The Overlap Integral is a quantitative measure of the overlap of atomic orbitals situated on different atoms. An orbital overlap is the amount of orbitals of adjacent atoms that are in the same regions of space. The overlap of the atomic orbital of an atom A and the atomic orbital of an atom B is called their overlap integral. It is defined as \( S_{AB} = \int \psi^{*}_{A} \psi_{B} \, dr \) extending over all space.

**Basic description**

To understand the overlap integral, consider the wave function \( \psi_{+} \) to calculate the energy of \( H^{+}_{2} \) as a function of internuclear separation, R.

The energy associated with \( \psi_{+} \), \( E_{+} \) has the equation

\[
\hat{H} \psi_{+} (r; R) = E_{+} \psi_{+} (r; R)
\]

Multiply the left by \( \psi^{*}_{+} (r; R) \) and then integrate over the allowed values of r to get \( E_{+} \)

\[
E_{+} = \frac{\int \psi^{*}_{+} \hat{H} \psi_{+}}{\int \psi^{*}_{+} \psi_{+}}
\]

The wave function \( \psi_{+} \) is given by \( \psi_{+} = c(1s_{A} + 1s_{B}) \). To normalize this wave function, \( \int \psi^{*}_{+} \psi_{+} = 1 \), so

\[
\int \psi^{*}_{+} \psi_{+} = \int dr (1s_{A}^{*} + 1s_{B}^{*})(1s_{A} + 1s_{B})
\]

\[
= \int dr 1s_{A}^{*}1s_{A} + \int dr 1s_{A}^{*}1s_{B} + \int dr 1s_{B}^{*}1s_{A} + \int dr 1s_{B}^{*}1s_{B}
\]

The first and fourth integrals are simply the normalization expressions of the hydrogen atomic orbitals, so

\[
\int dr 1s_{A}^{*}1s_{A} = \int dr 1s_{B}^{*}1s_{B} = 1
\]

The second and third integrals involve the product of the hydrogen atomic orbital focus on nucleus A and the hydrogen atomic orbital focus on nucleus B. This product is larger when the two atomic orbitals have a larger overlap. These two integrals equal each other because the hydrogen atomic 1s orbital is expressed by a real function, or \( 1s^{*}(r) = 1s(r) \), and S is the overlap integral, so

\[
\int dr 1s_{A}^{*}1s_{B} = \int dr 1s_{B}^{*}1s_{A} = S
\]

This then gives

\[
\int \psi^{*}_{+} \psi_{+} = 1 + S + S + 1 = 2 + 2S
\]
Thus, the denominator is

\[
\int dr (1s^*\{A\} + 1s^*\{B\})(1s\{A\} + 1s\{B\}) = 2 + 2S
\]

Example \(\PageIndex{1}\): Determine the normalized wave function for \(\psi_{+}\)

The wave function \(\psi_{+}\) is given by \(c(1s\{A\} + 1s\{B\})\). To normalize this wave function, \(\int dr \psi^{*}_{+} \psi_{+} = 1\), so

\[
1 = \int dr \psi^{*}_{+} \psi_{+}
\]

\[
1 = \int dr c(1s^*\{A\} + 1s^*\{B\}) c(1s\{A\} + 1s\{B\})
\]

\[
1 = c^2 \int dr (1s^*\{A\}1s\{A\} + 1s^*\{A\}1s\{B\} + 1s^*\{B\}1s\{A\} + 1s^*\{B\}1s\{B\})
\]

Using the concepts of the Overlap Integral, \(\int dr 1s^*\{A\}1s\{A\} = \int dr 1s^*\{B\}1s\{B\} = 1\) and \(\int dr 1s^*\{A\}1s\{B\} = \int dr 1s^*\{B\}1s\{A\} = S\), so

\[
1 = c^2 (1 + S + S + 1)
\]

\[
1 = c^2 (2 + 2S)
\]

\[
c^2 = \frac{1}{2(1 + S)}
\]

\[
c = \sqrt{\frac{1}{2(1 + S)}} = \frac{1}{\sqrt{2(1 + S)}}
\]

Thus, the normalized wave function is

\[
\psi_{+} = c(1s\{A\} + 1s\{B\})
\]

\[
\psi_{+} = \frac{1}{\sqrt{2(1 + S)}} (1s\{A\} + 1s\{B\})
\]

Advanced description

If the wave functions do not overlap, then the overlap integral is zero. The integral can also be zero if the wave functions have positive and negative aspects that cancel out. If the overlap integral is zero, then the wave functions are called orthogonal. As the distance of the functions get closer to \(R = 0\), then the overlap integral gets closer to the maximum overlap integral of \(S = 1\).
Figure \(\PageIndex{1}\): The wave functions of atomic orbitals decrease exponentially with distance. Orbital overlap is non-zero when two atoms are close together, as illustrated for 1s orbitals in the upper figure. The lower figure shows orbitals that are too far away to interact. In this case both S is close to zero.

Overall, the full equation for the overlap integral, which is hard to calculate but is explained here, is

\[
[S(R)= \left \langle 1s_A \mid 1s_B \right \rangle = e^{-R/a_0} \left (1 + \frac{R}{a_0} + \frac{R^2}{3a_0^2} \right )]
\]

Figure \(\PageIndex{2}\): The overlap integral at different proton separations.

Example \(\PageIndex{2}\): The overlap integral at different separations

\[
[S(R)= e^{-R/a_0} \left (1 + \frac{R}{a_0} + \frac{R^2}{3a_0^2} \right )]
\]

Calculating the different separations of Figure 1.2 above:

At \(\frac{R}{a_0}\) = 0,

\[
[S(0) = e^{-0}(1 + 0 + \frac{0}{a_0} + \frac{0^2}{3a_0^2}) = e^0(1 + 0 + 0) = 1(1) = 1]
\]

At \(\frac{R}{a_0}\) = 1,
\[ S(1) = e^{-1} (1 + 1 + \frac{1}{3}) = e^{-1}(1 + 1 + \frac{1}{2}) = e^{-1}(\frac{5}{2}) = 0.9197\]

At \( \frac{R}{a_0} = 2 \),
\[ S(2) = e^{-2} (1 + 2 + \frac{4}{3}) = e^{-2}(1 + 2 + \frac{4}{2}) = e^{-2}(1 + 2 + 2) = e^{-2}(5) = 0.6767\]

At \( \frac{R}{a_0} = 4 \),
\[ S(4) = e^{-4} (1 + 4 + \frac{16}{3}) = e^{-4}(1 + 4 + \frac{16}{2}) = e^{-4}(1 + 2 + 8) = e^{-4}(11) = 0.2015\]

As evident from these calculations, the distance of \( R/a_0 = 0 \) or \( R = 0 \) gives the maximum overlap integral of \( S = 1 \). After that, the overlap integral \( S \) decreases exponentially with distance \( R \).

**Contributors**
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