

## Perspective

# Perspective on “The physical nature of the chemical bond”

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### 1 Introduction

“I believe that a good theory combines mathematical rigor with physical interpretation.” With these words, Klaus Ruedenberg began a summary of the highlights of his scientific career in 1996. Many seminal papers by this giant in the field of quantum chemistry serve to illustrate this philosophy; none accomplish the task with more beauty and insight than “The physical nature of the chemical bond” [1]. This paper and those that followed it [2–4] represent the first rigorous, first-principles analysis of the fundamental quantum mechanical origins of covalent bonding which, as Mulliken [5] noted in 1977, “are commonly misunderstood”. With the insight that has become his trademark, Ruedenberg combined four fundamental precepts – the virial theorem, wave-particle duality, the variational principle and the decomposition of the total energy into kinetic and potential components – to devise a model that is both simple and broadly applicable. This paper clearly establishes the important point that it is “possible to extract from a rigorous wavefunction (or a bonafide approximation to it), in a quantitative fashion, a partitioning of the energy which justifies conceptual interpretations.”

The guiding principle in the “chemical bond” paper is the endeavor to isolate the energy-lowering that is associated with bond formation and then to further isolate that contribution to the energy-lowering that is fundamentally quantum mechanical in nature. This is accomplished by proposing a “reaction mechanism” that is constructed in such a way that the virial theorem and the variational principle combine to force the energy-lowering, thereby enabling the decomposition into kinetic and potential-energy contributions to emerge in a natural and easily understandable manner. This focus on the energy-lowering upon bond formation

is critical, since it is precisely with this lowering that we, as chemists, identify bond formation. Additionally, we associate the strength of a bond with the magnitude of the energy decrease. The use of the virial theorem allows for a direct connection with classical physical concepts as is illustrated beautifully in the 1970 paper by Feinberg et al. [2] in the section entitled “The paradox, analogy to space travel.”

### 2 Discussion

The underlying basis for the analysis of the chemical bond may be understood by considering the simplest chemical bond – that which is formed when a hydrogen atom and a proton combine to make  $H_2^+$ , the hydrogen molecule ion [3]:



In the simplest possible case, the two nuclear centers each support one  $1s$  (atomic) wavefunction with which to accommodate electronic motion, and one imagines the formation of a molecular wavefunction  $\Psi$  from the two atomic wavefunctions  $1s_a$  and  $1s_b$  as the two atoms come together,

$$\Psi = N(1s_a \pm 1s_b) , \quad (2)$$

where  $N$  is a normalization constant. The  $+$  and  $-$  in Eq. (2) correspond to the bonding and antibonding molecular wavefunctions, respectively, since they correspond to energy-lowering and energy-raising, respectively. For the bonding wavefunction,

$$N = [2(1 + S_{ab})]^{-1/2} , \quad (3)$$

where  $S_{ab}$  is the overlap of the two atomic wavefunctions. Then, the electron density for the wavefunction in Eq. (2) is

$$\rho_{qm} = \Psi^* \Psi = [2(1 + S_{ab})]^{-1} (1s_a + 1s_b)^2 . \quad (4)$$

A fundamental point regarding  $\rho_{qm}$  is to note that to obtain a quantum mechanical probability density, one first adds the appropriate wavefunctions. In contrast,

classically, one would simply add the corresponding densities to obtain the (normalized) composite probability density,

$$\rho_{\text{cl}} = 1/2(\rho_a + \rho_b) = 1/2(1s_a^2 + 1s_b^2) , \quad (5)$$

Therefore, the inherently quantum mechanical contribution to the density is the difference between  $\rho_{\text{qm}}$  and  $\rho_{\text{cl}}$ . Since this difference ultimately may be traced to the wave nature of our treatment of electrons, and, in particular to the interference of the waves that we refer to here as atomic wavefunctions, Ruedenberg termed this difference density the interference density,  $\rho_I$ :

$$\rho_I = \rho_{\text{qm}} - \rho_{\text{cl}} = [1 + S_{\text{ab}}]^{-1} \times (1s_a 1s_b - 1/2 S_{\text{ab}} [1s_a^2 + 1s_b^2]) . \quad (6)$$

Since both the classical and quantum mechanical densities must integrate to the correct number of electrons in the system (in this case, 1), the interference density must integrate to zero over all space. So, the interference density represents the rearrangement of electron density, with respect to the classical density of Eq. (5), that occurs when the two atoms approach each other. A plot of this rearrangement density along the internuclear axis for the bonding wavefunction at the equilibrium internuclear distance exhibits the well-known buildup of electron density in the bond region between the nuclei, at the expense of a concomitant depletion of electron density around the nuclei. The reverse would, of course, be true for the higher energy antibonding wavefunction.

This decomposition of the total density in terms of a classical and an inherently quantum mechanical interference contribution leads to an analogous resolution of the energy. By considering the energy in a similar light, one may approach the quantum mechanical origins of the energy-lowering responsible for covalent binding. In considering the energy changes due to formation of a covalent bond, Ruedenberg notes that the application of the variational principle to minimize the energy of the newly formed molecule necessarily (due to the virial theorem) requires the balance of two competing factors. This competition arises as a result of the alteration of the electron probability density from a compact distribution around two separated atoms to a more diffuse distribution of the electron density on the two, now bonded, atoms. Due to the nature of the kinetic-energy operator,

$$\mathcal{T} = -1/2\nabla^2 \quad (7)$$

this relaxation of electron density relieves the kinetic-energy pressure: i.e., it reduces the kinetic energy relative to the atoms. On the other hand, the same relaxation of the electron density distribution reduces the magnitude of the nuclear suction; i.e., the potential due to electron–nuclear attraction is attenuated since the electron density is less concentrated around the nuclei. It is the balance between these two competing phenomena that is critical in determining the nature of the chemical bond.

To place the foregoing on a more quantitative footing, consider the formation of  $\text{H}_2^+$  from  $\text{H} + \text{H}^+$  to occur in two steps. We begin with  $\text{H}$  described by the

exact  $1s$  wavefunction (exponent = 1.0), with an identical  $1s$  wavefunction centered on the infinitely separated proton. The electron density may then be described as either  $\rho = \rho_a$  or  $\rho = \rho_b$ , depending whether a or b is the proton. An energetically equivalent description is  $\rho = 1/2(\rho_a + \rho_b)$ . In the first step,  $\text{H}$  and  $\text{H}^+$  are brought from infinity to their equilibrium internuclear separation of 2.0 bohr in such a manner that the exponent on the  $1s$  wavefunctions remains 1.0. The energy change due to this step is almost certainly negative (ex-ergic), due to the formation of the covalent bond. The second step is simply to permit the molecular wavefunction, given by Eq. (2), to relax its exponent (and thereby the radial distribution) from 1.0 to the optimum 1.24 and thus re-establish the virial relation  $V = -2T$ . An energy decrease for this step is guaranteed by the variational principle. One may then calculate the changes in the total ( $E$ ), kinetic ( $T$ ) and potential ( $V$ , including nuclear repulsion) energies for each step and for the overall process. The results are presented in Table 1. In the first step, bond formation, the energy decrease is driven by release of the kinetic-energy pressure, due to the spreading out of the electron density over the two nuclear centers. In the second step, the electron density is contracted (the wavefunction becomes more compact) as the exponent of the wavefunction increases from 1.0 to 1.24. This causes an increase in the kinetic-energy pressure (illustrated by the positive value of  $\Delta T$  for this step) and a concomitant decrease in the potential-energy suction, as the electron density contracts around the nuclei; however, the total energy-lowering is smaller than for step 1.

Note that the energies quoted in Table 1 do not correspond to the exact  $\text{H}_2^+$  bond energy. This is because there is an additional step, in which polarization is introduced into the wavefunction. This is discussed in detail in the original papers by Ruedenberg and coworkers.

The foregoing analysis may be more directly connected with the decomposition of the electron density into classical and interference components by considering an alternative “mechanism” for the formation of  $\text{H}_2^+$ . In this second two-step mechanism, we first contract the  $\text{H}$  atom wavefunction by increasing its orbital exponent from the optimum value of 1.0 to the final  $\text{H}_2^+$  value of 1.24. One may think of this as a contractive promotion step, analogous to the hybridization of the orbitals of a carbon atom in preparation for the formation of methane. This step costs energy, but it is energy that will be recovered upon bond formation.

We next define the total molecular potential energy,  $V^{\text{mol}}$ , as

**Table 1.** Energetics (hartree) for two-step formation of  $\text{H}_2^+$

	$\Delta T$	$\Delta V$	$\Delta E$
Step 1	-0.1138	+0.0600	-0.0538
Step 2	+0.2009	-0.2336	-0.0327
Total	+0.0871	-0.1736	-0.0865

$$\begin{aligned}
V^{\text{mol}} &= -\langle \Psi | Z/r_a + Z/r_b | \Psi \rangle + Z/R_{ab} \\
&= -[2(1 + S_{ab})]^{-1} \\
&\quad \times \langle (1s_a + 1s_b) | Z/r_a + Z/r_b | (1s_a + 1s_b) \rangle + Z/R_{ab},
\end{aligned} \tag{8}$$

where  $Z$  is the nuclear charge,  $r_a$  is the distance from an electron on atom A from its nucleus, and  $R_{ab}$  is the internuclear distance.  $V^{\text{mol}}$  contains (a) the attractions of the electron density on an atom for its own nucleus, (b) the attractions of electron density on one atom for the other nucleus, and (c) the attraction of the interference density for both nuclei. To separate these contributions, we define  $V_A$  as the atomic attraction,  $V_{\text{QC}}$  as the two-center quasiclassical (QC) attraction, and  $V_I$  as the attraction due to interference:

$$\begin{aligned}
V_A &= -\langle 1s_a | Z/r_a | 1s_a \rangle \\
&= -1/2[\langle 1s_a | Z/r_a | 1s_a \rangle + \langle 1s_b | Z/r_b | 1s_b \rangle]
\end{aligned} \tag{9}$$

$$\begin{aligned}
V_{\text{QC}} &= -1/2[\langle 1s_a | Z/r_b | 1s_a \rangle + \langle 1s_b | Z/r_a | 1s_b \rangle] \\
&\quad + 1/R_{ab}
\end{aligned} \tag{10}$$

$$\begin{aligned}
V_I &= (1 + S_{ab})^{-1}[\langle 1s_a | -Z/r_a - Z/r_b | 1s_b \rangle \\
&\quad - 1/2S_{ab}(\langle 1s_a | -Z/r_a - Z/r_b | 1s_a \rangle \\
&\quad + \langle 1s_b | -Z/r_a - Z/r_b | 1s_b \rangle)]
\end{aligned} \tag{11}$$

$$V^{\text{mol}} = V_A + V_{\text{QC}} + V_I . \tag{12}$$

For the ground-state hydrogen atom,

$$V_H = -\langle 1s_a | Z/r_a | 1s_a \rangle . \tag{13}$$

For an exponent of 1.0,  $V_A = V_H$ , so upon bond formation at a fixed exponent of 1.0, the change in potential energy is given by

$$\Delta V = V_{\text{QC}} + V_I . \tag{14}$$

In general,

$$\Delta V = (V_A - V_H) + V_{\text{QC}} + V_I = V_{\text{CP}} + V_{\text{QC}} + V_I , \tag{15}$$

where  $V_{\text{CP}}$  is the energy increase due to the contractive promotion that occurs when the exponent is increased to 1.24. The kinetic energy can be partitioned in a similar manner, except, of course, that there is no analog for the two-center classical (QC) term:

$$\Delta T = T_{\text{CP}} + T_I . \tag{16}$$

These energy differences are summarized in Table 2. It is clear from Table 2 that

1. The driving force for covalent bonding in  $\text{H}_2^+$  is the constructive interference contribution to the kinetic energy.

2. The wavefunction contraction, and thus the lower final potential energy, is not directly due to the sharing of electrons as was generally believed prior to the publication of this paper. Rather, it is “atomic” in nature.

An examination of the antibonding wavefunction, at the ground-state equilibrium internuclear distance of 2.0 bohr, reveals an analogous energy decomposition: the energy increase arises from the destructive interference contribution to the kinetic energy. Similar conclusions were arrived at by the Ruedenberg group for studies on more complex molecules, and also by Kutzelnigg [6] and Mulliken [5].

The important role of the electronic kinetic energy, first established by Ruedenberg for covalent bonding has been demonstrated for many other important chemical phenomena such as steric repulsion [7], ionization potentials [8], three-center/two-electron bonding [9], and hydrogen bonding [10]. Thus, this very general conceptual framework serves to highlight the similarities and differences between these diverse situations.

### 3 Concluding remarks

The essence of this model of the chemical bond may be summarized as follows

1. The origins of covalent chemical bonding lie in the kinetic-energy lowering caused by interference effects that arise from the fundamentally quantum mechanical wave-particle duality. “...the interference energy owes its binding effect entirely to a lowering of the kinetic energy...the interference process is unfavorable as regards the potential energy. The ubiquitous statement that overlap accumulation of electrons in a bond leads to a lowering of the potential energy is based on fallacious reasoning.”

2. “The wave mechanical kinetic behavior, which differs typically from the classical behavior...is a fundamentally essential element of covalent bonding. Any explanation of chemical binding based essentially on an electrostatic, or any other nonkinetic concept, misses the very reason why quantum mechanics can explain chemical binding, whereas classical mechanics cannot.”

3. While the formulation of the model is most commonly made in terms of atomic orbital components, it does not rely on such a formulation and is quite general.

**Table 2.** Energetics (hartree) for bond formation in  $\text{H}_2^+$

	$\text{H}_2^+$ exponent = 1.0			$\text{H}_2^+$ exponent = 1.24		
	$\Delta T$	$\Delta V$	$\Delta E$	$\Delta T$	$\Delta V$	$\Delta E$
Contractive	0.0	0.0	0.0	0.2672	-0.2387	0.0285
Promotion two-center	0.0	0.0275	0.0275	0.0	0.0123	0.0123
Classical interference	-0.1138	0.0325	-0.0813	-0.1801	0.0528	-0.1273
Total binding	-0.1138	0.0600	-0.0538	0.0871	-0.1736	-0.0865

4. While any energy decomposition is necessarily arbitrary, such pictures are useful, since “they allow us to visualize and predict similarities and differences in the solution of the Schrödinger equation for different molecules without continuous appeal to an electronic computer.” This comment, expressed originally in 1962, is even more relevant today.

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