

The Concept of Resonance

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A recent article in this *Journal* advocates substituting the word “delocalization” for “resonance” (1). This recommendation should not be accepted because modern electronic structure theory shows that “delocalization” and “resonance” are not the same, nor is one a special case of the other.

Examples of Delocalization and Resonance

In electronic structure theory, we must include electronic spin in order to satisfy the Pauli principle. I will neglect spin-orbit coupling to make the arguments simpler. Then a suitable electronic wave function for an atomic or molecular system with N electrons must be antisymmetric under permutation (transposition) of two electrons and must correspond to a definite value S of total electronic spin. If the spatial part of the electronic wave function is formed from no more than N orbitals, each of which may be interpreted as the variationally best representation of an electron moving in the average field of the other electrons, then the electronic wave function including spin must be expressible as a permutation operator acting on product of N spatial orbitals times a spin function (2); this kind of approximate wave function is called a spin-coupling-optimized generalized valence bond wave function. In such a wave function, the orbitals do not need to transform according to the full symmetry of the molecule (2). Thus, for example, the orbitals can be localized even in symmetric systems (3).

By restricting the form of the wave function, one can obtain, as a special case, the Hartree–Fock molecular orbital method in which the wave function may be written as a Slater determinant of delocalized symmetry orbitals. In contrast, requiring the orbitals of the more general spin-coupling-optimized wave function to be delocalized symmetry functions would be a constraint that raises the energy and—by the variational principle—makes the wave function less accurate. This provides a very general example of where a delocalized description of a system is associated with a higher energy than the localized one; thus it is wrong to consider delocalization as equivalent to resonance stabilization. Alternative but equivalent explanations of delocalization are provided by other authors (4, 5).

One can consider another example, namely HCl. This may be considered a resonance hybrid of a covalent and an ionic structure (6).¹ In HCl, the covalent structure has a weight larger than 50%, and the ionic structure, therefore, has a weight less than 50%. Resonance stabilization of the dominant covalent structure by the ionic structure leads to the valence electrons being more localized on the chlorine and less delocalized over two centers than in the covalent structure.

These two examples show that delocalization is not the same concept as resonance.

Resonance in Quantum Mechanics

Probability

If one wishes to discuss a situation involving resonance without using the word “resonance”, the following general language is one correct way to do so. In quantum mechanics, an approximate description of the ground state of a system corresponds to a higher energy than the true energy. A quantum mechanical wave function is a probability amplitude. For example, an electron in a hydrogen atom has a nonzero probability to be near the nucleus and a nonzero probability to be far from it. Restricting the ground-state wave function so that any situation with a nonzero probability is excluded would correspond to a higher energy than the true ground-state energy and would be a more approximate description.

Similarly in the H_2 molecule there is a nonzero probability of observing a charge distribution that corresponds to our usual picture of a covalent bond. There are also nonzero probability amplitudes for observing structures that could be described as H^+H^- or H^-H^+ (these zwitterionic structures are usually called “ionic” in valence bond theory.) Restricting the wave function to exclude any of these contributions would correspond to a higher energy than the true ground state and to a less accurate description.

Sometimes one starts with the model wave function corresponding to the restricted wave function with just the covalent component. Then one proceeds to write a more accurate wave function that also includes the ionic contributions. The covalent and ionic contributions are sometimes called covalent and ionic configurations (or valence bond structures), and this process of adding the ionic contributions is sometimes called configuration mixing or configuration interaction. But the students need to be able to read the literature so one should add: this process is also called resonance stabilization, and the energy lowering in proceeding from the energy corresponding to the restricted wave function to the more accurate energy is called resonance energy.

Learning any scientific field includes not only learning the concepts of the field but also learning the language that is used by specialists in that field. This is required in order to understand lectures, to communicate with colleagues, and to read the literature. “Resonance” is an important and well established technical term in chemistry. Students should learn it. Even if it were possible to legislate it away (which seems impossible after 75 years of use), it would be wrong to replace it by “delocalization” since that is a different concept.

Wave Functions

Reference 1 also asks “What is resonating?” and concludes that “there is no oscillation of any kind.” One can give another answer to this question, but it requires a more advanced

understanding of quantum mechanics than the material discussed above. When one discusses molecular structure and energetics one is usually referring to the structure corresponding to the ground electronic state (7). Kerber's article (1) makes the important point that historically Pauling often used time-dependent language to discuss resonance. Since the ground state is a stationary state, it has a time-independent probability distribution (8), and therefore time-dependent language is incorrect. However, all wave functions (that is, all solutions of the time-dependent Schrödinger equation) are not necessarily stationary states. Superpositions of stationary states corresponding to different energies are called wave packets. A valence bond wave function corresponding to a single covalent or ionic structure is a wave packet, as is a linear combination of two such wave functions ψ_A and ψ_B . In principle one could create a laser pulse that would excite a state corresponding to such a wave packet. In the absence of decoherence, and if we assume that ψ_A and ψ_B are orthogonal and that ψ_A is only strongly coupled to ψ_B and vice versa, such a wave packet would physically oscillate between the two valence bond structures with a frequency ν (in cycles per second) given by

$$\nu = \frac{2}{h} \left(\frac{\Delta^2}{4} + \left| \langle \psi_A | \hat{H} | \psi_B \rangle \right|^2 \right)^{1/2} \quad (1)$$

where h is Planck's constant, \hat{H} is the Hamiltonian, and

$$\Delta = \langle \psi_B | \hat{H} | \psi_B \rangle - \langle \psi_A | \hat{H} | \psi_A \rangle \quad (2)$$

If the two structures are degenerate, then Δ is zero, and this is the frequency mentioned on page 224 of ref 1. In practice, even if one could devise such a laser pulse, and even if the assumptions mentioned above were valid, the perfectly resonating superposition would not last very long because the electronic wave function in a nonstationary state is subject to decoherence (which is defined here as the evolution of a pure state of the electronic subsystem of the molecular system to a mixed state; ref 9); even for a molecule isolated in space in an ultrahigh vacuum, the motion of the molecule's own nuclei causes decoherence of the electronic wave function (10). Nevertheless, at least in this idealized case, there does exist a physical resonating state, although it is not the same as the ground-state wave function one is usually discussing in the context of molecular structure and energetics.

Summary

The meaning of resonance energy as it appears in valence bond theory is the lowering of the calculated ground-

state electronic energy when one improves a quantum mechanical model containing a single valence bond structure in the wave function to include other significant valence bond structures, where "structure" is defined in Note 1. It is instructive to refer to several research publications where the concept of resonance is used correctly in the context of modern valence bond theory (5, 11).

Note

1. The word "structure" is used here in the valence bond sense of an electronic configuration state function corresponding to a single set of spin orbitals with a spin coupling corresponding to a particular covalent or ionic bonding scheme. A configuration state function is an antisymmetric many-electron trial function composed (usually) of the minimum number of Slater determinants required to obtain the correct spatial and spin symmetry.

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