



Probing the reactive center for site selective protonation in carbonyl sulphide in terms of conceptual density functional based site selectivity descriptors

Sandip Kumar Rajak

Department of Chemistry, Dumkal College, Basantapur, Murshidabad-742 406, West Bengal, India

E-mail: sandip1ku@gmail.com

Manuscript received online 12 October 2020, revised and accepted 27 November 2020

In the investigation of sufficient number of molecule species from the interstellar and circumstellar media with almost 80% of these cations are protonated molecules. The carbonyl sulphide (OCS) molecule being the interstellar molecule has three possible protonation sites (either O, S, or C). So, the investigation is performed to determine the best site for the protonation of carbonyl sulphide (OCS) theoretically. The physico-chemical process of protonation is allied with the energy lowering phenomenon. For ambivalent molecules having more than one lone pairs at different sites, the protonation occurs preferentially. Preferred site of protonation is an important physico-chemical input in suggesting and modeling reaction mechanism involving such molecules. Locating the preferred site of protonation in ambivalent molecules is a fascinating problem of experiment as well as theoretical chemistry. The present study has invoked local density functional descriptors governing electrophilic attack for Fukui function (f^+), local softness function (s^-) and local philicity function (ω^-) theoretically locating the preferred site of protonation, an electrophilic reaction, of the chosen ambidentate molecule whose preferred site of protonation are known experimentally. It is found that theoretical prediction in terms of computed theoretical descriptor values regarding the preferred sites of protonation in carbonyl sulphide (OCS) molecules have one to one correspondence with the experimental findings.

Keywords: Protonation, DFT, Fukui function.

Introduction

The protonation reactions or the physico-chemical process of protonation are ubiquitous in almost all the areas of chemistry and biochemistry¹⁻⁵. The chemical method of protonation is basic of many chemical rearrangements, and enzymatic reactions⁴. The resulting protonated molecule is frequently an essential intermediate that guides the succeeding steps of the overall process. The knowledge of the intrinsic basicity and the site of protonation of a compound are central for the understanding of the mechanism of chemical reactions. The legend proton affinity is defined as the negative of the enthalpy change of a protonation reaction at the standard conditions. The gas-phase proton affinities are a quantitative measure of the intrinsic basicity of a molecule⁶. The study of thermochemistry of the proton transfer reaction in the gas phase is well-known experiment of acid-base reaction⁷. Dynamics of proton transfer is also important for ionization processes in mass spectroscopy⁸.

In the investigation of ample number of molecule spe-

cies from the interstellar and circumstellar media with about 10% being cations and almost 80% of these cations are protonated molecules⁹⁻¹⁶. Jefferts *et al.*¹⁷ during their study, first detected the carbonyl sulphide (OCS) as a recognized interstellar molecule within the giant molecular Sagittarius B2 and was further confirmed in about ten interstellar sources¹⁸⁻²⁰. This interstellar molecule OCS participate a significant role in the global cycling of sulphur²¹ and it forms the major source of stratospheric aerosol²² due to its high abundance (about 500 ppm) in the troposphere.

Since, the OCS molecule has three possible protonation sites (either O, S, or C) so the purpose of this work was to determine the best site for the protonation of OCS theoretically which correspond with the experimental result²³⁻²⁸.

In the physico-chemical process of protonation, when a proton dynamically approaches towards a nucleophile from a long distance, it is attracted by the electron cloud of the molecule. Thus a proton acting as an electrophile starts soaking the electron density from the entire skeleton of the nu-

cleophile²⁹ and as a result, the electron cloud of the nucleophile is redistributed and remains under the influence of nucleus of the electrophile. Ultimately the proton fixes at a site of lone pair – the site of protonation, of the molecule. However, if there is no lone pair in the structure of the molecule, the proton remains weakly attached to the sphere of the charge cloud of the molecule. The polarizing power of the proton induces a physical process of structural and energetic changes in the molecule. This phenomenon is, in particular, at the origin of the site of protonation, has considerable effect on the strength and length of the bonds⁵. The structural and energetic changes induced by the polarizing power of the proton are expected to be at its maximum at the gas phase of the molecule. Thus, the gas-phase basicity is certainly the ideal revelator of the structural and energetic characteristics of the molecular protonation process.

If a molecule has more than one donor sites i.e. lone pairs and if a proton approaches such a molecule, the proton will not find all the donor sites to be attacked equally likely. The proton will select the most preferred site in the structure of the molecule. In the dynamic process of protonation reaction, the preferred site may be identified by the attaching proton in a kinetic and thermodynamic process. But the selection of preferred site will be decided by the thermodynamically controlled process. When the proton is fixed at the preferred site, the enthalpy change is more and when the proton fixes at non-preferred site liberation of energy is less. The procedure follows the hierarchical steps: (i) calculate energy of the molecule first, and (ii) then attach proton at different probable sites to generated protonated species one after another, and (iii) then compute the energy of the protonated species theoretically and/or experimentally.

The preferred site of protonation in ambidentate molecules can also predicted from the charge densities on atomic sites and also the hybridization of the lone pair that binds the proton^{5,29,30}. Introduction of Conceptual Density Functional Theory based global and local descriptors by Parr and co-workers^{31–34} made DFT more popularize and initiated a new arena of scientific research. Although, the global descriptors like electronegativity, hardness and electrophilicity index are hypothetical concepts^{35–47}, these descriptors are successfully used to predict several physico-chemical properties of molecules as well as the reaction surfaces^{45,47} and to probe

the site of chemical reaction of molecules⁴⁸. It is worth mentioning that the local descriptors are evolved from the global descriptors. Global quantities like hardness, softness deal with the stability and reactivity of different interacting fragments as a whole.

If a proton approaches dynamically towards a donor, what direction will be preferred from among several directions that can produce the same type of chemical bond between the proton and the donor? Since the purpose of this work here is to correlate the known site selectivity in terms of local density functional descriptors, so it is pertinent to discuss the local reactivity descriptors in brief.

The most popular method for predicting how and whether a reaction will take place is the frontier molecular orbital theory (FMO)⁴⁹. This method uses the shapes and symmetries of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) to indicate whether a reaction will occur or not. If the HOMO of the electron donor and the LUMO of the electron acceptor have the same shape (symmetry) and phase, then electron transfer from the HOMO of the first molecule to the LUMO of the second can occur, often forming a bond between the reagents⁵⁰. This motivated the definition of a function in the context of density functional theory (DFT) that encapsulates the essence of FMO^{31,51–53} but, in principle, includes both electron correlation^{31,54}. This function is known as the “Fukui function” $f(r)$. The quantity $f(r)$ is a local property depending on position, r and hence it possesses different value at different position in the chemical species. The Fukui function, $f^-(r)$, is defined as the change in density that one observes when one goes from N to $N - 1$ electrons (with the nuclear positions fixed) and within the frozen core approximation this is analogous to the density of the HOMO orbital. A similar function, $f^+(r)$, can be defined as the difference between the electron densities of the $N + 1$ and N electron systems; this is analogous to the LUMO orbital density. The Fukui function is labeled according to whether the system is acting as an electron acceptor or an electron donor. The $f^+(r)$ says where an electron will add to the molecule. The $f^-(r)$ says where an electron given to an electron acceptor will come from. Electron donors tend to attack the molecule where $f^+(r)$ is large because this is where the molecule “wants electrons”. The essence of the theoretical development is that the numerical

Rajak: Probing the reactive center for site selective protonation in carbonyl sulphide in terms of conceptual *etc.*

values of $f^+(r)$ and $f^-(r)$ in molecules predict the preferred sites for electrophilic or nucleophilic attack in the molecules. Electron acceptors tend to attack the molecule where $f^-(r)$ is large because this is where the molecule has electrons that it is "willing to give up"^{31,51}.

Notwithstanding some workers reported the failure of Fukui functions to predict the reaction site of a molecule³⁰, still the Fukui functions are used in several works as good descriptor of site selectivity^{48,51,55-60}.

Parr and Yang^{31,33}, on the basis of DFT, further introduced a new local DFT descriptor – the local softness (s) which have been found potentially useful to identifying the preferred sites of molecules prone to chemical reaction. The local softness can be considered as "local abundance" or "concentration" of their corresponding global properties. The conceptual structure and the necessary algorithm for this descriptor have crystallized a distinct branch of conceptual chemistry – the local Hard-Soft Acid-Base (HSAB) principle.

In order to provide a unified treatment of chemical reactivity and selectivity concept of philicity is introduced³⁰ through a resolution of identity.

Theoretical background

There is a paradigm shift in the realm of conceptual chemistry due to the density functional underpinning of Parr *et al.*^{31,32,52,61}. The useful qualitative entities like hardness, electronegativity and electrophilicity index which were abstract semiotic representations are now considered as theoretical quantities of cognitive representations. According to DFT, given the electron density function $\rho(r)$ of a chemical system and the ground state energy and everything can be determined. The chemical potential, μ of that system in equilibrium has been defined as the derivative of the energy functional $E(\rho)$ with respect to the electron density at fixed molecular geometry.

The chemical potential, μ , is given by⁶²

$$\mu = -\chi = [\delta E(\rho)/\delta \rho]_v \quad (1)$$

where v is the external potential acting on an electron due to the presence of nucleus.

The differential definition more appropriate to atomic system is on the basis that for a system of N electrons with ground state energy $E[N, v]$,

$$\mu = -\chi = [\partial E/\partial N]_v \quad (2)$$

The absolute hardness is defined⁶³ as

$$\eta = \frac{1}{2} [\partial \mu/\partial N]_v = \frac{1}{2} [(\partial^2 E/\partial N^2)]_v \quad (3)$$

The ansatz for hardness is mathematically difficult because the numerical method is required to be invoked to solve it⁶⁴. However, Parr and Pearson⁶³, invoking finite difference approximation, suggested an approximate formula for the evaluation of hardness and electronegativity as

$$\eta = \frac{1}{2} (I - A) \quad (4)$$

$$\chi = \frac{1}{2} (I + A) \quad (5)$$

where I is the ionization energy and A is the electron affinity of the chemical species. Pearson⁶⁵ proceeded further to evaluate ' I ' and ' A ' in terms of orbital energies of the highest occupied molecular orbital, HOMO and the lowest unoccupied molecular orbital, LUMO by connecting it with Hartree - Fock SCF theory and invoking Koopmans' theorem the hardness and electronegativity are reformulated as

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

$$\text{and } \chi = -\mu = -\frac{1}{2} (\epsilon_{\text{LUMO}} + \epsilon_{\text{HOMO}}) \quad (7)$$

where $I = -\epsilon_{\text{HOMO}}$, and $A = -\epsilon_{\text{LUMO}}$.

The inverse of hardness is defined as softness^{31,33}.

$$S = \frac{1}{2}\eta = (\partial N/\partial \mu)_v = 1/(I - A) \quad (8)$$

Parr *et al.*³⁴ defined another global parameter, the electrophilicity index (ω) as

$$\omega = (\mu)^2/(2\eta) \quad (9)$$

or,

$$\omega = \{(I + A)^2\}/8(I - A) \quad (10)$$

The Fukui function is defined as

$$f(r) = [\delta \mu/\delta v(r)]_N = [\partial \rho(r)/\partial N]_v \quad (11)$$

The Fukui function can give three predictions:

(i) governing electrophilic attack: $f^-(r) = [\partial \rho(r)/\partial N]^-_v$ (12)

(ii) governing nucleophilic attack: $f^+(r) = [\partial \rho(r)/\partial N]^+_v$ (13)

(iii) governing neutral (radical) attack:

$$f^0(r) = [\partial \rho(r)/\partial N]^0_v \quad (14)$$

The three cases have $\mu_S > \mu_R$, $\mu_S < \mu_R$ and $\mu_S \sim \mu_R$.

A "frozen core" approximation now gives $d\rho = d\rho_{\text{valence}}$ in each case, and therefore,

(a) governing electrophilic attack: $f^-(r) = \rho_{\text{HOMO}}(r)$ (15)

(b) governing nucleophilic attack: $f^+(r) = \rho_{\text{LUMO}}(r)$ (16)

(c) governing neutral (radical) attack:

$$f^0(r) \approx \frac{1}{2} [\rho_{\text{HOMO}}(r) + \rho_{\text{LUMO}}(r)] \quad (17)$$

where $\rho(r)$ is the electron density.

Local softness, $s(r)$, can be written by the formula

$$s(r) = S f(r) = (\partial \rho(r) / \partial \mu)_{T, V(r)} \quad (18)$$

There are three local softness functions:

(a) governing electrophilic attack: $s^-(r) = S f^-(r)$ (19)

(b) governing nucleophilic attack: $s^+(r) = S f^+(r)$ (20)

(c) governing neutral (radical) attack: $s^0(r) = S f^0(r)$ (21)

Here $s^-(r)$, $s^+(r)$ and $s^0(r)$ are the local softnesses corresponding to electrophilic attack, nucleophilic attack and radical attack respectively⁶⁶. The local philicity index³⁰ is given as

$$\omega(r) = \omega f(r) \quad (22)$$

There are three local philicity functions:

(a) governing electrophilic attack: $\omega^-(r) = \omega f^-$ (23)

(b) governing nucleophilic attack: $\omega^+(r) = \omega f^+$ (24)

(c) governing neutral (radical) attack: $\omega^0(r) = \omega f^0$ (25)

Propose of this study to locate the reactive centers for the chemico-physical process of protonation of representative molecule in terms of the computed values of local density functional descriptors.

Method of computation

Computational study is performed within *ab initio* framework and descriptors have been calculated using conceptual density functional theory. All the modeling and structural optimization of compounds have been performed using Gaussian 09 software package⁶⁷. For optimization purpose, Hartree-Fock with basis set 6-311G has been adopted.

The optimized structure for carbonyl sulfide are presented in Fig. 1.

All the global descriptor such as global hardness (η), chemical potential (μ), electronegativity (χ), global softness (S), and global electrophilicity index (ω) are computed for the molecules stated above using eq. (6), eq. (7), eq. (8) and eq. (10) respectively and are given in the Table 1.

The global descriptors are used to compute the local

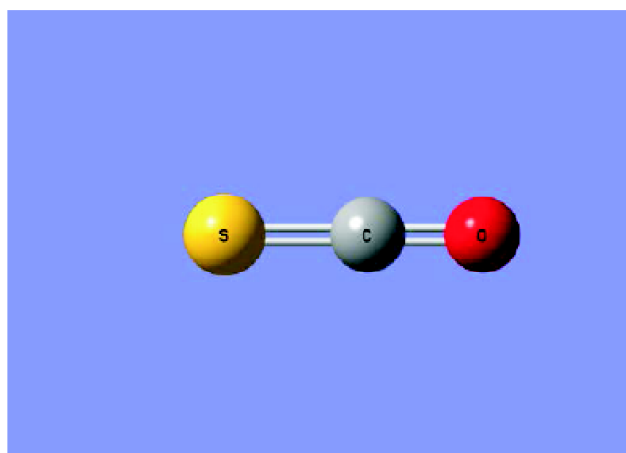


Fig. 1. Optimized structure of carbonyl sulfide.

Table 1. Global hardness (η), global softness (S), chemical potential (μ), and global electrophilicity index (ω) in eV

Molecules	η (eV)	μ (eV)	χ (eV)	ω (eV)	S (eV)
OCS	6.90112	-4.8611	4.8611	1.71207	0.1449

descriptors. Since proton is an electrophile and the site selectivity of the instant reactions will be decided by f^- , s^- and ω^- , so computation has done to calculate the values of Fukui function (f^-), local softness (s^-), local philicity index (ω^-) only using eq. (15), eq. (19) and eq. (23) respectively for all the probable donor centers of the chosen molecule and are given in the Table 2.

Table 2. The computed Fukui function (f^-), local softness (s^-), local philicity index (ω^-) in eV for different donor centers of carbonyl sulfide (OCS)

Center	f^-	s^-	ω^-
O	0.30078	0.043584	0.51495
C	0.03277	0.004748	0.0561
S	0.84815	0.122901	1.4521

Results and discussion

The structural formula shows that the molecule has three probable sites, 'O', 'S' and 'C' of protonation. The evaluated Fukui functions (f^-), the local softness (s^-) and local philicity (ω^-) for the three different donor centers O, S and C of the molecule OCS are presented in Table 2. It is the intrinsic characteristics of Fukui function that the numerical value of f^- measures the reactivity (nucleophilicity) of a particular

Rajak: Probing the reactive center for site selective protonation in carbonyl sulphide in terms of conceptual etc.

atomic site of a donor center towards an electrophile, the proton. Looking at Table 2, it can be seen that the f^- values of the different donor centers in the donor, OCS follows the order $S > O > C$ which clearly indicates that the S-center in OCS molecule is the more reactive center towards an electrophile.

In prediction based upon the calculated atomic charges, on the other hand, would be seriously in error. In OCS, the most negative atomic charge are found to be on O, S and C, $-0.4404, 0.197, 0.24338$ respectively, followed inconsistent with the experimental fact^{23,24-28} that S is the most attractive site of protonation attack.

So, the experiment^{23,24-28} and theory proceed hand in hand in the matter of selecting the preferred site of protonation in multi dented molecule like OCS and the theoretical tour is some local DFT descriptor.

Conclusion

Molecules may have more than one site having lone pair of electrons in its structure in terms of valence bond description. The lone pairs are the centre where an electrophile usually attaches during the course of chemical reactions between a nucleophilic and electrophile. Proton is an electrophile. It approaches kinetically towards a molecule and soaks electron density from the molecule. In the process energy lowering takes place. It is also quite expected that proton will prefer more polarizable site in the molecule for binding. The local Hard-Soft Acid-Base (HSAB) principle has introduced a cluster of local theoretical descriptors namely the Fukui functions, local softnesses and the local electrophilicity indices. The thermodynamic mechanism of protonation can be rationalized in terms of the local Hard-Soft Acid-Base (HSAB) descriptors. The gamut of the theory is that the site selectivity in the physico-chemical process of protonation can be predicted in terms of these theoretical descriptors.

In the present study, determined the preferred site of electrophilic reactions/protonation of such molecules in terms of the local descriptors discussed above and the result is 1 to 1 correspondence between the theoretical prediction and experimental finding. In other words, the preferred site of protonation can be rationalized in terms of the local density functional descriptors. The experiment and theory proceed hand in hand in the matter of selecting the preferred site of pro-

tonation in multidented compounds and the theoretical tour is some local DFT descriptor. But prediction based upon the calculated atomic charges, on the other hand, would be seriously in error.

References

1. R. Stewart, "The Proton: Appellation to Organic Chemistry", Academic Press, New York, 1985.
2. F. A. Carrol, "Perspectives on Structure and Mechanism in Organic Chemistry", Brooks-Cole, New York, 1998.
3. J. Zhao and R. Zhang, *Atmospheric Environment*, 2004, **38**, 2177.
4. R. A. Kennedy, Ch. A. Mayhew, R. Thomas and P. Watts, *Int. J. Mass Spectrom.*, 2003, **627**, 223.
5. G. Bouchoux, *Mass Spectrometry Reviews*, 2007, **26**, 775.
6. C. A. Deakyne, *Int. J. Mass Spectrom.*, 2003, **227**, 601.
7. S. G. Lias, J. F. Liebman and R. D. Levine, *J. Phys. Chem. Ref. Data*, 1984, **13**, 695.
8. A. Hansel, N. Oberhofer, W. Lindinger, V. A. Zenevich and G. B. Billing, *Int. J. Mass Spectrom.*, 1999, **559**, 185.
9. H. J. Fraser, M. R. S. McCoustra and D. A. Williams, *Aston. Geophys.*, 2002, **43**, 2.10-2.18.
10. A. G. G. M. Tielens, *Rev. Mod. Phys.*, 2013, **85**, 1021.
11. E. E. Etim and E. Arunan, *Planex Newslett*, 2015, **5**, 16.
12. E. E. Etim, P. Gorai, A. Das, S. K. Chakrabarti and E. Arunan, *Astrophys. J.*, 2016, **832(2)**, 10.3847/0004-637X/832/2/144.
13. E. E. Etim and E. Arunan, *Eur. Phys. J. Plus*, 2016, **131**, 10.1140/epjp/i2016-16448-0.
14. E. E. Etim and E. Arunan, *Adv. Space Res.*, 2017, **59**, 1161.
15. E. E. Etim, E. Arunan, *Astrophys. Space Sci.*, 2017, **362**, 1.
16. E. E. Etim, P. Gorai, A. Das and E. Arunan, *Eur. Phys. J. D*, 2017, **71**, 10.1140/epjd/e2017-70611-3.
17. K. B. Jefferts, A. A. Penzias, R. W. Wilson and P. M. Solomon, *Astrophys. J.*, 1971, **168**, L111-L113.
18. P. F. Goldsmith and R. K. Linke, *Astrophys. J.*, 1981, **245**, 482.
19. W. Fock and T. McAllister, *Astrophys. J.*, 1982, **257**, L99-L101.
20. M. E. Palumbo, T. R. Geballe and A. G. Tielens, *Astrophys. J.*, 1997, **479**, 839.
21. D. C. Thornton, A. R. Bandy, B. W. Blomquist and B. E. Anderson, *J. Geophys. Res.: Atmos.*, 1996, **101**, 1873.
22. K. Hiraoka, K. Fujita, M. Ishida, K. Hiizumi and F. Nakagawa, *J. Am. Soc. Mass Spectrom.*, 2005, **16**, 1760.
23. S. Saebo, M. M. Sanz and S. C. Foster, *Theoret. Chem. Accounts*, 1997, **97**, 271.
24. S. E. Wheeler, Y. Yamaguchi and H. F. Schaefer III, *Chem.*

- Phys.*, 2006, **124**, 10.1063/1.2150819.
25. R. C. Fortenberry, X. Huang, J. S. Francisco, T. D. Crawford and T. J. Lee, *J. Phys. Chem. A*, 2012, **116**, 9582.
 26. T. McAllister, P. R. Taylor and M. Scarlett, *Org. Mass Spectrom.*, 1986, **21**, 157.
 27. P. R. Taylor and M. Scarlett, *Astrophys. J.*, 1985, **293**, L49.
 28. J. Liu, B. van Devener and S. L. Anderson, *J. Chem. Phys.*, 2002, **117**, 8292.
 29. D. C. Ghosh, "A theoretical study of some selected molecules and their protonation by the application of CNDO method", Premchand Roychand Research Studentship Award, University of Calcutta, Calcutta, 1976.
 30. J. Melin, F. Aparicio, V. Subramanian, M. Galván and P. K. Chattaraj, *J. Phys. Chem. A*, 2004, **108**, 2487.
 31. R. G. Parr and W. Yang, *J. Am. Chem. Soc.*, 1984, **106**, 4049.
 32. R. G. Parr and W. Yang, "Density Functional Theory of Atoms and Molecules", Oxford, University Press, 1989.
 33. W. Yang and R. G. Parr, *Proc. Natl. Acad. Sci. USA*, 1985, **82**, 6723.
 34. R. G. Parr, L. V. Szentpaly and S. Liu, Electrophilicity Index, *J. Am. Chem. Soc.*, 1999, **121**, 1922.
 35. D. C. Ghosh and N. Islam, *Int. J. Quantum Chem.*, 2011, **111**, 2802.
 36. D. C. Ghosh and N. Islam, *Int. J. Quantum Chem.*, 2011, **111**, 2811.
 37. D. C. Ghosh and N. Islam, *Int. J. Quantum Chem.*, 2011, **111**, 1942.
 38. D. C. Ghosh and N. Islam, *Int. J. Quantum Chem.*, 2009, **110**, 1206.
 39. D. C. Ghosh, N. Islam and S. K. Rajak, *Int. J. Chem. Model*, 2009, **2**, 361.
 40. D. C. Ghosh, N. Islam and S. K. Rajak, *Int. J. Chem. Model*, 2009, **2**, 375.
 41. D. C. Ghosh and N. Islam, *Int. J. Quantum Chem.*, 2011, **111**, 1931.
 42. D. C. Ghosh and N. Islam, *Int. J. Quantum Chem.*, 2010, **111**, 1961.
 43. D. C. Ghosh and N. Islam, *Int. J. Quantum Chem.*, 2011, **111**, 40.
 44. N. Islam and D. C. Ghosh, *Mole Phys.*, 2011, **109**, 917.
 45. N. Islam and D. C. Ghosh, *European Physical Journal D.*, 2011, **61**, 341.
 46. N. Islam and D. C. Ghosh, *Int. J. Quantum Chem.*, 2011, **111**, 3556.
 47. N. Islam and D. C. Ghosh, *Eur. J. Chem.*, 2010, **1**, 83.
 48. D. C. Ghosh and S. Bhattacharyya, "DFT Correlation of the Site Selectivity of Donor–Acceptor Chemical Interaction, Nanoscience and Advancing Computational Methods in Chemistry: Research Progress", Apple Academic Press, Canada, 2011.
 49. T. A. Albright, J. K. Burdett and M. H. Whangbo, "Orbital Interactions in Chemistry", Wiley-Interscience, New York, 1985.
 50. J. S. M. Anderson, J. Melin and P. W. Ayers, *J. Chem. Theory Comput.*, 2007, **3**, 358.
 51. P. W. Ayers and M. Levy, *Theor. Chem. Acc.*, 2000, **103**, 353.
 52. W. Yang, R. G. Parr and R. Pucci, *J. Chem. Phys.*, 1984, **81**, 2862.
 53. P. W. Ayers and R. G. Parr, *J. Am. Chem. Soc.*, 2000, **122**, 2010.
 54. J. Melin, P. W. Ayers and J. V. Ortiz, *J. Chem. Sci.*, 2005, **117**, 387.
 55. P. Fuentealba and R. Contreras, in: "Reviews of Modern Quantum Chemistry: A Celebration of the Contributions of Robert G. Parr, K. D. Sen", World Scientific, Singapore, 2002.
 56. E. Chamorro, R. Contreras and P. Fuentealba, *J. Chem. Phys.*, 2000, **113**, 10861.
 57. P. Geerlings, F. De Proft and W. Langenaeker, *Chem. Rev.*, 2003, **103**, 1793.
 58. P. Pérez, Y. Simón-Manso, A. Aizman, P. Fuentealba and R. Contreras, *J. Am. Chem. Soc.*, 2000, **122**, 4756.
 59. L. T. Nguyen, T. N. Le, F. De. Proft, A. K. Chandra, W. Langenaeker, M. T. Nguyen and P. Geerlings, *J. Am. Chem. Soc.*, 1999, **121**, 5992.
 60. S. Pal and K. R. S. Chandrakumar, *J. Am. Chem. Soc.*, 2000, **122**, 4145.
 61. R. G. Parr, R. A. Donnelly, M. Levy and W. E. Palke, *J. Chem. Phys.*, 1978, **68**, 3801.
 62. E. P. Gyftopoulos and G. N. Hatsopoulos, *Proc. Natl. Acad. Sci.*, 1968, **60**, 786.
 63. R. G. Parr and R. G. Pearson, *J. Am. Chem. Soc.*, 1983, **105**, 7512.
 64. K. D. Sen and S. C. Vinayagam, *Chem. Phys. Lett.*, 1988, **114**, 178.
 65. R. G. Pearson, *Proc. Natl. Acad. Sci.*, 1986, **83**, 8440.
 66. D. C. Ghosh and J. Jana, *Int. J. Quantum Chem.*, 2003, **92**, 484.
 67. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Baron, B. Mennucci and G. A. Peterson, Gaussian 09, revision D.01, Gaussian, Inc., Wallingfort, CT, 2009.