

The solution to this puzzle, proposed by Linus Pauling in 1931, was that carbon atoms, when in molecules, did not have to conform to the constraints of a lone carbon atom as it appeared on the periodic table. He proposed a mathematical solution to the problem. And although his actual mathematics was complex, because of the equations involving atomic orbitals, his conceptual approach was really quite simple and logical. Pauling took what he had, on the one hand: a carbon with 4 nonidentical orbitals of unequal occupancy (1 s orbital with 2 electrons and 3 p orbitals with a total of 2 electrons). On the other hand, he wanted to form 4 equivalent orbitals with 1 electron each that could be pointed to the corners of a tetrahedron. Like Lewis, Pauling had also grown up believing that atoms were tetrahedral.

Pauling's strategy was exactly the same as solving a word problem from an elementary mathematics class.

Here are the conditions. You have a little bit of money: 400 cents. Of these 400 cents, 100 are from a single American dollar and 300 are from 3 euros. You can give gifts of 100 cents to your friends, so you are limited to a maximum of 4 gifts. Because your friends really like the American money, you agree to always give away the entire dollar, regardless of how many ways you divide up the cash. So, with the 100-cent limit, you will have leftover euro money if you make fewer than 4 gifts. What is the dollar-to-euro cent ratio if you make 100-cent gifts to 4 friends? To 3 friends? And to 2 friends?

You can do that math!

For 4 friends: each gift is a mixture (a hybrid gift) where each person gets 1/4 of the dollar (25 cents; 25% of a dollar) and 3/4 of a euro to make up the difference (75 cents; 75% of a euro). All of your money would be distributed and each of your 4 friends end up with 100 cents of currency, where the dollar-to-euro ratio is 1:3 (or the d^1e^3 hybrid gift).

For 3 friends: each gift is 1/3 of the dollar and 2/3 of a euro. You have 1 euro left over, and each of your 3 friends end up with 100 cents of currency, where the dollar-to-euro ratio is 1:2 (the d^1e^2 hybrid gift).

For 2 friends: each gift is 1/2 of the dollar and 1/2 of a euro. You have 2 euros left over, and both of your friends end up with 100 cents of currency, where the dollar-to-euro ratio is 1:1 (the d^1e^1 hybrid gift).

Pauling's task was exactly the same. On atomic carbon, he has a single s orbital (the dollar) and three p orbitals (the euros). For CH_4 , carbon has 4 friends, and Pauling wants to divide the 4 orbitals up to make 4 equal orbitals (equal gifts) because he believed atoms were perfectly tetrahedral and that CH_4 has 4 identical C-H bonds.

You can do Pauling's math. To make 4 equal orbitals from what he had, Pauling concluded that each orbital at carbon is a mixture (a hybrid orbital) where each one gets 1/4 of the original s orbital and 3/4 of an original p orbital. All 4 of your new orbitals would be equal, and each one ends up with an s-to-p ratio of 1:3 (or the s^1p^3 hybrid orbital). Pauling's process is called orbital hybridization, mixing together what you have to get what you want.

Hybridization of atomic orbitals is not a physical phenomenon; it is a mathematical model and there is no direct experimental measurement that can be made to help confirm or reject it. Orbital hybridization provides an intellectually satisfying way to reconcile the idea that the carbon atom in methane (CH_4) ought to have 4 equivalent valence electrons in 4 equivalent atomic orbitals so it can make its 4 equivalent C-H bonds, resolving the idea that the carbon of the periodic table does not provide an equivalent set of 4 electrons to work with. Pauling's idea was that a carbon atom in methane is not constrained to being the lone carbon of the periodic table, and he conserved orbitals by accounting for them.