

Chemical Bonding as a Superposition Phenomenon

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Chemistry and Wave Functions

Perhaps the most difficult conceptual jump in all of science is that from classical to quantum (“wave”) mechanics. Quantum mechanics forces us to surrender some of the most self-evident tenets of our classical (pre-1925) picture of physical reality and causality. Such “quantum weirdness” deeply disturbed Einstein, Schrödinger, de Broglie, and other pioneers of quantum theory (1). In recent years, increasingly stringent experimental tests (all passed with flying colors by quantum mechanics) have further underscored the remarkable dichotomy between common sense concepts and the observed behavior of matter in the quantum domain (2).

Chemists, above all, cannot escape the conceptual dilemma posed by quantum mechanics, for chemistry is in the deepest sense a quantum phenomenon. Put another way, elementary particles that follow the classical (rather than quantum) laws of physics cannot “do” chemistry. It therefore follows that the fundamental concepts of chemical bonding must be sought in the strange mathematical and logical rules of the quantum domain, rather than in the comforting images of 19th-century physics or their extensions in Bohr’s “old quantum theory” of atomic structure.

These days, beginning chemistry students are quickly plunged into the arcane conceptual constructs of quantum mechanics—“wave functions”, “orbital interactions”, “Pauli exclusion principle”, “hybridization”, “resonance”, and the like (if not into mathematical details of the Schrödinger equation itself). It is increasingly clear that such quantal concepts provide the unified framework for satisfactory elucidation of all chemical phenomena. Today, few scientists would dispute Dirac’s prophetic 1929 statement, “The underlying physical laws [for] the whole of chemistry are thus completely understood” (3), or Eyring’s similar 1944 conclusion, “In so far as quantum mechanics is correct chemical equations are problems in applied mathematics” (4).

Some Basic Wave Mechanics

The focal point of elementary bonding theory is the *orbital*. This can be defined as a 1-electron wave function, that is, a solution of Schrödinger’s equation that describes a possible state of a single electron in a specified potential field due to the nuclei and other electrons of the system.¹ More picturesquely, an orbital can be described as a “fuzzy orbit” or “square root of the electron density”. Essentially, each orbital $\phi(x)$ is a mathematical function of spatial position that associates a wave amplitude ϕ with each point x , such that the density $\rho(x)$ of the electronic distribution (the relative probability of finding the electron at point x) is given by

$$\rho(x) = |\phi(x)|^2$$

(More precisely, each [spin-] orbital is reserved for electrons of particular spin [α = “up” or β = “down”], but we shall initially restrict attention to the idealized single-electron case

where this complication can be ignored.) Whereas $|\phi(x)|^2$ is intrinsically a nonnegative quantity, as befits a probability, the orbital $\phi(x)$ itself typically oscillates between positive and negative values in “wavy” fashion, giving rise to the characteristic interference phenomena that underlie chemical bonding.

Each orbital ϕ of the full set of solutions of Schrödinger’s equation has potential chemical significance as a possible state of the electron, whether actually occupied or not. (For example, the transfer of the electron from one orbital state to another corresponds to a possible spectral excitation.) The Pauli principle imposes the important quantal restriction that no more than one electron (of given spin) may occupy a given orbital. Thus the manifold of occupied orbitals constitutes the “electron configuration” of an atom, while the manifold of low-lying unoccupied orbitals represents its capacity for electronic give-and-take in chemical interactions with other atoms.

The Schrödinger equation

$$\hat{\mathcal{H}}\phi_n(x) = E_n\phi_n(x) \quad (1)$$

allows us to associate each orbital ϕ_n with a definite energy E_n in a system described by quantum operator $\hat{\mathcal{H}}$. More generally, we can consider that quantum mechanics provides a functional $\mathcal{E}[\phi]$ (a “function of a function”) that associates a definite energy \mathcal{E} with each chosen orbital ϕ . Specifically, $\mathcal{E}[\phi]$ can be written as the Rayleigh–Ritz functional

$$\mathcal{E}[\phi] = \frac{\int_{-\infty}^{\infty} \phi^*(x) \hat{\mathcal{H}}\phi(x) dx}{\int_{-\infty}^{\infty} |\phi(x)|^2 dx} \quad (2)$$

whose stationary values are uniquely determined by eq 1. However, we need not be concerned about details of how the $\mathcal{E}[\phi]$ functional actually works in order to recognize some of its startling consequences. In the following, we cite some properties of the functional $\mathcal{E}[\phi]$ whose chemical consequences can be deduced from simple algebra.

Superposition and “Spooky Action at a Distance”

The most profound paradoxes of wave mechanics involve superposition, the mixing of orbitals with plus sign ($\phi_1 + \phi_2$, “in-phase”) or minus sign ($\phi_1 - \phi_2$, “out-of-phase”). Energetic consequences of quantum superposition follow from certain mathematical properties of the energy functional $\mathcal{E}[\phi]$ that may be quoted without proof:

Invariance to Overall Sign Change

$$\mathcal{E}[\phi] = \mathcal{E}[-\phi] \quad (3a)$$

This property shows that the orbital energy does not depend on the overall sign of $\phi(x)$ (though it is sensitive to relative sign *changes* within the orbital), consistent with the remark that only the square of the orbital is related to experimentally measurable probability density.

Invariance to Scale Change

$$\mathcal{E}[\lambda\phi] = \mathcal{E}[\phi] \quad (3b)$$

for any scale factor $\lambda \neq 0$. This property shows that the orbital energy is unaltered by an overall nonzero multiplicative factor (such as $\lambda = -1$, the special case of eq 3a). Only *relative* amplitude changes within the orbital have physical significance, and we can therefore ignore overall normalization factors that are sometimes included for mathematical convenience.

Nondistributive Character

$$\mathcal{E}[\phi_1 + \phi_2] \neq \mathcal{E}[\phi_1] + \mathcal{E}[\phi_2] \quad (3c)$$

In words, this inequality states that if $\epsilon_1 = \mathcal{E}[\phi_1]$ and $\epsilon_2 = \mathcal{E}[\phi_2]$ are the orbital energies of ϕ_1 and ϕ_2 , then the energy $\mathcal{E}[\phi_1 + \phi_2]$ of their in-phase superposition $\phi_1 + \phi_2$ is *not* simply $\epsilon_1 + \epsilon_2$. (Similarly, $\mathcal{E}[\phi_1 - \phi_2] \neq \epsilon_1 - \epsilon_2$ for an out-of-phase superposition, and more generally, for any linear combination of the orbitals.) As a useful general measure of this effect, we can define the quantity h_{12}

$$h_{12} = \frac{1}{2}\{\mathcal{E}[\phi_1 + \phi_2] - \mathcal{E}[\phi_1 - \phi_2]\} \neq 0 \quad (3d)$$

which corresponds to the energy “splitting” separating the orbital energies of in-phase and out-of-phase superpositions from their hypothetical average value.

Optimal Superposition of Two Orbitals

If $\epsilon_1 = \mathcal{E}[\phi_1]$ and $\epsilon_2 = \mathcal{E}[\phi_2]$ are the orbital energies of ϕ_1, ϕ_2 , and if h_{12} is as defined in eq 3d, then one can generally find an improved (lower energy) *optimal superposition* orbital Φ_{opt} of the form

$$\Phi_{\text{opt}} = c_1\phi_1 + c_2\phi_2 \quad (3e)$$

whose energy $\mathcal{E} = \mathcal{E}[\Phi_{\text{opt}}]$ is found as a solution of the 2×2 determinantal equation

$$\begin{vmatrix} \epsilon_1 - \mathcal{E} & h_{12} \\ h_{12} & \epsilon_2 - \mathcal{E} \end{vmatrix} = 0 \quad (3f)$$

The numerical values of the coefficients c_1, c_2 (dependent on $\epsilon_1, \epsilon_2, h_{12}$) will be discussed below.

Note that the form of the superposed orbital Φ_{opt} in eq 3e can persist even if the component orbitals ϕ_1, ϕ_2 of the superposition are separated by great distances. In fact, the Pauli occupancy restrictions and other quantal superposition constraints are maintained even if the distance between orbital centroids could not be traversed at the speed of light on the time scale of measurements on the separated distributions! The superposed orbital Φ_{opt} gives rise to probability distributions measurably distinct from those of ϕ_1, ϕ_2 or their uncorrelated average (e.g., with respect to the probability of finding the electron spins of a dissociated diatomic molecule “up” or “down” along chosen axis directions). Superposition therefore leads to persistent correlations between arbitrarily separated probability distributions that could not be caused by any physical signal traveling at less than the speed of light (“spooky action at a distance” [5]), and are thus disturbingly inconsistent with classical intuition.

The paradoxes associated with quantum superposition are usually discussed in terms of two-slit experiments (6), involving no specific assumptions about the nature of the particles (charge, mass, etc.) or obvious relevance to chemistry.

However, we can formulate additional consequences of eqs 3a–f whose implications for chemical bonding and electron delocalization are immediate and obvious.

The Donor–Acceptor Paradigm

Let us now specialize to the case in which ϕ_1, ϕ_2 are, respectively, an occupied (ϕ_o) and a vacant (ϕ_v) orbital on two nuclear centers. (For example, ϕ_o might represent the occupied 2s spin-orbital of a lithium atom and ϕ_v the unoccupied 3p spin-orbital of a chlorine atom.) At large separation, this system is adequately described by an orbital of the form eq 3e, with corresponding energy \mathcal{E} from solution of eq 3f. Solving the quadratic equation eq 3f in the usual manner, we obtain the two possible solutions, labeled \mathcal{E}_{\pm} ,

$$\mathcal{E}_{\pm} = \frac{\epsilon_v + \epsilon_o}{2} \pm \left\{ \left(\frac{\epsilon_v - \epsilon_o}{2} \right)^2 + h_{\text{ov}}^2 \right\}^{1/2} \quad (4)$$

We assume that the vacant orbital lies higher in energy than the filled orbital: $\epsilon_v > \epsilon_o$. For sufficiently large separation (small $|h_{\text{ov}}|$), the square root in eq 4 can be expanded as a Taylor series in powers of $|2h_{\text{ov}}/(\epsilon_v - \epsilon_o)|^2$ to give the expression

$$\mathcal{E}_{\pm} = \frac{\epsilon_v + \epsilon_o}{2} \pm \left[\frac{\epsilon_v - \epsilon_o}{2} + \frac{h_{\text{ov}}^2}{\epsilon_v - \epsilon_o} + \dots \right] \quad (5)$$

To leading order, the low-energy solution \mathcal{E}_- therefore becomes

$$\mathcal{E}_- = \epsilon_o - \frac{h_{\text{ov}}^2}{\epsilon_v - \epsilon_o} \quad (6)$$

The energy lowering $\Delta\mathcal{E}_{\text{DA}}$ resulting from this interaction of filled (“donor”) orbital ϕ_o with vacant (“acceptor”) orbital ϕ_v can therefore be expressed as

$$\Delta\mathcal{E}_{\text{DA}} = \frac{h_{\text{ov}}^2}{\epsilon_v - \epsilon_o} \quad (7)$$

Equation 7 can also be recognized as the familiar 2nd-order perturbation theory expression for the stabilizing effect of a 1-electron donor-acceptor interaction.

Note that although the specific approximate form of $\Delta\mathcal{E}_{\text{DA}}$, eq 7, is valid only under the assumptions of the derivation (particularly, $\epsilon_v \neq \epsilon_o$, $|h_{\text{ov}}| \ll |\epsilon_v - \epsilon_o|$), it can be shown more generally that the solutions are of the form

$$\mathcal{E}_- = \epsilon_o - \Delta\mathcal{E}_{\text{DA}} \quad (8a)$$

$$\mathcal{E}_+ = \epsilon_v + \Delta\mathcal{E}_{\text{DA}} \quad (8b)$$

where $\Delta\mathcal{E}_{\text{DA}}$ depends only on the *magnitude* of h_{ov} (for example, $\Delta\mathcal{E}_{\text{DA}} = |h_{\text{ov}}|$ when $\epsilon_v = \epsilon_o$). Whether we employ the approximate form in eq 7 or the exact expression for $\Delta\mathcal{E}_{\text{DA}}$ will not materially alter the following discussion.

Figure 1 schematically depicts the donor–acceptor interaction, showing how the initial orbital energies ϵ_o, ϵ_v are split to give net energy lowering of the occupied level (hence, mutual attraction between the systems). The occupied orbital Φ_- of the interaction system is now of delocalized superposition form (cf. eq 3e),

$$\Phi_- = c_o \phi_o + c_v \phi_v \quad (9a)$$

containing a partial admixture of the high-energy orbital ϕ_v .

Three aspects of such donor-acceptor interactions are particularly noteworthy.

First, the corresponding interactions of two *filled* (spin-) orbitals would not be similarly stabilizing. As eqs 8a,b and Figure 1 show, the two energy levels of the noninteracting system are split by essentially equal and opposite amounts, so the net stabilization of the interacting system would be nearly zero if both levels were occupied. In fact, consideration of higher-order terms shows that such filled-filled orbital interactions generally lead to net energy *increase*, corresponding to repulsions between the systems. Thus, the availability of an unoccupied orbital with which the filled orbital can interact (i.e., into which the electron can partially delocalize) is essential to the general attractive nature of superposition.

Second, the donor-acceptor energy lowering is generic, associated only with the general superposition expressions (eqs 3d-f), and virtually independent of the detailed form of \mathcal{H} . In particular, the energy lowering $\Delta\mathcal{E}_{DA}$ depends only on the magnitude of h_{ov} , not its sign, so *any* alteration of \mathcal{H} that increases this magnitude (e.g., by increasing or decreasing either kinetic or potential energy terms) would have an equivalent stabilizing effect. Of course, the details of the kinetic and potential energy terms in \mathcal{H} (and their mutual relationship required by the virial theorem [7]) are important for determining specific values of ϵ_o , ϵ_v , h_{ov} , and the quantitative energy lowering, but it is useful to recognize that the qualitative chemical stabilizing effects of donor-acceptor superposition are largely independent of these details. In particular, it is fundamentally misleading to attempt to rationalize the attractive chemical forces (e.g., in terms of classical images of individual kinetic or potential energy terms²) without reference to superposition.

Third, it is remarkable (and entirely characteristic) that the energy lowering $\Delta\mathcal{E}_{DA}$ is achieved by mixing the low-energy orbital with a higher-energy unoccupied orbital. Only in quantum mechanics can one hope to lower the energy of an object by “blending in” some object of higher energy! This counter-intuitive aspect of delocalizing interactions represents one of the deepest conceptual paradoxes of quantum theory, yet such interactions pervasively underlie practically all chemical phenomena.

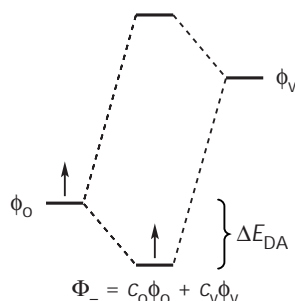


Figure 1. Schematic perturbation diagram for 1-electron donor-acceptor interaction between occupied (ϕ_o) and vacant (ϕ_v) spin-orbitals, leading to energy lowering $\Delta\mathcal{E}_{DA}$; cf. text eqs 8a,b.

Chemistry of Donor-Acceptor Interactions

Let us examine a few of the chemical phenomena that can be associated with donor-acceptor interactions. To make the connection between the form of the superposition wave function and the energetic quantities (eqs 6–8) more explicit, we can express eq 9a in the alternative form

$$\Phi_- = \cos(\theta) \phi_o + \sin(\theta) \phi_v \quad (9b)$$

where the mixing angle θ that determines the extent of superposition is given by

$$\tan(\theta) = -\Delta\mathcal{E}_{DA}/h_{ov} \quad (9c)$$

Note that eq 9c remains correct when the exact value of $\Delta\mathcal{E}_{DA}$ is used in place of eq 7, and reduces to the proper symmetric superposition, $\tan(\theta) = 1$, that is, $c_o = c_v$, in the limiting case $\epsilon_v = \epsilon_o$ where $\Delta\mathcal{E}_{DA} = |h_{ov}|$.

The specific example of the previous section alludes to the $\phi_o \rightarrow \phi_v$ interaction of two nonidentical neutral atoms (e.g., Li + Cl). But we might equally well apply Figure 1 to the case of a hydrogen atom interacting with a bare proton,



the prototype 1-electron chemical bond.³ In this case, ϕ_o and ϕ_v are hydrogenic 1s atomic orbitals of the separated atom and ion. At large separations of H and H^+ , where $|h_{ov}|$ is small and the superposition (eqs 9) is just beginning to develop, the electron remains primarily localized on one center ($c_o \gg c_v$). However, at smaller separations where the interactions $|h_{ov}|$ becomes sufficiently large, the symmetric ($c_o = c_v$) superposition becomes the optimal solution. This corresponds to the usual LCAO-MO form of the bonding σ orbital in the near-equilibrium region of H_2^+ ,

$$\sigma_{AB} = 2^{-1/2} \{1s_A + 1s_B\} \quad (11)$$

symmetrically delocalized between the nuclei A, B.

The corresponding 2-electron covalent interaction



can be considered as the composite of two such 1-electron interactions, one for α and one for β spin. If we assume that the α electron is initially on nucleus A and β on nucleus B, the two 1-electron interactions can be denoted (with “bar” denoting β spin)

$$\phi_o^A \rightarrow \phi_v^B, \quad \bar{\phi}_o^B \rightarrow \bar{\phi}_v^A \text{ (covalent)} \quad (13)$$

representing complementary delocalizations in opposite directions (favored). However, the same final H–H covalent bond orbital might arise from the coordinate covalent (“dative”) interaction of negative and positive hydrogen ions



expressed in terms of the two 1-electron interactions

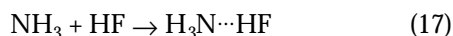
$$\phi_o^A \rightarrow \phi_v^B, \quad \bar{\phi}_o^A \rightarrow \bar{\phi}_v^B \text{ (dative)} \quad (15)$$

delocalizing in the same direction (anion \rightarrow cation). Such dative-type delocalizations (“2-electron stabilizing interactions” [8]), denoted $(\phi_o^A)^2 \rightarrow (\phi_v^B)^2$, can also occur between neutral species, as in the prototype Lewis base–Lewis acid reaction

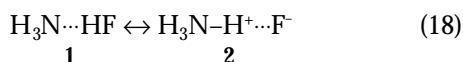


where ϕ_o^A is a nitrogen nonbonding n_N orbital and ϕ_v^B is a vacant boron $2p_B$ orbital. As previously remarked,¹ quantitative ab initio descriptions of eqs 12, 14, and 16 involve higher-level configuration interaction effects, but the physical gist of chemical bonding is well captured in all cases by the simple LCAO–MO picture based on eqs 3d–f.

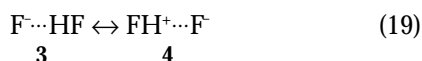
Weaker forms of 2-electron donor–acceptor interactions occur when the acceptor orbital ϕ_v is a vacant 2-center antibond orbital (rather than atomic orbital), with additional nodal structure, higher energy, and reduced acceptor strength. For example, the σ_{HF}^* antibond orbital of HF (the out-of-phase counterpart of the σ_{HF} bonding orbital) can interact with the ammonia lone pair, in a manner similar to eq 16, to give the weaker form of $(\phi_o^A)^2 \rightarrow (\phi_v^B)^2$ interaction that leads to a hydrogen bond,



with $\phi_o^A = n_N$, $\phi_v^B = \sigma_{HF}^*$. Such an interaction corresponds, in resonance terms, to a partial admixture of the alternative ion-pair resonance structure,

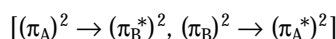


in which the roles of covalent bond and hydrogen bond are partially blurred. For this H-bonded complex, the weighting of the alternative ion-pair structure 2 is much smaller than that of 1 ($w_1 \gg w_2$), and the electrons remain well localized as pictured in structure 1. However, when the amine base NH_3 is replaced by the stronger (anionic) donor F^- , the resulting interaction

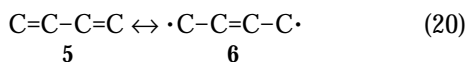


(with $\phi_o = n_F$, $\phi_v = \sigma_{HF}^*$) leads to the more strongly delocalized bifluoride ion FHF^- species, with *symmetric* equilibrium geometry and complete obliteration of the distinction between covalent bond and H-bond ($w_3 = w_4$). Such a donor–acceptor picture allows one to account for many of the known regularities of H-bonding in terms of simple Lewis acid–base concepts (9).

Still another well-known form of donor–acceptor interaction involves 2-center π orbitals as *both* donors and acceptors. A simple example is butadiene ($H_2C=CH-CH=CH_2$), whose classical Lewis structure contains two filled π bond orbitals (π_A , π_B) and the corresponding unfilled antibond orbitals (π_A^* , π_B^*), held in proximity by the underlying σ bond network. Each π bond interacts with the adjacent π antibond



to give the strong conjugative delocalizations characteristic of extended polyene systems



In butadiene and other cyclic polyenes, the $\pi \rightarrow \pi^*$ interactions are not sufficient to entirely erase the bond alternation pattern of the principal resonance structure ($w_5 > w_6$). However, in benzene and other cyclic aromatic systems, these delocalizing interactions are so strong as to obliterate the distinction between single and double bonds ($w_5 = w_6$), leading to a

symmetric equilibrium structure. (In this respect, benzene is somewhat analogous to the intermolecular limiting case [eq 19].) The propensity toward bond-equalization and delocalization in π -conjugated molecules can therefore be seen as a direct consequence of the strength of $\pi \rightarrow \pi^*$ donor–acceptor superposition.

Numerous other examples of donor–acceptor superposition might be cited, including “hyperconjugative” $\pi \rightarrow \sigma^*$, $\sigma \rightarrow \pi^*$, and $\sigma \rightarrow \sigma^*$ interactions of importance in spectroscopy (10), rotation barrier phenomena (11), hypervalency (12), and reactivity (13). However, the above examples may serve to illustrate the central role of the quantum mechanical superposition principles (eqs 3) in a broad array of chemical phenomena.

Teaching the Donor–Acceptor Concept

Although the donor–acceptor concepts sketched above are by now rather widely recognized in the chemistry research community, their influence on freshman chemistry textbook writers and curriculum reformers is as yet virtually imperceptible. This is unfortunate, for these concepts are inherently simpler and more highly visualizable (as well as substantially more accurate) than the familiar melange of freshman chemistry “rationalizations”. We briefly sketch how these concepts might be integrated into a reformed, unified framework that could truly serve as a “general chemistry” introduction to advanced studies in organic, inorganic, physical, and biochemistry.

A donor–acceptor-based freshman chemistry curriculum should generally emphasize quantal “orbital intuition”, including orbital visualization of interactions and charge distributions, rather than electron-counting schemes and quasi-classical particulate description of electron behavior. Topics to be promoted by this shift of emphasis include particle–wave duality, fractional charge, polar covalency, valence bond and antibond orbitals, and donor–acceptor mixing, as discussed below.

Particle–Wave Duality

As stressed throughout this article, teachers should emphasize the deeply counterintuitive implications of quantal particle/wave duality

$$\text{electron} \leftrightarrow \phi(x) \quad (21)$$

rather than attempt to rationalize quantum behavior in terms of comforting (but ultimately incorrect) classical models. This would tend to encourage student interest in more rigorous and mathematical treatment of particle–wave duality (e.g., in a future physical chemistry course), rather than complacency with misleading, infertile classical images.

Fractional Charge

The quantal association (eq 21) requires one to picture electronic charge in a *distributed* fashion (corresponding to the spatial distribution of $|\phi|^2$). Students should be taught to think in terms of fractional charges (“partial charges”) and molecular (or supramolecular) charge distributions, based on shapes of underlying orbitals. Less emphasis would thereby be placed on formal electron counting scheme (i.e., formal charge, oxidation number, VSEPR) and idealized atomic or ionic configurations of integer net charge.

Polar Covalency

Corresponding to eq 3e or eq 11, the electrons of a general A–B chemical bond should be pictured in terms of a general bond orbital function (in-phase superposition) of the form

$$\phi_{AB} = c_A h_A + c_B h_B \quad (22a)$$

where h_A , h_B are atomic hybrid orbitals and c_A , c_B are general polarization coefficients (satisfying the normalization condition $c_A^2 + c_B^2 = 1$) that vary smoothly between 0 and 1 according to the relative electronegativities of A and B. The simple relationships between hybrid character and bond polarity expressed by Bent's rule (14) should be strongly emphasized. As Sanderson (15) has pointed out, a polar covalent description properly expresses the continuous variation between covalent ($c_A = c_B$) and ionic ($c_A \gg c_B$) limits, correcting the unfortunate impression of extreme bonding "types" (each with atoms of integer electron and charge assignments) that still pervade many elementary discussions of bonding theory.

Valence Bond and Antibond Orbitals

Emphasis should be placed on recognizing the characteristic shapes of bond orbitals (eq 22a) corresponding to electron pairs of the localized Lewis structure diagram, as well as to the corresponding antibonding orbitals

$$\phi_{AB}^* = c_B h_A - c_A h_B \quad (22b)$$

which represent residual unfilled (acceptor) valence-shell capacity. Just as effort is expended to learn the shapes and energies of filled and unfilled atomic orbitals (to comprehend hybrid and bond formation), so should the shapes and energies of leading bond and antibond orbitals (eqs 22a, b) be mastered to explain *noncovalent* interactions and electron delocalization ("resonance") effects. This represents only a slight generalization of what is commonly taught in the standard "homonuclear diatomic molecules" module, but would considerably extend the pedagogical use of these orbitals (e.g., beyond the paramagnetism of O_2). Examples of the type of bond–antibond orbital diagrams that could enhance freshman chemistry books are shown in the *Encyclopedia of Computational Chemistry* (16).

Donor–Acceptor Mixing

The same type of reasoning and visualization that leads to formation of covalent bonds from overlapping hybrids h_A , h_B should be employed to describe the interactions of overlapping bond–antibond orbitals in forming delocalized molecular (or supramolecular) orbitals, using the mnemonic perturbation diagram (Fig. 1) or eqs 3–8 as a unifying framework. As described in the section on chemistry of donor–acceptor interactions, this leads naturally to unified treatment of a variety of conjugative, hyperconjugative, and noncovalent phenomena that are usually considered "beyond" freshman chemistry.

In summary, a donor–acceptor-based approach should aim to instill in the freshman chemistry student (i) increased awareness that many fundamental chemical phenomena can be traced back to basic wave-mixing principles embodied in Figure 1 and (ii) increased familiarity with the shapes and energies of leading atomic and bond–antibond orbitals needed to treat the phenomena of bonding "resonance" delocalization, hyperconjugation, and hydrogen bonding. The

benefits of such an approach might be realized with relatively subtle shifts of emphasis in concepts listed above.

Conclusion

The quantum superposition principle leads to a virtually certain mechanism for rewarding interactions of a chemical nature. Given that nature favors evolution of matter toward states of lower energy, it is virtually certain that two electronic systems, each allowed to probe the unoccupied orbitals of the other, will find at least one of the two possible superpositions ($\phi_o + \phi_v'$ or $\phi_o - \phi_v'$, for some scaled $\phi_v' = \lambda\phi_v$) to be energetically favorable. Hence, nature tends to favor bringing electronic systems into closer spatial proximity ("bonding") because this leads to nonvanishing interactions h_{ov} (of either sign) that will allow favorable $\phi_o \rightarrow \phi_v$ delocalizations to lower the energy.⁴

The examples of this paper show that many combinations of occupied and vacant orbitals (1-center or bond type, intramolecular or intermolecular, σ or π , etc.) can lead to donor–acceptor superposition and stabilization. The favorable superposition patterns can often be qualitatively predicted with only minimal knowledge of the actual form of \mathcal{H} . This justifies the conviction of many chemists that qualitative awareness of orbital shapes and mixing patterns (17) (rather than, for example, details of individual kinetic and potential energy contributions) provides the most important insight in understanding and predicting chemical phenomena.

Owing to its pervasive dependence on the superposition phenomenon, chemistry truly deserves to be called "the quantum science".

Notes

1. While more accurate treatment of Schrödinger's equation introduces further complexities, this simple "molecular orbital picture" is known to capture the essential physical gist of chemical bonding in all systems considered herein.

2. For example, freshman chemistry textbooks often attempt to "explain" chemical bonding in terms of "expanded box length" (to lower the kinetic energy) or "attraction of the electron to both nuclei" (to lower the potential energy). Each of these expresses only a partial truth.

3. In this case the formal symmetry-adapted eigenfunctions of \mathcal{H} contains equal contributions from two degenerate, localized, long-lived solutions of the time-dependent Schrödinger equation, only one of which is physically relevant. However, one can use a formal perturbative treatment, based on an initial neutral H atom perturbed by a distant proton, to obtain the unsymmetric solution that is appropriate in the present case.

4. Of course, general aggregation of matter is opposed by both steric forces (filled-filled orbital interactions) and the randomizing effects of ambient thermal energies.

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- (Jammer, ref 1, Sec. 5), was often echoed (in various languages) by pioneer quantum theorists. See, e.g., Ehrenfest, P. *Z. Phys.* **1932**, *78*, 555–559. Pauli, W. *Z. Phys.* **1933**, *80*, 573–586.
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