Pauling's Defence of Bent-Equivalent Bonds: A View of Evolving Explanatory Demands in Modern Chemistry

Summary

Linus Pauling played a key role in creating valence-bond theory, one of two competing theories of the chemical bond that appeared in the first half of the 20th century. While the chemical community preferred his theory over molecular-orbital theory for a number of years, valence-bond theory began to fall into disuse during the 1950s. This shift in the chemical community's perception of Pauling's theory motivated Pauling to defend the theory, and he did so in a peculiar way. Rather than publishing a defence of the full theory in leading journals of the day, Pauling published a defence of a particular model of the double bond predicted by the theory in a revised edition of his famous textbook, *The Nature of the Chemical Bond*. This paper explores that peculiar choice by considering both the circumstances that brought about the defence and the mathematical apparatus Pauling employed, using new discoveries from the Ava Helen and Linus Pauling Papers archive.

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Word Count: 8658 (9936 with footnotes)

1. Introduction

The problem of modelling the structure of molecules has tortured chemists from the 19th century to the present day. In the first half of the 20th century, two theories of how to model chemical bonds had emerged in response to quantum mechanics' revelations about the behaviour of electrons. The valence-bond theory, championed by Linus Pauling, experienced a decline in prominence over the second half of the century as the molecular-orbital theory rose to the fore. Pauling's theory was on the verge of becoming a historical artefact in 1960, when he was in the midst of revising his famous textbook, *The Nature of the Chemical Bond*. This is the story of what motivated Pauling to defend his theory and how that defence arose.

The third edition of Linus Pauling's famous textbook, *The Nature of the Chemical Bond*, contains a rarity among textbooks: an *apologia* for a then-nearly-dead idea. In it, Pauling argues that double bonds are 'bent equivalent,' or that the probability distribution of electrons in the bonds spreads evenly between two arcs rather than unequally between three, as the molecular-orbital approach's σ-π model of the double bond suggests.[1] Pauling put forth this conception of the structure of the double bond early in his career and stuck by it throughout his lifetime, even after the σ-π bond became the standard model. But he did not defend it in print until late in his career.

The aim of this essay is to uncover why Pauling's defence of the bent-equivalent model of the double bond occurred when it did, rather than earlier or not at all. The timing of Pauling's defence reflects, among other things, changes that occurred in the way chemistry was taught in the decades between Pauling's original work on valence-bond theory in the early 1930s and his rally behind bent-equivalent bonds in the late 1950s. In defending bent-equivalent bonds when he did, Pauling is responding to changing explanatory needs in the chemical community and attempting to change the scientific public's perception of his brand of chemistry.

At present, there is little historical work on Pauling's structural quantum chemistry or his work in chemical education, despite the proliferation of biographies and scholarly articles on his work in biochemistry and anti-nuclear activism.[2] There are of course exceptions,[3] but this work makes no explicit mention of Pauling's defence of bent-equivalent bonds. Likewise, a handful of more contemporary articles from the chemical and chemical-education literature have addressed the question of whether double bonds

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[1] Linus Pauling *The Nature of the Chemical Bond and the Structure of Molecules and Crystals; An Introduction to Modern Structural Chemistry*. 3 edn (Ithaca: Cornell University Press, 1960), pp. 136-142

[2] e.g. Thomas Hager, *Force of Nature: The Life of Linus Pauling*. (Simon & Schuster, 1995); Clifford Mead and Thomas Hager, *Linus Pauling: Scientist and Peacemaker*. (Oregon State University Press, 2001); Anthony Serafini, *Linus Pauling: A Man and His Science*. (Paragon House Publishers, 1991); Keith Manchester, 'Linus Pauling and Biochemistry: How Things were Shaping Up 50 Years Ago'. *South African Journal of Science* 95 (1999): 5-7

[3] e.g. Robert Paradowski, *The Structural Chemistry of Linus Pauling*. (Madison, WI: Ph. D. Dissertation, University of Wisconsin, 1972); Buhm Soon Park, 'Chemical Translators: Pauling, Wheland and Their Strategies for Teaching the Theory of Resonance'. *British Journal for the History of Science* 32 (1999): 21-46; Ana Simões, 'Chemical Physics and Quantum Chemistry in the Twentieth-Century', in Mary Jo Nye (ed.), *Modern Physical and Mathematical Sciences* (Cambridge: Cambridge University Press, 2003, vol.5 Cambridge History of Science Series), pp. 394-412; Martha L. Harris, 'Chemical Reductionism Revisited: Lewis, Pauling and the Physico-Chemical Nature of the Chemical Bond'. *Studies in History and Philosophy of Science Part A* 39, no. 1 (2008):78-90.

are better modelled as bent-equivalent bonds than σ-π bonds for explanatory purposes,[4] but none aim to reconstruct Pauling's own arguments or assess the historical context of the two models.

After familiarising the reader with the technical language used in this article in Section 2, I offer an overview of the changes Pauling made to his explanation of double bonds in his textbook between 1940 and 1960 (Section 3). In Section 4, I demonstrate that Pauling could have published a defence of the bent-equivalent double bond much earlier in his career, but that without pressure from the chemical community to do so, no such early defence was made public.

Section 5 demonstrates that three largely unrelated circumstances, uncovered in the archives of the Ava Helen and Linus Pauling Papers (hereafter Pauling Papers), brought the problem of modelling the double bond to Pauling's attention in the late 1950s. The first circumstance, namely the rise of molecular-orbital theory, provided Pauling with a motivation to defend the bent-equivalent model. The latter two clued him in to a means of mounting the defence and offered a ready forum for the dissemination of his results. Section 6 contains a reconstruction of the defence itself, and in Section 7 I argue that through the lens of the story of Pauling's defence, it is possible to gain a richer understanding of the shifting explanatory needs of the chemical community during the middle of the 20th century.

2. Using valence bonds and molecular orbitals to explain the double bond

The double-bond models of concern in this paper arise from two general theoretical models of the chemical bond that arose in the wake of the quantum revolution, namely valence-bond (VB) theory and molecular-orbital (MO) theory.[5] Early VB theory is most closely associated with the work of Heitler, London, Slater, and Pauling, and early MO theory with Hund, Mulliken, and Hückel. This section provides an overview of the conceptual differences between the theories and an introduction to the ways that each theory may represent double bonds. For a thorough overview of the development of these models, readers are advised to see Nye, Shaik and Hiberty, or any number of excellent historical articles.[6] Readers who are familiar with VB and MO are advised to skip to the closing paragraph of the section.

Both VB and MO aim to predict the behaviour of electrons in bonds by using quantum-mechanical results about the nature of electrons, specifically the Schrödinger equation. The Schrödinger equation, which can be used to describe the behaviour of an electron of a specific energy given information about other particles in the system, is mathematically intractable for most systems of chemical interest. VB and MO

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[4]   e.g. Palke William E., 'Double Bonds are Bent Equivalent Hybrid (Banana) Bonds'. *Journal of the American Chemical Society* 108, no. 21 (1986): 6543–6544; Peter Schultz and Richard Messmer, 'The Nature of Multiple Bonds'. *Journal of the American Chemical Society* 115 (1993): 10925–10937; and Kenneth Wiberg, 'Bent Bonds in Organic Compounds'. *Accounts of Chemical Research* 29, no. 5 (1996): 229–234

[5]   I use "theory" and "model" interchangeably in this paper, reflecting chemists' own tendencies to do so in discussing molecular orbitals and valence bonds, and with due apologies to the philosophical literature's careful investigations of the difference between the concepts associated with each term.

[6]   Mary Jo Nye, *Before Big Science: The Pursuit of Modern Chemistry and Physics*, 1800-1940. (Cambridge: Harvard University Press, 1999); Sason Shaik and Phillippe Hiberty, *A Chemist's Guide to Valence Bond Theory*. (Hoboken, NJ: Wiley Interscience, 2008)

approximate the Schrödinger equation using various mathematically- and empirically-derived shortcuts. They differ from one another in the ways they go about their approximations, although both make heavy use of group theory, and the models are sometimes empirically distinguishable.

The models also differ conceptually, as a result of the different interests and backgrounds of the researchers who developed the models. MO was born out of primarily physical interests and considers the electron as spread out over the entire system of atomic centres in a molecule. VB was born out of primarily chemical interests and considers the electron as localized to a defined range of atomic centres. VB retains many of the notions associated with G.N. Lewis' classical valence theory of chemical bonding, notably the idea that one electron from each atomic centre forms the electron-pair in a standard covalent bond. This latter idea appears as a restriction in the formalism of VB theory that is absent in MO theory.

Such conceptual differences are reflected in differences in the formalisms used by each model. Each formalism is twofold, composed of both mathematical approximations of the Schrödinger equation and of associated conceptual schema, in which the models define and depict patterns of electron movement called *orbitals*. The orbital schema represent the mathematical formalisms, and the two aspects of the formalisms interact closely.

The formalisms adopt different but related notations for electronic orbitals, or shapes of electron probability distribution curves, which will be referred to throughout this paper. Both models refer to the standard hierarchy of shapes of *atomic orbitals* as s, p, d, f, and both may refer to *molecular orbitals* associated with each shape as σ, π, ∂, etc., although MO makes heavier use of molecular orbitals than VB does. Each orbital is associated with a particular quantized electronic energy level, and pairs[7] of orbitals can exist at the same level in a given system. Pairs of multiples of this sort are called *degenerate*, and components of a pair of degenerate orbitals are sometimes distinguished from one another by adding a + or – superscript to the orbital.

For complex molecules, such as those that form double bonds, combinations of molecular orbitals are given to denote the total electron probability distribution over the system. MO arrives at these system-level distributions by simple combinations of the component molecular orbitals (whence originates the 'σ-π' terminology for double bonds described in MO models), whereas in VB, system-level distributions are given by weighted linear combinations of atomic orbitals, resulting in *hybrid orbitals*. Hybrid orbitals play a central role in Pauling's bonding theory — in particular the tetrahedral or sp^3 orbital, so named because it combines one s orbital and three p orbitals into four equivalent orbitals pointed at the four corners of a tetrahedron (see figure 2a below). The use of hybrid atomic orbitals rather than combinations of molecular orbitals marks the chief difference between the bent-equivalent bond (hereafter BEB) model from the σ-π model, and VB from MO more generally.

The formal differences give rise to different predictions of the system-level distribution of electron probability around a double bond. The distribution prediction by BEB (see figure 1, top) is of two arcs of equal size and density (i.e., two equivalently bent arcs, hence 'bent-equivalent') situated at 180º to one another and seated,

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[7]   It is possible to have larger sets of degenerate orbitals than just pairs, but they will not be discussed in this paper.

respectively, above and below the axis connecting the atomic centres. The arcs are curved at angles that resemble the curvature of a typical banana, suggesting the model's alternate name, the 'banana bond.' This distribution is markedly different from that predicted by the σ-π model, which proposes a dense core of electron density around the internuclear axis, surrounded by two lower-density arcs on either side (see figure 1, bottom).

In sum, MO and VB share a common conception that the Schrödinger equation governs the behaviour of electrons in molecules, and both acknowledge that solving the equation directly is computationally intractable for systems larger than a very few electrons, i.e. nearly all systems that are of chemical interest. The models offer differing conceptual and quantitative means of approximation, and the resulting differences in their systems of equations and orbital schema lead to different predictions about the expected shape of the electronic probability distribution, or structure, of a typical double bond.

One of the key concepts of Pauling's VB theory, which has no direct parallel in MO theory, is the concept of *resonance*. Resonance, or mesomerism, is often described conceptually as the oscillation between two or more degenerate quantum states, although chemistry students are often cautioned not to take this classical analogy too seriously. Resonance is represented diagrammatically by means of *contributing molecular structures*, similarly to VB's conception of overall bond structures in molecules in terms of contributing orbitals. In each case, combining component structures produces a hybrid structure that is considered to be the best overall representation of the bond structure of the system.

In terms of the formalism of VB, resonance offers a means of representing delocalized electrons and connected the phenomenon of delocalization to predicted or observed lowering of the overall energy of the bonds in a given system. The formalism of MO can represent delocalized electrons directly in its mathematical structure, but at the expense of the conceptual aid of resonance structures built out of their component contributing molecular structures. The role of resonance in Pauling's theory, and in the lead-up to his defence of BEB, is discussed at more length in Section 5.1.

Pauling's defence is ultimately a defence of the prediction of one formalism over the prediction of another. The formalisms themselves can provide some rationale for why a particular structure is expected or preferred, but arguing from the formalism alone is useless against an opponent who has other reasons for preferring the alternative formalism. So the defence is also a rationale for the use of the formalism of VB in the case of modelling double bonds, and as such it meets a demand for an explanation of why one formalism should be preferred in a given setting. As will be shown in the following sections, this is not a demand that students of chemistry would be expected to make in the early days of Pauling's work in theoretical structural chemistry, but it is one that students could conceivably make in the 1960s. This difference in expected explanatory demands provides a rationale for the timing of the defence's publication.

3. Textbook explanations

In 1938, Pauling gathered his principles and theories into a textbook entitled *The Nature of the Chemical Bond* (hereafter *NCB*). Many universities took up the book as a standard text for chemistry students,[8] and it remains a classic. In 1940 a second edition of the book appeared, largely because constraints imposed by Pauling's initial contract had

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[8]   Hager op. cit., p. 218

prevented him from collecting royalties on the first edition.[9] This edition changed very little from the first edition. The third and final[10] edition of the book, which contains substantial revisions, did not appear until 1960. In the first two editions of *NCB*, Pauling has little to say about the various models of double bond structure, except to point out that two existed and he believed his was the better. The whole double-bond section of these editions occupies less than one full page of the text, in which he writes:

> No general discussion of the orbitals involved in multiple-bond formation analogous to that just described for single bonds has been given... It seems probable that the orbitals involved in double-bond formation by a carbon atom in a molecule such as ethylene are of the following type.[11]

He then goes on to describe how two bond orbitals will be involved in the formation of the double bond, noting that the first will lie in the plane of the molecule and the second, 'with lobes extending above and below the plane of the molecule, is then involved in the formation of the second half of the double bond'.[12] He does not elaborate on the nature of this involvement.

By contrast, in the third edition, Pauling spends seven pages discussing the structure of the double bond. He introduces both the BEB and the σ-π model, summarising the views and giving contrasting diagrams (see figure 1 above):

> There are two alternative ways in which these orbitals have usually been described. In the first, the two orbitals for each atom have been assumed to be essentially tetrahedral orbitals… This leads to a description of the double bond, as involving two bent single bonds. … The other description of the double bond is in terms of a σ bond, formed by a σ orbital for each atom directed toward the other atom, and a π bond, formed by a π orbital for each atom… When the quantum mechanical equations are examined it is found that the two descriptions of the double bond are identical in the molecular-orbital treatment based on *s-p* hybrids. They are not identical in the valence-bond treatment, especially when the bond orbitals are concentrated about their bond directions by the assumption of *d* and *f* character… The greater separation of the electrons for the bent-bond structure with concentrated bond orbitals than for the σ-π structure may stabilize the bent-bond structure enough to make it the better approximation to use in discussing multiple bonds in general. In addition, it has the advantage of being more closely related to single bonds, whose properties are well known.[13]

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[9] Paradowski op. cit., p. 492

[10] Notes and publishers' contracts for a fourth edition of the book are available in the Pauling Papers, Boxes 5.004.12-5.004.16, but Pauling never put together manuscripts for a fourth edition. There are few notes on the section on double bonds in the suggested revisions for the fourth edition, excepting some notes in the margins of the section on double bonds to expand the section on restricted rotation. This only strengthens my argument, which we will see in Section 5.2, that it was thinking about restricted rotation that led Pauling to mount his defence of the BEB model.

[11] Linus Pauling, *The Nature of the Chemical Bond and the Structure of Molecules and Crystals. An Introduction to Modern Structural Chemistry*. 2 edn (Ithaca: Cornell University Press, 1940), p. 89

[12] Ibid., pp. 89-90

[13] Pauling 1960, pp. 136-138

In the section, Pauling makes five distinct arguments in defence of the BEB model: 1) Greater separation of bond orbitals increases stability, 2) Similarity to single bonds provides a cleaner *aufbau* of bonding properties, 3) BEB rationalises observed bond lengths in a way that σ-π cannot, 4) BEB rationalises some bond angles that σ-π cannot, and 5) BEB rationalises observed potential barriers to internal rotation and σ-π cannot.

Notice that the aim of each of these arguments is to provide a rationale, an explanation, for preferring BEB to σ-π, suggesting that Pauling has recognized an explanatory demand that needs to be met. Because Pauling's bonding model was the dominant one during the publication of the first edition of *NCB*, no such explanatory demand existed. In Section 5, I describe changes in the chemical community's dominant means of explaining bonding phenomena that occurred between the publication of the first and the third editions of *NCB*. These changes gave rise to the explanatory demand Pauling appears to have felt in the late 1950s, and so they provided a motivation for the publication of the defence. In the following section, I describe Pauling's double-bond model in more depth before laying out the circumstances that brought Pauling's attention back to the phenomenon of *concentration of bond orbitals*, which provided the means for making the latter three arguments that comprise the defence.

4. The origins of bent-equivalent bonds

Pauling was one of the first chemists to attempt a quantum theory of the chemical bond. In the early 20th century, chemists had observed that carbon has four tetrahedral bond sites; that is, that atoms bonding with carbon did so in groups of no more than four and were spaced about 109º apart from one another. This observation conflicted with early quantum mechanics, which predicted that carbon would bond with two other atoms strongly and two more weakly, at differing angles. Pauling's famous 1931 paper, 'On the Nature of the Chemical Bond,' resolved the conflict, providing a quantum-mechanical basis for the tetrahedral bonding behaviour of carbon.

In the 1931 paper, Pauling proposes the hybrid bond orbital model that is the hallmark of his approach to bonding. As discussed in Section 2, hybrid orbitals describe probability distributions for electrons by combining the wavefunctions for electrons in principled proportions. Hybrid orbitals provide a quantum-mechanically sound explanation of the observed tetrahedral bonding behaviour of carbon.

Carbon's tetrahedral bonding behaviour is crucial to the story of Pauling's conception of the structure of the double bond. Using hybridized orbitals, Pauling argues that carbon's bonding behaviour is analogous to the meeting of tetrahedra at their corners. The single bond is described by the joining of one pair of corners. Pauling then explains the double bond as the joining of two pairs of corners. He makes this picture evident in 1931 (see figure 2), solidifying the BEB model early on in his thinking about the nature of the double bond.

4.1 An early defence

A set of notes in the Pauling Papers form an early defence of BEB against the double-bond model of MO advocate Robert Mulliken. The notes are Pauling's handwritten reflections on a manuscript version of a paper by Mulliken, later published as 'Electronic Structures of Polyatomic Molecules and Valence II. General Considerations'.

Pauling's copy of the manuscript is lost, but the fact that he refers to different pagination than that in the printed version confirms he was reviewing a manuscript, and it dates the notes around early 1932. In the published paper, Mulliken lays out a general outline of MO theory and attacks VB theory, criticising VB as being less widely applicable[14] and more mathematically complex[15] than his MO theory. The paper also comments on VB's and MO's respective formulations of the structure of the double bond, and this is section Pauling comments on in the notes currently under consideration.

The prize of the notes is a series of figures Pauling draws to represent the difference between the BEB model of the structure of the double bond in O_2 and the structure Mulliken is proposing in the manuscript. Pauling draws a representation of O_2's bonding structure according to instructions given in Mulliken's manuscript[16] as well as the state as described by valence bond theory. The first picture (see figure 3, top) depicts three orbital lobes on each nucleus, one each in the axis of the bond on the far side of the bond to represent the lone pairs in O_2 and two each to represent a π molecular orbital perpendicular to the bond axis. Between the nuclei are wave drawings to represent the antisymmetric $\pi+$ and $\pi-$ orbitals Mulliken describes, as well as the electrons comprising the σ bond. A note beside the picture reads, 'Pretty good explanation of $^3\Sigma$ for O_2, but it may not be the whole story'. The '$^3\Sigma$' notation here is archaic notation for the expected distribution of molecular orbitals in the O_2 bonds.

Immediately below this picture appears another (see figure 3, bottom), labelled 'Better,' in which there is no depiction of the π orbitals but rather a series of wave drawings depicting the occupancies of different energy levels by different electrons and electron pairs, and beside it a primitive molecular orbital diagram assigning electrons to different orbitals. The molecular orbital diagram is labelled 'Quite arbitrary,' and a note at the bottom of the series reads 'But $^1\Sigma$ is O.K. unless we know sign of res. int. [resonance integral]', which indicates that Pauling is questioning even the basic distribution of molecular orbitals in O_2 proposed in Mulliken's paper.

The moral here is that Pauling is clearly trying to engage with molecular orbital theory here by following Mulliken's diagram and attempting to connect it to other parts of the nascent theory—the 'resonance integral' to which he refers was an artefact from Erich Hückel's earlier molecular orbital theory[17] that Pauling must have picked up on during his investigation of this method. But here too is an early rejection of the σ-π picture of the double bond: Pauling is unsatisfied with the σ-π picture in general, even if he considers it adequate for O_2, and he is finding reasons to reject it. His comment about the arbitrariness of the molecular-orbital assignment in his second picture indicates that he did not find it to be a satisfying alternative. Even this early in the development of the theory, Pauling is concerned with the ability of a model to provide a explanatory rationale for the structure of a bond.

Later in these notes, we see what may be the first depiction of BEB's hybrid bond orbitals themselves — the overlapping loops representing the regions where electrons can

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[14] Robert Mulliken, 'Electronic Structures of Polyatomic Molecules and Valence. II. General Considerations'. *Physical Review* 41, no. 1 (1932), p. 55

[15] Ibid., pp. 55-56

[16] Ibid., p. 55

[17] Erich Hückel, 'Zur Quantentheorie der Doppelbindung'. *Zeitschrift für Physik A: Hadrons and Nuclei* 60, no. 7 (1930): 423–456

be expected to be found (see figure 4). The notes demonstrate that Pauling is continuing to work through Mulliken's manuscript and comes to the section where Mulliken treats the dinitrogen ion, N_2^+.[18] Pauling again draws a version of a molecular-orbital diagram per Mulliken's description in his paper, depicting different waves, signifying how many electrons are on each and labelling each wave as one of the molecule's orbitals. But above this diagram he draws a counterpart that he labels 'my picture'. In it, three tetrahedral lobes from each nucleus join and the fourth lobe on each nucleus sticks out on the outside of the bond. This depiction of tetrahedral hybrid orbitals forming a triple bond may be the first diagram of a BEB structure on record, and so marks a development in the conceptual formalism of VB.

Pauling's notes are never assembled for publication, likely because Pauling felt no pressure to meet an explanatory demand in the chemical community at the time. Mulliken's work appeared in physics journals, and so the chemists to whom Pauling's articles were directed were largely unaware of Mulliken's approach — MO was still squarely in the domain of physics. Additionally, MO's empirical predictions were not as accurate as those of Pauling's method in 1932. Finally, Pauling had other publications to tend to, as well as teaching and supervision duties and the birth of his second son. Publishing a comparison of his and MO theory's views of the double bond may simply not have been worth his time. But these notes on Mulliken's paper demonstrate that Pauling was clearly thinking about the comparison at this stage in his career. He was beginning to see that MO theory would paint a picture of the double bond that contrasted with his own, and early on he was seeking methods to justify the use of his picture over the alternative, should he ever need to do so.

5. Catalysing the mature defence

When Pauling first published *NCB*, his VB model was at least as widely used as MO theory. Between the second and third editions of the book, however, MO theory gained popularity for the relative ease of calculation offered by its quantitative formalism, especially when applied to large organic molecules. Mulliken and others refined MO during the 1930s, and it acquired a number of followers in both physics and chemistry. These refinements, combined with increased interest in modelling organic compounds, brought MO to the forefront of many chemists' attention.

In the late 1940s, MO found a whole new range of uses. British chemists including Coulson and Longuet-Higgins[19] and Lennard-Jones[20] extended its application by developing an MO-based method known as a *generalized perturbation model*, which improved their ability to describe bonds in large organic compounds such as the particularly difficult-to-model conjugated bonds in aromatic compounds. The method

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[18] Mulliken 1932, p. 63

[19] Charles Coulson and Hugh Longuet-Higgins, 'The Electronic Structure of Conjugated Systems. I. General Theory'. *Proceedings of the Royal Society A: Mathematical, Physical and Engineering Sciences* 191, no. 1024 (1947): 39–60

[20] John Lennard-Jones, 'The Molecular Orbital Theory of Chemical Valency. I. The Determination of Molecular Orbitals'. *Proceedings of the Royal Society A: Mathematical, Physical and Engineering Sciences* 198, no. 1052 (1949): 1–13

was predictively accurate and its mathematics were simpler than either the early MO models of Mulliken et al. or the VB model.[21]

In the late 1940s and early 1950s, increased funding for organic and biological research had already piqued interest in organic chemistry, and the race to uncover the structure of DNA had begun.[22] In light of this culture of chemical interest in organic compounds, many chemists seized upon MO's new and relatively user-friendly method of making quantitative predictions of bond energies and lengths in organic compounds. So MO became the dominant model used in chemical research throughout the 1950s.

In the wake of all this excitement over MO, Pauling's VB theory received some criticism from the scientific community. While physicists and chemists publishing at the time did acknowledge that both the VB and MO 'have their own merits,'[23] the merits of MO were being hyped more frequently and more aggressively. For instance, consider the following passages from articles written between 1948 and 1955:

> The molecular orbital method has the merit of being more fundamental in its approach.[24]

> It is not surprising that [the valence-bond] approach is a particularly attractive one from the point of view of the chemist; but it is rather less pleasing from a mathematical standpoint, and even the simplest molecules have so far resisted any really satisfactory treatment along these lines.[25]

> The semiempirical LCAO MO method constitutes a very useful tool in investigation of molecular structure, and it may be considered as the next stage of evolution after Pauling's resonance theory.[26]

This new prominence of MO provided some motivation for Pauling to defend VB against increasing criticism, for he was never hesitant to defend ideas that he thought were good even when the scientific community was taking another direction — just consider his adamant advocacy of the miraculous benefits of Vitamin C throughout his late career. In the early 1930s, Pauling's model was clearly the most widespread among chemists. Back then, defending it against attacks from the MO camp, such as the one in the 1932 paper of Mulliken's from the previous section, was not a worthwhile project. But the scene had changed by the early 1950s.

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[21] John Pople, 'Molecular Orbital Perturbation Theory. I. A Perturbation Method Based on Self-Consistent Orbitals'. *Proceedings of the Royal Society A: Mathematical, Physical and Engineering Sciences* 233, no. 1193 (1955), p. 233

[22] Hager op. cit., p. 188

[23] Clemens Roothaan, 'New Developments in Molecular Orbital Theory'. *Reviews of Modern Physics* 23, no. 2 (1951), p. 69

[24] Lennard-Jones op. cit., p. 2

[25] Roy McWeeny, 'The Valence Bond Theory of Molecular Structure. I. Orbital Theories and the Valence-Bond Method'. *Proceedings of the Royal Society of London. Series A, Mathematical and Physical Sciences* 223, no. 1152 (1954), p. 63

[26] Camille Sandorfy, 'LCAO MO Calculations on Saturated Hydrocarbons and Their Substituted Derivatives'. *Canadian Journal of Chemistry* 33, no. 8 (1955), p. 1338. 'LCAO' here stands for 'linear combination of atomic orbitals.

Although his research was no longer primarily focused on the foundations of structural chemistry,[27] Pauling occasionally argued for the merits of VB throughout the 1950s. Notably, he defended VB in his Nobel lecture[28] after winning the Nobel Prize in Chemistry in 1954, as well as during a 1956 visit to the USSR in the wake of the Soviet resonance controversy (discussed in Section 5.1).[29] Throughout the decade, then, Pauling was beginning to acknowledge a need to defend VB, and when a new set of rationales defending the theory were presented to him through a seemingly unrelated correspondence, he seized the opportunity to develop a defence of VB by defending BEB.

5.1 Soviet suppression and pedagogical disfavour

While both VB and MO survived in the United States and western Europe, albeit with MO leading the field definitively, MO took an exclusive foothold in the Soviet Union. There, movements in socialist science went so far as to legally ban the use of Pauling's theory in Soviet-funded scientific research.[30] The move was inspired by parallel prohibitions of Mendelian methods in biology, which comprised the first instance of Lysenkoist science in the USSR. Soviet scientists attacked VB by arguing that the theory of resonance it put forth was 'senseless,' 'perverted,' and 'erroneous,'[31] and called *NCB* itself, 'Permeated with a Machistic and cosmopolitanistic ideology, by a slavish uncritical attitude toward bourgeois science and a contemptuous attitude toward native science.'[32] *NCB* was a prominent focus of Soviet criticism, due in part to a Russian translation of the book that came out shortly before the attacks on resonance and VB theory were published.[33]

Not only was VB theory being threatened generally, but *NCB* itself was coming under fire frequently, and all of the quotes used against Pauling in support of the Soviet viewpoint came from *NCB*. Some authors even criticized Pauling's theory of the double bond directly.[34] The *NCB* focus, while it is likely due solely to the availability in Russian of the book and corresponding lack of availability of research articles, challenged Pauling's writings in chemical education even more than it challenged his research. So the Soviet controversy provided a reason for the defence to appear in *NCB* instead of in a research journal.

Back in the West, the relative statuses of VB and MO in chemical education during the 1950s was somewhat less clear. Many textbooks, especially those in organic chemistry, had begun to use the concept of resonance to explain various observed

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[27] By this time, his grants were earmarked for organic research (Hager op. cit., p. 188), and he was wrapped up in the race for the structure of DNA and anti-nuclear activism.

[28] Linus Pauling, 'Modern Structural Chemistry'. *Science* (New York, N.Y.) 123, no. 3190 (1956): 255–258

[29] Ibid., *Materials re: Resonance Controversy, 1949-1983*. Courtesy Ava Helen and Linus Pauling Papers, Oregon State University Special Collections, Box 11.2.003 (1949-1983).

[30] Ibid.

[31] D.N. Kursanov, M.G. Gonikberg, et. al., trans. Irving Bengelsdorf, 'The Present State of the Chemical Structural Theory'. *Journal of Chemical Education* 29, no. 1 (1952): 2-13

[32] V. M. Tatevskii and M. I. Shakhparanov, trans. Irving Bengelsdorf, 'About a Machistic Theory in Chemistry and its Propagandists'. *Journal of Chemical Education* 29, no. 1 (1952): 13-14

[33] Ia. K. Syrkin and M. E. Diatkina published a Russian translation of NCB in 1947.

[34] Linus Pauling and N.D. Sokolov, *'S' Correspondence, 1957*. Courtesy Ava Helen and Linus Pauling Papers, Oregon State University Special Collections, Box 1.380.1

bonding phenomena.[35] But few introductory textbooks tarried on the theoretical underpinnings of the new, quantum-mechanically founded bonding theory. Those that introduced a formalism, which not many did, often adopted either a notation that was rough enough to fold both MO and VB under its umbrella or one that favoured MO. By the end of the decade, textbooks were using MO theory's molecular-orbital diagrams commonly, and the popularity of the diagrams was likely accompanied by a general preference for MO theory in instructional settings. On the turf of textbooks in the USSR and in the West, MO theory was again threatening VB theory.

5.2 Wilson

The Pauling Papers contain extensive correspondence between Pauling and his colleagues, friends, and various professional organizations. Among them lies a series of letters between Pauling and Edgar Bright Wilson, Jr. from late 1957-early 1958. This correspondence, which focused on the topic of restricted rotation in molecules, catalysed Pauling's defence of the BEB model. Restricted rotation occurs when electrostatic forces between nuclei prevent the free movement, or internal rotation, of one group of atoms in a molecule about a bond with another group of atoms.

Pauling saw a copy of a paper of Wilson's 'On the Origin of Potential Barriers to Internal Rotation,' in the last 1957 issue of the *Proceedings of the National Academy of Sciences,* and the article struck a chord. In a brief letter to Wilson dated 12 December,[36] Pauling explained that the article stimulated him to finish a manuscript on a similar subject. He sent a copy of the manuscript along with the letter to Wilson. The manuscript Pauling sent Wilson was published in the next issue of the *Proceedings of the National Academy of Science*[37], and it is recorded as being communicated to the journal before Wilson's first reply to Pauling arrived.

Restricted rotation, the subject of the two papers, played a key role in the development of Pauling's early picture of the BEB model. One of the central projects of any model of the chemical bond is to relate bond energies to the relative positions of participating atoms. Relative positions are often represented by planes of symmetry in molecules, which are given in terms of symmetry transformations to hybrid orbitals. Molecules that display restricted rotation are characterized by non-cylindrical symmetry, which is in turn used to represent differences in relative positions of atoms that correspond to observed variations in bond energy. Bond energy is directly proportional to bond strength.

Pauling's first picture of the double bond (see figure 2) was introduced in the midst of a discussion about restricted rotation, and without that discussion, Pauling would have had little motivation to discuss the structure of double bonds in 1931. In the 1931 paper, Pauling argued that in single bonds, the bond is cylindrically symmetric about the bond axis. This point is used to explain why the energy of a single bond does not, in general, depend on the relative orientation of the two atoms.

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[35] e.g. Hammett's *Physical Organic Chemistry*, 1940; Finar's *Organic Chemistry*, 1951; Partington's *A Textbook of Organic Chemistry*, 1951; and Royals' *Advanced Organic Chemistry*, 1954.

[36] Linus Pauling and Edgar Bright Wilson, *Correspondence with E. Bright Wilson, Jr.* Courtesy Ava Helen and Linus Pauling Papers, Oregon State University Special Collections, Box 1.438.5 (1957-58)

[37] Linus Pauling, 'The Nature of Bond Orbitals and the Origin of Potential Barriers to Internal Rotation in Molecules'. *Proceedings of the National Academy of Sciences* 44 (1958): 211–216

In the case of Pauling's double bond, he pointed out in 1931 that the two eigenfunctions representing hybrid orbitals participating in the double bond 'are not cylindrically symmetrical about the z-axis [bond axis] or any direction, nor are the two eigenfunctions on the [non-bonding] group'. He goes on to argue that this lack of cylindrical symmetry implies that the double bond can exist in just two maximal-energy, or strongest, states. In fact, his first picture of the tetrahedra that form the BEB model of the bond is meant to illustrate why rotation in the bond is restricted, rather than simply to propose that the orbitals of double bonds are BEB. The timing of his later work on the structure of the double bond suggests that continuing to puzzle over restricted rotation played a part in the development of his later defences of the BEB model.

In the 1931 paper, Pauling noted that some single bonds still succumb to restricted rotation. But Pauling could not give a rationale explaining the cause of the restriction in 1931; the hindrance was written off as a 'steric effect'[38] and the discussion was ended. And in the following decades, few attempts at a robust theoretical rationale for restricted rotation came to the surface. Restricted rotation often appeared as a rationale in papers that were accounting for a class of observed effects of some kinds of chemical systems, but the phenomenon serves more often as an *explanans* than an *explanandum*. Recognizing the need for further explanation of this phenomenon, Wilson attempted to provide a more satisfying rationale for restricted rotation with his 1957 paper. Wilson's research thus filled explanatory gaps in the same research arena — theoretical structural chemistry — that Pauling's defence eventually would.

Wilson's restricted-rotation project is thus functionally similar to Pauling's defence: both fill explanatory gaps in theoretical structural chemistry. This similarity in function or purpose plays a role in explaining why Wilson's work, rather than someone else's, inspired Pauling to return to the arena of theoretical structural chemistry to mount the defence when he did in the late 1950s. Of course, the fact that Wilson and Pauling were close colleagues and frequent correspondents also played a role, and the closeness of content of Wilson's restricted-rotation work and Pauling's defence offers perhaps the most direct link between the two programs.

In the 26 years between Pauling's first paper on the nature of the chemical bond and Wilson's paper, progress was inevitably made to explain the nature of the steric effects hindering rotation around single bonds. Wilson's paper summarizes some of this progress, and comes to the conclusion that recent research, especially on ethane (C_2H_6), shows that the distribution of electrons on either end of the main bond—that is, the electrons that are not participating in the carbon-carbon bond—is responsible for restricting rotation about single bonds. He suggests that the explanation for the observed potential barriers, or functions describing restricted rotation, lies in the quantum-mechanical description of the motion and energy of these axial electrons, and he recommends further research needs to be done to precisify the quantum-mechanical description of restricted rotation.

Pauling's 1958 paper attempts to provide an explanation for restricted rotation that is not directly quantum-mechanical. Instead, his paper suggests that a precise explanation for restricted rotation can be given in terms of his quantum-mechanically-based valence-bond model. In particular, Pauling claims that the phenomenon of concentrated bond

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[38] Ibid., 'The Nature of the Chemical Bond'. *Journal of the American Chemical Society* 53, no. 4 (1931), p. 1379

orbitals, a feature of the valence-bond model, plays a key role in explaining the restricted rotation around a single bond. The observed potential barriers are said to be a result of exchange interactions between the concentrated orbitals on the axial nodes of the molecule. Pauling gives a quantitative description of the phenomenon of concentration of bond orbitals before applying this description to an explanation of restricted rotation.

It is worthwhile to note two points here: First, there is a direct link between the Wilson correspondence and the BEB model. In the correspondence between Wilson and Pauling that followed the publication of these two papers, Pauling discusses the double bond explicitly. Pauling makes use of the BEB model to explain the relatively lower potential barrier around a double bond relative to that around two single bonds, alluding to the bending of the bond orbitals, which occurs as a result of concentration, as a factor. On 22 January 1958, he writes to Wilson, 'Because two bent bonds contribute less than two straight bonds in tetrahedral directions, the barrier would be predicted for the double-bonded structure to be somewhat less than that for methyl amine, probably about 1.2 kcal/mole'. (Letter is reprinted in figure 5.) So Pauling is thinking about the effects of his concept of concentrated bond orbitals on his description of double bonds.

Second, Pauling's 1958 paper is at least partially responsible for the section on concentration of bond orbitals in the third edition of *NCB*, and this section is directly relevant to the expansion of the double-bond section in the third edition. The equations and explanations of concentrated bond orbitals that Pauling gives in the paper are identical to those which appear in the third edition of *NCB*, and these equations and explanations were not present in earlier editions of the book. Further, there is no apparent evidence in his research notebooks, correspondence, or personal notes in the years between the editions of *NCB* to suggest an earlier origin for the equations for the concentration of bond orbitals. And the closing line of Pauling's 22 January letter to Wilson suggests that the subject is just now entering the forefront of Pauling's consciousness: 'I am planning to publish some more papers on the phenomenon of concentration of bond orbitals. This probably should have been done long ago'.[39]

5.3 Kekulé

On December 17, 1957, five days after he first wrote to Wilson about restricted rotation and concentration of bond orbitals, Pauling received an invitation to speak at the 1958 Symposium of the International Union of Pure and Applied Chemistry.[40] The conference was honouring August Kekulé. Kekulé is best known for proposing the hexagonal structure of the benzene molecule, where six carbon nuclei are linked by alternating double and single bonds. In correspondence with the organizers of the symposium, Pauling suggests that his talk will be on Kekulé and the double bond,[41] in order to pay homage Kekulé's work with double bonds in benzene. Pauling composed a speech for the symposium entitled 'The Nature of the Double Bond and of Conjugated[42] Aromatic Molecules'.

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[39] Ibid.

[40] Ibid., *Abstract and Notes, 'Kekulé and the Chemical Bond' speech*. Courtesy Ava Helen and Linus Pauling Papers, Oregon State University Special Collections, Box 4.1958s2.4 (1958)

[41] Ibid.

[42] Conjugated molecules are those in which alternating double and single bonds can be seen. They are most commonly organic molecules, such as the aromatic compounds, and the alternating double and single bonds are nearly always chains or rings of carbon bonds.

A manuscript of the speech, as well as Pauling's notes toward the manuscript, is available at the Pauling Papers.[43] By going through the manuscript and notes, I discovered that for this speech, Pauling composed a preliminary version of the defence of the BEB model of double bonds that would appear in the third edition of *NCB*. He discussed the concentration-of-bond-orbitals argument at length, occasionally pointing to Wilson in his discussion of restricted rotation. He also pointed to empirical evidence about bond lengths and bond angles and explained how his model, but not the σ-π model, could explain phenomena such as the relationship between the internuclear distances in the carbon-carbon single bond and the carbon-carbon double bond—the ratio, he argued, was the ratio between a straight line and an arc along the tetrahedral bond distance.

Looking at a page from Pauling's notes for the Kekulé speech (see figure 6) offers a snapshot of the history of the defence. The page is scribbled with the phrases, 'σ+π? I say no. Bent bonds are better!' 'resonance – USSR' and 'concentration of bond orbitals – Wilson'. The arguments for the defence are headed 'theory,' 'distances,' and 'angles' before a section on restricted rotation is introduced. Clearly, this is where Pauling's defence came together.

Pauling's speech at the Kekulé conference was edited and published in the proceedings from the conference in 1959, but no other articles on the defence appeared. Rather, the major release of the BEB model occurred in the 1960 edition of *NCB*. This suggests that the argument is primarily targeted not at chemists on the frontiers of research, but at chemical educators and students of chemistry. The conceptual apparatus contained in the BEB model is meant as a tool to guide thought about the nature of the chemical bond, not as a discovery of novel or ground-breaking insight into the mechanics of the bond.

6. Concentrating Bond Orbitals into a Defence

Thinking about the concentration of bond orbitals in the late 1950s led Pauling to revisit what some advocates of MO had to say about the structure of double bonds in the early 1950s. His argument against their conclusions comprises the formal basis of his defence, from which he draws the inferences that make up the list of arguments found in the third edition *NCB* and described in Section 3 of this paper.

The argument is contained in Pauling's 23rd research notebook and is dated 13 August 1958, less than a year after Pauling's correspondence with Wilson brought the concentration of bond orbitals back to his attention. To introduce Pauling's opponents in the argument, it is necessary to return briefly to the rise of the MO model.

As MO grew in popularity, many chemists and physicists were eager to explicate the similarities and differences between MO theory and the valence bond models of resonance theory. In 1950, a group of four chemists at Cambridge University[44] published the first in a series of more than 15 articles collectively titled 'The Molecular Orbital Theory of Chemical Valency,' hoping to bring molecular orbital theory to more chemists' attention and to pinpoint its relationship to resonance theory. In 1951, G.G. Hall and Sir John Lennard-Jones published the seventh article in the series, subtitled 'Molecular

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[43] Ibid.
[44] Namely Lennard-Jones, Hall, Pople, and Hurley

Structure in Terms of Equivalent Orbitals'.[45] In this article, they claimed that the molecular-orbital and valence-bond treatments of double bonds produce identical predictions for bond energy, and they argued for the general quantitative equivalence of the two methods.

When the article came out, Pauling found no need to respond to the claim that the two methods produced equivalent predictions—he never mentioned the claim either in his early 1950s publications or in the course of his regular correspondence with Lennard-Jones.[46] It was not until seven years later, a few months after his exchange with Wilson on the concentration of bond orbitals and during his work on the third edition of *NCB*, that Pauling took issue with the Hall and Lennard-Jones claim of equivalence. Again, this suggests that Pauling does not see the conflict between BEB and the σ-π model as a matter of pressing concern for research; rather, the issue is pedagogical and requires addressing for the sake of providing chemical educators and students with a more thorough set of explanations of the mechanics of the double bond.

In his 23rd research notebook, Pauling develops an argument using the concentration of bond orbitals to the conclusion that the σ-π model does not produce results equivalent to the valence-bond's BEB model, and further that the results produced by the BEB model are more predictively accurate and tell a more cohesive story about the nature of the double bond.

The confrontation with Hall and Lennard-Jones lies on pages 162-165 of the notebook (see figure 7). The section is titled '*d* Character of Double Bonds' and dated 13 August 1958. The notes are fluidly organized, containing few scribbles or redirections. This suggests that Pauling probably worked out the calculations on scrap paper before committing them to the notebook, but the fact that the argument makes extensive use of the concentration of bond orbitals, coupled with the timing—a few months after his correspondence with Wilson—implies that the argument was developed in the wake of the Wilson correspondence.

Pauling begins the argument by pointing out that Hall and Lennard-Jones' claim that the BEB model and the σ-π model are equivalent is intended to hold only when the same sets of orbitals are used in each model. Specifically, because the σ-π model requires the use of only *s* and *p* orbitals, the models are equivalent only when the orbitals involved in creating the hybrid orbitals of the bent bonds are restricted to *s* and *p* orbitals alone. Pauling then makes two claims: first, that the models would produce different pictures if *d* orbitals were introduced into each, and second, that introducing *d* orbitals is the most natural thing to do from the bent-bond perspective because these additional orbitals are required to *concentrate* the orbitals of the bent bonds.

There is no argument for the second conclusion in these notes, presumably because Pauling sees no need for one: concentrating bond orbitals by adding higher-orbital character is doing no more than adding an additional correction term in the approximation of the wavefunction, so of course the bent-bond orbitals will be better characterized by the addition of *d* character.

[45] George Hall and John Lennard-Jones, 'The Molecular Orbital Theory of Chemical Valency. VII. Molecular Structure in Terms of Equivalent Orbitals'. *Proceedings of the Royal Society A: Mathematical, Physical and Engineering Sciences* 205, no. 1082 (1951): 357–374

[46] Linus Pauling and John Lennard-Jones, *Correspondence with John Lennard-Jones.* Courtesy Ava Helen and Linus Pauling Papers, Oregon State University Special Collections, Box 1.215.4 (1950s)

The argument for the first conclusion runs as follows. Pauling gives equations for the five standard d orbitals and takes the bond plane to be the xz plane, so that the z-axis is the bond axis and the lobes or π portions of the double bond are aligned along the xz plane. He then assumes 0.04 is good coefficient for the d term in each model.[47] Then, he selects the d orbitals that will comprise the d term for each model. He justifies each choice: in the σ-π model, the d_z (or, in contemporary terms, $d_{z\text{-squared}}$) orbital is added to the σ bond to concentrate it, because all other d orbitals have a node along the z axis, and the σ bond has no such node. The π bond is concentrated with d_{xz}, because the bond plane is the xz plane. Then all that is needed to concentrate the bonds with 0.04 d character is to add a term for .04 d_z to the σ bond orbital equation and another for 0.04 d_{xz} to the π bond orbital equation.

In the BEB model, orbitals cannot be combined so straightforwardly, because the bond orbitals for the double bond are pointing in tetrahedral directions, and the lobes of the d orbitals are not. So the d orbitals themselves need to be hybridized in order to be concentrated. To hybridize the d orbitals, Pauling takes the d_{xz} and the d_{x+y} orbitals, which are a 45º rotations of one another in Cartesian coordinates. Since the bond orbitals of the bent double bonds do not point at 45º to the z axis, but rather at around 54º44', unequal amounts of the two d orbitals are needed for the concentration. Pauling concludes that the d_{xz} orbital will contribute about twice as much as the d_{x+y} orbital, giving the coefficients 0.0533 and 0.0267, respectively, to the orbital terms for an overall d character of 0.04.

The conclusion follows relatively obviously, once the calculations are muddled through. In the σ-π model the d terms added are 0.04 d_z and 0.04 d_{xz}. In the BEB model, the d terms added are 0.0533 d_{xz} and 0.0267 d_{x+y}. These are different terms. Therefore the two models are inequivalent. Pauling elaborates slightly on the argument, showing that in order to get the numbers for the bent-bond model to start approaching those of the σ-π model, the angle between the bond orbitals would have to be less than 54º, or less than half the angle predicted by the tetrahedral model.

This is the first place that Pauling makes mature calculations on the structure of the double bond for both models. The argument he gives is a convincing one: the math checks out, and the assumptions about how orbitals are distributed are natural ones given the basic tenets of valence-bond theory—in other words, the argument should serve as a satisfactory explanation to students familiar with the basics of Pauling's theory of how orbitals combine.

If Wilson had not stuck the concentration-of-orbitals bee in Pauling's bonnet, though, the argument may never have occurred. Pauling recognized the importance of these calculations quickly, and less than three weeks after the date of the argument in the research notebook he began presenting his results in public.

7. Conclusions

While Wilson's correspondence returned Pauling's attention to concepts relevant to the debate, it alone does not explain why it is significant that Pauling developed and disseminated the defence where and when he did. To understand the timing of the defence, it is necessary to look at the chemical community's changing perceptions of VB

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[47] He gives an argument why this is the appropriate coefficient in the manuscript of the Kekulé speech.

theory over the middle of the 20th century: shifting explanatory demands gave Pauling new motivation to justify the use of his theory rather than MO theory. To understand the location, the Soviet resonance controversy must be taken into account, but so must Pauling's interest in teaching and preserving his highly conceptual brand of thinking about problems in chemistry.

Pauling had a number of reasons for holding BEB to be preferable to the σ-π model: not only was it born directly out of his theory rather than the competing MO theory, but it incorporated important concepts from the conceptual scheme associated with the VB formalism — hybridization, the relation between single and double bonds, and other geometrical considerations. In pedagogical settings, this meant BEB would serve as a particularly effective concept-builder in a way the σ-π model could not. Additionally, BEB was easily visualizable, and throughout his career Pauling strove to anchor abstract and difficult chemical concepts in visualizable models and pictures.[48] While it was possible to produce a picture of the σ-π model, that picture does not provide an anchor for the bonding concepts, such as hybridization, that Pauling saw as central.

These reasons alone, though, were not sufficient to motivate Pauling to publicly defend BEB when the model first entered caught his spying attention. As discussed in Section 4.1, Pauling saw no need to publish an early defence of BEB, although he was formulating one well before the first edition of *NCB* appeared in chemistry classrooms. It was not until VB theory was under attack in the chemical community that Pauling was moved to rise to its defence. Criticisms from his colleagues in West created a need for Pauling to defend VB theory, and Soviet attacks on *NCB* offered him an opportunity to take a stand from a pedagogical perspective.

In response to the chemical community's shifting explanatory demands, Pauling needed a means of defending VB if he was to save it from sinking slowly into oblivion, leaving only the concept of chemical resonance behind. Wilson's correspondence and the invitation to the Kekulé conference opened his eyes to a line of attack: his theory said something quite different from MO theory about the structure of the double bond. If his theory's model of the structure of the double bond could be shown to be preferable to MO theory's model, it would give chemists reason to keep VB around.

This is exactly what Pauling aimed to show in the defence that appears in the third edition of *NCB*. He used the concentration of bond orbitals (Section 6), which was born of a difference in mathematical formalism of the two theories and inspired by Wilson, to show that BEB and the σ-π model make different predictions about the distribution of electron probability density in a double bond. Then he demonstrated, using empirical data and analogy to other parts of VB theory, that the picture given by BEB can be rationalized conceptually, where the picture given by σ-π has no such advantage; it requires a stauncher faith in the mathematical formalism.

The problem of where to anchor one's faith in the formalism of a model — whether in the mathematics or in the conceptual framework — is one that troubles many chemists and students of chemistry, and the BEB defence demonstrates that Pauling wanted students of his to consider the latter at least as earnestly as the former. While the Soviet

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[48] Evidence on this point includes Pauling's extensive collection of hand-made and store-bought molecular and crystal-structure models, currently available to view in the Pauling Papers, as well as his lifelong correspondences with architecturally inclined artists, including sculptor Alexander Calder, and a book he published in 1964 with artist and architect Roger Hayward entitled *The Architecture of Molecules*.

resonance controversy provided an external motivation for defending VB theory in the text of *NCB* itself, the fact is that Pauling was reaching his most impressionable audience by publishing the defence in the textbook rather than in research journals: Most established researchers would have already decided how much faith to lay in which part of the formalism. But convincing students that the conceptual framework of VB theory was worth keeping around would mean greater odds of his theory's survival as these students matured into researchers and teachers in their own rights. For a theory on the edge of extinction, giving young minds a set of reasons for keeping it around was perhaps the best way to ensure the theory's survival.
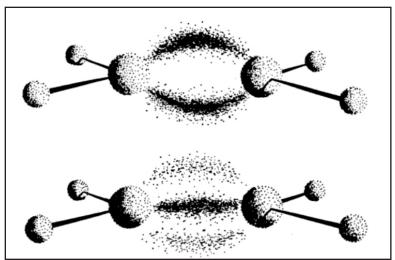
Figure 1: Pauling's 1960 images depicting th structure of the double bond in the bent-equivalent (top) and sigma-pi (bottom) models. *Courtesy Cornell University Press*.
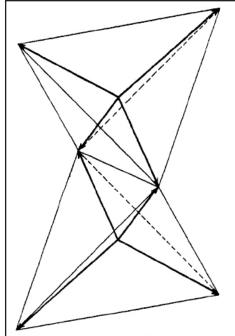

Fig. 5.—Directions of maxima of tetrahedral eigenfunctions in two atoms connected by a double bond.

Figure 2: Pauling's first published representation of the bent-equivalent bond, shown as two tetrahedral orbitals joining along two corners. *Courtesy American Chemical Society Publications*.
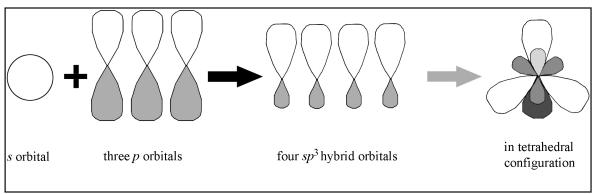

s orbital   three p orbitals   four sp^3 hybrid orbitals   in tetrahedral configuration

Figure 2a: Schematic diagram of tetrahedral bonding orbitals according to Pauling's theory of hybridization. *Author's Diagram*.

Figure 3: Excerpt from Pauling's 1931 or 1932 notes on Mulliken's manuscript for "Electronic Structure of Polyatomic Molecules and Valence: General Considerations." *Courtesy Pauling Papers*.
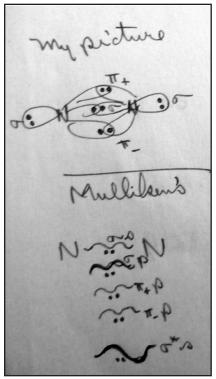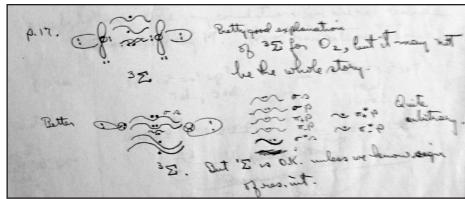
Figure 4: Pauling's representation of his (top) and Mulliken's (bottom) description of the triple bond in dinitrogen. *Courtesy Pauling Papers*.

22 January 1958

Professor E. Bright Wilson, Jr.
Department of Chemistry
Harvard University
12 Oxford Street
Cambridge 38, Massachusetts

Dear Bright:

I am pleased to continue the discussion of the theory of restricted rotation. I may say that I still not know, as I had surmised from your paper, whether you had the feeling that it would turn out that the axial bond itself was responsible for the restriction of the rotation.

With respect to your general comment about my highly simplified quantum mechanical discussion, I may say that I bend more and more to the opinion that it is the highly simplified discussions that are of greater value to chemistry than the complicated and detailed numerical calculations. I still do not know of any chemical discovery that has been made through the extremely complicated numerical calculations that many people are now carrying out. In general, I have greater confidence in the results of the very simple calculations than in the results of the very complicated ones.

Arguments for the use of the bond strength as a measure of bond-forming power were given in my 1931 paper. The angular dependence of the wave function gives a first-order effect, which may be very great, whereas the differences in the radial parts of the wave function, for different angular dependences, give a second-order effect. Except in the immediate neighborhood of the nucleus, the radial parts for different angular dependence may be essentially the same. I think that in general the different radial parts would be expected to be essentially identical in the region where the overlap occurs. It is, of course, possible to have the radial parts exactly the same, but the promotion energy is then somewhat larger.

As to the matter of coulombic interaction, in general the exchange terms may be expected to be much larger than the coulomb terms, roughly ten times as large.

I am glad to make predictions about the molecules that you mention. I am sure that you can make them just as well.

For CH₃NCS the principal structure involves double bond between nitrogen and carbon. Because two bent bonds contribute less than two straight bonds in tetrahedral directions, the barrier would be predicted

Professor Wilson   Page 2, 22/1/58

for the double-bonded structure to be somewhat less than that for methyl amine, probably about 1.2 kcal/mole. Moreover, there is expected to be some contribution of structures with a single bond or a triple bond between nitrogen and carbon, which would cut down the barrier further, causing me to make a rough estimate of 0.8 kcal/mole as the height of the barrier. The stable configuration would, of course, be that in which a methyl hydrogen atom is eclipsed relative to the NCS group.

For cis-fluoropropylene I would predict the same barrier as for the trans compound. There might be a small steric repulsion between the eclipsed hydrogen atom and the fluorine atom, possibly causing as much as 10 percent decrease in the height of the barrier.

For cis and trans methyl formate I would predict essentially the same barrier height. For the carboxylate ester group I expect about 70 percent contribution of the structure with a single bond to the oxygen atom with methyl attached, and 30 percent contribution of the structure with double bond in this position. The first structure corresponds to the staggered configuration, and the second to the eclipsed configuration. For the first structure the barrier height would be predicted to be about 1 kcal/mole, as in methanol, and for the second about 1.5 kcal/mole. Accordingly we conclude that the actual barrier height should be about 0.3 kcal/mole, with the staggered configuration stable. This conclusion applies to both the cis isomer and the trans isomer.

Please let me know if there are any other molecules for which you would like me to make predictions.

I am planning to publish some more papers on the phenomenon of concentration of bond orbitals. This probably should have been done long ago.

With best regards, I am

Sincerely yours,

Linus Pauling:w

Figure 5: Pauling's letter to Edgar Bright Wilson, 22 January 1958. Note especially discussion of bent bonds at bottom of page 1 and closing paragraphs. *Courtesy Pauling Papers*.

We have become so accustomed to the power of chemical structure theory that Kekulé's diffidence may surprise us:

"FINALLY I HAVE TO MENTION THAT I MYSELF LAY ONLY SMALL VALUE ON CONSIDERATIONS OF THIS SORT... BUT THESE IDEAS SEEM TO ME TO GIVE A SIMPLE AND RATHER GENERAL EXPRESSION OF RECENT DISCOVERIES, AND PERHAPS THEIR USE WILL HELP IN FINDING SOME NEW FACTS".

HAVE THERE BEEN GREAT ADDITIONS ? (TETRAHEDRAL, RESONANCE)
$\sigma \& \tau$?
I SAY NO.   BENT BONDS ARE BETTER ! 'USSR THEORY.
ARGUMENTS: DISTANCES : 1.32/1.33   1.18/120Å
            ANGLES ⌒ 124.8° PROPYLENE
(122.0° E.D., 121.3° IR ETHYLENE)

Rotation : CONCENTRATION OF BOND ORBITALS
            KEMP & PITZER . 1937.   WILSON

Figure 6: Manuscript notes for Pauling's 1958 Kekulé address. *Courtesy Pauling Papers.*
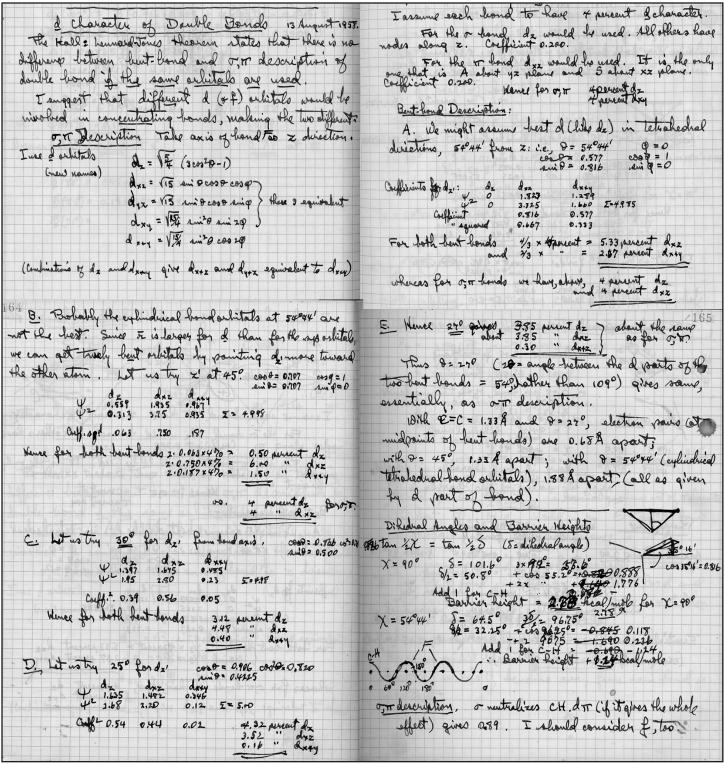
Figure 7: Pages 162-165 of Pauling's 23rd research notebook, dated 13 August 1958. Detailed calculations for the inequivalence of the two bonding models using concentration of bond orbitals. *Courtesy Pauling Papers*.