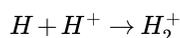


3.10: Three Mechanisms for Bond Formation in the Hydrogen Molecule Ion

Introduction

Ruedenberg's innovative analysis of the covalent bond (1-2) has received considerable attention in the pedagogical literature (3-13) as well as a number of excellent reviews in the primary literature that are accessible to non-specialists (14-16). The purpose of this study is analyze three mechanisms for covalent bond formation in H_2^+ that are suitable for an undergraduate course in quantum chemistry and reveal Ruedenberg's central message - a full understanding of the nature of the chemical bond requires consideration of the role of electron kinetic energy.

All three mechanisms postulate a single intermediate state for the reaction for H_2^+ bond formation.



Scaled hydrogenic wave functions will be used to calculate the initial atomic state, the final molecular state and the intermediate states. Mathematical details can be found in the Appendix.

The Hydrogen Atom

Using the following 1s orbital

$$1s(\alpha, R) = \sqrt{\frac{\alpha^3}{\pi}} \exp(-\alpha R)$$

in a variational calculation on the hydrogen atom yields the following result for the energy in atomic units.

$$E_H = \frac{\alpha^2}{2} - \alpha$$

The first term is electron kinetic energy and the second term is electron-nucleus potential energy. Minimization of E_H with respect to α yields $\alpha = 1$, and the following result for the ground state energy.

$$E_H = T + V = 0.50 - 1.0 = -0.50$$

The Hydrogen Ion Molecule

The H_2^+ molecular orbital is written as a linear superposition of scaled hydrogenic orbitals centered on the two hydrogen nuclei, a and b.

$$\Psi_{bmo} = \frac{1s_a(\alpha, r_a) + 1s_b(\alpha, r_b)}{\sqrt{2 + 2S_{ab}(\alpha, R_{ab})}}$$

S_{ab} is the overlap integral,

$$S_{ab}(\alpha, R_{ab}) = \exp(-\alpha R_{ab}) \left[1 + \alpha R_{ab} + \frac{\alpha^2 R_{ab}^2}{3} \right]$$

A variational calculation using Ψ_{bmo} yields the results in the following table.

	Initial Atomic State		Final Molecular State
o	$H_{atom} + H_{ion}$	o	$\Psi_{mo} = \frac{a+b}{\sqrt{2+2S}}$
o	$\alpha = 1$	Δ	$\frac{\alpha=1.238}{R=2.003}$
T	0.5	0.0865	0.5865
V	-1.0	-0.1730	-1.1730
V_{ne}	-1.0	-0.6723	-1.623
V_{nn}	0	0.4993	0.4993
E	-0.50	-0.0865	-0.5865

Table 1 shows that the atomic and molecular states individually satisfy the virial theorem ($E = V/2 = -T$), as does the bond formation process ($\Delta E = \Delta V/2 = -\Delta T$). At first glance Table 1 and the virial theorem suggest that chemical bonding is governed solely by electrostatics. In bond formation, in the transition from atoms to a molecule, kinetic energy increases, potential energy decreases, and total energy decreases. From this perspective, clearly potential energy must be the key factor in the formation of a stable molecule, because it has the same sign as the change in total energy, and a decrease in energy is the signature of stability. That this sort of reasoning leads to an incorrect interpretation of the covalent bond will be illustrated by the mechanistic analyses that follow.

Mechanism I

The first mechanism is one that might appear familiar to general chemistry students. For example, when we describe the bonding in methane to undergraduates we generally invoke a mechanism that uses the concepts of atomic promotion [$2s^2 2p^2 \rightarrow 2s^1 2p^3$], hybridization [$2s^1 2p^3 \rightarrow (sp^3 \text{ hybrids})^4$], and bond formation through the overlap of atomic orbitals. The H_2^+ bond formation mechanism described here consist of just two steps: atomic promotion and covalent bond formation ($H + H^+ \rightarrow H^* + H^+ \rightarrow H_2^+$). This simple mechanism has previously been discussed in the review literature (16) and has been invoked in a study of the covalent bond in H_2 (10).

$$H(\alpha = 1) + H^+ \rightarrow (\alpha = 1.238) + H^+ \rightarrow H_2^+(\alpha = 1.238, R = 2.003)$$

	Initial Atomic State	o	Intermediate Excited Atomic State	o	Final Molecular State
	$H_{atom} + H_{ion}$	o	$H_{atom} + H_{ion}$	o	$\Psi_{mo} = \frac{a+b}{\sqrt{2+2S}}$
	$\alpha = 1$	Δ	$\alpha = 1.238$	Δ	$\frac{\alpha=1.238}{R=2.003}$
T	0.50	0.2663	0.7663	-0.1798	0.5865
V	-1.0	-0.2380	-1.2380	0.0650	-1.1730
V_{ne}	-1.0	-0.2380	-1.2380	-0.4343	-1.6723
V_{nn}	0	0	0	0.4993	0.4993
E	-0.50	0.0283	-0.4717	-0.1148	-0.5865

In the first step the hydrogen atom orbitals prepare for bonding by contracting from $\alpha = 1$ to $\alpha = 1.238$, the optimum value of the final molecular wave function. This step is atomic and endoergic (+0.0283 E_h), increasing the kinetic energy more (+0.2663 E_h) than it decreases the potential energy (-0.2380 E_h). The potential energy decreases because the electron is drawn closer to the nucleus. The kinetic energy increases because of the increased confinement of the electron in the contracted atomic orbital - kinetic energy is inversely proportional to the square of the average distance of the electron from the nucleus, or inversely proportional to volume of the electron distribution raised to the 2/3 power, $V^{-2/3}$.

The second step consists of the formation of a molecular wave function by the superposition (linear combination) of the promoted atomic orbitals. The electron density of this molecular orbital is,

$$(|\Psi_{bmo}|)^2 = \left(\left| \frac{a+b}{\sqrt{2+2S}} \right| \right)^2 = \frac{a^2 + 2ab + b^2}{2 + 2s}$$

Molecular orbital formation distributes the electron density over the entire molecule and this charge delocalization brings about a significant decrease in kinetic energy (-0.1798 E_h). Potential energy increases slightly (0.0650 E_h) because nuclear repulsion (0.4993 E_h) more than offsets the increase in electron-nuclear attraction (-0.4343 E_h) due to the fact that the electron now interacts with both nuclei. This step is exoergic (-0.1148 E_h) because kinetic energy decreases more than potential energy increases. In other words, in this mechanism charge delocalization funds (drives) the formation of the chemical bond.

Mechanism II

Mechanism II postulates an intermediate non-bonding molecular state that has the equilibrium values of α and R . The non-bonding character this state is revealed by examining its electron density.

$$(|\Psi_{nmo}|)^2 = \left(\left| \frac{a+b}{\sqrt{2}} \right| \right)^2 = \frac{a^2}{2} + \frac{b^2}{2}$$

The electron density has no interference term and simply places half the electron density in each atomic orbital. The energy of the non-bonding state as a function of α and R and is provided in the Appendix. This intermediate state subsequently relaxes to the

final molecular bonding state. The calculations for this mechanism are summarized in Table III.

	<u>Initial</u> Atomic State	<i>o</i>	<u>Intermediate</u> Non Bonding State	<i>o</i>	<u>Final</u> Molecular State
<i>o</i>	$H_{atom} + H_{ion}$	<i>o</i>	$\Psi_{nmo} = \frac{a+ib}{\sqrt{2}}$	<i>o</i>	$\Psi_{mo} = \frac{a+b}{\sqrt{2+2S}}$
<i>o</i>	$\alpha = 1$	Δ	$\frac{\alpha=1.238}{R=2.003}$	Δ	$\frac{\alpha=1.238}{R=2.003}$
<i>T</i>	0.50	0.2663	0.7663	-0.1798	0.5865
<i>V</i>	-1.0	-0.2258	-1.2258	0.0528	-1.1730
<i>V_{ne}</i>	-1.0	-0.7251	-1.7251	0.0528	-1.6723
<i>V_{nn}</i>	0	0.4993	0.4993	0	0.4993
<i>E</i>	-0.50	0.0407	-0.4595	-0.1270	-0.5865

Formation of the non-bonding molecular state is endoergic (+0.0407 E_h) because orbital contraction increases kinetic energy (+0.2664 E_h) more than it decreases potential energy (-0.2258 E_h). The kinetic energy increase for this intermediate state is identical to that in Mechanism I. The potential energy decrease is less than that for Mechanism I because nuclear-nuclear repulsion (+0.4993 E_h) in the intermediate state is greater than "electron-other-nucleus" attraction [-0.4871 E_h = -0.7251 E_h - (-0.2380 E_h)]

The subsequent relaxation to the bonding molecular state is exoergic (-0.1270 E_h) because charge delocalization decreases kinetic energy (-0.1799 E_h) more than charge redistribution to the bond region increases electron-nucleus potential energy (+0.0528 E_h). As in Mechanism I we have an endoergic atomic step followed by an exoergic molecular step.

This mechanism clarifies an important issue. It is commonly thought, and frequently taught, that from a potential energy point of view the internuclear region is the most favorable place for electron density because it is midway between to nuclei. However, this mechanism clearly shows that the redistribution of charge into the internuclear region due to the interference term in the bonding electron density occurs with an increase in potential energy. That this is not some arcane quantum mechanical phenomenon is revealed by a simple classical electrostatic calculation [11]. From a purely electrostatic perspective the preferred location for an electron is in the nucleus.

If a stable chemical bond is due to the build-up of charge density in the internuclear region, then this mechanism shows that kinetic energy plays a crucial role in bringing about this effect.

Mechanism III

The third mechanism postulates an initial molecular state, rather than a promoted atomic state or a non-bonding molecular state for the intermediate. The initial molecular state has the equilibrium bond length, but the atomic value for the orbital scale factor, α . The calculations based on this mechanism are shown below.

$$H(\alpha = 1) + H^+ \rightarrow H_2^+(\alpha = 1, R = 2.003) \rightarrow H_2^+(\alpha = 1.238, R = 2.003)$$

	<u>Initial</u> Atomic State	<i>o</i>	<u>Intermediate</u> Bonding State	<i>o</i>	<u>Final</u> Molecular State
<i>o</i>	$H_{atom} + H_{ion}$	<i>o</i>	$\Psi_{imo} = \frac{a+b}{\sqrt{2+2S}}$	<i>o</i>	$\Psi_{mo} = \frac{a+b}{\sqrt{2+2S}}$
<i>o</i>	$\alpha = 1$	Δ	$\frac{\alpha=1}{R=2.003}$	Δ	$\frac{\alpha=1.238}{R=2.003}$
<i>T</i>	0.50	-0.1138	0.3862	0.2003	0.5865
<i>V</i>	-1.0	0.0599	-0.9401	-0.2329	-1.1730
<i>V_{ne}</i>	-1.0	-0.4394	-1.4394	-0.2329	-1.6723
<i>V_{nn}</i>	0	0.4993	0.4993	0	0.4993
<i>E</i>	-0.5	-0.0539	-0.5539	-0.0326	-0.5865

The intermediate molecular state is calculated at the equilibrium bond length ($R = 2.003 a_0$) for a molecular orbital with $\alpha = 1.0$. Charge delocalization over the two nuclear centers on the formation of the molecular orbital brings about a large decrease in kinetic energy (-0.1138 E_h). Potential energy (+0.0599 E_h) increases because nuclear repulsion (0.4993 E_h) is larger, as in Mechanism II, than electron-other-nucleus attraction (-0.4394 E_h). This step is exoergic and we see again that it is kinetic energy drives covalent bond formation.

In the second step of this mechanism the atomic orbitals making up the molecular orbital contract (α increases from 1 to 1.238) to achieve the final equilibrium molecular state. This orbital contraction decreases electron-nucleus potential energy (-0.2329 E_h)

more than it increases kinetic energy (+0.2003 E_h), so this step is also exoergic. However, as Ruedenberg pointed out, this step is essentially atomic in character. Orbital contraction draws electron density out of the bond region back toward the nuclei. In other words it returns some of the charge density transferred to the bond region in the first step back to the nuclear centers.

Summary

The three mechanisms examined postulate three different intermediate states: (1) promoted atomic; (2) non-bonding molecular; (3) intermediate molecular. However, they all tell the same story; kinetic energy plays a crucial role in chemical bond formation, and therefore viable models for the covalent bond require a consideration of both kinetic and potential energy. The virial theorem notwithstanding (as Ruedenberg has said), the formation of a chemical bond is not simply an electrostatic phenomena.

Appendix: Computational Details

Atomic energy contributions

$$E_H(\alpha) = \frac{\alpha^2}{2} - \alpha \quad T_H(\alpha) = \frac{\alpha^2}{2} \quad V_H(\alpha) = -\alpha$$

Bonding molecular energy contributions:

$$S(\alpha, R) = \exp(-\alpha, R) \left(1 + \alpha R + \frac{\alpha^2 R^2}{3} \right) \quad T_{bmo}(\alpha, R) = \frac{\alpha^2}{2} \frac{1 + \exp(-\alpha, R) \left(1 + \alpha R - \frac{\alpha^2 R^2}{3} \right)}{1 + S(\alpha, R)}$$

$$V_{bmo}(\alpha, R) = \frac{-\alpha - \frac{1}{R} + \frac{1}{R} (1 + \alpha R) \exp(-2\alpha R) - 2\alpha (1 + \alpha R) \exp(-\alpha R)}{1 + S(\alpha, R)} + \frac{1}{R}$$

$$E_{bmo}(\alpha, R) = T_{bmo}(\alpha, R) + V_{bmo}(\alpha, R)$$

Non-bonding molecular energy contributions:

$$T_{nbmo}(\alpha, R) = \frac{\alpha^2}{2} \quad V_{nbmo}(\alpha, R) = -\alpha + \left(\alpha + \frac{1}{R} \right) \exp(-2\alpha R) \quad E_{nbmo}(\alpha, R) = T_{nbmo}(\alpha, R) + V_{nbmo}(\alpha, R)$$

Initial Atomic State

$$T_H(1) = 0.5000 \quad V_H(1) = -1.0000 \quad E_H(1) = -0.5000$$

Final Molecular State:

$$T_{bmo}(1.238, 2.003) = 0.5865 \quad V_{bmo}(1.238, 2.003) = -1.1730$$

$$E_{bmo}(1.238, 2.003) = -0.5865$$

Mechanism I - Intermediate - Excited Atomic State

$$T_H(1.238) = 0.7663 \quad V_H(1.228) = -1.2380 \quad E_H(1.238) = -0.4717$$

Mechanism II - Intermediate = Nonbonding Molecular State

$$E_{nbmo}(1.238, 2.0033) = -0.4595 \quad T_{nbmo}(1.238, 2.0033) = 0.7663 \quad V_{nbmo}(1.238, 2.0033) = -1.2258$$

Mechanism III - Intermediate Bonding Molecular State

$$T_{bmo}(1, 2.003) = 0.3862 \quad V_{bmo}(1, 2.003) = -0.9401 \quad E_{bmo}(1, 2.003) = -0.5539$$

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Added references: Recently Klaus Ruedenberg and former student (now colleague) Mike Schmidt published two exhaustive studies on the quantum mechanical principles of the covalent bond.

- "Why Does Electron Sharing Lead to Covalent Bonding? A Variational Analysis" *J. Comput. Chem.* **2007**, *28*, 391-410.
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