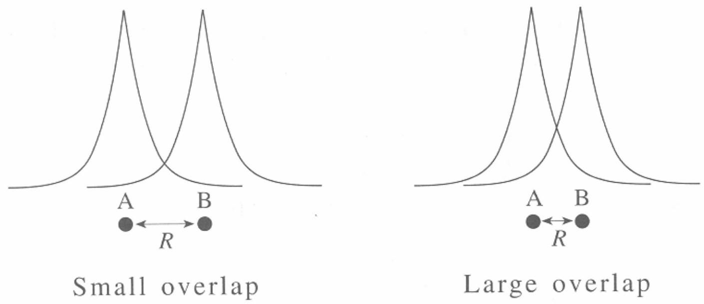

FIGURE 9.4
The overlap of the 1s orbitals centered on hydrogen nuclei located at A and B, a distance R apart.

For two 1s orbitals, it can be shown that their overlap integral is

$$S(R) = e^{-R}\left(1 + R + \frac{R^2}{3}\right) \tag{9.11}$$

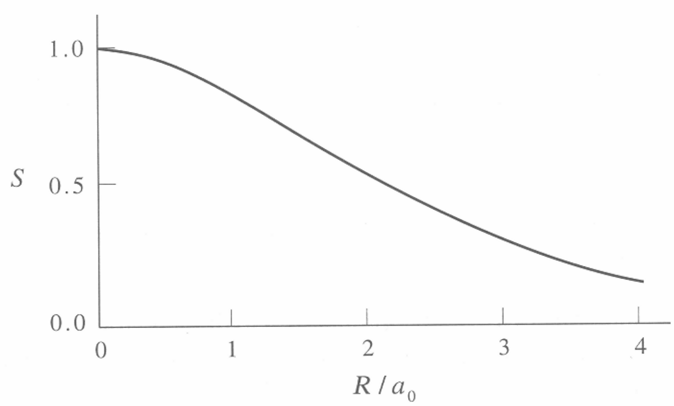

FIGURE 9.5
The overlap integral $S(R)$, Equation 9.11, for two hydrogen atom 1s orbitals plotted versus the internuclear separation in atomic units.

Donald A. McQuarrie and John D. Simon, *Physical Chemistry*: *A Molecular Approach*; University Science Books: Sausalito, CA; 1997

Evaluate numerator:

$$\int \Psi_+^* \hat{H} \Psi_+ \, d\tau = \int \Psi_+^* \left[-\frac{\hbar^2}{2m}\nabla^2 + \frac{e^2}{4\pi\varepsilon_0}\left(-\frac{1}{r_A} - \frac{1}{r_B} + \frac{1}{R}\right)\right] \Psi_+ \, d\tau$$

$$= \int \Psi_+^* \left[-\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{r_A} + \frac{1}{r_B}\right)\right] \Psi_+ \, d\tau$$

$$+ \int \Psi_+^* \left[\frac{e^2}{4\pi\varepsilon_0 R}\right] \Psi_+ \, d\tau$$

$$\equiv \text{I} + \text{II}$$

where $\text{II} = \dfrac{e^2}{4\pi\varepsilon_0 R} \displaystyle\int \Psi_+^* \Psi_+ \, d\tau = \boxed{\dfrac{e^2}{4\pi\varepsilon_0 R} 2N^2 [1 + S(R)]}$

τ not integrating over R

Evaluate I by substituting in LCAO expression:

$$\text{I} = \int N(A+B) \left[-\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{r_A} + \frac{1}{r_B}\right)\right] N(A+B) \, d\tau$$

Don't multiply out to get 12 terms!

$$\text{I} = N^2 \int (A+B) \left[-\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{r_A} + \frac{1}{r_B}\right)\right] A \, d\tau$$

$$+ N^2 \int (A+B) \left[-\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{r_A} + \frac{1}{r_B}\right)\right] B \, d\tau$$

and $\left[-\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0 r_A}\right] A = E(1s)\, A$ (eigenfunction!)

$\uparrow$ e^- motion (no nuclear motion)

$\uparrow$ distance of e^- in ψ_{1s_A} from nucleus A

and $\left[-\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0 r_B}\right] B = E(1s)\, B$ (eigenfunction!)

$$\text{so } (I) = N^2\int (A+B)\left[E(1s) - \frac{e^2}{4\pi\varepsilon_0 r_B}\right] A\, d\tau$$
$$+ N^2\int (A+B)\left[E(1s) - \frac{e^2}{4\pi\varepsilon_0 r_A}\right] B\, d\tau$$

$$\text{and } \int (A+B)\, E(1s)\, A\, d\tau = E(1s)\left[\int A^2 d\tau + \int BA\, d\tau\right]$$
$$= E(1s)\left[1 + S(R)\right]$$
$$= \int (A+B)\, E(1s)\, B\, d\tau$$

$$\text{so } (I) = N^2 E(1s)\left[1+S(R)\right] - N^2\int (A+B)\left[\frac{e^2}{4\pi\varepsilon_0 r_B}\right] A\, d\tau$$
$$+ N^2 E(1s)\left[1+S(R)\right] - N^2\int (A+B)\left[\frac{e^2}{4\pi\varepsilon_0 r_A}\right] B\, d\tau$$

We will not calculate, but we will label and interpret, the remaining integrals!
(I'll follow Atkins' notation on p.371)

Let $j \equiv \int A \left[\frac{e^2}{4\pi\varepsilon_0 r_B}\right] A\, d\tau = \frac{e^2}{4\pi\varepsilon_0}\int \frac{A^2}{r_B}\, d\tau$

This measures the interaction of the probability density of the left orbital (ψ_{1s_A}) with the right nucleus (N_B)

By symmetry, must also be true that

$$j = \int B \left[\frac{e^2}{4\pi\varepsilon_0 r_A}\right] B\, d\tau = \frac{e^2}{4\pi\varepsilon_0}\int \frac{B^2}{r_A}\, d\tau$$

Let $k \equiv \int B \left[\frac{e^2}{4\pi\varepsilon_0 r_B}\right] A\, d\tau = \frac{e^2}{4\pi\varepsilon_0}\int \frac{AB}{r_B}\, d\tau$

This measures the interaction of the overlap density with the right nucleus.

Again, by symmetry, must also be true that

$$k = \int A \left[\frac{e^2}{4\pi\varepsilon_0 r_A}\right] B\, d\tau = \frac{e^2}{4\pi\varepsilon_0}\int \frac{AB}{r_A}\, d\tau$$

So I $= 2N^2 E(1s)\,[1 + S(R)] - N^2(j+k) - N^2(k+j)$

$$\boxed{\text{I} = 2N^2 E(1s)\,[1 + S(R)] - 2N^2(j+k)}$$