed that the electronic energy (E_{el}) and nuclear repulsion energy (V_{nn}) are roughly perfect mirrors of each other and so are η and μ . This confirms the analysis of Gazquez *et al.*²⁶ that in case μ is a constant, a maximum or a minimum, the minimum (minimum) at E_{el} corresponds to maximum (minimum) in η . Under the similar conditions for μ , the maxima (minima) in V_{nn} and η coincide⁴⁴ as has been predicted by Parr and Gazquez²⁴.

Variation of hardness and torsional potential energy as a function of torsional angle is studied⁵⁶ in the context of internal rotation. An analytical formula has been obtained for activation hardness in terms of the activation energy and the difference in energies of two reference conformations. *Ab initio* SCF results of the internal rotation of nitrous acid and hydrogen persulphide are analyzed in terms of this formula. For both the molecules PMH has been found to be valid. For HONO, both cis and trans planar conformers are stable and are connected by a barrier where η is a minimum. On the other hand, a maximum

in η has been found for the stable gauche conformer of HSSH, placed about midway between the unstable *cis* and *trans* planar conformers.

Aromaticity

Statement: *A harder molecule is more aromatic than a softer one.*

Aromaticity is a popular concept associated with cyclic conjugated molecules. Aromatic molecules generally possess high stability, low reactivity and sustained induced ring current. Resonance energy per π -electron (REPE) has been considered⁵⁷⁻⁵⁹ to be an adequate measure of aromaticity. It was observed by Haddon and Fukunaga⁶⁰ that the resonance energy and aromatic character of $(4n+2)$ -annulenes correlate well with the HOMO-LUMO gap. The REPE values for several benzenoid hydrocarbons, nonalternate hydrocarbons and heterocycles have been plotted^{15,16} against their hardness values calculated within Hückel theory as well as from experimental *I* and *A* values. Good linear correlation is observed^{15,16} in all cases. For the benzenoid hydrocarbons studied, benzene is the most stable (least reactive) and with the largest η value and pentalene is the most reactive and with the smallest η value. Zhou and Navangul⁶¹ have calculated η values within MNDO theory and found that η_{MNDO} is linear with η_{HMO} and η_{expt} . They have shown⁶¹ that REPE of the benzenoid hydrocarbons is linear to η_{MNDO} as well. Through extended HMO calculation^{61a} it has been revealed that η is also a good measure of aromaticity in organometallic compounds.

A new concept of relative hardness (η_r) has been introduced by Zhou and Parr¹⁵ as the difference of hardness values of a conjugated molecule and a corresponding hypothetical acyclic reference structure. In general η_r correlates well with η . It has been prescribed¹⁵ that molecules with large positive η_r values are aromatic and with large negative η_r values are antiaromatic while those with η_r values close to zero are nonaromatic. They have categorized some 216 cyclic conjugated molecules and 96 other molecules in this way which conforms to their physical and chemical properties. For these molecules, REPE varies linearly with η_r .

Chemical Reactions

There are several ways of understanding the implications of PMH in the context of chemical reactions. Separate statements followed by supportive numerical examples are presented below.

Statement: *In a chemical reaction the hardest possible species lies in the product side and the average hardness of products is greater than that of reactants.*

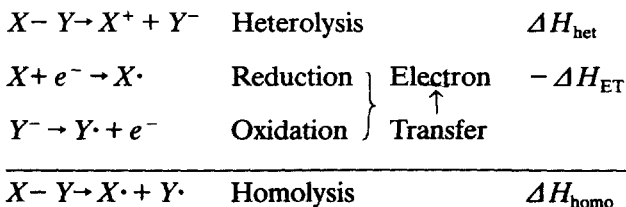
Datta⁶² has studied some 35 exchange reactions of the type, $PQ + RS = PR + QS$. Hardness values for all species taking part in the reaction are calculated using MNDO theory and also with experimental *I* and *A* values. He⁶² observed that the hardest possible species is one of the products and the average hardness of reactants is less than that of products in most cases. Similar observation has been made⁴⁸ through *ab initio* SCF calculations on some proton transfer reactions involving silicon hydrides and analogous carbon com-

pounds. Pearson and Palke²⁸ have shown that for simple reactions like $N(g) + 3H(g) = NH_3(g)$ hardness increases⁶⁴ from reactants to products in the energetically favourable direction, which is, however, not necessarily true for the reactions where very large molecules or crystals of a solid are formed. They²⁸ have calculated η using experimental I and A values and in case of a mixture (N and H in the reactants, say) they have used the formula^{17,63}, $\eta = (I_{\min} - A_{\max})/2$. It is known⁶⁵ for a long time that reactions of the type: $CH_3X + CH_3Y = CH_4 + XCH_2Y$; $X, Y = F, OH, NH_2$ for all combinations products are thermochemically more stable than the reactants due to "anomeric effect". Pearson⁶⁶ made an attempt to explain anomeric effect in terms of hardness. Calculating η at the MNDO level and also by using experimental I and A values Hati and Datta⁶⁷ have shown that in most cases the hardest species lies on the product side to have its least reactivity otherwise the back reaction will be favoured. In place of C, use of Si as the central atom has been shown to give similar results.

Chattaraj and Schleyer⁶⁸ have studied through *ab initio* calculations, a series of acid-base reactions leading to binary complexes. They⁶⁸ have found that above conclusions are generally not true for these reactions but PMH can be understood in the light of HSAB principle. *Ab initio* calculations on some protonation reactions have been performed by Chattaraj and Nath⁶⁹. They⁶⁹ have observed that protonated species is always harder than the corresponding unprotonated ones suggesting that the studied protonation reactions correspond to energetically favourable processes. Similar conclusions have been reached at⁴⁸ for some hydrogenation reactions via *ab initio* calculations. In both these cases^{48,69} neither of Datta's conclusions⁶² have been found to be true. It appears that those conclusions⁶² are valid for exchange reactions and not for the reactions where two reactants combine to give a single adduct.

Statement: Higher the value of the pair hardness, the greater the stability towards heterolytic cleavage.

Consider the following set of reactions⁷⁰



So

$$\Delta H_{\text{het}} = \Delta H_{\text{homo}} + \Delta G_{\text{ET}}, \quad \dots (36)$$

in case the entropy change for the electron transfer processes is small which is true for several reactions^{71,72}.

Now,

$$\Delta G_{\text{ET}} \approx \Delta H_{\text{ET}} = I_x - A_y = I_{\min} - A_{\max} = 2\eta^* \quad \dots (37)$$

where η^* is the pair hardness^{17,63}.

Again, it has been observed experimentally⁷⁰⁻⁷² that for a series of anions reacting with a cation ΔH_{homo} is roughly a constant. Thus,

$$\Delta H_{\text{het}} = \text{constant} + 2 \eta^*, \quad \dots (38)$$

Above linear relation has been found to be true for several reactions⁷⁰ involving cleavage around C-C⁷³, C-N⁷⁴, C-O⁷⁵ and C-S⁷⁶ bonds.

Statement: *Smaller the activation hardness faster the reaction.*

Zhou and Parr¹⁷ have introduced the concept of activation hardness (η_a) in order to predict the orientation of electrophilic aromatic substitution reactions. It has been defined¹⁷ as the negative of the change in hardness in going from reactant to transition state⁷⁷ and is equal to half of the activation energy. A reaction is faster if η_a is smaller. Wheland's⁶² cation localization energy and η_a behave in a similar manner¹⁷ when plotted against Hammett's σ^+ constants for several benzenoid hydrocarbons, heterocycles, substituted benzene and azulene and 1-chloronaphthalene. They have concluded that¹⁷, "Activation hardness appears to be an excellent index for predicting the orientation of electrophilic aromatic substitution. Other things being equal, the softer the reactant is the better, and the harder the transition state is the better".

Statement: *Minimum (maximum) energy configuration on the potential energy surface corresponds to maximum (minimum) hardness value.*

Datta⁵⁵ has computed the hardness profiles associated with ammonia inversion and intramolecular proton transfer in malonaldehyde by using MNDO method. Hardness has been found to be minimum at the transition state (TS) for both the processes. Therefore, the chemical species is the softest and the most reactive at TS. It has been argued⁵⁵ that the use of bond order⁷⁸ to locate the TS (other than the conventional total energy criterion) is not helpful for reactions where no bond is being broken or formed like in ammonia inversion or for stereochemical changes in other fluxional molecules. In these cases the minimum hardness condition would be very useful in locating the TS. Although bond order is not a good index for locating TS in certain reactions⁵⁵, a related quantity, molecular valency^{78a-d}, is generally a maximum at the minimum energy conformation for covalent or slightly polar covalent molecules⁴³. Later on the validity of the "maximum molecular valency principle"⁴³ was further verified through *ab initio* calculation on various physico-chemical properties^{44,46,47,78e}. Extremal behaviour of η and its relation to the extrema in PES has been a subject matter of research for quite a sometime^{10-14,23}.

Similar conclusions have been reached at through *ab initio* studies of phosphine inversion⁴³, a proton transfer reaction⁴⁶, rotational isomerizations^{47,56} 1,2-hydrogen shift reactions^{43,44} etc. It has also been shown²⁶ through *ab initio* calculation on the reaction $\text{H}^- + \text{SiH}_4 \rightarrow \text{SiH}_4 + \text{H}^-$ that a stable intermediate state with minimum energy corresponds to maximum hardness. The location of the hardness minimum as a function of the reaction coordinate may serve^{46,56} as an index of determining whether the TS would be reactant-like or product-like, in the spirit of Hammond's principle⁷⁹.

Statement: *When two reactants approach each other the hardness increases to a maximum value.*

In a chemical reaction, the electronegativity difference drives the electron transfer until electronegativities of all species get equalized⁸⁰. During molecule formation the electronegativity of an atom changes until it becomes equal to the 'molecular' electronegativity and its hardness also gets maximized as a consequence of PMH. Therefore, a chemical reaction dynamics can be envisaged in terms of temporal evolution of electronegativity⁸¹ and hardness⁸²⁻⁸⁴ during a chemical reaction. A quantum fluid density functional (QDFD) approach⁸⁵⁻⁸⁷ has been adopted to study the time evolution of electronegativity⁸¹ and hardness⁸² during a collision process between a nitrogen atom and a proton. Here hardness is calculated as a time dependent density functional. Recently it has been shown that hardness can be obtained variationally^{87a} and also as the electrostatic potential due to Fukui function^{87b} at covalent radius. This method (QDFD) has also been supplemented by *ab initio* calculations on Be-H⁺ system. Hardness has been found to increase as the proton approaches the atom and remains more or less constant after attaining a high value which may be considered as a "dynamical variant" of PMH.

Hard-Soft Acid-Base (HSAB) Principle

Statement: *HSAB principle is a consequence of the principle of maximum hardness.*

Hard-Soft Acid-Base (HSAB) principle is given by Pearson⁶. It states that, "Hard acids prefer to coordinate with hard bases and soft acids prefer to coordinate with soft bases for both their thermodynamic and kinetic properties." Chattaraj *et al.*⁸⁸ have provided two formal proofs of this principle one of which shows explicitly the connection between HSAB principle and PMH. Consider the reaction of an acid *A* and a base *B* taking place in two steps, viz., 1) Charge transfer to produce a common chemical potential and 2) redistribution of charges at constant μ and T . While first step is governed by minimisation of energy, the second step is driven by hardness maximization. They⁸⁸ have argued that the simultaneous satisfaction of these two criteria implies HSAB principle. It has also been proposed⁸⁸ that a reaction $AB + CD \rightarrow AC + BD$ is hardness raising or softness-lowering process if $S_A = S_C$ and $S_B = S_D$. This statement has been numerically verified^{48,62}. A local version of HSAB principle has also been established^{27,89}. Impurity segregation at grain boundary of germanium can be thought⁹⁰ of as a chemical reaction between the impurity and the interface and PMH and HSAB principle have been used⁹⁰ to predict the most probable sites of impurity accumulation.

Chattaraj and Schleyer⁶⁸ have studied HSAB principle through several acid-base reactions at the *ab initio* SCF, MP2 and QCISD(T) levels. Complexes of HF and Ag⁺ with HF, HCl, HBr, H₂O, H₂S, H₂Se, NH₃, PH₃ and AsH₃ have been considered for this purpose. Reactions of H⁺, Li⁺ and Na⁺ have also been studied. It has been observed that HSAB principle is valid in most cases. For reactions with HF the η values are calculated at the HF level. Neither of Datta's conclusions is found to be valid for complexation reactions. How-

ever, it has been observed⁶⁸ that HSAB principle is a consequence of PMH. HF being a hard acid its preference to bind with bases according to HSAB principle would be^{6,91}, $F \gg Cl > Br$, $O \gg S > Se$, and $N \gg P > As$. The calculated η values of binary complexes of HF with these bases follow exactly the same order⁶⁸. Chattaraj and Nath⁶⁹ have studied the protonation reactions at the *ab initio* SCF level. It has been observed that complexation energies sometimes do not follow the order predicted by HSAB principle but hardness does it in all cases.

Statistical Distributions

Statement: *As a chemical species approaches equilibrium at a given μ and constant temperature from a nearby nonequilibrium state its softness most often approaches a minimum value.*

The formal proof of PMH given by Parr and Chattaraj¹⁸ was originally meant for statistical distributions of a specific type²⁰. For the Gyftopoulos-Hatsopoulos⁹² three-level model it has been further analyzed²⁵ (see statement 6 of Section 2). Numerical calculations have been performed²⁵ for sodium atom at different temperatures where the nonequilibrium states are generated by changing μ and $\langle N \rangle$ has been taken as N_0 . It has been observed that $\bar{s}/\langle s \rangle$ is a minimum and equal to 1 at $\Delta\mu/kT=0$. Later it has been numerically verified⁹³ for oxygen atom that if the temperature is small ($< 10^4$ k) inclusion of any number of levels and/or excited states gives the same result described above. Exponential and quadratic models at low temperature behave similarly⁹³. At low temperature, PMH is shown to be valid⁹³ for the discrete model if $\langle N \rangle$ is an integer or half integer.

Summary

A chemical species with large HOMO-LUMO gap is generally stable and a reaction where such a species is formed is favourable. Several formal proofs towards a principle of maximum hardness have been presented. Supportive numerical examples are reviewed in order to know the implications of such a principle in stabilities of closed-shell species and isomers, molecular vibrations and internal rotations, aromaticity, chemical reactions, HSAB principle and statistical distributions. It can now be stated with some confidence that the maximum hardness condition complements the minimum energy criterion for molecular stability. In general, a stable configuration (like the least energy equilibrium structure or an intermediate) corresponds to the maximum hardness value and a transition state is associated with the minimum hardness value. Formation of the hardest possible species drives a chemical reaction.

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