Chem Rep, 2025, 6(1): 325-330
DOI: 10.25082/CR.2025.01.003

RESEARCH ARTICLE

Clarifying Aromaticity and Delocalization with the Principle of π-Electron Pair Interaction (PEPI)

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Received: August 2, 2025;
Accepted: November 4, 2025;
Published: November 12, 2025.

Citation: Ji HF. Clarifying Aromaticity and Delocalization with the Principle of π-Electron Pair Interaction (PEPI). *Chem Rep*, 2025, **6**(1): 325-330. https://doi.org/10.25082/CR.2025.01.003

Abstract: Valence Bond (VB) theory and Molecular Orbital (MO) theory are foundational approaches to understanding chemical bonding. While MO theory describes delocalized orbitals across the molecule and offers quantitative rigor, VB theory aligns closely with classical chemical concepts, using localized bonds and hybridization for intuitive understanding. However, VB theory's treatment of delocalized systems, such as aromatic compounds, relies on resonance structures, which are less efficient and may cause misconceptions compared to the methodology of MO theory. To address this, the *Principle of π-Electron Pair Interaction* (PEPI) is introduced as a heuristic framework to extend the qualitative power of VB theory. A visual guide is provided by PEPI to aid in understanding when π-electrons may resist delocalization due to pairing constraints. The model is intended to complement MO theory and is presented not as a physical principle, but as an interpretive aid that offers clarity in systems such as butadiene, benzene, and selected pericyclic reactions. It is demonstrated how PEPI can illuminate concepts such as aromaticity, antiaromaticity, misinterpretations of resonance, and stereoelectronic trends in a conceptually accessible manner. PEPI proposes that electron spin should be taken into account when evaluating resonance structures, particularly in the context of aromaticity. By reframing PEPI as a pedagogical tool, alignment is achieved with quantum mechanical models while the intuitive appeal of VB theory is preserved.

Keywords: π-Electron Pair Interaction (PEPI), Valence Bond Theory (VB Theory), aromaticity, π-electron delocalization, heuristic model

1 Introduction

In chemistry, VB theory and MO theory are the two primary frameworks in quantum chemistry for the explanation of chemical bonding [1]. VB theory emphasizes localized bonding interactions and hybridization, making it useful for drawing analogies to Lewis structures and classical models [2–5]. However, it struggles to account for phenomena like aromaticity, where electron delocalization dominates [6–10]. In contrast, MO theory treats electrons as occupying delocalized orbitals across entire molecules and provides a more direct path to understanding aromatic stabilization, Hückel's 4n+2 rule, and bond equalization in aromatic compounds [11–13].

While VB theory has often represented aromatic systems using resonance structures, a chemical interpretation of VB theory with Pauling's resonance theory, this approach can create ambiguity—particularly when resonance forms appear equally valid for both aromatic and antiaromatic systems (Figure 1). To address this, PEPI is introduced as a pedagogical framework that uses the idea of electron pair interaction patterns to help interpret π-electron delocalization behavior.

2 Discussion

Before introducing the concept, it is necessary to briefly review several foundational concepts in VB theory. In VB, the concept of electron spin is crucial for understanding how atomic orbitals overlap to form covalent bonds [14]. Spin represents the intrinsic angular momentum of an electron, which generates a magnetic dipole moment [15]. Charge and spin are intrinsically linked, as all charged particles inherently possess spin. These two properties are fundamental to

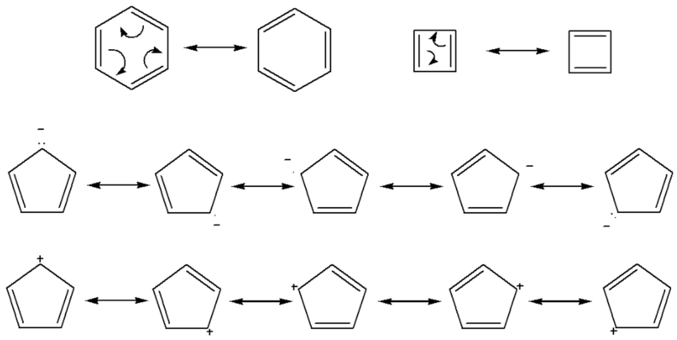

Figure 1 Examples of ring systems with both 4n and 4n+2 π electrons can be represented with resonance forms, incorrectly suggesting that both are stable.

the nature of electrons and naturally arise from the relativistic invariance of the wave equation. According to the Dirac equation, both charge and spin are essential characteristics that define the behavior of electrons [16].

Pauli exclusion principle states that two electrons cannot occupy the same quantum state within a system, so when forming a single bond between two atoms, two electrons will have opposite spins (one spin up and one spin down) [17]. There are three sets of forces in a bond: 1) Attraction forces between each electron with both nuclei of the bonded atoms. 2) Electrostatic repulsion between two electrons due to coulombic repulsion. 3) a much weaker magnetic attraction between two electrons due to the spin-spin attraction, i.e. the attraction between two opposite magnetic moments. The net result is an overall attractive force that holds the atoms together at a certain distance in a molecule. While electron spins are fundamentally a property of wave functions and its transformations can be described using Pauli matrices, electrons can be treated simply as tiny magnets due to their spin, or angular momentum, causing them to either attract or repel one another.

2.1 PEPI and Conjugation in Butadiene

In conjugated systems such as butadiene, delocalization is traditionally explained by MO theory as arising from constructive interactions of p orbitals across adjacent atoms, forming π-molecular orbitals. The highest occupied molecular orbital (HOMO) in butadiene (Figure 2 left) features a node between the central carbon atoms, and its electron density distribution explains the observed bond length alternation: shorter C1–C2 and C3–C4 bonds and a longer central C2–C3 bond.

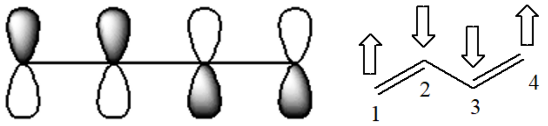

Figure 2 Left: the HOMO state of butadiene in MO theory. Right: Spin states of π-electrons in butadiene as suggested by PEPI. It is noteworthy that these symbolic arrows do not imply the presence of additional electrons when discussing the PEPI.

This node between the middle two carbons in butadiene suggests that the two adjacent electrons in the two π-electron pairs must have different spins, as dictated by the orbital phase relationships. As such, in the PEPI framework, this trend is interpreted qualitatively by assigning symbolic spin orientations to π-electron pairs. The idea is that adjacent π-electron pairs on neighboring carbons resist pairing if their spatial arrangement leads to same-spin interaction—which is depicted symbolically rather than representing actual spin polarization (Figure 2 right). According to this concept, the two π electrons adjacent to each other between two double bonds, i.e. between C2 and C3 in butadiene, exhibit the same spin. In other words, the spins of the electrons on the carbon atoms between two double bonds are not paired. This symbolic opposition mimics resistance to full delocalization, offering an intuitive way to explain why the central bond remains single-like, not double.

PEPI is supported by a key observation: if the spins of the adjacent electrons were opposite, they would likely pair or engage to form a double bond between the central two carbons, or the central bond would exhibit a stronger double-bond character like those in aromatic systems. However, experimental measurements of bond lengths and strengths indicate that this is not the case - the C=C double bond length in butadiene is approximately 1.338 Å, while the central

C-C single bond length is around 1.454 Å. This spin arrangement contrasts significantly with the patterns observed in aromatic (the C-C length in benzene is 1.39 Å) or resonance systems where the spins are opposite, as will be discussed in the next section.

However, I now explicitly clarify that this representation is pedagogical. Atoms in closed-shell ground states do not exhibit real spin polarization, and the PEPI diagram should not be taken as physically literal. Delocalization, as explained by MO theory, remains the more accurate quantum description, but PEPI provides a parallel interpretive lens grounded in VB-style reasoning.

2.2 PEPI and Aromaticity: Benzene and Cyclobutadiene

Aromaticity is most accurately described using MO theory, which explains that cyclic systems with (4n+2) π-electrons form completely filled bonding molecular orbitals, leading to exceptional stability. In contrast, 4n π-electron systems such as cyclobutadiene possess partially filled degenerate orbitals that result in antiaromatic instability.

While VB theory can represent both 4n+2 and 4n π-electron ring systems using resonance forms with alternating single and double bonds, this approach does not distinguish between aromatic and antiaromatic behavior. As a result, it may misleadingly suggest that both types of systems are similarly stabilized, which contradicts experimental observations and Hückel's rule.

PEPI provides an interpretive framework for visualizing how symbolic spin patterns influence delocalization in these systems (Figure 3). In benzene, the closed-loop conjugation results in symbolic electron pairings that cannot avoid pairing at multiple points, leading to complete delocalization and consistent with MO theory's prediction of equal bond lengths. In contrast, cyclobutadiene's electron arrangement—when interpreted with PEPI—leads to two unpaired spins in adjacent positions, symbolizing repulsive interactions that inhibit delocalization. These double repulsive forces significantly destabilize the system, making cyclobutadiene reactive so it dimerizes before it can be isolated. Consequently, the molecule exhibits antiaromatic behavior.

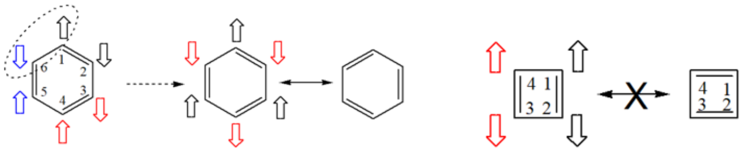

Figure 3 Effect of π-electron spins on the full delocalization of π-electrons in benzene and repulsion of two π-electron pairs in cyclobutadiene. In benzene, if the electrons were not delocalized and behaved like those in a conjugated alkene (e.g., π-electron pairs 1-2, 3-4, and 5-6), paring between π-electrons 6 and 1 cannot be avoided. In cyclobutadiene, electrons 2-3 and 4-1 remain unpaired, and consequently no resonance forms for cyclobutadiene.

Again, PEPI is not intended to replace the MO-derived understanding of aromaticity but to provide an intuitive, VB-aligned way of recognizing when delocalization may or may not be favored. It is a heuristic model used to support chemical reasoning in contexts where resonance structures may be misleading or ambiguous.

2.3 Misleading Resonance Interpretations: Cyclopentadienyl Systems

Certain systems like the cyclopentadienyl anion and cation are often presented in textbooks using resonance forms that may overstate their delocalization or stability. In MO theory, aromaticity in the cyclopentadienyl anion is understood to arise from the closed-shell (4n+2) π-electron configuration that fills the bonding orbitals. Conversely, the cyclopentadienyl cation, with 4 π-electrons, is antiaromatic due to its open-shell configuration and the resulting instability.

PEPI provides a heuristic visualization by examining potential pairing conflicts between electrons in the cyclic π-system (Figure 4). In the anion, symbolic pairing arrangements naturally lead to delocalization and resonance, which aligns with its aromatic nature. In the cation, any spin-like assignment across the ring produces a symbolic repulsion, consistent with its antiaromatic behavior, suggesting resonance forms cannot be applied to this type of molecules.

Again, this model is not proposed as a replacement for orbital-based reasoning. Rather, PEPI helps illustrate why resonance may be suppressed in some systems despite their apparent formal similarity to aromatic compounds.

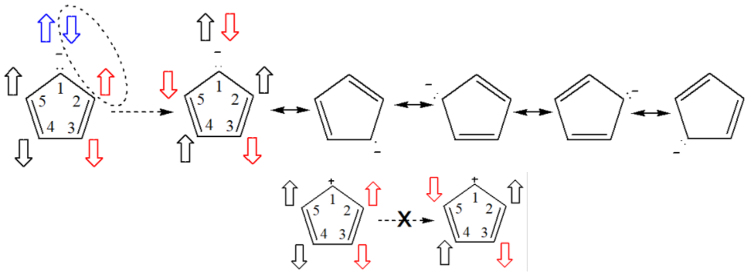

Figure 4 The misleading case of resonance forms in both cyclopentadienyl anion and cation. In cyclopentadienyl anion with six π-electrons, the two electrons in the p-orbital of C-1 would have opposite spins, if the electrons were not delocalized and behaved like those in a conjugated alkene, one of the two electrons on C-1 would inevitably pair with the electrons on either C-2 or C-5, resulting in the delocalization of all π-electrons across the anion and five resonance forms. In contrast, for the cyclopentadienyl cation with four π-electrons, the electrons on C-2 and C-5 have the same spin. As a result, they remain unpaired, leading to repulsive interactions rather than delocalization of π-electrons.

The same analysis applies to the cycloheptatrienyl cation/anion, polycyclic aromatic hydrocarbons (PAHs), and all the 2D aromatic/antiaromatic molecules I have tested, without exception, highlighting the significance of spin pairing in determining aromatic and antiaromatic character.

2.4 PEPI for Diels-Alder (DA) Reactions

Beyond explaining delocalization, PEPI can be effectively utilized to account for the regioselectivity of Diels-Alder (DA) reactions.

Diels–Alder reactions are well-described by the Woodward–Hoffmann rules and frontier molecular orbital (FMO) theory, which account for the symmetry and phase relationships of interacting orbitals during concerted bond transformations. DA reaction is a thermally allowed [4+2] cycloaddition. In the dienophile, the electrons are located near the electron-withdrawing group (W), making the carbon farther from the W group partially positive (δ+) and the carbon with the W group partially negative (δ-). The spin states of the pi-electrons of both diene and dienophile are illustrated in Figure 5.

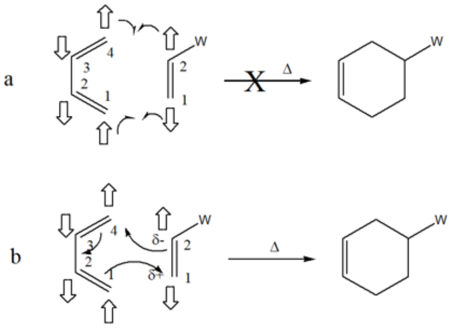

Figure 5 The reaction mechanism of Diels-Alder (DA) reaction with PEPI

The prevailing view on DA reactions is that they proceed as polar reactions via a concerted mechanism [18, 19], rather than as radical reactions [20]. Consequently, mechanism *a* in Figure 5 is incorrect, indicating that matching the frontier electron spins between C1 of the diene and C1 of the dienophile, and between C4 of the diene and C2 of the dienophile, is not required.

In the polar reaction mechanism (Figure 5b), the electron density on C1 and C2 of the dienophile suggests they play different roles. The partially positive (δ+) C1 carbon in the dienophile acts as an electron acceptor, attracting electrons from the diene, while the C2 carbon (δ-) in the dienophile functions as an electron donor, pushing away electrons on the diene. The opposite spin alignment between C1 in the dienophile and C1 in the diene enhances this attraction, while the same spin alignment between C2 in the dienophile and C4 in the diene facilitates the electron-pushing process, completing the reaction. This mechanism can be described as a “push-pull” process, where electron movement between the diene and dienophile enables the simultaneous formation of two bonds.

For DA reactions, PEPI’s symbolic scheme of ‘push–pull’ spin alignment mimics the electron density shifts predicted by FMO theory. However, these depictions are not rigorous representations of electronic spin or wavefunction behavior and should not replace orbital analyses. Instead, PEPI offers an accessible way to visualize regio- and stereoselectivity in pericyclic reactions from a VB-style perspective.

This model is heuristic, intended to support intuition rather than predict reactivity quantitatively. The frontier orbital theory uses the interaction between the HOMO of one molecule and LUMO of another to explain selectivity.[7] In contrast, PEPI avoids involving the LUMO state of molecules in its explanation.

3 Conclusion

This work introduces the PEPI as a conceptual tool that complements traditional VB theory in interpreting π-electron behavior in conjugated systems. Rather than proposing a new physical model, PEPI offers a symbolic and intuitive framework for visualizing when and how π-electrons may favor or resist delocalization based on qualitative interaction patterns. By applying PEPI to classical systems such as butadiene, benzene, cyclobutadiene, and select pericyclic reactions, its utility is demonstrated in rationalizing patterns of aromaticity, misleading in resonance forms, bond alternation, and stereoelectronic effects.

Importantly, PEPI is presented as a heuristic aid rather than a substitute for MO theory or rigorous quantum chemical methods. Integrating the PEPI principle enhances VB theory's power while maintaining its simplicity and compatibility with chemical intuition. It is most effective in an educational context, where it can help bridge the gap between resonance structures and the underlying electronic phenomena they attempt to represent. Future work may explore computational or pedagogical validation of PEPI's effectiveness in teaching and interpreting aromaticity, particularly in introductory organic and physical chemistry settings.

Conflicts of Interest

The author declares no conflict of interest.

References

[1] Murrell JN, Kettle SFA, Tedder JM. The Chemical Bond (2nd ed.). 1985. John Wiley & Sons. ISBN 0-471-90759-6.

[2] Xu LT, Cooper DL, Dunning TH. Resolving a puzzling anomaly in the spin-coupled generalized valence bond description of benzene. Journal of Computational Chemistry. 2020, 41(15): 1421-1426. https://doi.org/10.1002/jcc.26185

[3] Xu LT, Dunning TH. Orbital Hybridization in Modern Valence Bond Wave Functions: Methane, Ethylene, and Acetylene. The Journal of Physical Chemistry A. 2019, 124(1): 204-214. https://doi.org/10.1021/acs.jpca.9b11054

[4] Radenković S, Danovich D, Shaik S, et al. The nature of bonding in metal-metal singly bonded coinage metal dimers: Cu_2, Ag_2 and Au_2. Computational and Theoretical Chemistry. 2017, 1116: 195-201.

[5] Shaik S, Danovich D, Galbraith JM, et al. Charge-Shift Bonding: A New and Unique Form of Bonding. Angewandte Chemie International Edition. 2019, 59(3): 984-1001. https://doi.org/10.1002/anie.201910085

[6] Bury CR. Langmuir's Theory of the Arrangement of Electrons in Atoms and Molecules. Journal of the American Chemical Society. 1921, 43(7): 1602-1609. https://doi.org/10.1021/ja01440a023

[7] Cooper DL, Gerratt J, Raimondi M. The electronic structure of the benzene molecule. Nature. 1986, 323(6090): 699-701. https://doi.org/10.1038/323699a0

[8] Vemulapalli GK. Theories of the chemical bond and its true nature. Foundations of Chemistry. 2008, 10(3): 167-176. https://doi.org/10.1007/s10698-008-9049-2

[9] Shurki A, Hiberty PC, Dijkstra F, et al. Aromaticity and antiaromaticity: what role do ionic configurations play in delocalization and induction of magnetic properties? Journal of Physical Organic Chemistry. 2003, 16(10): 731-745. https://doi.org/10.1002/poc.658

[10] Karadakov PB, Cooper DL, Gerratt J. Modern Valence-Bond Description of Chemical Reaction Mechanisms: Diels-Alder Reaction. Journal of the American Chemical Society. 1998, 120(16):

3975-3981.
https://doi.org/10.1021/ja9741741

[11] Shaik S, Danovich D, Hiberty PC. Valence Bond Theory-Its Birth, Struggles with Molecular Orbital Theory, Its Present State and Future Prospects. Molecules. 2021, 26(6): 1624.
https://doi.org/10.3390/molecules26061624

[12] Woodward RB, Hoffmann R. The Conservation of Orbital Symmetry. Angewandte Chemie International Edition in English. 1969, 8(11): 781-853.
https://doi.org/10.1002/anie.196907811

[13] Fukui K, Yonezawa T, Shingu H. A molecular orbital theory of reactivity in aromatic hydrocarbons. The Journal of Chemical Physics. 1952, 20(4): 722-725.

[14] Dunning TH, Xu LT, Cooper DL, et al. Spin-Coupled Generalized Valence Bond Theory: New Perspectives on the Electronic Structure of Molecules and Chemical Bonds. The Journal of Physical Chemistry A. 2021, 125(10): 2021-2050.
https://doi.org/10.1021/acs.jpca.0c10472

[15] Eisberg R, Resnick R. Quantum Physics of Atoms, Molecules, Solids, Nuclei, and Particles (2nd ed.). 1985. Wiley. pp. 272–273.

[16] Gorbar EV, Miranskij VA, Shovkovy IA, et al. Electronic Properties of Dirac and Weyl Semimetals. 2021, World Scientific Publishing.

[17] Krane KS. Introductory Nuclear Physics. Wiley. 1987. ISBN 978-0-471-80553-3.

[18] Houk KN, Lin YTsong, Brown FK. Evidence for the concerted mechanism of the Diels-Alder reaction of butadiene with ethylene. Journal of the American Chemical Society. 1986, 108(3): 554-556.
https://doi.org/10.1021/ja00263a059

[19] Goldstein E, Beno B, Houk KN. Density Functional Theory Prediction of the Relative Energies and Isotope Effects for the Concerted and Stepwise Mechanisms of the Diels-Alder Reaction of Butadiene and Ethylene. Journal of the American Chemical Society. 1996, 118(25): 6036-6043.
https://doi.org/10.1021/ja9601494

[20] Dewar MJS, Olivella Santiago, Stewart JJP. Mechanism of the Diels-Alder reaction: reactions of butadiene with ethylene and cyanoethylenes. Journal of the American Chemical Society. 1986, 108(19): 5771-5779.
https://doi.org/10.1021/ja00279a018