

chemistry. The model we use is the familiar minimal basis MO-LCAO description of H_2 .

In this model, each hydrogen atom has a $1s$ atomic orbital and, as the two atoms approach, molecular orbitals (MOs) are formed as a linear combination of atomic orbitals (LCAO). The coordinate system is shown in Fig. 2.5. The first atomic orbital, ϕ_1 , is centered on atom 1 at \mathbf{R}_1 . The value of ϕ_1 at a point in space \mathbf{r} is $\phi_1(\mathbf{r})$ or, since its value depends on the distance from its origin, we sometimes write $\phi_1 \equiv \phi_1(\mathbf{r} - \mathbf{R}_1)$. The second atomic orbital is centered on atom 2 at \mathbf{R}_2 , i.e., $\phi_2 \equiv \phi_2(\mathbf{r} - \mathbf{R}_2)$. The exact $1s$ orbital of a hydrogen atom centered at \mathbf{R} has the form

$$\phi(\mathbf{r} - \mathbf{R}) = (\zeta^3/\pi)^{1/2} e^{-\zeta|\mathbf{r} - \mathbf{R}|} \quad (2.54)$$

where ζ , the orbital exponent, has a value of 1.0. This is an example of a *Slater orbital*. In this book we will be concerned mostly with *Gaussian orbitals*, which lead to simpler integral evaluations than Slater orbitals. The $1s$ Gaussian orbital has the form

$$\phi(\mathbf{r} - \mathbf{R}) = (2\alpha/\pi)^{3/4} e^{-\alpha|\mathbf{r} - \mathbf{R}|^2} \quad (2.55)$$

where α is the Gaussian orbital exponent. For the present, we need not be concerned with the particular form of the $1s$ atomic orbitals. The two atomic orbitals ϕ_1 and ϕ_2 can be assumed to be normalized, but they will not be orthogonal. They will *overlap*, such that the overlap integral is

$$S_{12} = \int d\mathbf{r} \phi_1^*(\mathbf{r}) \phi_2(\mathbf{r}) \quad (2.56)$$

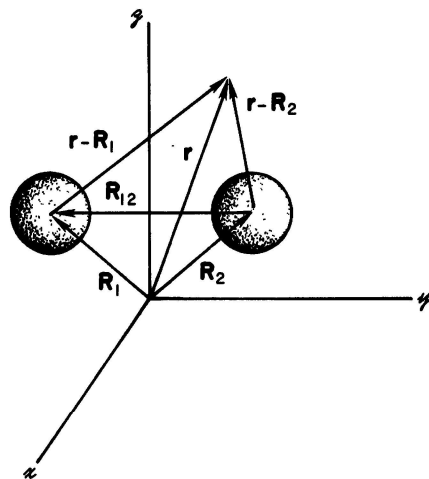


Figure 2.5 Coordinate system for minimal basis H_2 .