

Talking to Pauling's ghost

Michelle Francl dusts off Pauling's notes on bonding to explore the illusory link between electron promotion and hybridization.

Pauling haunts my classes. Metaphorically, and sometimes I suspect, literally.

In the fall of 1957, Linus Pauling paid an impromptu visit to Bryn Mawr College to hear my colleague Frank Mallory, a new faculty member and CalTech alumnus, speak¹. Pauling sat in the front row, four feet from the lecturer's table; four feet from where I now teach first-year chemistry. Each time I turn to the periodic table on the wall and encourage students to think about atomic valences or electronegativity, I catch a glimpse of Pauling in his prime, still stretched out in my front row, iconic black beret on his head, holding forth in his Oregon twang.

Even when I'm not teaching in that particular classroom, Pauling's shade insinuates itself into my syllabus, driving what I teach — and sometimes what I'm trying to unteach. Pauling's hybrid orbitals are a de facto language for organic chemistry. They are one of our most beloved and powerful loci of argument, invoked to explain phenomena ranging from conformational preferences to bond lengths to acidity. But imbued with such power, orbitals have taken on a reality they do not actually possess. The claims of orbital tomographers are to the contrary²: there are no such observables as orbitals — hybrid, atomic or molecular. My introductory quantum-chemistry students, after a year of mentally tagging every carbon atom they encounter with its hybridization and seeing pi clouds floating high above phenyl rings, enticing targets for electrophiles, are loath to believe me when I insist orbitals are nothing more than a mathematical convenience, figments of quantum mechanics' imagination. Ironically, the power of Pauling's approach is one reason quantum mechanics is a routine part of a chemist's training.

Chemists' contentions as to the material reality of orbitals — atomic or molecular — aren't what concern me here. Buu Pham and Mark Gordon, among others, have cogently laid out the reasons why orbitals cannot be observed³⁻⁵. I've nothing to add to this, other than to say Pauling didn't believe orbitals were observable either⁶. Instead, I'd like to take a step back and examine the narratives (or perhaps I should say 'myths') we use to explain to new students

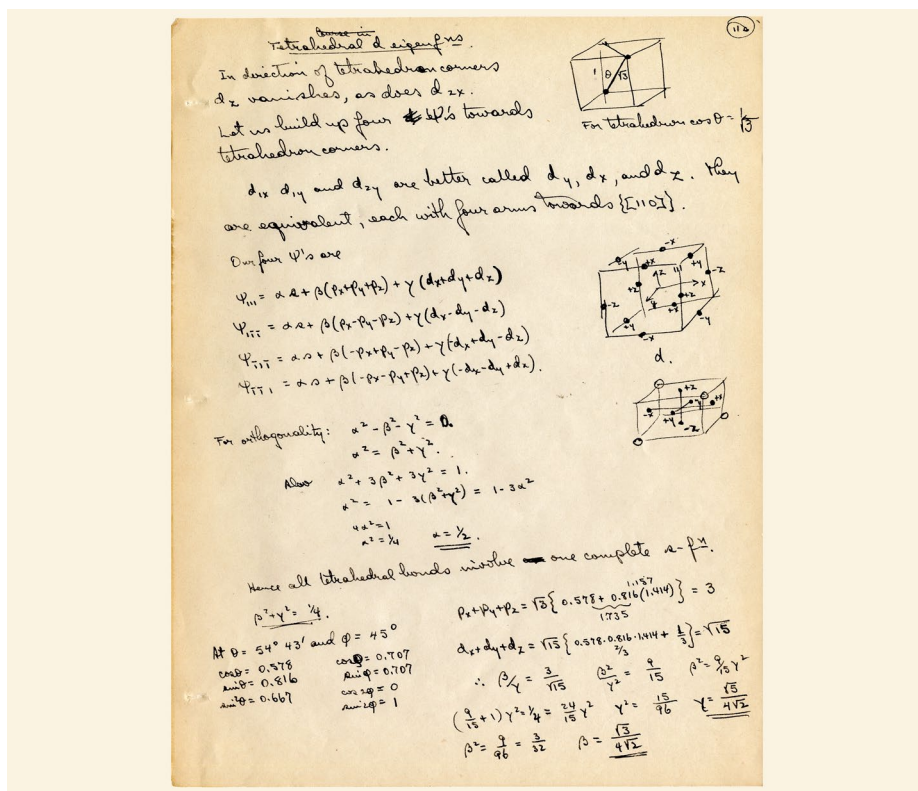


Fig. 1 | A page from Linus Pauling's notes. Written on a single evening in December 1930, Pauling's derivation of a tetrahedral set of hybrid orbitals using s, p and d functions. Photograph courtesy of Ava Helen and Linus Pauling Papers, Oregon State University Libraries.

how hybrid orbitals emerge from the canonical set of atomic orbitals. At the very moment we introduce them to a quantum-mechanical view of chemistry, we unnecessarily ignore the quantum-mechanical underpinnings and send our students down a rabbit hole that can be hard to get them out of later.

In many, if not most, general chemistry texts, the introduction of hybrid orbitals begins by noting that the ground-state electron configuration for carbon has a filled 2s subshell, which makes those electrons unavailable for forming a two-electron bond and limits carbon to the formation of, at most, two bonds. In order to account for the known tetravalence of carbon, textbook authors often suggest that an electron from the 2s subshell is first promoted to the 2p level, the cost of this promotion being recouped from the extra bonds the atom can

now form. As a result of this promotion, the narrative implies that not only do you have the ability to form four bonds, you can make new hybrid orbitals. Authors generally note that you can't make the same argument for either oxygen or nitrogen.

But how does this promotion of an electron connect to the formation of hybrid orbitals? The texts are silent on this. As they then immediately apply those hybrid orbitals to both nitrogen and oxygen compounds, my alert students are left rightfully confused about the connection between promotion and hybridization. Despite what the text says, I assure them, notions of electron promotion have no bearing on Pauling's creation of sp^n hybrids.

I've wondered for years how this misplaced notion found its way into general chemistry textbooks. Pauling never mentions the promotion of an electron in

the foundational papers on the nature of the chemical bond^{6,7} — or in the notes he made on a December night in 1930 when his thinking about hybrids crystallized (Fig. 1)⁸. Neither is such an explanation found in Pauling's own general chemistry textbook⁹ nor in the lectures he recorded on the nature of the chemical bond¹⁰. Examples can be found in general chemistry, organic chemistry and physical chemistry texts for at least the past 40 years. Since a substantial collection of Pauling's own notes on the theory of bonding have been digitized by Oregon State University archives, I dug into them to see if I could find the seed of the promotion myth. I suggest there are two potential sources for this confounding of promotion and hybridization.

Pauling's hybrid orbitals emerge from his attempts to show that the tetrahedral nature of carbon, first proposed by van 't Hoff in 1874, could be derived *a priori* from the principles of quantum mechanics. Pauling's first foray involved reducing a bond to the interaction of two atoms, A and B, each of which was described by a collection of one-electron eigenfunctions⁷. He treated the approach of the two atoms as a perturbation and noted that in some cases the quantization of the *s* and *p* orbitals was 'destroyed' by a strong interaction. In contemporary terms, the set of unperturbed functions on the two atoms that gave the most stable interaction was not the canonical *s* and *p* subshells, but a degenerate set of four linear combinations of those orbitals with a different energy than either the *s* or *p* levels.

Pauling later asserts that comparing the interaction energy and the energy separation between the *s* and *p* subshells provides a rough criterion for whether this 'change in quantization' was important: if the bond energy was greater than the *s*–*p* gap, use the linear combinations⁶. I wonder if this is the source of the current explanation that the cost of promotion is balanced by the bond energy, but I note that Pauling wasn't constructing his perturbation diagram from an excited atomic state, but from a new state, with a fourfold degenerate shell at a new energy, a subtlety lost in translation over the years.

The second potential source stems from Pauling's 1931 paper: "The nature of the chemical bond," in which he brought variational theory to bear on the problem, again treating a bond as the interaction between two atomic wavefunctions built from single-electron functions. A single such function on each atom would overlap to create a two-electron bond. In the days before the available computational machinery could tackle the calculation of the integrals for finding the variational energy, Pauling had to make reasonable guesses as to the most important terms contributing to the variational energy and what they depended on. He expressed⁶ the energy of the interaction as:

$$E = W_A + W_B + J_E + J_X - \sum_Y J_Y - 2 \sum_Z J_Z$$

Pauling considered the terms W_A , W_B and J_E to be independent of any interaction between the atoms. Though he was unable to quantitatively calculate the exchange terms, J_X , J_Y and J_Z , he assumed them to be negative based on the value of similar known integrals. The best variational energy would thus be obtained when J_X , the exchange term between the bonding orbitals, was maximized. As the exchange terms were directly proportional to the overlap of the orbitals involved, the best basis functions for the molecule would have their maxima directed along the bond axis.

To find the best functions under these constraints, Pauling took linear combinations of the canonical *s* and *p* functions. Drawing on his perturbation theory analysis, he assumed that the quantization of the subshells was destroyed, which would make the radial parts of *s* and *p* identical and radically simplify his calculations. This assumption is another possible source of the promotion myth, as it is tantamount to moving the energy of the *s* orbital to match that of the *p* orbital.

It was now straightforward to show that an *sp* hybrid had a larger value along the bond axis than either a pure *s* or *p* orbital⁸. Creating a function orthogonal to this hybrid, its maximum is found to be at the tetrahedral angle. Thus, Pauling brilliantly

used a quantum-mechanical framework to show that quadrivalent carbon had to be tetrahedral.

My reading of Pauling's work is that the formal promotion of electrons has nothing to do with his hybridization theory, and we should summarily exorcise it from the textbooks (along with a number of other myths)¹¹. Pauling's own qualitative reasoning is accessible to undergraduates, the only math you need is trigonometry. It has the advantage of showing them the route from quantum mechanics to chemical structure, as well as setting the stage for those who will go on in chemistry to understand orbitals as mathematical constructs, not real objects. But perhaps most importantly, we miss an opportunity to help students see equations not as machines that spit out numbers, but as another way to describe the natural world. They can and should appreciate the power of qualitatively 'reading' the mathematical expressions that were at the core of the groundbreaking connection Pauling forged between quantum mechanics and chemical structure. If Pauling's ghost is going to haunt our classrooms, we should take a moment to listen to what he has to say. □

Michelle Franci^{1,2}

¹Department of Chemistry at Bryn Mawr College, Bryn Mawr, PA, USA. ²Vatican Observatory, Vatican City, Vatican City.

Twitter: @MichelleFranci

e-mail: mfranci@brynmawr.edu

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