

3.2: The Covalent Bond in the Hydrogen Molecule

Introduction

The covalent chemical bond is a difficult concept that is frequently oversimplified as a purely electrostatic phenomenon in textbooks at all levels of the undergraduate chemistry curriculum. Therefore, the purpose of this paper is to provide an elementary quantum-mechanical analysis of the covalent bond appropriate for an undergraduate course in physical or advanced inorganic chemistry. It is important to emphasize that there is no acceptable classical electrostatic explanation for the covalent bond, just as there is no classical explanation for atomic stability or atomic structure. Quantum-mechanical principles are required to understand atomic and molecular stability and structure.

Background

Forty years ago, Ruedenberg and his collaborators undertook a detailed study of the covalent bond in H_2^+ [1-3]. This thorough and incisive theoretical analysis revealed that chemical-bond formation was not simply an electrostatic phenomenon as commonly thought, but that electron kinetic energy also played an essential role. Ruedenberg's contribution to our current understanding of the physical nature of the chemical bond has been discussed in a number of publications in the pedagogical literature in chemistry and physics [4-9]. In addition, there are excellent critiques and summaries elsewhere that are accessible to the interested nonspecialist [10-12]. It should be noted that Slater also recognized the importance of electron kinetic energy in chemical bond formation in a benchmark paper published in the inaugural volume of the *Journal of Chemical Physics* [13]. He returned to the subject subsequently [14], but never pursued it at the depth that Ruedenberg and his colleagues did.

Ruedenberg chose to study H_2^+ because, as the simplest molecule, he could easily extract detailed information about all the contributions to the total energy from its one electron wave function. In the present study the simplest electron-pair bond, H_2 , will be examined. The analysis is carried out at a much more elementary level, but the same message emerges—electron kinetic energy plays a crucial role in chemical bond formation. Theoretical analysis shows that H-H bond formation, $2H \rightarrow H_2$, is an exothermic process that obeys the virial theorem: $\Delta E = \Delta V/2 = -\Delta T$ [15]. Noncritical use of the virial theorem, therefore, may lead one to believe that stable bond formation is solely an electrostatic potential-energy effect, and that consideration of kinetic energy is neither relevant nor necessary. However, H-H bond formation can be thought of as a very simple chemical reaction, and we know that it is never justified to assume that the balanced chemical equation is also the mechanism for the reaction. For example, even a simple first-order isomerization reaction ($R \rightarrow P$) requires the formation of an activated form of the reactant ($R \rightarrow R^* \rightarrow P$).

Similarly, to study the covalent bond it is instructive to postulate a "mechanism" for bond formation, a sequence of hypothetical steps that are equivalent to the overall process $2H \rightarrow H_2$. Unlike a traditional chemical mechanism, it cannot be tested empirically and, therefore, its value or validity rests on the clarity and cogency of its basic premises. There are actually several plausible mechanisms, but our attention will be restricted to one that might appear especially cogent to undergraduate audiences. For example, when we describe the bonding in methane to students, 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 in this paper will consist of two steps: atomic promotion and overlap of atomic orbitals ($2H \rightarrow 2H^* \rightarrow H_2$). This simple mechanism has previously been used to analyze the bonding in H_2^+ [12]. It should be noted that the individual steps of the mechanism do not satisfy the virial theorem, but, of course, collectively they do. To carry out a quantum-mechanical analysis of bond formation in H_2 , it is necessary to decide at what level of theory to work. In this analysis scaled hydrogenic 1s orbitals will be used for the atomic orbitals. At the molecular level, both molecular orbital (MO) and valence bond (VB) wave functions will be considered. Labeling the nuclei a and b, and the electrons 1 and 2, the atomic orbitals are,

$$1s_a = \sqrt{\frac{\alpha^3}{\pi}} \exp(-\alpha r_a) \quad 1s_b = \sqrt{\frac{\alpha^3}{\pi}} \exp(-\alpha r_b)$$

Table 1. Variational Results for the MO and VB Wave Functions

	MO	VB
α	1.197	1.166
T/E_b	1.1282	1.1389
V/E_b	-2.2564	-2.2778

E/E _b	-1.1282	-1.1389
% Error	3.95	3.04
R _e /α ₀	1.38	1.41
% Error	1.43	0.71

Table 2. Bond Formation Mechanism Results for the Molecular Orbital Wave Function

	2 H(α=1)		2H*(α=1.197) ^a		H ₂ (α=1.197)
T/E _h	1.00	0.4328	1.4328	-0.3046	1.1282
V/E _h	-2.00	-0.3940	-2.3940	0.1376	-2.2564
E/E _h	-1.00	0.0388	-0.9612	-0.1670	-1.1282

^aEq 4 is used to calculate the entries in this column.

Table 3. Bond Formation Mechanism Results for the Valence Bond Wave Function

	2 H(α=1)		2H*(α=1.166) ^a		H ₂ (α=1.166)
T/E _h	1.00	0.3596	1.3596	-0.2207	1.1389
V/E _h	-2.00	-0.3320	-2.3320	0.0542	-2.2778
E/E _h	-1.00	0.0276	-0.9724	-0.1665	-1.1389

^aEq 4 is used to calculate the entries in this column.

Using this basis set, the MO and VB wave functions are (neglecting spin),

$$\Psi_{MO} = N_{MO} [1s_a(1) + 1s_b(1)] [1s_a(2) + 1s_b(2)]$$

$$\Psi_{VB} = N_{VB} [1s_a(1)1s_b(2) + 1s_a(2)1s_b(1)]$$

In these equations the scale factor, α is a variational parameter which controls how rapidly the atomic wave function decays to zero, and N_{MO} and N_{VB} are the appropriate normalization constants.

The Hydrogen Atom

Using a scaled hydrogenic wave function (see eq 1) in a variational calculation for the hydrogen atom yields the following expression for the energy in atomic units (m_e = e = ħ = 1),

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

where the first term is the electron kinetic energy, and the second term is the electron-nucleus potential energy. Minimization of E_H with respect to α yields,

$$\alpha = 1 \rightarrow E_H = \langle T \rangle + \langle V \rangle = \frac{1}{2} - 1 = -\frac{1}{2}$$

where and represent the expectation values for kinetic and potential energy, respectively.

The Hydrogen Molecule. The results for the variational calculations on the hydrogen molecule using the molecularorbital and valence-bond wave functions, and the Born-Oppenheimer energy operator,

$$\hat{H} = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{1}{r_{a1}} - \frac{1}{r_{a2}} - \frac{1}{r_{b1}} - \frac{1}{r_{b2}} + \frac{1}{r_{12}} + \frac{1}{R_{ab}}$$

are presented in Table 1. The table provides the optimum value of α, the total energy, and the equilibrium bond length for both wave functions as reported in the literature [16]. The kinetic and potential contributions to the total energy are obtained using the

virial theorem. The experimental values [17] for the ground-state energy and the equilibrium bond distance are, respectively, $-1.1746 E_h$ ($1 E_h = 27.2114 \text{ eV} = 2.6255 \text{ MJ mol}^{-1}$) and $1.40 a_0$ ($1 a_0 = 52.92 \text{ pm}$).

The Mechanism

For both wave functions, the bond formation mechanism is the same. In the first step, atomic promotion, the hydrogen atom orbitals prepare for bonding by contracting from $\alpha = 1$ to the optimum α value of the final molecular wave function. This step is atomic and endothermic, increasing the kinetic energy more than it decreases the potential energy. The potential energy decreases because the electrons move closer on average to their respective nuclei. The kinetic energy increases because of the greater confinement of the electrons in the contracted orbitals; kinetic energy is inversely proportional to the square of the average distance of the electron from the nucleus.

The second step consists of the formation of a molecular wave function by overlap of the promoted atomic orbitals. The constructive interference that accompanies orbital overlap brings about charge delocalization and charge redistribution. Charge delocalization distributes the electron density over the molecule as a whole (each electron now belongs to both nuclei) and brings about a significant decrease in kinetic energy. Charge redistribution transfers some electron density from the neighborhood of the nuclei into the inter-nuclear region, which involves an increase in electron potential energy. The second step is exothermic because kinetic energy decreases more than potential energy increases—charge delocalization funds the redistribution of charge from the area around the nuclei into the bond region. The results for both molecular wave functions are summarized in Tables 2 and 3. In summary, this simple two-step mechanism clearly shows that covalent bond formation in H_2 is driven by a decrease in kinetic energy brought about by the charge delocalization that accompanies the overlap of atomic orbitals. This is also the basic conclusion of Ruedenberg's more-detailed and sophisticated analysis for H_2^+ .

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