One Electron Covalent Bond

What Do You Think?

- Electron holds nuclei together?
- Atoms (sic) “share” electron?
- Electron occupies bonding orbital?

QM

- Construct model wavefn(s)
- Evaluate model energy using Hamiltonian
- What kind of model predicts a bond?
- What “mechanism” inside the model is responsible for the bond?
- If we find a good model, are other good models precluded?

\[
\Psi_{g,u} = N_{g,u} \left( 1s_a \pm 1s_b \right)
\]

\[
E_g = \frac{H_{aa} + H_{ab}}{1 + S_{ab}} = E_{1s} + V_{nn'} - J - \left( \frac{K - J S_{ab}}{1 + S_{ab}} \right)
\]

\[
E_u = \frac{H_{aa} - H_{ab}}{1 - S_{ab}} = E_{1s} + V_{nn'} - J + \left( \frac{K - J S_{ab}}{1 - S_{ab}} \right)
\]
\[ \Psi_{g,u} = N_{g,u} \left( 1s_a \pm 1s_b \right) \]

\[ E_g = \frac{H_{aa} + H_{ab}}{1 + S_{ab}} = E_{1s} + V_{nn'} - J - \left( \frac{K - J S_{ab}}{1 + S_{ab}} \right) \]

\[ E_u = \frac{H_{aa} - H_{ab}}{1 - S_{ab}} = E_{1s} + V_{nn'} - J + \left( \frac{K - J S_{ab}}{1 - S_{ab}} \right) \]

Standard situation: Calculation ≠ Explanation
Can you tell if \( E_g \) supports your idea of the chemical bond?

Both models contain delocalized electron
\( E_{1s} = \) H atom energy (non-bonded reference point?)
\( V_{nn'} \) & \( J = \) interatomic Coulomb energies (depend on \( R \))
\( K = \) interatomic Exchange energy (depends on \( R \))
\( S = \) overlap (depends on \( R \))

\[ V_{nn'} - J \]
\[ K - JS_{ab} \]

\( K \) appears because electron is delocalized
\( \pm K \) creates repulsion (attraction)

\[ K - J S_{ab} = \int \left( \phi_b - S \phi_a \right) \frac{e^2}{4 \pi \varepsilon_0 r_b} \phi_a \]
Not So Fast!

\[ \Psi = N (1s_a + i 1s_b) \]

\[ E = E_{1s} + V_{nn'} - J \]

delocalized electron doesn’t give attraction or repulsion (except at short \( R \))

More “causes” for bonding

- **1s\(_a\) + 1s\(_b\)**
  \[ \Psi^2 = a^2 + b^2 + 2S_{ab} \]
  node, enhanced e density btw p* positive overlap

- **1s\(_a\) - 1s\(_b\)**
  \[ \Psi^2 = a^2 + b^2 - 2S_{ab} \]
  node, reduced e density btw p* negative overlap

- **1s\(_a\) + i 1s\(_b\)**
  \[ \Psi^* \Psi = a^2 + b^2 \]
  no node, slightly enhanced e density imaginary overlap

Energy

- As potential wells overlap…
  - Wave function curvature / decay changes \( \to \) KE
    \[ \phi (r) = N (\xi) e^{-\xi (r/a_0)} \]
  - 1 (isolated H), 1.24 (H\(_2^+\) at 2.00 a\(_0\))
  - Effects are directional (\( \perp \) \( \parallel \) to bond axis)

- e\^- moves inward (\( \perp \)) and outward (\( \parallel \))
  - Inward \( \to \) lower PE, higher KE (smaller box)
  - Outward \( \to \) higher PE, lower KE (larger box)
Energy “Decomposition”

Table 1. Bond Energy Contributions for $H_2^+$

<table>
<thead>
<tr>
<th></th>
<th>(a) Bonding</th>
<th>(b) Nonbonding</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta T/\text{hartree}$</td>
<td>-0.17985</td>
<td>0.26636</td>
<td>0.08651</td>
</tr>
<tr>
<td>$\Delta V/\text{hartree}$</td>
<td>0.05284</td>
<td>-0.22585</td>
<td>-0.17301</td>
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<tr>
<td>$\Delta E/\text{hartree}$</td>
<td>-0.12702</td>
<td>0.04051</td>
<td>-0.08651</td>
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“nonbonding” portion – exponent increases $\rightarrow$ large $\Delta PE$ & $\Delta KE$ ~cancel
“bonding/interference” portion – overlap reduces $\Psi$ curvature & KE (small $\Delta PE$)

Virial theorem is satisfied by combining these results
Can’t just point to increased internuclear electron density & say “stabilizing”

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Points for Criticism

- Argument is based on model wave fn
Points for Criticism

• Argument is based on possibly artificial distinction

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