

Chapter 11 Web Appendix

OVERLAP INTEGRALS OF ATOMIC WAVEFUNCTIONS

The normalization of molecular wavefunctions that are formed as combinations of atomic orbitals involves evaluation of so-called *overlap integrals* having the general form

$$\int \psi_a^*(\mathbf{r}) \psi_b(\mathbf{r} - \mathbf{R}) dV \quad (11.23)$$

Such integrals are evaluated here for the case where ψ_a and ψ_b are wavefunctions for the hydrogen ground state:

$$\psi_a(r) = \psi_b(r) = \frac{1}{\sqrt{\pi}} a_0^{-3/2} e^{-r/a_0} \quad (11.24)$$

The analysis is most transparent when carried out in atomic units, where distances are measured in bohrs (a_0) and energies in rydbergs ($ke^2/2a_0$). In such units r/a_0 becomes simply r , and ke^2/r becomes $2/r$, and so on.

Now the hydrogen ground-state orbital is an s state and, therefore, spherically symmetric; that is, ψ_a is a function only of $|\mathbf{r}| = r$. Likewise, $\psi_b(\mathbf{r} - \mathbf{R})$ will depend only on

$$|\mathbf{r} - \mathbf{R}| = \sqrt{r^2 + R^2 - 2\mathbf{r} \cdot \mathbf{R}}$$

If we orient the coordinate axes so that the z -axis lies along the direction of \mathbf{R} , then $\mathbf{r} \cdot \mathbf{R} = rR \cos \theta$, where θ is the polar angle in spherical coordinates. Since the volume element in spherical coordinates is $dV = r^2 dr d\Omega$, where the element of solid angle $d\Omega = \sin \theta d\theta d\phi$, the integration over angle can be carried out using the substitution $u^2 = r^2 + R^2 + 2rR \cos \theta$ (so that $udu = rR \sin \theta d\theta$). For $\theta = 0$, $u = |r - R|$ ($= u_1$), while $\theta = \pi$ implies $u = |r + R|$ ($= u_2$). Then

$$\begin{aligned} \int \psi_b(\mathbf{r} - \mathbf{R}) d\Omega &= \frac{1}{\sqrt{\pi}} a_0^{-3/2} \left(\frac{2\pi}{rR} \right) \int_1^{u_2} u e^{-u} du \\ &= -\frac{2\sqrt{\pi}}{rR} a_0^{-3/2} (1 + u) e^{-u} \Big|_{u_1}^{u_2} \\ &= \frac{2\sqrt{\pi}}{rR} a_0^{-3/2} \{ (1 + |r - R|) e^{-|r - R|} - (1 + |r + R|) e^{-|r + R|} \} \end{aligned}$$

and the full overlap integral becomes

$$\begin{aligned} \int \psi_a^*(\mathbf{r}) \psi_b(\mathbf{r} - \mathbf{R}) dV &= \frac{2}{R} \left\{ \int_0^\infty r e^{-r} (1 + |r - R|) e^{-|r - R|} dr \right. \\ &\quad \left. - \int_0^\infty r e^{-r} (1 + |r + R|) e^{-|r + R|} dr \right\} \end{aligned}$$

Since r and R are both nonnegative, $|r + R| = r + R$, and the second of the two integrals on the right can be integrated immediately using

$$\int_0^\infty x^n e^{-x} dx = n!$$

to get

$$\begin{aligned} \frac{2}{R} e^{-R} \int_0^\infty r(1+r+R)e^{-2r} dr &= \frac{1}{R} e^{-R} \int_0^\infty \left(\frac{x}{2}\right) \left(1 + \frac{x}{2} + R\right) e^{-x} dx \\ &= \left(\frac{1}{R} + \frac{1}{2}\right) e^{-R} \end{aligned}$$

The first integral must be evaluated separately in the two intervals $r < R$ and $r > R$. For $r < R$, we have $|r - R| = R - r$ and we find

$$\frac{2}{R} e^{-R} \int_0^R r(1+R-r) dr = [R(1+R) - 2R^2/3] e^{-R}$$

while for $r > R$ we obtain (with $x = r - R$)

$$\begin{aligned} \frac{2}{R} \int_0^\infty r(1+r-R)e^{(-2r+R)} dr &= \frac{2}{R} e^{-R} \int_0^\infty (x+R)(1+x)e^{-2x} dx \\ &= \left(\frac{1}{R} + \frac{3}{2}\right) e^{-R} \end{aligned}$$

Combining all the preceding results gives the overlap integral as

$$\int \psi_a^*(\mathbf{r}) \psi_b(\mathbf{r} - \mathbf{R}) dV = \left(1 + R + \frac{R^2}{3}\right) e^{-R} \quad (11.25)$$

With only minor alterations, the same method may be used to obtain the expressions given in the text for the energies E_+ and E_- of the lowest bonding and antibonding states, respectively, of H_2^+ .

Overlap integrals figure prominently in the calculations needed to normalize molecular wavefunctions built up from atomic orbitals. To see how this works, consider the molecular wavefunction ψ_\pm built from the symmetric (antisymmetric) combination of two atomic orbitals ψ_a , one centered at the origin and the other centered at $\mathbf{r} = \mathbf{R}$:

$$\psi_\pm(\mathbf{r}) = \psi_a(\mathbf{r}) \pm \psi_a(\mathbf{r} - \mathbf{R})$$

We assume the atomic wavefunctions ψ_a are already normalized. The normalization integral for ψ_\pm is

$$\begin{aligned} \int |\psi_\pm|^2 dV &= \int |\psi_a(\mathbf{r})|^2 dV + \int |\psi_a(\mathbf{r} - \mathbf{R})|^2 dV \\ &\quad \pm \int \psi_a^*(\mathbf{r}) \psi_a(\mathbf{r} - \mathbf{R}) dV \\ &\quad \pm \int \psi_a(\mathbf{r}) \psi_a^*(\mathbf{r} - \mathbf{R}) dV \end{aligned}$$

Since the atomic wavefunctions are already normalized, the first two integrals on the right are both unity. If \mathbf{R} is large, the last two integrals can be neglected, since the integrand for each is the product of one atomic function centered at $\mathbf{r} = 0$ with another centered at $\mathbf{r} = \mathbf{R}$. The resulting product is small everywhere provided \mathbf{R} is sufficiently large, and these integrals—the *overlap integrals* described previously—are very nearly zero. Thus, in the lowest approximation

$$\int |\psi_\pm|^2 dV \approx 2$$

and approximately normalized molecular wavefunctions can be had by multiplying ψ_\pm by the factor $1/\sqrt{2}$.

In a more refined treatment, the overlap integrals have to be evaluated. For the hydrogen atom in the ground state, the overlap integrals are both given by Equation 11.25 above. Denoting these integrals by Δ , we find

$$\int |\psi_{\pm}|^2 dV \approx 2 \pm 2\Delta$$

and the proper normalization factor for the wavefunction ψ_{\pm} becomes $1/\sqrt{2(1 \pm \Delta)}$.