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## What is a hydrogen bond? Resonance covalency in the supramolecular domain

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We address the broader conceptual and pedagogical implications of recent recommendations of the International Union of Pure and Applied Chemistry (IUPAC) concerning the re-definition of hydrogen bonding, drawing upon the recommended IUPAC statistical methodology of mutually correlated experimental and theoretical descriptors to operationally address the title question. Both direct and statistical lines of evidence point to the essential *resonance covalency* of H-bonding interactions, rather than the statistically insignificant “dipole–dipole” character that is persistently advocated in current textbooks. The revised conception of H-bonding is both supported by modern quantum chemical technology and consistent with the pre-quantal insights of G. N. Lewis and other bonding pioneers. We offer specific suggestions for how relatively minor changes in the usual discussion of Lewis-structural and resonance concepts—supported by modern web-based computational modeling tools—can readily accommodate this fundamental change of perspective.

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### Introduction

*“Any other situation in quantum mechanics, it turns out, can be explained by saying, ‘You remember the case of the experiment with the two holes? It’s the same thing’.”—Richard P. Feynman*

Chemistry is often characterized as “the molecular science” (Moore *et al.*, 2010). This description implicitly narrows chemistry’s presumed intellectual domain to polyatomic species linked by covalent bonds, the signature feature of molecule formation. Indeed, a widely held view is that chemical covalency forces extend only to the boundaries of the molecule, whereas remaining forces of intermolecular attraction (such as those responsible, *e.g.*, for condensed phase formation, biological self-assembly, and related *supramolecular* phenomena) are perforce identified as “noncovalent” interactions. The former are generally recognized to be of essential *quantal* nature, whereas the latter are assumed to be describable by simpler potential forms such as those of classical electrostatics, free of the exchange-type superposition phenomena (“quantum weirdness”) and associated computational complexities that are characteristic of the covalent bonding regime.

Hydrogen bonding is arguably the most important “type” of such supramolecular interaction, currently featured as a primary

term in the title, abstract, or keyword list of more than 10 000 research publications per year. The manner in which H-bonding is defined and discussed in introductory textbook and classroom presentations is of corresponding importance in the educational domain. Envisioned distinctions between H-bonding and other “bond types” commonly lead to pedagogical confusion that is well documented in the chemical education literature, reflecting both the problems in learning that arise from problematic teaching as well as the need for more accurate, clear, and up-to-date accounts of chemical bonding concepts. As pointed out by Henderleiter *et al.* (2001), an understanding of the common textbook presentation of H-bonding is so complex that students typically rely on rote memorization to determine which elements could be considered to be involved. Taber (1998) has commented on the tendency of many chemistry textbooks to refer to H-bonding (as well as other van der Waals interactions) not as “chemical bonds” but as “just forces”. In a recent review of 14 general chemistry textbooks, Tsapalis and Pappa (2011) reported that one book presents intermolecular bonds without referring to their “types,” four books refer to existence of intermolecular bonds but describe only the hydrogen bond, and nine books follow different order of presentation of the types of intermolecular bonds, with most books concurring that covalent and ionic bonding are true bonding, whereas H-bonding and other intermolecular interactions are just “forces”.

Problems of teaching H-bonding are evidently connected to broader issues in the teaching of “ordinary” valency and chemical bonding concepts. As suggested by Taber and Coll (2002), usual presentations of the “octet” framework may lead to learning impediments, in that any form of interaction that

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does not apparently lead to atoms having filled electron shells appears mysterious. Students thereby have difficulty accepting anything that is not clearly explicable in “octet” terms as being a chemical bond, and H-bonding (unless properly presented in resonance terms; see below) apparently cannot be readily fitted into such a scheme. Further study and discussion of chemical bonding can be found in Levy Nahum *et al.* (2007, 2008, 2010, 2013), Yayon *et al.* (2012), Taber (2013), and Tsapalis and Sevan (2013). Although our present discussion is couched in terms of “freshman chemistry” textbooks of the US university model, analogies may be inferred to other teaching levels and geographical settings (Harrison and Treagust, 2000), (Coll and Taylor, 2001, 2002), (Taber *et al.*, 2012). From all perspectives, the current tendency to strongly separate discussion of “true” chemical bonding from H-bonding and related electrostatic-type “forces” is deeply entrenched.

Indeed, common definitions of H-bonding in current textbooks are nearly uniform in advocating an electrostatic “dipole-dipole” rationale, as shown in the following representative examples (highly conserved from edition to edition):

“a type of dipole-dipole interaction” (Brown *et al.*, 2012),  
 “a special type of dipole-dipole interaction” (Burdge, 2011),  
 “particularly strong dipole-dipole forces,” (Zumdahl and Zumdahl, 2012),  
 “an extreme form of dipole-dipole interaction,” (Kotz *et al.*, 2009),  
 “especially enhanced dipole-dipole forces” (Siska, 2005),  
 “a special kind of dipole-dipole force” (Moore *et al.*, 2010),  
 “a sort of *super* dipole-dipole force” (Tro, 2011),  
 and many similar. The current *Wikipedia* entry for “hydrogen bond” (accessed February 19, 2014) also includes firm declarative statements such as

“The hydrogen bond is the electromagnetic attractive interaction between polar molecules. . . it is not a true bond but a particularly strong dipole-dipole attraction, and should not be confused with a covalent bond”.

Similar presumptions are reflected in all recent articles pertaining to H-bonding in the *Journal of Chemical Education*. Still stronger assertions can be found in the research literature that the resonance-type “charge transfer” component of H-bonding is not merely of secondary importance, but “ill-defined” and “part of the induction (polarization)” component that “vanishes in the limit of a complete basis” (Stone, 1993).

Similar electrostatics-type assumptions are deeply embedded in the empirical point-charge potentials of widely used molecular dynamics (MD) and Monte Carlo (MC) simulation methods (Leach, 2001). These methods make no pretense to describe chemical bonding and reactivity phenomena, but are widely presumed to adequately describe H-bonding phenomena. The ubiquity of such simulation potentials in many areas of materials and biochemical research tends to reinforce and perpetuate the corresponding electrostatics-type rationalizations of H-bonding in elementary textbooks. Neither the manner in which H-bonding is now taught to beginning students nor how it is “simulated” in MD/MC potentials has changed appreciably in the past half-century.

Electrostatics-based assumptions about the nature of H-bonding were also long canonized in the “Gold Book” (McNaught and Wilkinson, 1997) definitions of the International Union of Pure and Applied Chemistry (IUPAC). In recent years, however, a distinguished international committee was convened to reformulate the IUPAC definition of H-bonding, based on accumulated experimental and theoretical evidence of its substantial inadequacy. The final committee definition (Arunan *et al.*, 2011b) is a rather ponderous composition [*ca.* 700 words (about eight times the original), plus another 900 words of footnotes and an 8-page supplementary “Account” of supporting rationale] that challenges easy textbook synopsis. Moreover, the committee document takes no firm stand as to which among a number of listed theoretical factors should be singled out for primary pedagogical emphasis. Nevertheless, the committee achieves genuine progress by endorsing a sensible evidence-based *operational* procedure for determining what is (or is not) a hydrogen bond, based on a *composite array of correlated experimental properties* (including familiar X-ray, infrared, and NMR features) that are regarded as reliable signatures of H-bonding.

Such fundamental operational criteria for deciding “What is a hydrogen bond?” provide the starting point for systematically improving both experimental and theoretical characterizations of the H-bonding phenomenon. In principle, the IUPAC approach allows entirely new experimental methods to be added to the “best current” definition, based on evidence of mutually consistent correlations with previously established criteria. In analogous manner, any proposed *theoretical* descriptor can be tested for inclusion in this evolving consensus. More importantly for our considerations, the methodology suggests how one can apply standard regression techniques to quantify the relative weightings assignable to *competing* theories of H-bonding, with considerable conceptual and pedagogical implications.

As described in a recent study (Weinhold and Klein, 2012), such regression-based testing can be applied to resolve the long-standing controversies between electrostatic “dipole-dipole” vs. “partial covalency” descriptions of H-bonding. Contrary to common textbook presumptions, all such evidence points to the superiority of covalency-based descriptors of hydrogen bonds, corresponding to intrinsic conceptual formulation as resonance-type *fractional chemical bonds*. The present article aims to bring this work to the attention of a broader audience of chemical educators and outline its major pedagogical implications.

Such a revised perspective on H-bonding presents both challenges and opportunities to chemical educators, extending covalency and resonance concepts into a broad new landscape of biochemical and other “soft matter” phenomena. We include suggestions for how improved H-bonding concepts can be achieved rather directly by linking the introductory teaching of covalency and resonance topics more closely to modern computational chemistry technology. The ready availability of computational chemistry discovery tools in the WiFi classroom makes such integrated improvement of chemical bonding and H-bonding topics both practically feasible and

ideally suited to newer “active learning” strategies throughout the science curriculum.

## Resonance covalence in NBO perspective

Arguments about the nature of H-bonding can be traced to two illustrious pioneers of modern bonding theory—Gilbert Newton Lewis and Linus Pauling. Although Pauling makes reference to an earlier report of H-bonding effects by Moore and Winmill (1912), broader recognition of the phenomenon and its importance to the general theory of bonding is primarily due to the Berkeley group surrounding G. N. Lewis. Shortly before the discovery of quantum mechanics, Lewis concluded that H-bonding manifested a “bivalent” aspect of the hydrogen atom that should be considered the most important extension of his electron-pair theory of chemical covalency (Lewis, 1923). Lewis’s viewpoint was subsequently challenged by the young Linus Pauling, who pointed out (Pauling, 1928) that the hydrogenic 2s solution of Schrödinger’s equation (erroneously presumed to be necessary for H-bonding) lies about 235 kcal mol<sup>−1</sup> above the ground 1s state, far too high to be involved in H-bonding (true, but irrelevant). The prevailing electrostatics-based textbook picture can be traced back to Pauling’s influential conclusion (repeated in successive editions of *The Nature of the Chemical Bond*) that H-bonding must be primarily “ionic” in nature. For a comprehensive account of the historical evolution of H-bonding concepts, see Quane (1990).

As the quantum theory of H-bonding advanced, the covalency concept was advocated in the varied terminology of “covalent-ionic resonance” (Coulson, 1957), “3-center molecular orbitals” (Pimentel and McClellan, 1960), “charge transfer” (Ratajczak, 1972), and “intermolecular donor–acceptor interactions” (Weinhold and Landis, 2005). All such formulations make reference to what is now commonly described as “3c/4e” (3-center/4-electron) interaction (Pimentel, 1951; Rundle, 1962; Coulson, 1964; Munzarova and Hoffmann, 2002; Weinhold and Landis, 2005, p. 278ff), the simple extension of Lewis’s original 2c/2e electron-pair bond concept that underlies important resonance-type phenomena in both intra- and intermolecular domains.

The qualitative concepts underlying both the original localized 2c/2e Lewis structure picture and its resonance-type 3c/4e extensions can be quantified with natural bond orbital (NBO) analysis of modern wavefunctions (Weinhold and Landis, 2005; Glendening *et al.*, 2013). NBO analysis is implemented in a widely used computer program (currently, *NBO 6.0*, <http://nbo6.chem.wisc.edu>) which is routinely available through the *WebMO* website (<http://www.webmo.net/>) and is interfaced to many popular program suites ([http://nbo6.chem.wisc.edu/affil\\_css.htm](http://nbo6.chem.wisc.edu/affil_css.htm)). Some general aspects of NBO analysis are briefly described below or accessible in pedagogical introductions (Suidan *et al.*, 1995; Weinhold 1999; Weinhold and Landis, 2001), whereas more technical details of NBO program usage and the underlying computational algorithms are available elsewhere (Weinhold, 1998; Glendening *et al.*, 2012; Weinhold and Landis, 2012).

The primary task of NBO analysis is to find the best single “natural Lewis structure” (NLS) representation of the chosen

NBO	parent NLS	CT resonance
amide $n_{\text{N}} \rightarrow \pi_{\text{CO}}^*$		
vicinal $\pi_{\text{CC}} \rightarrow \pi_{\text{CC}}^*$		
vicinal $\sigma_{\text{AX}} \rightarrow \sigma_{\text{BY}}^*$		
geminal $\sigma_{\text{AX}} \rightarrow \sigma_{\text{AY}}^*$		
H-bond $n_{\text{B}} \rightarrow \sigma_{\text{AH}}^*$		

Fig. 1 Generic “arrow-pushing” diagrams, comparing NBO donor–acceptor description (left) with corresponding parent NLS (middle) and secondary charge-transferred resonance structures (right) for various conjugative and hyperconjugative motifs.

wavefunction or density. For a typical molecular species, the NLS provides explicit optimized forms of the lone pairs ( $n_{\text{A}}$ ) and bonds ( $\sigma_{\text{AB}}$ ,  $\pi_{\text{AB}}$ , *etc.*) of the formal Lewis diagram, represented by Lewis-type “donor” NBOs that commonly describe *ca.* 99% or more of the total electron density. Residual donor–acceptor corrections to the localized NLS density are associated with the weak occupancy of remaining non-Lewis-type “acceptor” NBOs, such as the valence antibonds ( $\sigma_{\text{AB}}^*$ ,  $\pi_{\text{AB}}^*$ , *etc.*) that are formally vacant in the elementary Lewis structure picture.

This NBO donor–acceptor description is closely connected to the usual “resonance theory” description of electronic delocalization effects, as first popularized by Pauling and others (Pauling and Wheland, 1933; Wheland, 1955; Pauling, 1960). Indeed, each possible NBO donor–acceptor correction to the elementary Lewis picture (such as the  $n_{\text{N}} \rightarrow \pi_{\text{CO}}^*$  delocalization of amides or the  $\pi_{\text{CC}} \rightarrow \pi_{\text{CC}}^*$  delocalizations of aromatics) can be equivalently expressed† as a contributing “charge-transferred” resonance structure according to familiar arrow-pushing mnemonics, as illustrated for common intramolecular and intermolecular

† For examples of the orbital configuration shifts and determinantal algebra underlying the mappings of Fig. 1, see (Weinhold and Landis, 2005, p. 20), (Weinhold and Landis, 2012, p. 99ff).

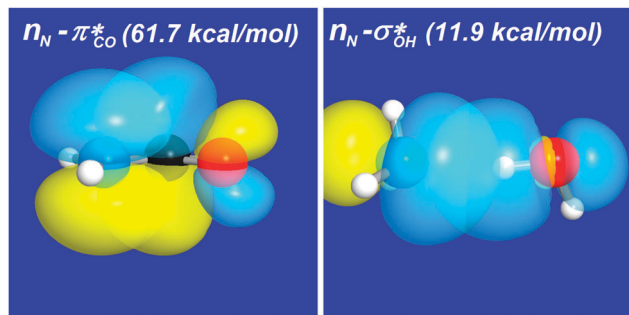


Fig. 2 NBO overlap diagrams for contrasting intramolecular  $n_N \rightarrow \pi^*_{CO}$  (formamide; left) vs. intermolecular  $n_N \rightarrow \sigma^*_{OH}$  (H-bonded  $NH_3 \cdots H_2O$  complex; right) donor–acceptor interactions (cf. upper and lower panels of Fig. 1), with parenthesized perturbative estimates of interaction energy.

bonding motifs in Fig. 1. With this mapping, the qualitative concepts of H-bond covalency can be discussed with no specific reference to NBO methodology, yet with easy connection to the usual discussions of resonance in benzene, amides, carboxylates, and other familiar examples of the molecular domain.

The resonance stabilization provided by each such donor–acceptor delocalization can be estimated by simple perturbation-theoretic or orbital deletion methods (Weinhold and Landis, 2012, Sections 5.2 and 5.3). Consistent with the variety of orbital types and bonding motifs represented in Fig. 1, these donor–acceptor interactions range over a wide variety of stabilization energies and forms, as illustrated in Fig. 2 for the strong  $\pi$ -type intramolecular  $n_N \rightarrow \pi^*_{CO}$  resonance of formamide ( $NH_2CHO$ ) vs. the weaker  $\sigma$ -type intermolecular  $n_N \rightarrow \sigma^*_{OH}$  resonance of the H-bonded ammonia–water species ( $H_3N \cdots HOH$ ).

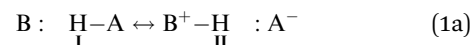
The resonance-theoretical description can be further quantified with NBO-based natural resonance theory (NRT) (Glendening and Weinhold, 1998), which provides optimized numerical resonance weightings ( $w_I, w_{II}, \dots$ ) of contributing resonance structures **I**, **II**,... as well as the composite *bond orders* ( $b_{AB}$ ) that best express the strength of resonance-weighted chemical bonding between any atom pair (A, B). Donor–acceptor interactions thereby lead to the well-known *fractional bond orders* (e.g.,  $b_{NC} = 1.305$ ,  $b_{CO} = 1.743$  in formamide) that are indicative of resonance-type conjugative or hyperconjugative effects in the intramolecular domain.

The corresponding *intermolecular* resonance effects are found to be quite analogous and no less important. The principal difference is that the fractional resonance-type contribution to bond order is not supplemented by the usual integer contribution from an underlying Lewis-structural skeletal network of covalent bonds.<sup>‡</sup> From this perspective, it can be seen that the intermolecular variant of resonance covalency represents the sub-integer “tail” of the *continuous* distribution of interatomic

<sup>‡</sup> In the usual order of perturbative precedence, the optimal Lewis structure (NLS) provides the idealized *integer* (Lewis-type) contribution to bond order, whereas the weighting with secondary resonance structures leads to *fractional* (resonance-type) corrections to bond order, as in the familiar examples of benzene or amides. In the H-bonding case discussed below, the Lewis-type integer contribution is absent in the idealized NLS limit (**I**) but the fractional bond order contribution remains in the composite resonance hybrid (**I**  $\leftrightarrow$  **II**).

$A \cdots B$  orders that are apparently possible in the periodic table (Weinhold and Landis, 2007). “Intermolecular resonance” therefore refers specifically to the important *sub-integer* range of covalent bond orders that are accessible to *all* elements of the material world.

For the specific case of  $B \cdots H-A$  hydrogen bonding, the essence of the intermolecular  $3c/4e$  picture is expressed by the resonance hybrid of asymmetrically weighted neutral (**I**) and proton-transferred (**II**) resonance forms, *viz.*,



with

$$w_I \geq w_{II} \quad (1b)$$

It is evident from (1b) that the bond orders for the covalent ( $b_{HA}$ ) and H-bond ( $b_{B \cdots H}$ ) linkages are related to the resonance weightings and to one another by

$$b_{B \cdots H} = 1 - b_{HA} = w_{II} = 1 - w_I \quad (1c)$$

Relationship (1c) directly expresses the important concept that the resonance *is* the binding (Herzberg, 1966).

Despite differences in magnitude and orbital form (Fig. 2), Fig. 1 suggests the many parallels between intramolecular and intermolecular resonance stabilization. These parallels are consistent with the fact that the underlying quantal Hamiltonian operator makes *no* distinction between electronic interactions that are classified by the chemist as “intramolecular” vs. “intermolecular”. Perceived differences in resonance-type aspects of the two regimes must ultimately reflect superficial matters of degree, not of underlying quantum mechanical nature.

## Direct and regression-based evidence

By its own account (Arunan *et al.*, 2011a), the IUPAC committee was strongly influenced by more recent experimental measurements of hitherto unknown properties of H-bonded systems that defy plausible classical electrostatic explanation. These include studies of Compton scattering (Isaacs *et al.*, 1999) and NMR *J*-couplings *through* H-bonds (Dingley and Grzesiek, 1998; Cornilescu *et al.*, 1999; Golubev *et al.*, 1999) that demand exchange-type “communication” between H-bonded species, as well as striking atomic force microscopy imagery of H-bonds as fibrous “bridges” between molecules (Zhang *et al.*, 2013), all outside the framework of classical electrostatic theory. Other studies of more strongly (Cleland and Kreevoy, 1994; Frey 2002) and weakly (Desiraju and Steiner, 1999) H-bonded systems have shown that characteristic structural and spectroscopic signatures persist over a far broader span of interaction energies (*ca.*  $kT < \Delta E_{HB} < 45 \text{ kcal mol}^{-1}$ ) than were contemplated in the former IUPAC definition. Both ends of this range challenge electrostatic orthodoxy. Particularly telling are the many known examples of weak apolar (or *reversed* polarity§) interactions that

§ For the instructive example of  $CO \cdots HF$  vs.  $OC \cdots HF$  complexes, see Curtiss *et al.* (1985).



nevertheless comply faithfully with established operational criteria for H-bonding. All such examples offer direct evidence against the textbook dipole-dipole rationale.

Similar inferences can be drawn more quantitatively from regression-based analysis of any representative sample of H-bonded species. In our recent study (Weinhold and Klein, 2012), the sample consisted of twenty  $B \cdots HA$  binary complexes, formed from a variety of simple closed-shell neutral, cationic, and anionic monomers. The selected complexes were chosen to more-or-less uniformly span the range of interaction energies  $\Delta E_{HB}$  from lowest (e.g.,  $B = H_2O$ ,  $HA = CH_4$ ;  $\Delta E_{HB} \approx 0.5 \text{ kcal mol}^{-1} \approx kT$ ) to highest (e.g.,  $B = F^-$ ,  $HA = HF$ ;  $\Delta E_{HB} \approx 45 \text{ kcal mol}^{-1}$ ), all evaluated at the B3LYP/aug-cc-pVTZ theory level (Foresman and Frisch, 1995). For each complex, we evaluated a variety of experimentally measurable descriptors, e.g.,

- $\Delta\nu_{AH}$  (IR frequency shift of the hydride bond)
- $\Delta R_{B \cdots H}$ ;  $\Delta R_{HA}$  (H-bond penetration distance; covalent bond length shift)

- $\Delta\sigma_H$  (NMR proton shielding shift)

We also evaluated theoretical descriptors that are related to intermolecular  $B \cdots HA \leftrightarrow BH^+ \cdots A^-$  resonance covalency, e.g.,

- $Q_{CT}$  (intermolecular  $B \rightarrow HA$  charge transfer,  $Q_{CT} = Q_B = -Q_{HA}$ )
- $b_{B \cdots H}$ ,  $b_{AH}$  (H-bond order; covalent bond order)

or to dipole-dipole models of H-bonding, e.g.,

- $|\mu_B| \cdot |\mu_{AH}|$  (product of monomer dipole moments)

Standard  $|\chi|^2$  correlation coefficients were evaluated to relate each descriptor  $d_i$  (experimental or theoretical) to the principal target property,  $\Delta E_{HB}$ , as well as to one another. For any pair of descriptors  $d_i$ ,  $d_j$  we also obtained regression coefficients ( $a_{ij}$ ,  $b_{ij}$ ) for the optimal least-squares correlation of the form  $d_i = a_{ij}d_j + b_{ij}$  that allows one descriptor to be related to another. Because the data set involves H-bonds from a variety of groups, periods, and charge states, for which bond order-bond energy and similar relationships are expected to display varying proportionality factors, the correlations are understandably somewhat “noisy”. Additional statistical noise arises from secondary background effects due to variations in electrostatics, dispersion, or couplings of H-bonds to other intramolecular structural variations. Nevertheless, the surviving correlations (typically,  $|\chi|^2 > 0.9$ ) provide highly significant statistical evidence for the conclusions to be quoted.

The major results of our study can be summarized rather succinctly: As expected, the gold standard experimental signatures of H-bonding ( $\Delta\nu_{AH}$ ,  $\Delta R_{B \cdots H}$ ,  $\Delta\sigma_H$ ) exhibit robust correlations with  $\Delta E_{HB}$  and with one another ( $|\chi|^2 \approx 0.92$ ). Covalency-based descriptors such as charge transfer ( $Q_{CT}$ ) or bond order ( $b_{B \cdots H}$ ) exhibit still *higher* correlations ( $|\chi|^2 \approx 0.95$ ) with  $\Delta E_{HB}$  than those exhibited by experimental  $\Delta\nu_{AH}$ ,  $\Delta R_{B \cdots H}$ , or  $\Delta\sigma_H$  values, and the  $Q_{CT}$ ,  $b_{B \cdots H}$  values tend to be *better* correlated with  $\Delta\nu_{AH}$ ,  $\Delta R_{B \cdots H}$ , and  $\Delta\sigma_H$  than are the latter with one another. In contrast, the dipole-dipole descriptor  $|\mu_B| \cdot |\mu_{AH}|$  exhibits essentially *negligible* correlation ( $|\chi|^2 < 0.2$ ) with  $\Delta E_{HB}$  or other known signatures of H-bonding.

The high correlation ( $|\chi|^2 \approx 0.99$ ) between charge transfer-type ( $Q_{CT}$ ) and resonance-type bond order ( $b_{B \cdots H}$ ,  $b_{AH}$ ) descriptors of H-bonding is also noteworthy. Fig. 3 displays this

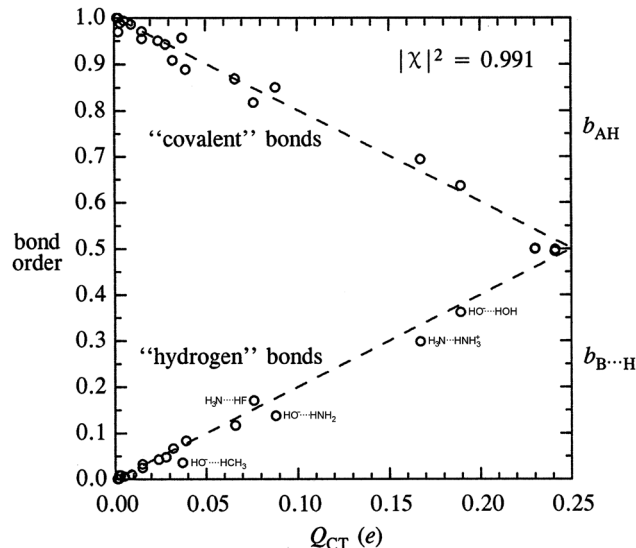


Fig. 3 Correlation of hydride bond orders ( $b_{HA}$ ,  $b_{B \cdots H}$ ) and intermolecular charge transfer ( $Q_{CT}$ ) for the statistical distribution of H-bonded complexes, showing the close adherence to the idealized  $3c/4e$  resonance eqn (2) (dashed lines) and *continuous* distribution of bond orders across the arbitrary dividing line ( $b_{HA} = b_{B \cdots H} = 1/2$ ) between so-called “covalent” (upper half) vs. “hydrogen” (lower half) bonds. (A few representative H-bonds are labelled between extremal  $H_2O \cdots HCH_3$  and  $F^- \cdots HF$  species.)

correlation for the full set of binary complexes and bond orders, whether of “covalent bond” ( $b_{AH} > 0.5$ ; upper half) or “hydrogen bond” type ( $b_{B \cdots H} < 0.5$ ; lower half). The dashed lines represent the 2-resonance relationship, eqn (2), between  $Q_{CT}$  and bond order,

$$1/2 Q_{CT} = b_{B \cdots H} = 1 - b_{HA} \quad (2)$$

which corresponds to the idealized limit in which the intrinsic *univalency* of the H atom is divided (symmetrically or asymmetrically) between the “covalent bonded” and “hydrogen bonded” resonance structures, with *no* discontinuous boundary or change of character except arbitrary re-labelling of which is which after the dashed lines cross at  $Q_{CT} = 0.25e$ . For the entire distribution of binary complexes, the plotted values closely adhere to this idealized limit *throughout* the range of H-bond strengths, passing seamlessly from one side to the other of the (arbitrarily chosen)  $b_{HA} = b_{B \cdots H} = 1/2$  “dividing line” at  $Q_{CT} = 0.25e$ . In this light, we may conclude that perceived *distinctions* between covalent and hydrogen bonds (including their characteristic correlations with experimental X-ray, IR, and NMR properties) merely reflect an arbitrary labeling convention, rather than any statistically significant change of character.

Further details of these regression studies need not be repeated here. The statistical methodology is intended to be open-ended to continual refinements as new experimental or theoretical techniques, or results from new classes of H-bonded systems, are included for consideration. Indeed, the interested reader is invited to repeat the statistical comparisons with an independent selection of H-bonded complexes, improved theory level, alternative choice of dipole-dipole descriptor, or other

variations that may serve to test the general robustness of the above conclusions.

The foregoing is not to deny that contributions of point charge ( $R^{-1}$ ), dipole-dipole ( $R^{-3}$ ), or London dispersion ( $R^{-6}$ ) forms may become dominant features of the potential in the asymptotic long-range limit where intermolecular separation exceeds van der Waals contact distance and exchange-type contributions are negligible. However, the cited evidence indicates that in the actual near-equilibrium geometry of H-bonded systems such classical-like polynomial contributions (if present at all) appear statistically *insignificant* compared to the *exponential* contributions of quantal exchange-type interactions. As in the familiar conjugative and aromaticity effects of  $\pi$ -bonded systems, polarity variations may exert secondary influences on the strength of resonance interactions, but are inessential to the underlying phenomenon. Accordingly, the dipole-dipole rationalizations of current textbooks can be recognized as misleading representations of the actual resonance-type interactions that govern H-bonded systems. The latter should be given primary pedagogical emphasis as the basis for proper *chemical* understanding of supramolecular H-bonding phenomena.

## What should be taught?

In essence, questions concerning “What should be taught?” involve both narrow replacement definitions of H-bonding as well as broader changes of perspective in the teaching of Lewis structural and resonance concepts. The following recommendations (R1–R5) therefore address both aspects of the question.

### (R1) Define H-bonding more accurately in terms of underlying charge transfer, donor-acceptor, and 3c/4e resonance concepts

In the earlier study (Weinhold and Klein, 2012), we suggested a variety of Gold Book-like, short-form, and long-form definitions of H-bonding to serve various purposes. For textbook purposes, the short-form definition may be suitable:

- A *fractional chemical bond due to partial intermolecular*  $A-H \cdots B \leftrightarrow A: \cdots H-B^+$  *resonance delocalization (partial 3-center/4-electron proton-sharing between Lewis bases), arising most commonly from quantum mechanical*  $n_B \rightarrow \sigma_{AH}^*$  *donor-acceptor interaction.*

[The “most commonly” makes provision for alternative  $\pi_B \rightarrow \sigma_{AH}^*$  cases where the donor orbital is a  $\pi$ -bond rather than lone pair of the Lewis base (Nishio *et al.*, 1998).] Successively simplified phrasings, with reduced technical references to 3c/4e electronic character, may also be considered:

- The *stabilizing attraction associated with resonance-type*  $n_B \rightarrow \sigma_{AH}^*$  *“charge transfer” delocalization from a lone pair ( $n_B$ ) of the Lewis base to the proximal hydride antibond ( $\sigma_{AH}^*$ ) in a general*  $B \cdots HA$  *acid-base complex.*

- The *resonance-type attraction associated with proton sharing (partial proton-transfer) between competing*  $A: \cdots B:$  *Lewis bases, with fractional bond orders*  $b_{AH}, b_{BH}$  *divided between alternative*  $A-H \cdots B$  *vs.*  $A: \cdots H-B^+$  *bond patterns of the*  $A: \cdots H \cdots B$  *triad*

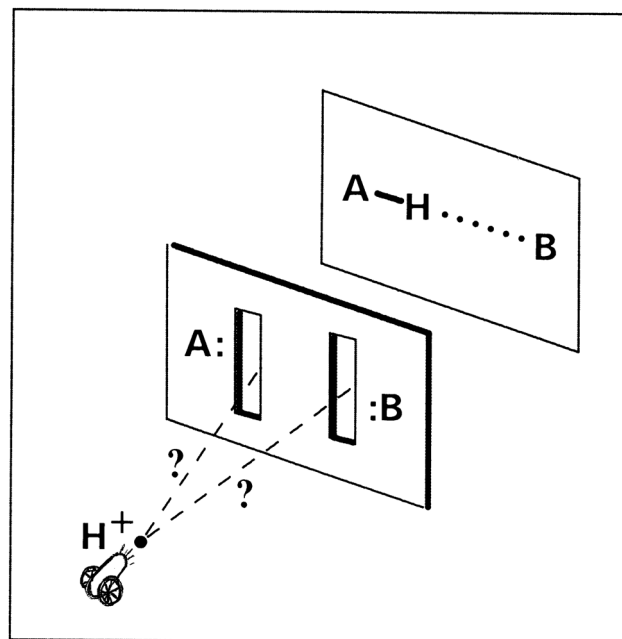


Fig. 4 H-bonding depicted as a resonance-type two-slit superposition phenomenon.

- The *weaker of the two competing donor-acceptor bonds* ( $n_B \rightarrow \sigma_{AH}^*$  vs.  $n_A \rightarrow \sigma_{BH}^*$ ) *in a general*  $A: \cdots H \cdots B$  *triad*
- The *minority fraction of a general*  $A-H \cdots B \leftrightarrow A: \cdots H-B^+$  *resonance hybrid*

All such phrasings emphasize the collective *triad* and competing *resonance* aspects of the H-bonding phenomenon, which can serve to introduce more general 3c/4e resonance concepts that play an important role in the structural and reactive chemistry of both main group and transition metal species.

### (R2) Embrace the weirdness of quantum superposition

A previous paper (Weinhold, 1999) highlights the deep relationships between chemical bonding and the *quantum* logic of the two-slit experiment (Feynman and Hibbs, 1965). Specific pedagogical suggestions were offered for diminishing emphasis on arcane quasi-classical pictures of Bohr orbits and electron counting schemes in favor of the wave-like *continuity* and phase-superposition concepts that underlie all forms of “quantum weirdness”.¶ Suitably chosen lecture demonstrations with optical analogs (Rioux, 2005) or web-based animations (<http://www.youtube.com/watch?v=DfPeprQ7oGc>) can also smooth this important conceptual transition for chemistry students. As quoted at the top of this article and illustrated in cartoon imagery of Fig. 4, Feynman’s apt aphorism

¶ As Feynman explained to his freshman physics students (Feynman *et al.*, 1963, pp. 37–42): “We choose to examine a phenomenon which is impossible, *absolutely* impossible to explain in any classical way, and which has in it the heart of quantum mechanics. In reality, it contains the *only* mystery. We cannot explain the mystery in the sense of ‘explaining’ how it all works. We will *tell* you how it works. In telling you how it works we will have told you about the basic peculiarities of all quantum mechanics”.

(Feynman, 1967) applies to *all* chemical bonding phenomena, including H-bonding.

### (R3) Expose students ASAP to modern theoretical discovery tools

The ready web-based availability of *WebMO* and other resources for calculating and visualizing accurate wavefunctions places a powerful tool in the hands of chemical educators and their laptop-toting students in the modern WiFi-activated classroom. With suitable guidebooks or on-line tutorials [*e.g.*, Marcel Patek (<http://www.youtube.com/watch?v=2Sqo8T1Fong>), Christopher C. Cummins (<http://youtu.be/-veQ3IdYs7s>), or other web-based tutorial materials listed in [http://nbo6.chem.wisc.edu/tutor\\_css.htm](http://nbo6.chem.wisc.edu/tutor_css.htm) or [http://nbo6.chem.wisc.edu/biblio\\_css.htm](http://nbo6.chem.wisc.edu/biblio_css.htm)], students can soon be using the same powerful computational tools that are driving chemical discovery in research laboratories around the globe. With such access, the student's laptop or mobile device can serve not only as an in-class discovery tool but also as a patient tutor and pedagogical "oracle" to provide accurate answers (and vivid graphical imagery) concerning details of valency, hybridization, and bonding in chosen chemical species, long before mathematical mastery of the underling quantum theory is attained.

### (R4) Expand the scope and accuracy of hybridization and Lewis structural description

The association of molecular geometry with electronic structure is now commonly attempted with VSEPR-style (valence shell electron pair repulsions) reasoning, which "works" (for coincidental reasons) only in selected cases. As currently taught, VSEPR theory carries inaccurate connotations concerning hybrid composition (including misleading "rabbit ears" imagery), Lewis-structural pattern, and the nature of steric repulsions.\*\*

In the main group, where VSEPR logic often proves "right" for wrong reasons, increased attention should focus on how general  $sp^{\lambda}$  hybrids are intrinsically related to continuously variable s/p mixing ratio [ $\lambda = (\% - p)/(\% - s)$ ], inter-hybrid bond angle [ $\theta = \cos^{-1}(-1/\lambda)$ ], and the electronegativity difference between central atom and bonding ligand. The latter relationship is elegantly captured in Bent's rule (Bent, 1961), which easily accounts for the usual VSEPR examples but adds considerable quantitative detail and perceptive electronic rationale.

Still further benefits accrue from the powerful analogies that allow successful extension of Lewis-like concepts to transition metal (TM) species. In this extension, the octet rule of the

P-block is replaced by the corresponding "duodectet (12e) rule" of the D-block (s/5d) valence shell, giving rise to  $sd^n$  hybrids whose relationships to percentage s/d mixing [ $\mu = (\% - d)/(\% - s)$ ], inter-hybrid bond angle [ $\theta = \cos^{-1}[\pm(\mu - 2)/2\mu]^{1/2}$ ], and electronegativity are perfectly analogous to those of the main group. (Subsequent 3c/4e ligand coordinations to the Lewis-like parent species are also analogous to the intermolecular H-bonding interactions described above.) In contrast to the general success of Lewis-like structural predictions, many VSEPR-style predictions are found to fail *spectacularly* in the TM domain. Whether or not freshmen are allowed a glimpse of modern organometallic chemistry, proper grounding in main-group Lewis-structural and hybridization concepts provides the easy on-ramp to further exploration of the inorganic domain.

### (R5) Make things as simple as possible, but no simpler

Einstein's advice can be taken to guide the pruning that allows new ideas to find space in the freshman syllabus. As suggested above, VSEPR-style rationalizations are prime candidates for deprecation, but equally disposable are *faux*-rigorous attempts to introduce "completely delocalized" concepts of numerical Hartree-Fock theory, based on superfluous (physically meaningless) transformation properties of single-determinant wavefunctions. Excessive focus on "canonical molecular orbitals" may only serve to sow confusion at the freshman level by obscuring the essentially *local* character of electron pairs, as properly depicted in Lewis and resonance-structural bonding diagrams (Weinhold, 2012). Any intrusion of oversimplified MD-type potential concepts should also be treated as false economy that obfuscates the essential quantal aspects of intermolecular interactions and arguably does more harm than good at the freshman level. Pedagogical investment in more accurate quantal concepts and tools can therefore prove worthwhile both in adding enriched content as well as allowing the offsetting elimination of anachronistic fixtures of the freshman curriculum that must often be "unlearned" as the student progresses to higher levels (Schreiner, 2002).

## Summary and conclusions

In this paper we have attempted to build on recent IUPAC initiatives to reformulate the definition of hydrogen bonding in an operational manner that is more consistent with best current experimental and theoretical understanding. Evidence-based regression methods point instead to resonance-type "charge transfer" superposition of competing  $A-H \cdots B$  vs.  $A: \cdots H-B^+$  bond patterns as the defining characteristic of H-bonding, whereas classical-type (exchange-free) London dispersion and electrostatic "dipole-dipole" forces play only a secondary role. Proper explanations of H-bonding should therefore trace back to the underlying quantum mechanics of "the experiment with the two holes," in accordance with Feynman's keen insight.

We have also argued for upgrading the teaching of bonding concepts with earliest possible student introduction to molecular modeling and analysis tools. The suggested reforms mesh

|| As described elsewhere (Weinhold, 1999), Feynman's characterization of the two-slit experiment in terms of quantal superposition of "interfering alternatives" (Feynman and Hibbs, 1965) can be adapted as well to alternative electronic association with atoms A or B (2-center chemical bonding), alternative orbitals s or p (angular hybridization), alternative Lewis structures I or II (resonance), and so forth. In each case, deep quantum principles dictate that *some* superposition (in-phase mixture) of the interfering alternatives must lie *lower* in energy than *either* alternative in the absence of "interference" (interaction), thereby allowing one to appreciate the profound truth of the statement that "chemistry is quantum science" (<http://condensedconcepts.blogspot.com/2012/09/chemistry-is-quantum-science.html>).

\*\* Further details of NBO-based hybridization and bonding to be mentioned below can be found in Weinhold and Landis (2001), ch. 4 of Weinhold and Landis (2012), and references therein.



with other strategies for implementing “bottom up” teaching approaches (Kronik *et al.*, 2008) as well as meeting the challenge to incorporate active science inquiry into all introductory college science classes (Alberts, 2013). All such changes should serve to impress students with the generality and power of the modern quantum description of matter and the need for basic competency in its concepts and computational methods as a stepping stone to advanced molecular and supramolecular studies throughout the natural sciences.

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