CHAPTER 2

Theoretical background

2.1.

QUANTIFICATION OF AROMATICITY

Aromaticity has been considered as an abstract concept from philosophical point of view by Cryansli et al.[1] Whereas, from another perspective, the event of aromaticity can be regarded as multidimensional since it cannot be described definitely by any single property based index and all indices do not always give consistent results. Due to all these problems the quantification of aromaticity still remains a challenging and fundamental problem. Also, Minkinet al.[2] has described in their book "Aromaticity and Antiaromaticity, Electronic and Structural Aspects", eight different types of aromaticity namely, (i) Aromaticity, (ii) Antiaromaticity, (iii) Homoaromaticity, (iv) Heteroaromaticity, (v) In-plane aromaticity, (vi) Three- dimensional aromaticity and (vii) Spherical aromaticity.

On the basis of available literature, the criteria for the quantification of aromaticity can be divided into the following four basic categories. (1) Chemical behavior: Electrophilic aromatic substitution reactions are the characteristic reactions of the aromatic systems but it is difficult to define aromaticity with the help of the chemical behavior of the molecule. (2) Structural pattern: Aromatic systems are mainly planar systems. The characteristic property of an aromatic system is that its bond lengths are all equal and π-electrons are delocalized. The direct determination of bond lengths gives us valuable information regarding the extent of delocalization. (3) Aromaticity has long been connected to the enhanced resonance energies (REs) and the aromatic stabilization energies (ASEs). Even the $(4n+2)$ π- electron rule of Hückel is based on energetic criterion. The energetic measure of aromaticity and antiaromaticity is based on evaluations of energies relative to the reference systems such as conjugated polyenes or olefins.[3] (4) Magnetic Criteria: The anomalous diamagnetization of benzene has been related to the delocalization of π-electrons since the early days of quantum chemistry. The aromatic molecules demonstrate relatively strong diamagnetism when placed in a magnetic field; this is due to the generation of an opposing magnetic field by the induced ring currents. The magnetic criteria of aromaticity are dependent on the specific reaction of the aromatic compounds to externally applied uniform magnetic field which is placed perpendicular to the molecular plane. This contribution of π-electrons to the magnetic susceptibility component which is placed perpendicular to the molecular plane was chosen as an indicator of aromaticity. While the direction of an induced current in a loop is determined by the relative orientation of the magnetic field and the loop's movement but the direction of the current in a molecule also depends on the type of the system. Generally in a system containing 4nπ electrons, an external magnetic field induces a paratropic ring current (i.e. in the opposite direction relative to a classic loop) while a system containing (4n+2) π electrons shows a diatropic ring current (i.e. in the same direction as a classic loop).[4] In detail analysis of the magnetic criteria of aromaticity is described in the third chapter in the form of a mini review article.

Aromaticity is not a physically observable quantity so defining it precisely is still a challenge. Quantification of aromaticity is a major challenge to the theoretical and the computational chemists till date. Whether aromaticity is a multidimensional phenomenon or it can be defined by a universal single unique criterion is a debatable topic. The journey of aromaticity from Kekulé's definition of benzene has been extensive and the recent developments in this field provide a considerable better insight into the concept. It is aptly said by Schleyer that, "aromaticity has been a time-dependent phenomenon." The perception of aromaticity is different in terms of its properties and characteristics to chemists with diverse backgrounds

Aromaticity being a multidimensional phenomenon, the effect that aromaticity applies on different structural, energetic, chemical and magnetic properties have led to the development of various aromaticity indices. The different aromaticity indices that have been employed in this thesis are briefly described in the following subsections.

2.1.1. Nucleus Independent Chemical Shifts (NICS)

The most efficient method of quantifying aromaticity is NICS, which was postulated by Schleyer and his co-workers.[6] The negative value of the absolute magnetic shielding gives the definition of NICS. NICS method uses a ghost atom namely Bq (named after the ghost Banquo from Shakespeare's Macbeth), it is devoid of any electrons, protons and neutrons. Initially it was placed at the centre of the system [NICS (0)], then later at a distance of 1 Å above the plane [NICS (1)]. This ghost atom is like a sensor for the magnetic environment at the position at which it is placed. The ghost atom senses this magnetic environment and reports the chemical shielding values through the use of computational technique like GIAO.[7-10] The NICS values are computed by placing the ghost atom at the centre of the ring [NICS (0)] to account for the contribution of the σ-electrons to aromaticity and 1 Å above and below the plane i.e., [NICS (1)] and [NICS (-1)] respectively to estimate the π-

aromaticity of the systems (Figure 2.1). The NICS values were reported with reversed signs, in agreement with NMR chemical shift convention. Positive NICS value indicates a paratropic magnetic field whereas a negative NICS value indicates a diatropic magnetic field, thus a negative NICS value would mean that a system is aromatic and a positive NICS value would correspond to an antiaromatic system. After their initial publication, Schleyer and his co-workers noted the problem in using NICS for 3-membered systems due to the local shielding effects of the neighboring σ-bonds. So they introduced two modifications in the following year.[51] The first modification was that the bq was raised 1 Å above the molecular plane, which was termed as NICS (1). Since σ-contributions are short ranged, so NICS (0) has greater σ-contributions, so by raising the bq by 1 Å, the σ-contributions are effectively reduced. Secondly, the total NICS value was separated into σ and π contributions. Since aromaticity results from π contributions, so NICS (1) is a better aromaticity criterion than NICS (0).

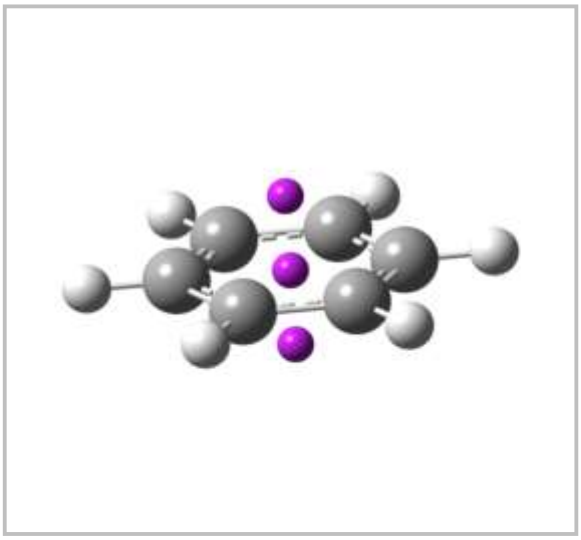

Figure 2.1. Representation of the ghost atoms placed at the centre and 1 Å above and below the plane of the benzene molecule.

2.1.2. Dissected Canonical Molecular Orbital NICS (CMO-NICS)

Later refinement of the original NICS technique offered better understanding of the aromatic systems which include the Dissected NICS technique which consists of the CMO-NICS method. This dissected NICS technique has been termed MO−NICS by Heine et al.,[11] but CMO−NICS is preferable to avoid ambiguity. This method for calculating the dissected NICS rigorously focuses on the employment of canonical MOs. Individual canonical molecular orbital (CMO) contributions to the magnetic shielding of atoms and to the NICS of aromatic compounds can be calculated by the extensively used GIAO method. CMO−NICS is based on the uncoupled form of current-density functional theory and is limited to purely DFT calculation (i.e., hybrid functional are not used). The shielding tensor is written as a sum of canonical orbital contributions.

Therefore, the NICS dissection into canonical molecular orbital contributions corresponds to the CMO-NICS as expressed in eq (1).

$$\sigma_{tot} = \sum_{i=1}^{occ} \sigma_{CMO_i} \tag{2.1}$$

2.1.3. Multi-centre indices

Giambiagi first developed an index to measure multicenter bonding.[12] The similar expression applied to a molecular ring was represented as I_{ring} to account for aromaticity.[13]

$$I_{ring}(A) = \sum_{i_1, i_2 \ldots, i_n} S_{i_i i_2}(A_1) \ldots . S_{i_n i_1}(A_n) \tag{2.2}$$

where $n_i = [0,1]$ is the occupancy of the corresponding natural orbital and $S_{ij}(A_1)$ is the atomic overlap matrix (AOM) of atom A_1,

$$S_{ij}(A_1) = \int_{A_1} d_1 \phi_i^*(1) \phi_j(1) \tag{2.3}$$

where $\phi_i(1)$ is a natural orbital. I_{ring} depends on the order of the atoms in the string for n > 3. MCI was suggested by Bultinck et al[14] which is an improvement over I_{ring} that takes into account the delocalization across a ring and is calculated by adding up all the possible I_{ring} contributions obtained from the permutations of the atoms in A,

$$MCI(A) = \frac{1}{2n} \sum_{P(A)} I_{ring}(A) \tag{2.4}$$

where P is an operator acting on A that generates all the n! permutations of its atoms. A higher positive MCI values signifies higher aromaticity in the ring.

2.1.4. Electron Localization Function (ELF)

As electron delocalization constitutes the genesis of aromaticity so another important index for quantifying aromaticity is the ELF. ELF is a measure of the probability of finding an electron in the vicinal area of a reference electron positioned at a given point with a similar spin. So, this quantifies the degree of spatial localization of the reference electron physically and can be applied for the mapping of electron pair probability in multielectronic systems. Its usefulness lies in the fact that it permits the analysis of electron localization in a chemically intuitive manner. The ELF is a mathematical description of the valence shell electron-pair repulsion (VSEPR) theory and was originally defined by Becke and Edgecomb in the year 1990.[15] The first measure of the electron localization as given by them was

$$D_\sigma(r) = \tau_\sigma(r) - \frac{1}{4}\frac{(\nabla_{\rho\sigma}(r))^2}{\rho_\sigma(r)}, \tag{2.5}$$

where ρ represents the electron spin density and τ is the kinetic energy density. D is the contribution due to fermions so the second negative term represents the bosonic kinetic energy density. In those regions of space where the probability of finding the localized electrons are high, D is anticipated to have a smaller value. The ratio,

$$\chi_\sigma(r) = \frac{D_\sigma(r)}{D_\sigma^0(r)} \tag{2.6}$$

is a dimensionless localization index, where $D_\sigma(r)$ is the electron localization that has been defined in equation and the uniform electron gas with spin density equal to $\rho(r)$ is given by

$$D_\sigma^0(r) = \frac{3}{5}(6\pi^2)^{2/3}\rho_\sigma^{5/3}(r). \tag{2.7}$$

Then finally the ELF is defined in terms of χ by mapping its values on to the range $0 \leq$ ELF ≤ 1 as

$$ELF(r) = \frac{1}{1 + \chi_\sigma^2(r)} \tag{2.8}$$

The ELF values ranges between 1 and 0, where a perfect localization is in correspondence to an ELF value of 1. The original derivation was based on Hartree–Fock theory. The approach was generalized by Savin in 1992 for Density Functional Theory.[16] The π-component of the electron localization function (ELF_π) is normally used as an indicator of aromaticity.

2.1.5. Aromatic Stabilization Energy (ASE)

The aromaticity of the studied systems is calculated using a recently proposed theoretical model where quantification of aromaticity is done with respect to the energy stabilization owing to the circular π-electrons delocalization, termed as the Aromatic Stabilization Energy (ASE).[17] This theoretical model is obtained by localizing unpaired p_z electrons on each individual carbon atom of benzene (Figure 2.2). In this model, the neighbouring antiparallel p_z-spins are in such an orientation so as to spread into one another's non-orthogonal overlapping orbitals stabilizing the entire system. In this theoretical model, ASE is related to the molecular energy stabilization due to electron delocalization in the framework of second order perturbation theory consequential from atom to atom charge transfer.[18-20]

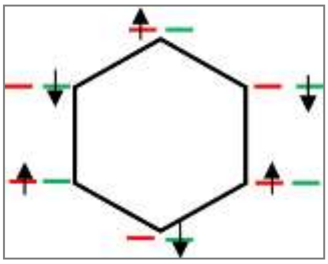

Figure 2.2. A schematic representation of benzenoid aromatic systems with localized π-electrons on the p_z orbitals of carbon atoms. Orbitals for (α) up-spin and (β) down-spin are represented by red and green lines respectively.

The theoretical model proposes the inter-site hopping integral (t_{ij}) and the onsite repulsion energy (U) to be responsible for the electron delocalization. The population of the electrons participating in delocalization is obtained as a product of spin-orbital population ($n_{i\sigma}$

and $n_{j\sigma'}$) within the unrestricted framework and the level of delocalization is projected from electron localization function (ELF) as

$$ASE = \sum_{i,j} \frac{t_{ij}^2}{U}\left(n_{i\sigma} n_{j\sigma'} + n_{i\sigma'} n_{j\sigma}\right) ELF^2 \tag{2.9}$$

As already mentioned, the above equation is applicable for benzene like aromatic molecules, which are different from the studied system in terms of the electronic structure and aromaticity type. In the systems studied in this work, specifically the migration of the lone pair of electrons in between the boron and fluorine completes the loop of electronic circulation and thus makes the pattern of electron delocalization unique and different to conventional aromatic systems. To agree with this representation of electron delocalization, the above equation is divided into two components as

$$ASE = \sum_{B,X} \frac{2t_{ij}^2}{U}\left(n_{B\sigma} n_{X\sigma'} + n_{B\sigma'} n_{X\sigma}\right) ELF^2 + \sum_{F,B} \frac{2t_{ij}^2}{U}\left(n_{F\sigma} n_{B\sigma'} + n_{F\sigma'} n_{B\sigma}\right) ELF^2 \tag{2.10}$$

Here, the first part stands for the electron delocalization within B-X ring, it is multiplied by two to account for two lone pair of electrons of the heteroatom X and the second part quantifies stabilization for electron delocalization within Lewis acid-base pair. The probability of the lone-pair transfer from F to B is taken into consideration by multiplying by two.

Since theoretical study of novel aromatic systems is the main objective of this thesis, so various theoretical indices that could indicate the structural integrity of the proposed molecular systems are discussed in the following as in order to understand function, first we need to comprehend the structure and vouch for its viability.

2.2.

INDICES OF STABILITY

2.2.1. Energy Decomposition Analysis (EDA)

The structural reliability of the molecular systems is established through Energy Decomposition Analysis (EDA) based on the approach of Ziegler and Rauk.[21] The individual atomic fragments are taken into consideration for the EDA. In this method the interaction energy (ΔE_{int}) is divided into three major components namely electrostatic interaction (ΔV_{elstat}), Pauli repulsive orbital interaction (ΔE_{pauli}) and attractive orbital interaction (ΔE_{orb}) as shown,

$$\Delta E_{int}=\Delta V_{elstat}+\Delta E_{pauli}+\Delta E_{orb} \tag{2.11}$$

Here, the ΔV_{elstat} represents the classical electrostatic interaction between the fragments as they are brought together to form the final complex. ΔE_{pauli} corresponds to the repulsive interaction between the filled orbital, generally termed as steric interaction.[22] ΔE_{orb} corroborates the interactions between the occupied orbitals of one fragment to the unoccupied orbitals of the other fragment and also takes into account the interactions between the occupied and virtual orbitals of the same fragment.

Another important tool to quantitatively analyze chemical bonds, merging the extended transition state (ETS) method[21] for energy decomposition analysis combined with the natural orbitals for chemical valence (NOCV) theory[23] is the extended transition state method and natural orbital for chemical valence scheme (ETS-NOCV).[24]

Here, they have further combined the NOCV and ETS methods in a ETS-NOCV charge and energy decomposition scheme by providing an expression for ΔE_{orb}.

The term ΔE_{orb} is given by:

$$\Delta E_{orb} = E[\rho] - [\rho^0] \tag{2.12}$$

where $E[\rho]$ is the energy of the final molecule and $E[\rho^0]$ is the energy E^0 associated with the normalized and antisymmetrized wave function Ψ^0. The ETS-NOCV charge and energy decomposition scheme provides a condensed picture of chemical bond formation within one common theoretical framework as illustrated in the following Figure 2.3.

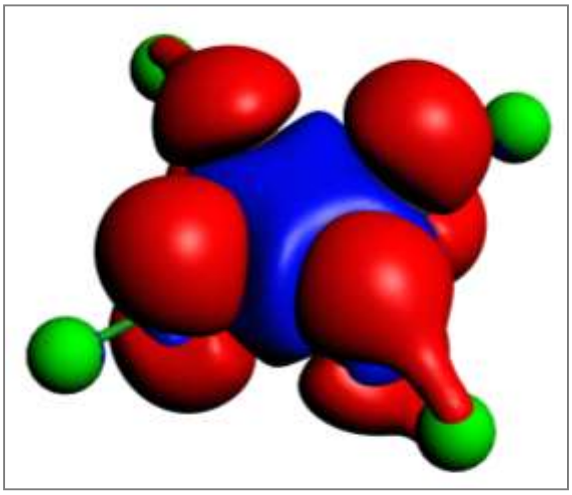

Figure 2.3. The ETS-NOCV difference density plot corresponding to −100 kcal/mol stabilization. The blue and red surfaces represent regions of the electron concentration and electron depletion (isosurface of 0.003 a.u.) respectively.

2.2.2. Ring Strain Energy (RSE)

Ring Strain Energy serves as an important measure for the stability of small ring systems. The ring strain is calculated with the aid of Bader’s Quantum theory of Atoms in Molecules (QTAIM)[25] The Lagrange kinetic energy density value G(r) computed at the Ring Critical Point (RCP) can be used to evaluate the ring strain in these small rings, with the application of the Regression equation, RSE= {337.72 × G(r) – 8.115}.[26]

2.2.3. Adaptive Natural Density Partitioning (AdNDP) Analysis

The most important aspect of this thesis is the bonding analysis of the novel aromatic systems and the best way to understand and get a visual illustration of the bonding is the AdNDP method (Figure 2.4). Adaptive Natural Density Partitioning is a theoretical analysis which provides a very proficient and an illustrative method to the understanding of the molecular orbital dependent wave functions. It is a recently developed method which was proposed in the year 2008 by Zubarev and Boldyrev[27] for determining chemical bonding patterns in general molecular systems. This method is based on the simple Lewis concept that describes the chemical bonding with respect to the electron pair thereby characterizing the electronic structures as n-centered-2 electron bonds where the value of n ranges from 1 to the total number of atoms present in the studied molecular systems. It figure outs the elements responsible for Lewis bonding and also the elements responsible for delocalized bonding which can be correlated with the concepts of aromaticity and antiaromaticity. AdNDP is an overview of NBO analysis as was proposed by Weinhold from a computational view point on the basis of the diagonalization of the blocks of the first order density matrix based on natural atomic orbitals.[28,29] AdNDP bonding patterns are in consonance with the point group symmetry of the molecular systems and resonating structures are generally avoided. The main advantage of this method is that it effortlessly links the Canonical Molecular Orbitals (CMO) and the Natural Bonding Orbitals (NBO).

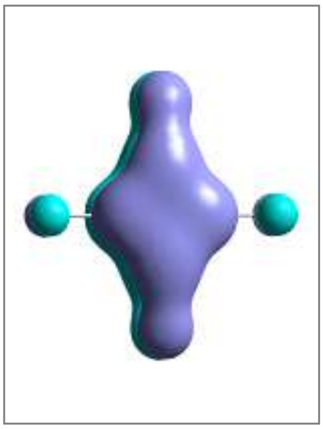

Figure 2.4. The top-view of the AdNDP orbitals of $C_2B_2F_4$.

2.2.4. Atom Centered Density Matrix Propagation (ADMP)

ADMP is based on the theory for an extended Lagrangian molecular dynamics trajectory method that employs atom-centered basis function and density matrix propagation.[30-33] This approach is well fitting for the dynamics of chemical systems such as clusters and gas-phase reactions. For ADMP the Lagrangian for the system can be written as

$$L = \frac{1}{2} Tr\left[V^T MV\right] + \frac{1}{2} Tr\left[\left\{\mu^{1/4} W \mu^{1/4}\right\}^2\right] - E(R,P) - Tr\left[\Lambda(PP-P)\right] \tag{2.13}$$

where R, V, and M are the nuclear positions, velocities and masses; P and W are the density matrix and the density matrix velocity respectively. The fictitious mass for the electronic degrees of freedom, μ, is chosen as a diagonal matrix with larger values for the core orbitals. Constraints on the total number of electrons and the idempotency of the one particle density matrix enforce N-representability and are imposed using the Lagrangian multiplier matrix Λ. The energy is calculated using the McWeeny purification of the density,[34] $\overline{P} = 3P^2 - 2P^3$.

2.3.

CONCEPTUAL DFT BASED REACTIVITY DESCRIPTORS

2.3.1. Global reactivity descriptors

Global reactivity descriptors are an important tool in predicting the structural stability of the molecules. It is established that hardness (η) and electrophilicity (ω) can give us an idea regarding the stability of molecular systems in conjunction with the associated electronic structure principles, viz., the maximum hardness principle (MHP)[35-40] and the minimum electrophilicity principle (MEP).[41-43] The electronegativity (χ),[44-46] hardness (η)[47,48] and electrophilicity (ω)[49] of an N-electron system can be defined as follows:

$$\chi = -\mu = -\left(\frac{\partial E}{\partial N}\right)_{\upsilon(\vec{r})} \tag{2.14}$$

$$\eta = \left(\frac{\partial^2 E}{\partial N^2}\right)_{\upsilon(\vec{r})} \tag{2.15}$$

$$\omega = \frac{\mu^2}{2\eta} = \frac{\chi^2}{2\eta} \tag{2.16}$$

E, μ, and $v(\vec{r})$ are the total energy of the N-electron system, chemical potential and external potential respectively.

Employing a finite difference approximation to Eqs. 2.14 and 2.15 one can achieve:

$$\chi = \frac{I + A}{2} \tag{2.17}$$

and $$\eta = I - A \tag{2.18}$$

where I and A indicate the ionization potential and electron affinity of the cluster, respectively, and they are calculated using Koopmans' theorem.[50,51]

2.3.2. Local reactivity descriptors (Fukui functions)

The Fukui functions are employed to describe local electrophilicity and nucleophilicity factors. Removal of an electron from the molecule, called the Fukui function for electrophilic attack, is described as $f^{-}$and the Fukui function for *addition* of an electron to the molecule, called the Fukui function for nucleophilic attack is denoted as f^{+}. The understanding of the quantitative values of the Fukui function is that a large value of f^{-}, signifies that a molecule *donates* electrons, whereas a larger value of f^{+} denotes where a molecule *accepts* electrons. The Fukui functions can be defined using finite differences of the electronic density

$$f^{-}=\rho(N)-\rho(N-1) \tag{2.19}$$

$$f^{+}=\rho(N+1)-\rho(N) \tag{2.20}$$

where the densities of the cation ($N-1$), the neutral (N), and the anion ($N+1$) are employed. Here, chemical reactivity is described on an atom-by-atom basis via a "condensed" Fukui function. The condensed Fukui function is computed as

$$f_k^{-}=q_k(N)-q_k(N-1) \tag{2.21}$$

$$f_k^{+}=q_k(N+1)-q_k(N) \tag{2.22}$$

where q_k is the charge at atomic center k.[52-56] Here Hirschfeld charges are used in Multiwfn[57] software.

2.4.

REFERENCES

1. Cryański, M. K.; Krygowski, T. M.; Katritzky, A. R.; Schleyer, P. v. R. *J. Org. Chem* **2002,** *67*, 1333.
2. Minkin, V.; Glukhovtsev, M.; Simkin, B. In *Aromaticity and Antiaromaticity*; Wiley Interscience, New York, **1994**.
3. Schleyer, P. v. R.; Jiao, H. **1996,** *68*, 209.
4. Poranne, G. P.; Stranger, A. *Chem. Soc. Rev.* **2015**, *44*, 6597.
5. Schleyer, P. v. R. *Chem. Rev.* **2001**, *101*, 1115.
6. Schleyer, P. v. R.; Maerke, C.; Dransfeld, A.; Jiao, H.; Hommes, N. J. R. v. E. *J Am Chem Soc* **1996**, *118*, 6317.
7. London, F. *J. Phys. Radiu.* **1937**, *8*, 397.
8. Cheeseman, J. R.; Trucks, G. W.; Keith, T. A.; Frisch, M. J. *J. Chem. Phys.* **1996**, *104*, 5497.
9. Schreckenbach, G.; Ziegler, T. *J. Phys. Chem*. **1995**, *99*, 606.
10. Schreckenbach, G.; Ziegler, T. *Theor. Chem. Acc.* **1998**, *99*, 71.
11. Heine, T.; Schleyer, P. v. R.; Corminboeuf, C.; Seifert, G.; Reviakine, R.; Weber, J. *J. Phys. Chem. A* **2003**, *107*, 6470.
12. Giambiagi, M.; de Giambiagi, M. S.; Mundim, K. C. *Struct. Chem.* **1990**, *1*, 423–427.
13. Giambiagi, M.; de Giambiagi, M. S.; dos Santos Silva, C. D.; de Figuereido, A. P. *Phys. Chem. Chem. Phys*. **2000**, *2*, 3381–3392.
14. Bultinck, P.; Ponec, R.; Van Damme, S. *J. Phys. Org. Chem.* **2005**, *18*, 706–718.
15. Becke A. D.; Edgecomb K. E. *J. Chem. Phys.* **1990**, *92*, 5397-5403.
16. Savin, A.; Jepsen, O.; Flad, J.; Andersen, O. K.; Preuss, H.; von Schnering, H. G. (1992). "Electron localization in solid-state structures of the elements – the diamond structure". *AngewandteChemie International Edition in English*. **31** (2): 187–188.
17. Paul, S.; Goswami, T.; Misra, A. *AIP Advances,* **2015**, **5**, 107211.
18. Anderson, P. W. *Phys. Rev.* **1950**, *79*, 350.
19. Anderson, P. W. *Phys. Rev.***1959**, *115*, 2.
20. Anderson, P. W. Theory of the magnetic interaction: exchange in insulators and superconductors. In solid state physics; Turnbull, F., Seitz, F., Eds.; Academic Press: New York, 1963; Vol. 14, p 99.
21. Ziegler, T.; Rauk, A. *Theor. Chim. Acta* **1977**, *46*, 1.
22. Pinter, B.; Fievez, T.; Bickelhaupt, F. M.; Geerlings, P.; DeProft, F. *Phys. Chem. Chem. Phys.* **2012**, *14*, 9846.
23. Michalak, A.; Mitoraj, M.; Ziegler, T. *J. Phys. Chem. A* **2008**, *112*, 1933.
24. (a) Mitoraj, M.; Michalak, A. *J. Mol. Model.* **2007**, *13*, 347–355; (b) Mitoraj, M. P.; Michalak, A.; Ziegler, T. *J. Chem. Theory Comput.*, **2009**, *5*, 962–975.
25. Bader, R. F. W. *Atoms in Molecules: A Quantum Theory;* Oxford University Press Oxford UK, 1990.

26. Bauzá, A.; Quiñonero, D.; Deyà, P. M.; Frontera, A. *Chem. Phys. Lett*. **2012**, *536*, 165.
27. Zubarev, D. Yu.; Boldyrev, A. I. *Phys. Chem. Chem. Phys.* **2008**, *10*, 5207.
28. Foster, J. P.; Weinhold, F. *J. Am. Chem. Soc*. **1980**, *102*, 7211.
29. Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899.
30. Marx, D.; Hutter, J.; J. Grotendorst (Ed.), Proceedings of Modern Methods and Algorithms of Quantum Chemistry, John von Neumann Institute for Computing, Jurich, Germany, 2000.
31. Schlegel, H. B.; Millam, J. M.; Iyengar, S. S.; Voth, G. A.; Daniels, A. D.; Scuseria, G. E.; Frisch, M. J. *J. Chem. Phys.***2011**, *114*, 9758-9763.
32. Iyengar, S. S.; Schlegel, H. B.; Millam, J. M.; Voth, G. A.; Scuseria, G.E.; Frisch, M. J. *J. Chem. Phys.* **2011**, *115*, 10291-10302.
33. Schlegel, H. B.; Iyengar, S. S.; Li, X.; Millam, J. M.; Voth, G. A.; Scuseria, G. E.; Frisch, M. J. *J. Chem. Phys.* **2002**, *117*, 8694-8704.
34. McWeeny, R. *Rev. Mod. Phys*. **1960**, *32*, 335.
35. Pearson, R. G. Recent Advances in the Concept of Hard and Soft Acids and Bases. *J. Chem. Edu.***1987**, *64*, 561-567.
36. Parr, R. G.; Chattaraj, P. K. *J. Am. Chem. Soc.* **1991,** *113*, 1854-1855.
37. Ayers, P. W.; Parr, R. G. *J. Am. Chem. Soc.* **2000**, *122*, 2010-2018.
38. Chattaraj, P. K.; Sengupta, S. *J. Phys. Chem.* **1996**, *100*, 16126-16130.
39. Fuentealba, P.; Simon-Manso, Y.; Chattaraj, P. K. *J. Phys. Chem. A* **2000**, *104*, 3185-3187.
40. Pan, S.; Solà, M.; Chattaraj, P. K. *J. Phys. Chem. A* **2013**, *117*, 1843-1852.
41. Saha, R.; Pan, S.; Chattaraj, P. K. *Molecules* **2016**, *21*, 1477-1493.
42. Chamorro, E.; Chattaraj, P. K.; Fuentealba, P. *J. Phys. Chem. A* **2003**, *107*, 7068-7072.
43. Parthasarathi, R.; Elango, M.; Subramanian, V.; Chattaraj, P. K. *Theo. Chem. Acc.* **2005**, *113*, 257-266.
44. Geerlings, P.; De, P. F.; Langenaeker, W. *Chem. Rev.* **2003**, *103*, 1793-1874.
45. Chattaraj, P. K. *J. Indian. Chem. Soc.* **1992**, *69*, 173-183.
46. Parr, R. G.; Donnelly, R. A.; Levy, M.; Palke, W. E. *J. Chem. Phys.* **1978**, *68*, 3801.
47. Chattaraj, P. K.; Sarkar, U.; Roy, D. R. *Chem. Rev.* **2006**, *106*, 2065-2091.
48. Chattaraj, P. K.; Roy, D. R. *Chem. Rev.* **2007**, *107*, PR46-PR74.
49. Parr, R. G.; Szentpaly, L. v.; Liu, S. *J. Am. Chem. Soc.***1999**, *121*, 1922-1924.
50. Koopmans, T. A. *Physica* **1993**, *1*, 104-113.
51. Janak, J. F. *Phys. Rev. B.* **1978**, *18*, 7165.
52. Roy, R.K.; Pal, S.; Hirao, K. *J. Chem. Phys*. **1999**, *110*, 8236
53. Roy, R.K.; Pal, S.; Hirao, K. *J. Chem. Phys*. **2000**, *113*,1372
54. Ayers, P.W.; Morrisson, R.C.; Roy, R.K. *J. Chem. Phys*. **2002**, 116, 8731.
55. Hocquet, A.; Toro-Labbé, A.; Chermette, H. *J. Mol Struc (THEOCHEM)* **2004**, 686, 213-218.
56. Melin, J.; Aparicio, F.; Subramanian, V.; Galván, M.; Chattaraj, P.K. *J. Phys. Chem. A* **2008**, *108*, 2487-2491.
57. Lu, T.; Chen, F. *J. Comp. Chem.* **2012**, *33*, 580-592.