In the Classroom

Kinetic Energy and the Covalent Bond in H_2^+

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*Using a reasonably accurate wave function, he described the formation of the chemical bond in terms of **both** kinetic and potential energy.*

A modified version of Ruedenberg's innovative analysis of the chemical bond in the hydrogen molecule ion is presented that factors the bond energy into bonding and nonbonding contributions. This simplified approach clearly illustrates Ruedenberg's main thesis: chemical bond formation is driven by a decrease in electron kinetic energy.

Introduction

In 1962, Ruedenberg [1] published a persuasive quantum mechanical analysis of the hydrogen molecule ion that challenged the prevailing opinion that covalent bonding is simply an electrostatic phenomenon, by demonstrating the crucial importance of kinetic energy in chemical bond formation. In the ensuing years, Ruedenberg, in collaboration with others, extended and refined his original study [2–4]. While this important work has received some attention in the pedagogical literature [5–7], and brief treatment in a few

advanced texts [7–11], chemistry textbooks currently in use throughout the undergraduate curriculum present exclusively the conventional view that the covalent bond can be understood solely in terms of electrostatic potential energy.

Ruedenberg revealed the critical role of kinetic energy in bond formation by partitioning the bond energy into three contributions that he called quasi-classical, promotion, and interference [4]. In an effort to make this important conclusion accessible to undergraduates, this paper employs a more elementary analysis that partitions the bond energy into just two contributions: bonding and nonbonding. The nonbonding term is the sum of Ruedenberg's quasi-classical and promotion contributions, and the bonding term is identical to his interference term. This simplification comes at some cost in understanding the finer details of chemical bond formation, but the main message comes across clearly: kinetic energy plays an essential role in the formation of a stable covalent bond.

Calculating the Ground State of H_2^+

Writing the molecular orbital in H_2^+ as a linear combination of scaled hydrogenic $1s$ orbitals centered on nuclei a and b, as was first suggested by Finkelstein and Horowitz [12], we have

$$\Psi = \frac{a + b}{\sqrt{2 + 2S}} \tag{1}$$

where,

$$a = \sqrt{\frac{\alpha^3}{\pi}} \exp(-\alpha r_a) \qquad b = \sqrt{\frac{\alpha^3}{\pi}} \exp(-\alpha r_b) \qquad S = \langle a | b \rangle \tag{2}$$

The scale factor or decay constant, α, is a variational parameter that controls the spatial extent of the wave function.

The variation integral is,

$$E_{H_2^+} = \langle \Psi | H | \Psi \rangle = \frac{\langle a + b | H | a + b \rangle}{2 + 2S} = \frac{H_{aa} + H_{ab}}{1 + S} \tag{3}$$

where due to the symmetry of the molecule $H_{aa} = H_{bb}$ and $H_{ab} = H_{ba}$. The energy operator is given by,

$$H = -\frac{1}{2}\nabla^2 - \frac{1}{r_a} - \frac{1}{r_b} + \frac{1}{R} \tag{4}$$

In eq 4, the first term is the electron kinetic energy operator, the second and third terms represent the electrostatic interaction between the electron and the two nuclei, and the last term the operator for nuclear–nuclear repulsion. The energy operator above and the calculation outlined below are expressed in atomic units ($|e| = m_e = h/(2\pi) = 4\pi\varepsilon_0 = 1$).

When the matrix elements are evaluated, the following expression in the scale factor, α, and the internuclear separation, R, is obtained [13].

$$E_{H_2^+} = -\frac{\alpha^2}{2} + \frac{\alpha^2 - \alpha - \frac{1}{R} + \left(\frac{1}{R} + \alpha\right)\exp(-2\alpha R) + \alpha(\alpha - 2)(1 + \alpha R)\exp(-\alpha R)}{1 + \exp(-\alpha R)\left(1 + \alpha R + \frac{\alpha^2 R^2}{3}\right)} + \frac{1}{R} \tag{5}$$

Minimization of the energy with respect to α as a function of R yields the molecular potential-energy curve shown in Figure 1. Minimization of the energy simultaneously with respect to α and R locates the H_2^+ ground state at $R_e = 2.0033$ bohr, with $\alpha = 1.2387$ and $E_{H_2^+} = -0.5865$ hartree.

For the ground state calculated above, the electron density in a plane containing the bond axis is shown in Figure 2, with both surface and contour representations.

$$\left|\Psi^2\right| = \frac{a^2 + b^2 + 2ab}{2 + 2S} \tag{6}$$

Identifying the Nonbonding Electron Density

An important question at this point is how much of the electron density represented by $|\Psi|^2$ contributes to bonding. Fortunately, it is possible to construct a nonbonding state within the LCAO-MO approach and subtract it from $|\Psi|^2$ to get a physical picture of the nature of the chemical bond. In other words, it is possible to resolve the total
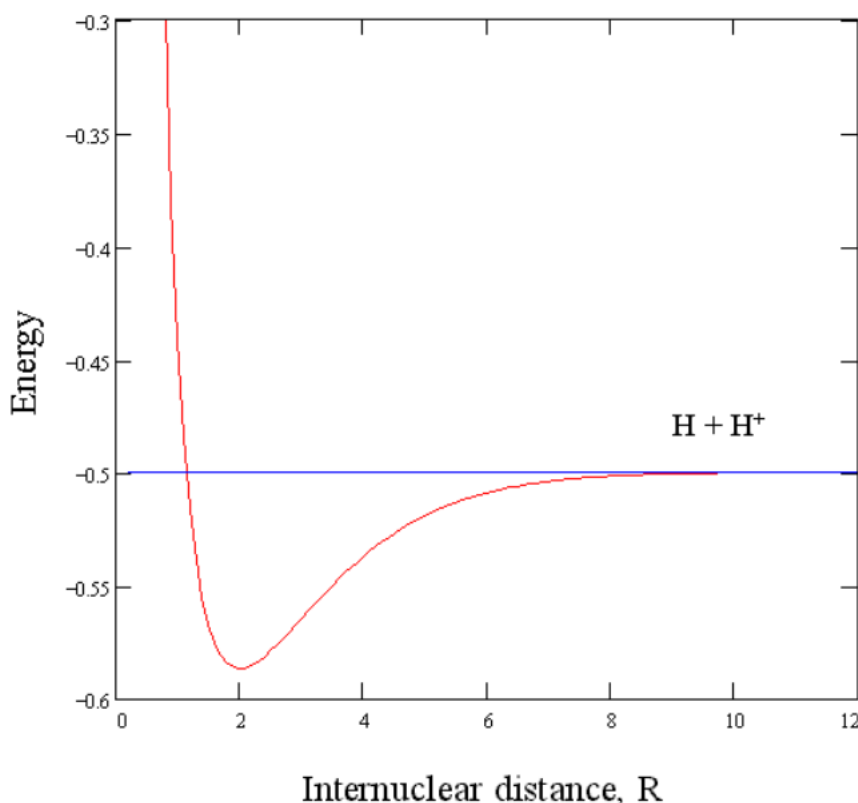
FIGURE 1. MOLECULAR POTENTIAL-ENERGY CURVE FOR H_2^+.

electron density into atomic and molecular contributions. The nonbonding electron density is described by a wavefunction in which the hydrogen atomic orbitals are $90°$ out of phase [14].
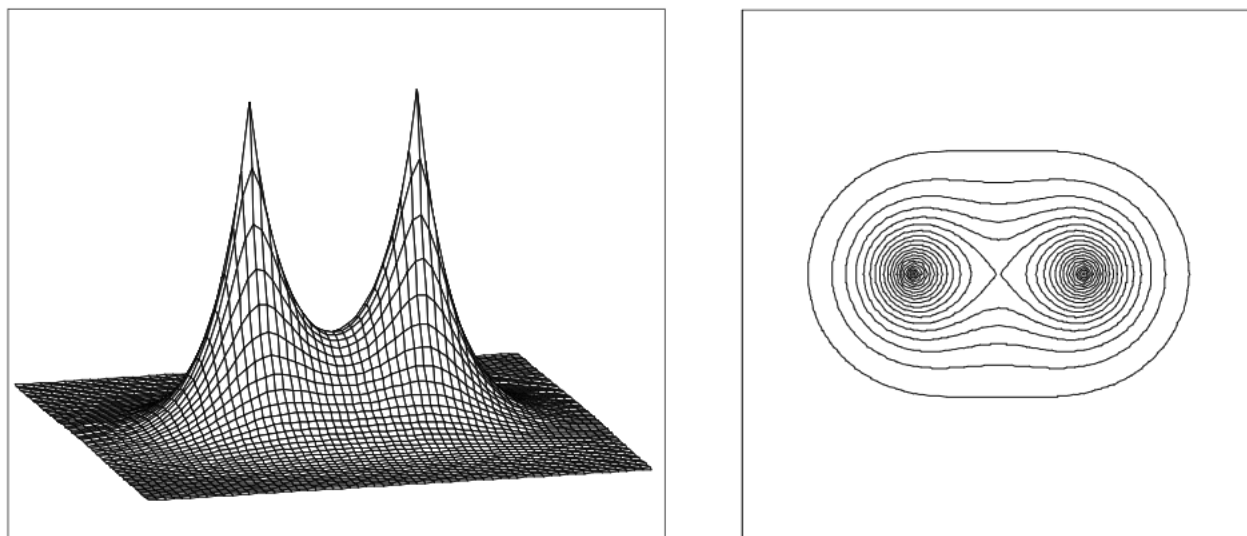
$$\Psi_n = \frac{a + ib}{\sqrt{2}} \tag{7}$$

The energy associated with the nonbonding electron density is

$$E_n = \langle \Psi_n | H | \Psi_n \rangle = \frac{\langle a - ib | H | a + ib \rangle}{2} = \frac{H_{aa} + H_{bb}}{2} = H_{aa} \tag{8}$$

The explicit form of E_n in terms of α and R can be shown to be [13]

$$E_n = \frac{\alpha^2}{2} - \alpha - \left[\frac{1}{R} - \left(\alpha + \frac{1}{R} \right) \exp(-2\alpha R) \right] + \frac{1}{R} \tag{9}$$
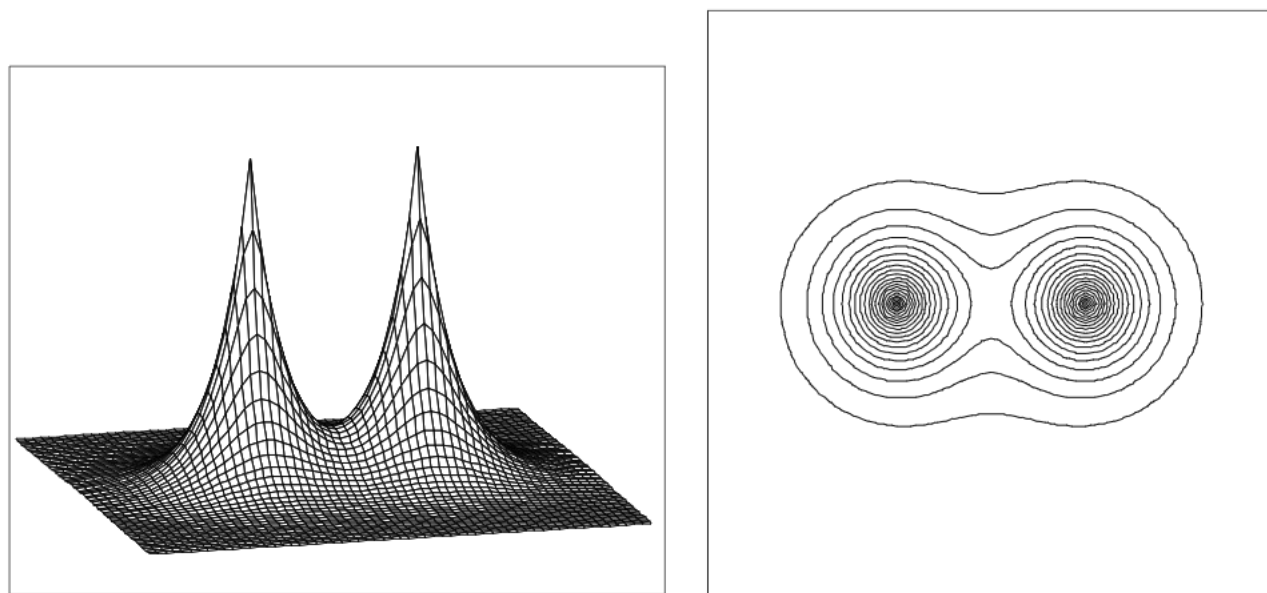
FIGURE 2. TOTAL ELECTRON DENSITY, $|\Psi|^2$.

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where the first term on the right is the kinetic energy of the electron in orbital a, the second term is the electron's electrostatic interaction with nucleus a, the third term is its interaction with nucleus b, and the fourth term is the nuclear–nuclear repulsion.

Figure 3 shows surface and contour plots of the nonbonding electron density.

$$|\Psi_n|^2 = \frac{a^2 + b^2}{2} \tag{10}$$

A qualitative comparison of Figures 2 and 3 shows that there is less electron density in the internuclear region in the nonbonding state. The distribution of contours also confirms that the nonbonding state has more atomic character. Later we will be able to show exactly how much charge density difference there is between these two wave functions in the internuclear region.

FIGURE 3. NONBONDING ELECTRON DENSITY, $|\Psi_n|^2$.

Isolating the Bonding Electron Density

It is now possible to partition $E_{H_2^+}$ into bonding and nonbonding contributions using $E_n = H_{aa}$,

$$E_{H_2^+} = \frac{E_n + H_{ab}}{1 + S} = E_n + \frac{H_{ab} - SH_{aa}}{1 + S} = E_n + E_b \qquad (11)$$

where E_b is the energy due to the bonding electron density, which has its origin in the constructive overlap of the atomic orbitals.

This expression can be used to examine the behavior of the bond energy as a function of the internuclear separation, R.

$$\Delta E_{bond} = E_{H_2^+} - E_H - E_{H^+} \qquad (12)$$

Combining eqs 11 and 12, while noting that $E_H = -0.5$ hartree and $E_{H^+} = 0$, yields

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$$\Delta E_{bond} = \left(E_{H_2^+} + \frac{1}{2} \right) = \left(E_n + \frac{1}{2} \right) + E_b \tag{13}$$

These terms are plotted as a function of R in Figure 4. This figure clearly shows that E_b is the cause of stable bond formation, and that the state represented by Ψ_n is indeed nonbonding for all values of R. Furthermore, when E_b is separated into its kinetic and potential energy components, Figure 5 shows that the T_b term is responsible for the energy minimum in the hydrogen molecule ion. Table 1 provides a breakdown of the contributions to the H_2^+ bond energy, based on the partitioning given in eq 13. More will be said about these entries in a moment.

A graphical representation of the covalent bond in H_2^+ can be found by isolating the bonding energy term and extracting from it the bonding electron density.

$$E_b = E_{H_2^+} - E_n \tag{14}$$

$E_{H_2^+}$ is the energy associated with the total electron density, $|\Psi|^2$. E_n is the energy associated with the nonbonding electron density, $|\Psi_n|^2$. Therefore, $|\Psi|^2 - |\Psi_n|^2$ is the bonding electron density with energy E_b.

$$|\Psi_b|^2 = |\Psi|^2 - |\Psi_n|^2 = \frac{2ab - Sa^2 - Sb^2}{2 + 2S} \tag{15}$$

The bonding electron density, $|\Psi_b|^2$, is shown in Figure 6 as both surface and contour plots. This figure clearly shows the buildup of charge in the internuclear region; this is frequently referred to as the glue that holds the nuclei together in a chemical bond. It also shows that this charge buildup came from the regions immediately around the nuclei. This explains why V_b is positive in Figure 5; transferring electron density from the nuclei to the internuclear region increases potential energy. This increase in potential energy is funded by a larger decrease in kinetic energy due to the delocalization of electron density. In other words, the formation of a stable chemical bond by transfer of charge into the internuclear region, electron sharing, is driven by a decrease in kinetic energy.
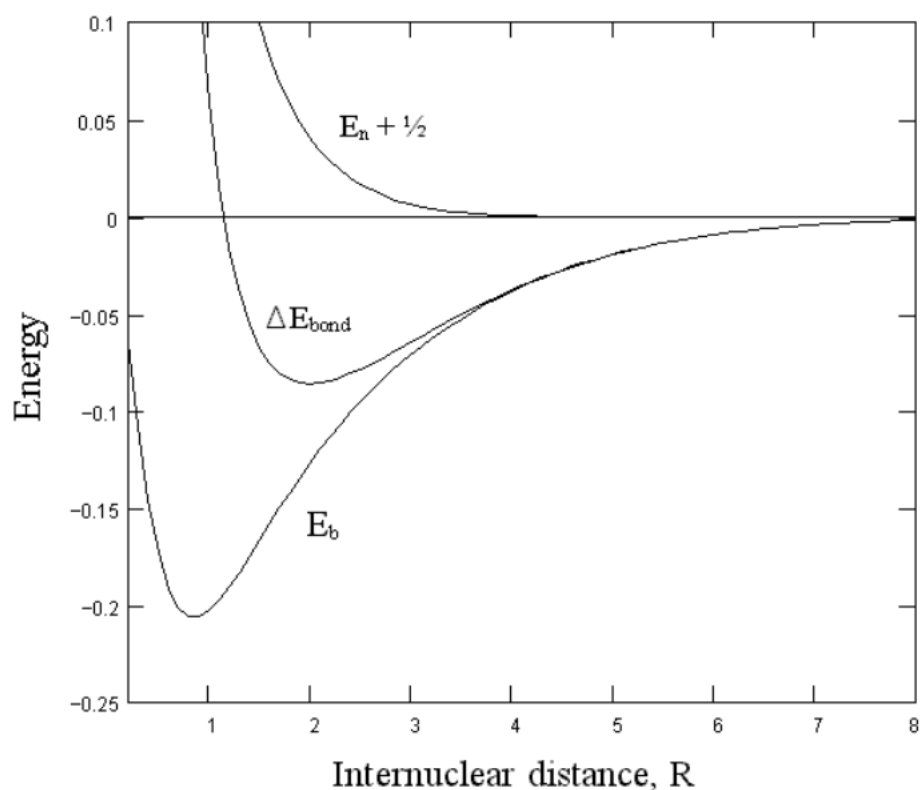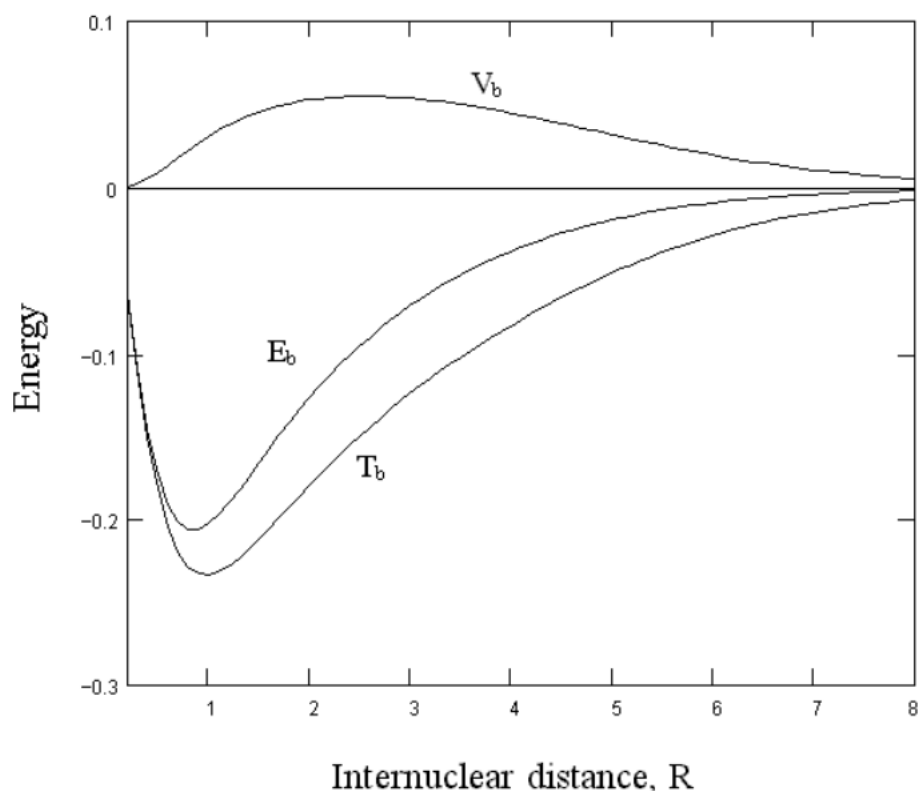
FIGURE 4. PARTITIONING OF BOND ENERGY INTO BONDING AND NONBONDING CONTRIBUTIONS.

Table 1. Bond Energy Contributions for H_2^+

|	(a) Bonding	(b) Nonbonding	Total
ΔT/hartree	−0.17985	0.26636	0.08651
ΔV/hartree	0.05284	−0.22585	−0.17301
ΔE/hartree	−0.12702	0.04051	−0.08651

FIGURE 5. PARTITIONING OF BONDING ENERGY INTO KINETIC (T_b) AND POTENTIAL (V_b) ENERGY CONTRIBUTIONS.

Mechanism for Covalent Bond Formation

Figure 7 juxtaposes plots of the total electron density, bonding density, and nonbonding density along the bond axis. Both it and Table 1 can now be used to provide a synopsis of covalent bond formation in the hydrogen molecule ion. Experiment yields a target bond energy while a quantum mechanical model (Born–Oppenheimer approximation, LCAO-MO, Finkelstein–Horowitz wave function, etc.) enables us to calculate a theoretical bond energy. If the comparison is favorable, we gain confidence in the model, and may use it to create a mechanism for bond formation whose individual steps, however, cannot be subjected to direct empirical test.

On the basis of the model presented in this study, the formation of a covalent bond is interpreted in terms of two phenomena: charge delocalization and orbital contraction. (a) Under the LCAO-MO approximation, constructive interference due to the overlap
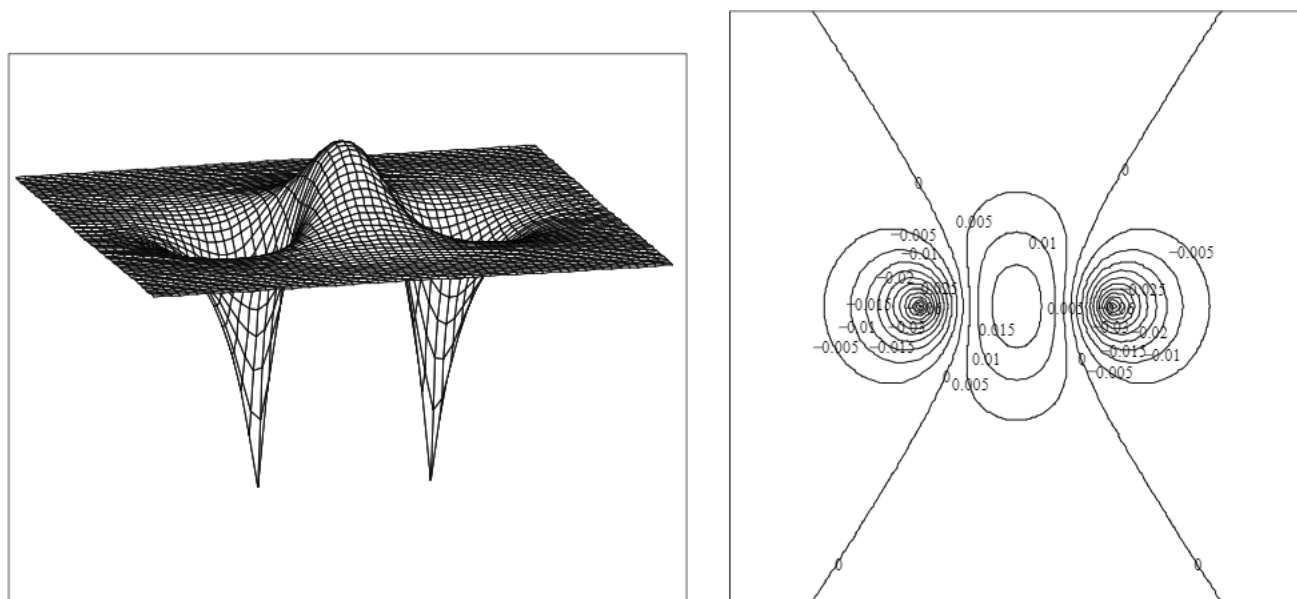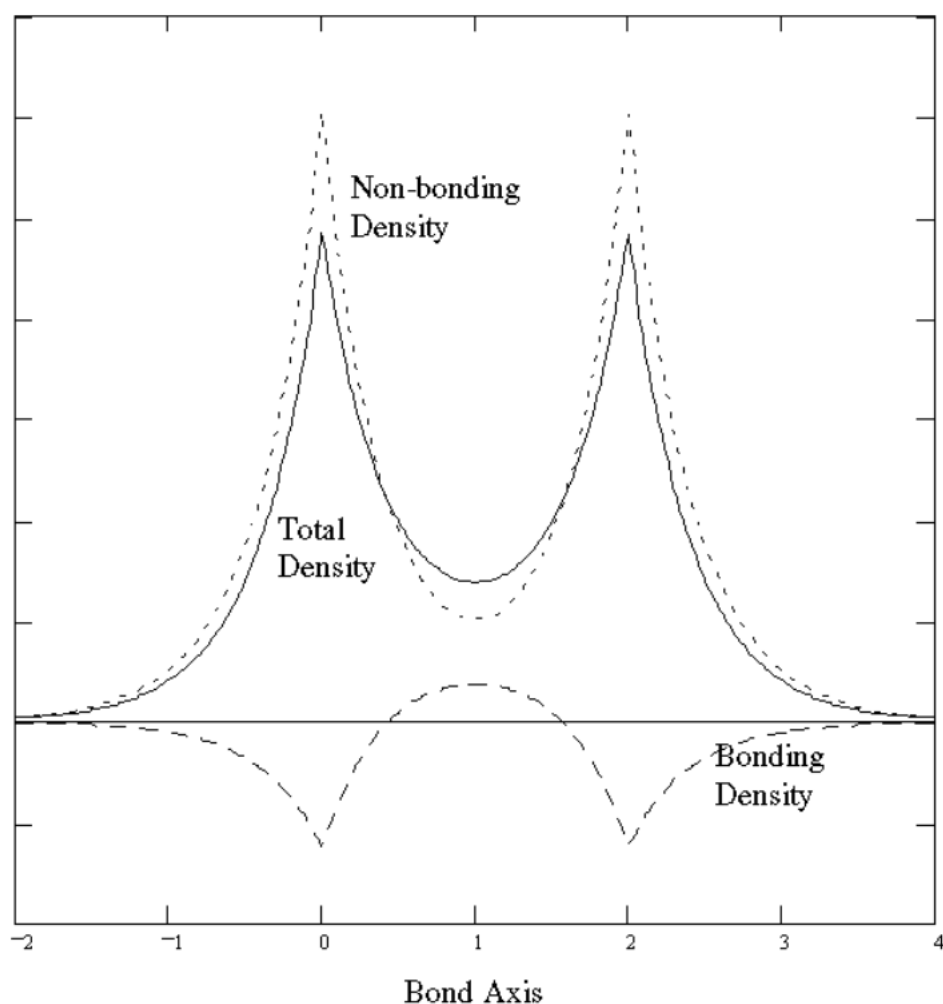
FIGURE 6. BONDING ELECTRON DENSITY, $|\Psi_b|^2$.

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of atomic orbitals transfers charge from the nonbonding areas immediately surrounding the nuclei to the internuclear region. This delocalization of electron density decreases kinetic energy more than it increases potential energy (see the bonding column in Table 1). (b) The consequent reduction of electron density at the nuclear centers allows the atomic orbitals to contract (increasing the scale factor, α), causing a large decrease in potential energy and a slightly larger increase in kinetic energy (see the nonbonding column in Table 1).

Process (a) is molecular or bonding, and exothermic. Process (b) is atomic or nonbonding, and endothermic. Looking at the last row (ΔE) of Table 1, we see that the sum of processes (a) and (b) is, of course, negative, indicating molecular stability for H_2^+. Overall, ΔT is positive and ΔV is negative, and their ratio satisfies the virial theorem ($\Delta V = -2\Delta T$, or $\Delta E = \Delta V/2$). This is the origin of the widely held, but erroneous belief, that chemical bonding can be understood solely in electrostatic terms.

The large drop in potential energy in step (b), by which the virial theorem is satisfied, is caused by a contraction of atomic orbitals that actually draws electron density out of the bond region toward the nuclei, as Figure 7 clearly shows.

FIGURE 7. TOTAL ELECTRON DENSITY, $|\Psi(x)|^2$; NONBONDING ELECTRON DENSITY, $|\Psi_n(x)|^2$; AND BONDING ELECTRON DENSITY, $|\Psi_b(x)|^2$, ALONG THE BOND AXIS.

Now we deal with the question of how much charge is actually transferred to the internuclear region. This is calculated as the electron density between the hyperbolic nodes shown in Figure 6. Ruedenberg [4] showed that for the Finkelstein–Horowitz wave function used in this study, the amount of charge within this region is given by a polynomial in the overlap integral, S.

$$\text{Bonding Charge} = 0.738S(1-S)(1-0.577S^2) \tag{16}$$

For $\alpha = 1.2387$ and $R = 2.0033$, the overlap integral is 0.4631, and the charge transferred to the bonding region is calculated to be 0.16 electrons, or 16%. This small

percentage is in striking contrast to the kind of electron sharing that is implied by qualitative, non-quantum-mechanical models for chemical bonding. These models frequently describe an electron-pair bond as a sharing of electrons *between* the nuclei, not simply a sharing *by* the nuclei.

Conclusion

This brings us to the necessity and importance of models. As Melrose et al. note, "At the fundamental level there is only one theory of binding in H_2^+, and that corresponds to an exact solution of the Schrödinger equation" [14]. However, as Robert Mulliken observed, "the more accurate the calculations became the more the concepts tended to vanish into thin air" [15]. Therefore, we explore different levels of theory and propose models of varying degrees of sophistication to find explanations that are intelligible in terms of familiar concepts, but also consistent with rigorous quantum mechanical principles. This is what Ruedenberg accomplished in his compelling analysis of the chemical bond. Using a reasonably accurate wave function, he described the formation of the chemical bond in terms of *both* kinetic and potential energy.

Actually Ruedenberg's finding about the importance of kinetic energy in chemical bonding should not be surprising. The seminal idea in quantum theory is de Broglie's hypothesis that matter has wavelike properties and a wavelength that is inversely proportional to its momentum. This equation is easily transformed into the following expression for the kinetic energy,

$$T = \frac{h^2}{2m\lambda^2} \tag{17}$$

Confinement of charge restricts λ to small values, which increases kinetic energy and explains why electrons, for example, do not collapse into the nucleus under the attractive electrostatic interaction. Conversely, delocalization of charge decreases kinetic energy and, as Ruedenberg has shown, is a mechanism for funding the transfer of charge into the bond region.

The importance of kinetic energy is also manifested by changes in mass, as eq 17 suggests. A dramatic example of this occurs when the electron in H_2^+ is replaced by the negative muon (μ^-), which has a mass 207 times that of the electron. The kinetic

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energy initially decreases, allowing the atomic orbitals to shrink, and the molecule achieves a new equilibrium configuration with a bond length approximately 200 times shorter than that for H_2^+ [16]. Electrostatically, nothing is changed by this electron–muon exchange, so the phenomenon can be attributed solely to the effect of mass on kinetic energy. And, of course, similar effects are observed at the atomic level with species like positronium and muonium. When we perform ab initio quantum mechanical calculations on atoms and molecules, we minimize the total energy (kinetic and potential) with respect to variational parameters built into the trial wave function. Therefore, we should expect that a correct interpretation of the results of the calculations requires consideration of both kinetic and potential energy contributions.

The model for covalent bonding outlined here has been presented using only the most elementary principles of ab initio quantum mechanics, and is therefore appropriate for a physical chemistry course that includes the study of quantum chemistry, or for any advanced course dealing with chemical bonding that has the appropriate physical-chemistry prerequisite. However, it is also possible to prepare a qualitative summary of the most important features of the model, based solely on Figures 2, 3, 6, and 7. Such a qualitative approach could be used in general chemistry, for example, to present an alternative to the strictly electrostatic model of covalent bonding that Ruedenberg has so effectively criticized.

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