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Unveiling the Nature of Chemical Bonds

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Abstract

From Newton's early suppositions about infinitesimal forces to Pauling's ground- breaking studies, scientists have been fascinated by the chemical bond, one of the most essential sundries in chemistry. There are easily bonds between titles, but defining what they are, how they're generated, and how to categorize them has proven to be a substantial challenge. The original models centered on electrostatic magnets, but the discovery of electron- brace relations and the development of mechanics, particularly molecular orbital (MO) and valence bond (VB) propositions, led to a better understanding. Weak relations, Ulti-electron correlations, and agitated countries may now be duly studied thanks to ultramodern computational chemistry styles like VBSCF, BOVB, SCGVB, CASSCF, and high- performance computing. The physical parcels, features, and analysis of chemical bonds, as well as their significance in chemical processes, intermolecular relations, and computational approaches, are stressed in this paper. The combined papers reveal how our understanding of bond conformation, electrical structure, and molecular behavior has progressed as a result of new theoretical and computational methodologies. They give us fresh perceptivity on and tools for detecting chemical cling in complicated systems.

Keywords: Chemical bond, Valence bond theory, Molecular orbital theory, Computational chemistry, Bond energy.

1. Introduction

From the theories of Isaac Newton about the "forces" binding atoms together, through the popular book by Linus Pauling of the same title, the nature of the chemical bond has always captivated the imagination of chemists and chemist-historians [1]. Although chemists are sure that the bonds exist between the atoms of a molecule, they are not sure of the nature of the chemical bonds, the way they are classified, or the reasons for the existence of chemical bonds. In order to explain the binding between the atoms of the many inorganic molecules, the early explanations of the nature of the chemical bond focused on the interaction between the electrical charges of opposite polarity. What, however, about the binding between the atoms of the countless organic molecules that did not have any net electrical charge? Over a century ago, the chemical bond was found by Lewis to be somehow associated with the "electron pairs" [2]. Immediately after the development of the wave equation by Irwin Schrödinger, Heitler and London showed that the quantum mechanical approach, later termed the "Valence Bond" (VB) method, was capable of describing the binding of the

extremely unlikely H2 molecule [3].

Chemists have been able to gain new knowledge through the progress of chemical theories and computational methods in accordance with the ability of electronic processors to examine the properties of various types of bonds, including the case in which two objects have a weak attraction to each other. These modifications have led to the replacement of Heitler and London's classic VB theory of the chemical bond with more sophisticated and accurate versions, including the Valence Bond Self-Consistent Field (VBSCF) [4], Breathing Orbital Valence Bond (BOVB) [3], and Spin-Coupled Generalised Valence Bond (SCGVB) [5] theories. These theories, through their improvement of the used orbitals in the wave function, make it possible to liberate the results from any assumptions about the properties of the used atomic orbitals. A different point of view regarding the electronic structure of molecules was offered by the molecular orbital (MO) theory and its computational version, the limited Hartree-Fock theory, which were frequently used to describe the ground and excited states of molecules, including O2 molecules. Edmiston and Ruedenberg revealed a strong correlation between VB and MO theories, in spite of the fact that the MO theory, characterized by the presence of molecular orbitals delocalized over the whole molecule, seems to provide a completely different point of view on the bonding in molecules. They have shown that doubly occupied orbitals, which correspond to lone pairs and two-electron bonds, differ from delocalised molecular orbitals in conventional MO theory by no more than a unitary transformation (see Refs. 9-12 for preliminary thoughts on this subject). Finally, multiconfigurational wave functions, the full optimised reaction space method (FORS) [13], and the complete active space SCF (CASSCF) wave functions were developed by Ruedenberg and his co-workers and Roos. These wave functions resolved the major difficulties connected with the RHF wave function and made it possible to make new discoveries in the electronic structure of molecules and in the nature of chemical bonds.[15] VBSCF and SCGVB methods, especially the second one (see explanation in Ref. 5), are very close to these new multiconfigurational methods. In the previous decade, China, Japan, the United States, and the European Union have all purchased new petascale and exascale computers. These extremely powerful computers are based on modern computing technologies; the existing sets of electronic structural approaches must be upgraded. The US Department of Energy's Exascale Computing Project is funding the development of exascale versions of NWChem, GAMESS, EXAALT, and QMCPACK.[16]. These modifications will greatly enhance the accuracy with which the correlated electrons and the active areas of the orbitals can be computed with the help of highly correlated methods. It will also enhance the overall functionality of the electronic structure code suites. It is believed that with the help of the computational tools developed with the help of these new tools for modelling the molecules, the nature of the chemical bond will be better comprehended. The first two pieces presented here are contributed by Professor Klaus Ruedenberg and Professor Sason Shaik. In the early 1960s, Professor Ruedenberg posed a challenge to the conventional knowledge on the physical reason for the covalent bond between two hydrogen atoms in the H2 molecule by showing that the bond's energy decrease was caused by a drop in the electrons' (interference) kinetic energy rather than an increase in the electrons' potential energy. His work has been significant for the understanding of the chemical bond [3]. The MO theory was the "theory of choice" in the early 1960s because the use of orthogonal molecular orbitals facilitated the calculations. Professor Shaik was instrumental in reviving the VB theory in chemistry [5]. This is because computers are faster today, and new methods for calculating the non-orthogonal orbitals have been developed. However, the main reason is the natural affinity of chemists for the concepts presented by the VB theory and the localized molecular orbitals of the MO theory, such as hybrid orbitals, bond pairs, lone pairs, resonance, etc. One of the most interesting things about the new ab initio VB theories (VBSCF, BOVB, and SCGVB) is the way they introduce new concepts which will help chemists with their ever-deepening inquiry into the molecular world.

2. Overview of Key Topics Featured in the Special Issue

The Special Issue of the Journal of Chemical Physics on the "Nature of the Chemical Bond" contains six primary types of articles. These include the physical nature of the chemical bond, its features, analysis of the chemical bond, chemical reactions and the chemical bond, molecular interactions, and computational methodologies and benchmarks. There are also some items that do not fall into any of the other categories. We'll now provide a brief overview of the articles in each of these categories.

3. Fresh Perspectives

Ruedenberg contributed two articles. The first article showed the electronic wave function in quasi-atomic orbitals. This gave a global energy expression for various forms of chemical bonds through physical interactions. Ruedenberg then proceeded to examine the manner with which different molecules bond with each other [8]. In the second article, Ruedenberg utilized a variety of intrinsic molecular orbitals and configurational transformations of the wave function. This gave a delineation of the energy of formation of a molecule in terms of intra-atomic variation of energy, interference energies, quasi-classical, non-classical, and charge transfer Coulombic interactions. This gave an algorithm for the quantitative analysis of bond energies [10]. Shaik et al. gave a complete summary of the properties of chemical bonds using the valence bond theory. This covered both single and multiple bonds, and charge shift bonds [9]. It also showed how an effective strategy is employed to ensure the description of the electrical structure of unusual molecules such as C_2 and O_2 is as brief as possible. It then proceeds to show how π and σ influence the geometric preferences of unsaturated molecules compared with those based on Si-analogs. It then proceeds to show how univalent metal atoms form groups. Such atoms only have parallel spins; however, they still manage to bond with each other through numerous resonance interactions. Finally, it shows the singlet excited states of ethylene, ozone, and sulphur dioxide. This offers new information on the electronic structure of these molecules.

4. Understanding the Physical Nature Behind Chemical Bond

Arasaki and Takatsuka investigate the physical properties of the chemical bond via the lens of energy natural orbitals, focusing on the essence of chemical bonding in three low-lying electronic states of the hydrogen molecule [11]. Bacskay quantified the kinetic energy changes that occur within and between fragments. These modifications primarily demonstrate how orbital contraction impacts a diverse spectrum of diatomic and polyatomic compounds [12]. Ruedenberg and Shaik both produced essays about this topic.

5. What Defines a Chemical Bond?

The bonding in the ground and low-lying electronic states of HfO and HfB has been studied by Ariyarathna et al. to obtain information about different catalysts and materials that have Hf-O or Hf-B moieties in their structure. These studies have used DFT results compared to coupled cluster results for dissociation energy, excitation energy, and ionization energy calculations [13]. Bressanini proved that a positron could bind to the PsH2 molecule to form a stable species that has three positrons. The potential energy curve for this species indicates that this species has equilibrium at 8 bohr with a binding energy of 11.5(5) mhartree with respect to the dissociation products PsH + e^+PsH [14]. Chen and Yang have studied the bonding in cerium oxide compounds and proved that the overlap between (Ce4f, O2p) orbitals with increasing coordination in Ce atoms makes the Ce-O bond covalent, leading to a specific shape in the molecule.

Scientists such as Depastas and his group have also identified the bonding and dissociation energies, together with the spectroscopic signatures, for seven different Mo_2 states, all of which are linked to the ground-state atoms. In the study, the group determined that the ground state has a sextuple chemical bond, while the other six states have one less bond than the one preceding them. Fletcher and his group have also designed a theoretical framework for understanding the correlations of individual electron pairs through the use of the variational subspace valence bond (VSVB) wave function, where the inter-electronic coordinate vectors are incorporated. Florez and his group have also conducted a thorough investigation of the closed-shell element Flerovium, aiming to make predictions about the behavior of the element in a solid, including the melting point, by dissecting the energy of the element into its various many-body interactions. Although Flerovium is a closed-shell element, it does not behave like other noble gas elements. Jackson and Miliordos have also investigated the beryllium ammonia dimers linked by linear hydrocarbon spacers, where the electrons of the compound are found in dispersed, singly occupied s-type orbitals, much like the electrons of the H_2 compound, where the electrons have the ability to couple either in a singlet or a triplet manner.

For long chains of hydrocarbons, the ground state is an open-shell singlet, very close to the triplet state. For n = 1, the molecule is a closed-shell singlet, just like the σ-bond in H_2. Kalemos studied the conventional CH4 molecule and its various formation mechanisms. These mechanisms include the reactions of

$$CH_n + (4 - n)H \rightarrow CH_4 (n = 0, 1, and 2)$$

Lucci et al. applied experimental and theoretical techniques to calculate the bond energies of AuSc, AuTi, and AuFe diatomic molecules.53 Mato et al. have studied the many-body expansion of energy for alkaline earth metal clusters Be, Mg, and Ca_n = 4, 5, and 6 using various theoretical techniques. The results showed that the geometrical configuration plays an important role in the behavior of the many-body expansion and, to some extent, the applied theoretical method. [15] McCutcheon et al. have studied the bonding properties of 15 ruthenium-ligand complexes and have provided a new computational toolbox for the analysis of bonding properties in these complexes. [16] Montero-Campillo et al. researched the ways of improving the weak acid properties of the triazoles and tetrazoles by binding them with beryllium complexes. It was found that the formation of the complexes of the basic centers of the azoles and the beryllium of the BeF_2 molecules, and also of the $(BeF_2)_2$ molecules, leads to a considerable disruption of the chemical bonds of the subunits participating in the complex formation. Rask and Zimmerman have studied the Fe(II) porphyrin complexes and found that the strong metal d-d and macrocycle π-π orbital interactions sustain the $^3A_{2g}$ state, while the d-π interactions sustain the ^3E_g state [18]. Ren et al. have studied the application of compact yet precise ab initio valence bond wave functions for the characterization of the electron transfer process of the classic but complex covalent/ionic interaction of LiF [19]. Simons has studied the possibility of a Rydberg radical forming a covalent bond either with another Rydberg radical or a regular valence orbital. It was found that any covalent bonds formed by the radicals are weak, and the molecules formed by them are prone to exothermic fragmentations requiring little energy for initiation. Shui et al. used bonding analysis techniques to study the bond between metal atoms in $Lu_2(C_{2n})$ (2n = 76-88) fullerenes, identifying a singular (two-center, two-electron) σ covalent bond between the two Lu ions. Tzeli and Xantheas applied the method of many-body expansion to the issue of the dissociation of covalent bonds and made this method much more effective. In two separate works, Xu and Dunning examined the behavior of dynamical correlation energy with inter-nuclear distance for covalent bonds in AH molecules, where A = B-F, and for recoupled pair two-center-three-electron bonds in CH and CF molecules. They found that the variation in dynamical correlation energy was non-monotonic, indicating changes in the molecular orbital structure. Zhao et al. used experimental and

computational techniques to describe uranium nitride-oxide cations and their complexes with equatorial N2 ligands, concluding that the bond lengths and vibrational modes could be explained by cooperative covalent and dative triple bonds [20].

6. Breaking Down the Chemical Bond

Hagebaum-Reignier et al., in their research on valence bond wave functions, established the concept of density as a differential with a quasi-state comprising identical orbitals [21]. Menéez-Herrero et al., using the Born maximum as a descriptor for the shell structure of ground-state atoms with atomic numbers Z = 1-36, analyzed the spatial arrangement of the N electrons inside the atom at the peak of the square of the wavefunction and compared it with other available indexes [22]. Nakatani et al. created a method for the analysis of chemical bonds inside the electronic wavefunctions of molecules using "local spin" - a form of spin correlation. This allowed them to easily comprehend the link between the concept of "spin correlations" and conventional chemistry notions such as the concept of resonance. The problem associated with the identification of the key points inside the electronic density using Bader's QTAIM methodology on a 3D regular grid was solved by Otero-de-la-Roza.68 Reuter et al. analyzed different forms of multicenter bonds using probability density analysis and compared the results with the valence bond methodology [22]. Scemama and Savin studied the impact of uncertainty on the probabilities of finding a specific number of electrons within specific geographic domains, and they also provided a way of easily selecting the domains. Silvi and Alikhani have also provided a way of dividing the atomic and molecular charge density into non-overlapping regions, which are chemically significant, by developing a method for the separation of the atomic and molecular charge density into non-overlapping regions. This has also provided a way of determining "good boundaries" by using information theory and simple statistical methods. Sousa and Nascimento have also used interference energy analysis for the study of the bonds, which are of the (three-center, two-electron) type, and have concluded that the interactions between the atoms A and C, which are part of the bond A-B-C, are as significant as the interactions between the atoms A, B, and C. Weinhold has also used natural bond orbital and natural resonance theory for the study of the puzzling properties of the C_{2v}-symmetric isomer of the chlorine dioxide radical ClO_2, where he observed that the molecule has a bonding configuration that has "different Lewis structures for different spins." In order to analyze all the interactions by making use of all the self-consistent charge type density functional tight binding methods, Xu et al. have provided a general strategy for the energy decomposition analysis of the intermolecular interactions by making use of a tight binding scheme. Zhao et al. used the EDA-NOCV method to investigate the characteristics of the interatomic interactions in LiF, BeO, and BN. Careful consideration and comparison of the results with QTAIM, NBO, and Mayer methodologies [23].

7. The Bond Behind Every Reaction

Starting from localised hole states, Danilov et al. used the quantum Ehrenfest approach to study the nuclear and electron dynamics in the glycine cation. They then used the Fourier transform of the spin densities to determine the normal modes of the electron dynamics [24]. David et al. studied the C_{4n} cyclacenes, which are characterized by significant bond alternation in the equilibrium geometries, and the physical aspects of the energy differences between the isomers and the barrier heights [25]. In order to better understand the phenomenon of electron transfer, Ebisawa et al. have utilized a new orbital analysis technique termed the natural reaction orbital method, where the orbital pairing is carried out automatically. Electron transfer occurs mostly near the transition states and the regions where the shoulder characteristics can be observed in the energy profile along the intrinsic reaction coordinate [26]. Molina Aguirre et al. found that a two-step mechanism with an intermediate diamond-core structure resembling diborane drives the gas-phase halogen

exchange reaction between boron and aluminium halides [27]. Sandoval-Pauker and Pinter have described the change in the electronic structure of the catalyst during the process of oxidative and reductive quenching of a photoredox catalyst by the use of quasi-restricted orbitals, fluctuations of electron density, and spin densities.

For the determination of whether the process of stereo-inversion competes with other chemical reactions such as reductive H2-elimination or hydride loss, and if so, the pathway of the reaction, Sigmund et al. have calculated the potential energy surfaces of fifteen tetrahedral p-block element hydrides [28].

8. Interactions Between Molecules

In their paper, Fan et al. studied the chalcogen bonds in some complexes formed by negatively charged bidentate chalcogen donors and chloride anions and proposed an inter-anion chalcogen bond. Harville and Gordon studied the intramolecular hydrogen bonding in salicylic acid and an intermediate compound in the synthesis of aspirin using the quasi-atomic orbital bonding analysis method and came to the conclusion that each intramolecular hydrogen bond is a (three-center, four-electron) bond. Herman et al. propose a classical electrostatic induction model to evaluate the three-body ion-water-water and water-water-water interactions in aqueous solutions of ions using an accurate dataset of three-body terms for 13 monatomic and polyatomic cation and anion systems. For a number of intermolecular complexes, including the one between dimethyl sulphide and sulphur dioxide, Nottoli et al. used charge displacement analysis to determine the charge redistribution profile along a designated contact axis [29]. In order to illustrate the role of the solvent molecules in π–π interactions of the benzene dimer, Sirianni et al. performed a quantum-chemical calculation of π–π interactions in an aqueous solution, using a T-shaped benzene dimer and a cationic pyridinium benzene dimer solvated in 28 or 50 water molecules [18]. The authors of the study concluded that the interactions involving nearby solvent molecules strongly affected the contacts in the cationic pyridinium benzene dimer, but only weakly affected the solute-solute interactions in the benzene dimer.

9. Exploring Computational Approaches and Standards

Almeida et al. estimated the dissociation energies of lanthanide sulphides and selenides using an f-block ab initio correlation-consistent composite approach [19]. Aldossary and Head-Gordon suggested a non-iterative method forcreating a molecule-specific minimum basis set and valence antibonding molecular orbitals [5]. With regard to singlet triplet gaps in biradicals, Chakraborty et al. developed a benchmark for the semi-stochastic CC(P,Q) technique [10]. Feller et al. used a systematic composite process to estimate the benchmark quality isotropic hyperfine characteristics for first-row elements (B–F) [21]. For spin-orbit vibronic interactions in molecules with tetrahedral and octahedral symmetries, Pradhan et al. presented a complete one-electron Hamiltonian framework that addresses all spin-orbit Jahn-Teller and pseudo-Jahn-Teller problems within these symmetries, independent of the kinds and numbers of vibrational modes involved [23]. Vila et al. presented novel coupled cluster techniques that allow for the calculation of the spectrum function and ionisation potential of molecular systems over a wide energy range, from valence to core binding levels [24]. In their study, Zheng et al. presented a novel hybrid density functional method based on the valence bond self-consistent field method and Kohn-Sham density functional theory.

10. Conclusion

One of the most fundamental concepts in chemistry is the chemical bond, and the articles in this Special Issue of the Journal of Chemical Physics demonstrate how much we have learned about it. In the past, especially for compounds that are covalently bound, it was unclear what held the atoms in a molecule together. The initial

applications of quantum theory to comprehend the chemical bond in the late 1920s and early 1930s showed great promise, but they were thwarted by challenging computational issues. Thankfully, thanks to digital computers, this is no longer the case. Strict theoretical underpinnings now underpin our current understanding of the chemical bond. These advancements are the result of advancements in computational and theoretical chemistry. We can now examine how molecules bond, how the electronic density in those molecules' functions, and what factors contribute to the bond energy using improved theoretical and computational methods. As we and our colleagues continue our research in the future, we hope to further advance our understanding of the chemical connection.

Declaration of Conflicting Interests

The authors declare no potential conflicts of interest with respect to the research, authorship and publication of this article.

References

[1] Pauling, Linus. *The nature of the chemical bond and the structure of molecules and crystals: an introduction to modern structural chemistry*. Vol. 18. Cornell university press, 1960.

[2] G. N. Lewis, J. Am. Chem. Soc. 38, 762 (1916).

[3] Heitler, W., & London, F. (2000). Interaction between neutral atoms and homopolar binding according to quantum mechanics. In *Quantum Chemistry: Classic Scientific Papers* (pp. 140-155).

[4] Wu, W., Su, P., Shaik, S., & Hiberty, P. C. (2011). Classical valence bond approach by modern methods. *Chemical Reviews*, *111*(11), 7557-7593.

[5] Dunning Jr, T. H., Xu, L. T., Cooper, D. L., & Karadakov, P. B. (2021). Spin-Coupled Generalized Valence Bond Theory: New Perspect i ves on the Electronic Structure of Molecules and Chemical Bonds. *The Journal of Physical Chemistry A*, *125*(10), 2021-2050.

[6] Mulliken, R. S. (1931). Bonding Power of Electrons and Theory of Valence. *Chemical Reviews*, *9*(3), 347-388.

[7] Roothaan, C. C. J. (1951). New developments in molecular orbital theory. *Reviews of modern physics*, *23*(2), 69.

[8] Edmiston, C., & Ruedenberg, K. (1963). Localized atomic and molecular orbitals. *Reviews of Modern Physics*, *35*(3), 457.

[9] Coulson, C. A. (1942). The dipole moment of the C—H bond. *Transactions of the Faraday Society*, *38*, 433-444.

[10] Lennard-Jones, J. E. (1949). Equivalent orbitals in molecules of known symmetry. *Proceedings of the Royal Society of London. Series A. Mathematical and Physical Sciences*, *198*(1052), 14-26.

[11] Hall, G. G., & Lennard-Jones, J. E. (1950). The molecular orbital theory of chemical valency. III. Properties of molecular orbitals. *Proceedings of the Royal Society of London. Series A. Mathematical and Physical Sciences*, *202*(1069), 155-165.

[12] Lennard-Jones, J. E., & Pople, J. A. (1950). The molecular orbital theory of chemical valency. IV. The significance of equivalent orbitals. *Proceedings of the Royal Society of London. Series A. Mathematical and Physical Sciences*, *202*(1069), 166-180.

[13] Ruedenberg, M. W. (1982). Schmidt, and MM Gilbert. *Chem. Phys*, *71*, 51.

[14] Frenking, G., & Shaik, S. (Eds.). (2014). *The chemical bond: fundamental aspects of chemical bonding*. John Wiley & Sons.

[15] Vogiatzis, K. D., Ma, D., Olsen, J., Gagliardi, L., & De Jong, W. A. (2017). Pushing configuration-interaction to the limit: Towards massively parallel MCSCF calculations. *The Journal of chemical physics*, *147*(18).

[16] Brabec, J., Brandejs, J., Kowalski, K., Xantheas, S., Legeza, Ö., & Veis, L. (2021). Massively parallel quantum chemical density matrix renormalization group method. *Journal of Computational Chemistry*, *42*(8), 534-544.

[17] West, A. C., Schmidt, M. W., Gordon, M. S., & Ruedenberg, K. (2015). A comprehensive analysis in terms of molecule-intrinsic, quasi-atomic orbitals. II. Strongly correlated MCSCF wave functions. *The Journal of Physical Chemistry A*, *119*(41), 10360-10367.

[18] Jackson, B. A., & Miliordos, E. (2022). The nature of supermolecular bonds: Investigating hydrocarbon linked beryllium solvated electron precursors. *The Journal of Chemical Physics*, *156*(19).

[19] Lucci, E., Giarrusso, S., Gigli, G., & Ciccioli, A. (2022). The AuSc, AuTi, and AuFe molecules: Determination of the bond energies by Knudsen effusion mass spectrometry experiments combined with ab initio calculations. *The Journal of Chemical Physics*, *157*(8).

[20] Mato, J., Tzeli, D., & Xantheas, S. S. (2022). The many-body expansion for metals. I. The alkaline earth metals Be, Mg, and Ca. *The Journal of Chemical Physics*, *157*(8).

[21] Simons, J. (2022). Do not forget the Rydberg orbitals. *The Journal of Chemical Physics*, *156*(10).

[22] Xu, L. T., & Dunning, T. H. (2022). Dynamical electron correlation and the chemical bond. I. Covalent bonds in AH and AF (A= B–F). *The Journal of Chemical Physics*, *157*(1).

[23] Sandoval-Pauker, C., & Pinter, B. (2022). Electronic structure analysis of copper photoredox catalysts using the quasi-restricted orbital approach. *The Journal of Chemical Physics*, *157*(7).

[24] Nakatani, K., Higashi, M., & Sato, H. (2022). Extraction of local spin-coupled states by second quantized operators. *The Journal of Chemical Physics*, *157*(1).

[25] Silvi, B., & Alikhani, E. (2022). Electron group localization in atoms and molecules. *The Journal of Chemical Physics*, *156*(24).

[26] Chakraborty, A., Yuwono, S. H., Deustua, J. E., Shen, J., & Piecuch, P. (2022). Benchmarking the semi-stochastic CC (P; Q) approach for singlet–triplet gaps in biradicals. *The Journal of Chemical Physics*, *157*(13).

[27] David, G., Ben Amor, N., Zeng, T., Suaud, N., Trinquier, G., & Malrieu, J. P. (2022). Difficulty of the evaluation of the barrier height of an open-shell transition state between closed shell minima: The case of small C4n rings. *The Journal of Chemical Physics*, *156*(22).

[28] Ebisawa, S., Tsutsumi, T., & Taketsugu, T. (2022). Extension of natural reaction orbital approach to multiconfigurational wavefunctions. *The Journal of Chemical Physics*, *157*(8).

[29] Zheng, P., Gan, Z., Zhou, C., Su, P., & Wu, W. (2022). λ-DFVB (U): A hybrid density functional valence bond method based on unpaired electron density. *The Journal of Chemical Physics*, *156*(20).