Table 2.2 Notations for one- and two-electron integrals over spin (χ) and spatial (ψ) orbitals

SPIN ORBITALS

$$[i|h|j] = \langle i|h|j\rangle = \int d\mathbf{x}_1\, \chi_i^*(\mathbf{x}_1) h(\mathbf{r}_1) \chi_j(\mathbf{x}_1)$$

$$\langle ij|kl\rangle = \langle \chi_i\chi_j|\chi_k\chi_l\rangle = \int d\mathbf{x}_1\, d\mathbf{x}_2\, \chi_i^*(\mathbf{x}_1)\chi_j^*(\mathbf{x}_2) r_{12}^{-1} \chi_k(\mathbf{x}_1)\chi_l(\mathbf{x}_2) = [ik|jl]$$

$$[ij|kl] = [\chi_i\chi_j|\chi_k\chi_l] = \int d\mathbf{x}_1\, d\mathbf{x}_2\, \chi_i^*(\mathbf{x}_1)\chi_j(\mathbf{x}_1) r_{12}^{-1} \chi_k^*(\mathbf{x}_2)\chi_l(\mathbf{x}_2) = \langle ik|jl\rangle$$

$$\langle ij||kl\rangle = \langle ij|kl\rangle - \langle ij|lk\rangle = \int d\mathbf{x}_1\, d\mathbf{x}_2\, \chi_i^*(\mathbf{x}_1)\chi_j^*(\mathbf{x}_2) r_{12}^{-1}(1 - \mathscr{P}_{12})\chi_k(\mathbf{x}_1)\chi_l(\mathbf{x}_2)$$

SPATIAL ORBITALS

$$(i|h|j) = h_{ij} = (\psi_i|h|\psi_j) = \int d\mathbf{r}_1\, \psi_i^*(\mathbf{r}_1) h(\mathbf{r}_1) \psi_j(\mathbf{r}_1)$$

$$(ij|kl) = (\psi_i\psi_j|\psi_k\psi_l) = \int d\mathbf{r}_1\, d\mathbf{r}_2\, \psi_i^*(\mathbf{r}_1)\psi_j(\mathbf{r}_1) r_{12}^{-1} \psi_k^*(\mathbf{r}_2)\psi_l(\mathbf{r}_2)$$

$J_{ij} = (ii|jj)$ Coulomb integrals

$K_{ij} = (ij|ji)$ Exchange integrals

For one-electron integrals over spin orbitals, the chemists' and physicists' notations are essentially the same.

$$[i|h|j] = \langle i|h|j\rangle = \int d\mathbf{x}_1\, \chi_i^*(\mathbf{x}_1) h(\mathbf{r}_1) \chi_j(\mathbf{x}_1) \tag{2.100}$$

Table 2.2 summarizes all the notations for one- and two-electron integrals used in this book. When we consider the reduction of integrals over spin orbitals to integrals over spatial orbitals later in this chapter, we will introduce a new notation for spatial integrals, which we have included in the table for the sake of completeness and ease of future reference.

2.3.3 General Rules for Matrix Elements

We have seen that it is fairly easy to evaluate matrix elements between two-electron Slater determinants. The N-electron case is more complicated, and here we simply present a set of rules that can be used to evaluate matrix elements and leave their derivation to the next subsection, which can be skipped, if desired.

There are two types of operators in quantum chemistry. The first type is a sum of one-electron operators

$$\boxed{\mathcal{O}_1 = \sum_{i=1}^{N} h(i)} \tag{2.101}$$

where $h(i)$ is any operator involving only the ith electron. These operators represent dynamic variables that depend only on the position or momentum