The Chemical Bond in H$_2$: An Orbital Exchange Calculation

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Abstract

This paper extends the orbital exchange method calculation of H$_2$ to include the possibility of a [HH,H+H-] resonance. The impact of the resonance on the orbitals’ overlaps and on the kinetic energy is described. The bond energy for H$_2$ is found by varying the parameters associated with the compression (orbital reduction) and polarization of the 1s bonding orbitals of H and H-, and the extent of resonance, to obtain the maximum bond energy with the bonding overlap $\leq 1.0$. The solution finds a binding energy, $D_e$, of 4.752 e.v. at a bond length of 0.733 Å with resonance fraction of 0.377. This is to be compared with the accepted value for $D_e$ of 4.75 e.v. at 0.741 Å. The success of this calculation strongly supports the hypothesis that overlapping bonding orbitals are not completely distinguishable and the efficacy of the orbital exchange method.

I. INTRODUCTION

An earlier paper introducing the orbital exchange method$^1$ as a method for calculating the chemical bond described the bonding in several di-atoms as well as the hydrogen molecule, H$_2$. Although the orbital exchange method produced better agreement between theory and experiment than previous methods$^{2,3}$, the agreement was not as good for H$_2$ as that for other di-atoms and the chemical bonds in other materials. The initial orbital exchange method treatment of H$_2$ did not consider the possibility of a [HH,H+H-] resonance. This paper considers this possibility and includes resonance in the calculation of the bond length and bond energy of H$_2$.

The orbital exchange method does not assume that the electrons in the overlapping orbitals of the chemical bond can be completely distinguished. That the electrons in the bonding orbitals cannot be completely distinguished in the overlap region has many implications. The most straightforward of these implications is the reduction in kinetic energy resulting merely from the overlap of the orbitals. Also, the orbital exchange method implies that bond lengths should be found at that point where overlap equals 1.0, since the overlap of the bonding orbitals cannot exceed 1.0.

II. SIGMA RESONANCE

To understand sigma bonding resonance, one needs to understand how bonds are counted. A typical chemical bond entails the left-hand side’s sigma bonding orbital overlapping the bonding orbital on the right side while at the same time the right-hand side’s sigma bonding orbital overlaps that on the left side. This has been defined as one bond. Since, it is possible, during resonance or in other circumstances, for one side of the bond to bond differently than the other, or for one side to bond and the other not, it is necessary to introduce the concept of the half

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bond. The left side orbital overlapping the right is one half of the bond while the right-side orbital overlapping the left is the other half of the bond. [In retrospect, the bond might have been better defined otherwise, but to change at this point would cause confusion.]

Resonance need not be complete. A bond may resonate for a portion of the time and not for the balance. While resonating, the H₂ bond has a charged component, H+H- or H-H+, and an uncharged component HH. The fraction of the charged component is termed fract_ion and the fraction of resonance is 2 times fract_ion. The non-resonance balance of the bond is (1-2 fract_ion).

A. Resonance Overlaps

The overlap while not resonating is overlap_{HH}. While in the HH part of a [HH,H+H-] resonance the overlap is 0.5 overlap_{HH} (left to right) and 0.5 overlap_{HH} (right to left). While in the H+H- part of the [HH,H+H-] resonance, there are two parallel 0.5 overlap_{HH} (right to left) overlaps. While [H+H-], the right has two bonding electrons while the left has none. It is important to recognize the parallel bonding here because, when parallel bonding, it is fraction_bonding (fraction_bonding=overlap/(1.0+overlap)) that is summed to obtain the total effective overlap, rather than simply summing the overlaps as in the serial bond (Parallel bonding is explained in Reference 1.) The overlap_{HH} is somewhat greater than the overlap_{HH} because the H- 1s orbitals are larger than the H 1s orbital. While [H+H-], there is a 1 in 5 chance that there will be a direct [H-H+,H+H-] resonance. In this case there will be two parallel 0.5 overlap_{H-H-} (right to left) overlaps. The overlaps sum as follows:

\[
\text{Overlap}_{\text{total serial}} = (1-2 \text{ fract}_\text{ion}) \text{ overlap}_{HH} + \text{ fract}_\text{ion} 0.5 \text{ overlap}_{HH} + 2 \text{ fract}_\text{ion} 0.5 (0.80 \text{ overlap}_{HH} + 0.20 \text{ overlap}_{H-H-}).
\]

The factor of 2 appears in the latter term because the resonance electron transitions both from left to right and from right to left.

\[
\text{Fraction}_\text{bonding}_{\text{total serial}} = \frac{\text{overlap}_{\text{total serial}}}{(1+\text{overlap}_{\text{total serial}})}.
\]

\[
\text{Fraction}_\text{bonding}_{\text{parallel}} = 2 \text{ fract}_\text{ion} 0.5 (0.80 \text{ fraction}_\text{bonding}_{HH} + 0.20 \text{ fraction}_\text{bonding}_{H-H-}).
\]

The factor of 2 appears in fraction_bonding_{parallel} because of both [HH,H+H-] and [HH,H-H+].

\[
\text{Fraction}_\text{bonding}_{\text{total}} = \text{fraction}_\text{bonding}_{\text{total serial}} + \text{fraction}_\text{bonding}_{\text{parallel}}.
\]

\[
\text{Overlap}_{\text{total}} = \frac{\text{fraction}_\text{bonding}_{\text{total}}}{(1 - \text{fraction}_\text{bonding}_{\text{total}})}.
\]

B. Resonance Kinetic Energy

The kinetic energy calculation mirrors the overlap calculation. Resonance contributions are separate from non-resonance contributions. To calculate the non-resonance kinetic energy, one needs the non-resonance overlap.

\[
\text{Overlap}_{\text{non-resonce}} = (1-2 \text{ fract}_\text{ion}) \text{ overlap}_{HH} + \text{ fract}_\text{ion} 0.5 \text{ overlap}_{HH}.
\]
KE_{non-resonance} = (1 / (1 + \text{overlap}_{non-resonance}) \times ((1 - 2 \text{ fract}_\text{ion}) \times \text{overlap}_{HH} \times KE_{net}_{HH} + \text{fract}_\text{ion} \times 0.5 \times \text{overlap}_{HH} \times KE_{net}_{HH})

KE_{net} is the kinetic energy reduction resulting from the identification ambiguity associated with the overlap of bonding orbitals. The calculation of KE_{net} is explained in reference 1.

Resonance kinetic energy is calculated as if the overlap were complete (overlap = 1.0).
KE_{resonance}_{HH} = 0.5 \times KE_{net}_{HH} \quad KE_{resonance}_{H-H} = 0.5 \times KE_{net}_{H-H}.

Total kinetic energy is:
KE_{total} = 2 \times KE_{non-resonance} + 2 \times \text{fract}_\text{ion} \times (0.80 \times KE_{resonance}_{HH} + 0.20 \times KE_{resonance}_{H-H}).

C. Energy Impact of H and H- Compression and Polarization

In the H\(_2\) molecule the orbital radii of both H and H- will be compressed (the orbital scale factors increased) and the orbitals polarized. The orbitals are polarized by altering the 1s functions of H and H- with a small amount of the functional form of 2p\(_z\). This has the effect of adding electron charge between the H atoms and lessening it on the periphery. There is an orbital scale factor associated with each of the added 2p\(_z\) functions. The energy penalty associated with compressing/polarizing the H and H- 1s orbitals is calculated and included in the result.

To establish the impact of compressing/polarization of H- it is first necessary to calculate the energy of H- in isolation (not bonding). This entails varying the H- orbital to find the best energy. The H- radius is found at an orbital expansion factor of 0.6910. At this radius the potential energy of each of the two electrons is 18.8044 e.v. and the kinetic energy is -6.4984 e.v.. The electron repulsion is -11.7589 e.v.. The energy of H- in isolation is 12.8531 e.v.. This equates to an electron affinity of 0.7526 e.v.. The accepted value for the electron affinity\(^4\) is 0.7542 e.v..

The potential energy, kinetic energy, and electron repulsion of the bonding H- are calculated and differences from those of the isolated H- determined. These quantities determine the energy impact of H- compression/polarization and are included in the energy required to make the transition [HH] to [H+H-].

III. CALCULATIONS

As in previous work, the calculations were performed numerically with operations on huge numeric arrays representing the orbitals. The numerical methods are described in detail in reference 1. Orbital exchange calculations require a software program which can perform mathematical calculations on, and between, arrays of numbers representing atomic orbitals or hybrid atomic orbitals.

The H\(_2\) bonding results are obtained by varying the parameters associated with compressing/polarizing the H 1s orbitals, the extent of resonance, and the bond length to find the
optimum energy with the overlap ≤ 1.0. Table I provides a detailed breakdown of the optimum result. This solution finds a binding energy, $D_e$, of 4.752 e.v. at a bond length of 0.733 Å with a resonance fraction of 0.377. This is to be compared with the accepted values\textsuperscript{5,6} for $D_e$ of 4.75 e.v. at a bond length of 0.741 Å.

An estimate of the accuracy of the calculations can be obtained from results for atomic H. Using the same scale factors as those used for the molecular calculation one obtains 1.000276 a.u. (vs. 1.000000) for the potential energy of the H electron and -0.499986 a.u. (vs -0.500000) for the kinetic energy. These results imply an accuracy of about 0.004% for kinetic energy and about 0.03% for the potential energy. [Calculation of the potential energy for atomic H is particularly difficult because of the high charge density near the nucleus.]

Table I. Components of the H\textsubscript{2} Calculation at 0.733 Å (Energy in electron volts)

The table below describes the maximum binding energy solution for the H\textsubscript{2} molecule at the limiting overlap (overlap=1.0). The bond energy maximum is found when H-H+ of the [HH,H-H+] resonance = 0.1885 (fraction resonating=0.377) and with the orbital parameters below.

<table>
<thead>
<tr>
<th>Component</th>
<th>Value</th>
<th>Change</th>
</tr>
</thead>
<tbody>
<tr>
<td>Orbital Parameters</td>
<td></td>
<td></td>
</tr>
<tr>
<td>orbital scale factor for H orbital</td>
<td>1.179</td>
<td></td>
</tr>
<tr>
<td>orbital scale factor for H polarizer (2p\textsubscript{z} function)</td>
<td>4.15</td>
<td></td>
</tr>
<tr>
<td>fraction 2p\textsubscript{z} function for H orbital</td>
<td>0.005</td>
<td></td>
</tr>
<tr>
<td>orbital scale factor for H- orbital</td>
<td>1.018</td>
<td></td>
</tr>
<tr>
<td>orbital scale factor for H- polarizer (2p\textsubscript{z} function)</td>
<td>2.50</td>
<td></td>
</tr>
<tr>
<td>fraction 2p\textsubscript{z} function for H- orbital</td>
<td>0.053</td>
<td></td>
</tr>
<tr>
<td>Overlaps</td>
<td></td>
<td></td>
</tr>
<tr>
<td>overlap \textsubscript{HH}</td>
<td>0.75135</td>
<td></td>
</tr>
<tr>
<td>overlap \textsubscript{HH-}</td>
<td>0.85058</td>
<td></td>
</tr>
<tr>
<td>overlap \textsubscript{H-H}</td>
<td>0.93061</td>
<td></td>
</tr>
<tr>
<td>$\text{Overlap}<em>{\text{total}}$ = (1-2 $\text{frac}</em>\text{ion}$) overlap \textsubscript{HH} + $\text{frac}<em>\text{ion}$ 0.5 overlap \textsubscript{HH} + 2 $\text{frac}</em>\text{ion}$ 0.5 (0.80 overlap \textsubscript{HH-} + 0.20 overlap \textsubscript{H-H}).</td>
<td>0.70226</td>
<td></td>
</tr>
<tr>
<td>$\text{Fraction}<em>{\text{bonding}}</em>{\text{total}}$ = overlap \textsubscript{total} / (1 + overlap \textsubscript{total}).</td>
<td>0.41254</td>
<td></td>
</tr>
<tr>
<td>$\text{Fraction}<em>{\text{bonding}}</em>{\text{parallel}}$ = 2 $\text{frac}<em>\text{ion}$ 0.5 (0.80 $\text{fraction}</em>{\text{bonding}}$ \textsubscript{HH} + 0.20 $\text{fraction}_{\text{bonding}}$ \textsubscript{H-H}).</td>
<td>0.08748</td>
<td></td>
</tr>
<tr>
<td>$\text{Overlap}<em>{\text{total}}$ = $\text{fraction}</em>{\text{bonding}}<em>{\text{total}}$ / (1 - $\text{fraction}</em>{\text{bonding}}_{\text{total}}$).</td>
<td>1.00011</td>
<td></td>
</tr>
</tbody>
</table>

Calculation of Kinetic Energy Contributions
\[ \text{Overlap}_{\text{non-resonance}} = (1-2 \text{ fract}_\text{ion}) \text{ overlap}_{\text{HH}} + \text{ fract}_\text{ion} 0.5 \text{ overlap}_{\text{HH}} \]

\[ \text{KE}_{\text{non-resonance}} = (1 / (1 + \text{overlap}_{\text{non-resonance}})) \]
\[ (1-2 \text{ fract}_\text{ion}) \text{ overlap}_{\text{HH}} \text{KE}_{\text{net HH}} + \text{ fract}_\text{ion} 0.5 \text{ overlap}_{\text{HH}} \text{KE}_{\text{net HH}}. \]
\[ \text{KE}_{\text{net HH}} = 5.20495 \]

\[ \text{KE}_{\text{resonance}}_{\text{HH}} = 0.5 \text{ KE}_{\text{net HH}} \]
\[ \text{KE}_{\text{net HH}} = 3.85596 \]

\[ \text{KE}_{\text{resonance}}_{\text{H-H}} = 0.5 \text{ KE}_{\text{net H-H}} \]
\[ \text{KE}_{\text{net H-H}} = 2.448124 \]

\[ \text{KE}_{\text{total}} = 2 \text{ KE}_{\text{non-resonance}} + 2 \text{ fract}_\text{ion} (0.80 \text{ KE}_{\text{resonance HH}} + 0.20 \text{ KE}_{\text{resonance H-H}}). \]

### Potential Energy Terms

- **C nuclear - C nuclear repulsion energy**
  -19.64721

- **H nuclear to opposite H orbital energy**
  \[ 2 (1 - \text{ fract}_\text{ion}) \text{ times} \]
  18.67311

- **H nuclear to opposite H- orbital energy**
  \[ 2 \text{ fract}_\text{ion} \text{ times} \]
  19.54662

- **H electron - H electron repulsion energy**
  \[ (1 - \text{ fract}_\text{ion}) \text{ times} \]
  -16.24719

### Resonance Energy and Energy to Compress/Polarize H and H-

- **Energy to compress/polarize H**
  \[ 2 (1 - \text{ fract}_\text{ion}) \text{ times} \]
  -0.64088

- **Energy to compress/polarize H-**
  -5.03180

- **Resonance energy** = H ionization + Affinity + Energy to compress/polarize H- \[ \text{ fract}_\text{ion} \text{ times} \]
  -8.94163

**Total Energy**

4.7518

### IV. CONCLUSION

Previous work\(^1,7,8\) has shown that the chemical bonds in chemicals as diverse as nitrogen, methane, diamond and lithium metal find their bond lengths at that point where the bonding orbitals’ overlap (synchronous overlap) equals 1.0, as postulated by the orbital exchange method. The finding that bond lengths are usually found where synchronous orbital overlap
equals 1.0 leaves little opportunity for misinterpretation since the radii of the bonding orbitals are known to within a tight range.

The successful calculation of the H₂ bond provides additional strong support for the orbital exchange method and the hypothesis that overlapping bonding orbitals are not completely distinguishable. The H₂ bond calculation does not require orbital orthogonalization nor any intraatomic orbital changes. The calculation has a minimum of complexities. There is no opportunity for unjustified optimizations. The parameters are clearly defined and reasonable ranges are known. Searching for the best bond energy by varying the orbital parameters and the extent of resonance while keeping the total overlap less than or equal to 1.0 yields a single result. This result is in excellent agreement with the accepted experimental data.