Permutational Symmetries of One- and Two-Electron Integrals

C. David Sherrill
School of Chemistry and Biochemistry
Georgia Institute of Technology

October 2005

Most algorithms in *ab initio* electronic structure theory compute quantities in terms of one- and two-electron integrals. Let us consider the form of these integrals and their permutational symmetries. Here we find it helpful to employ the notation of Szabo and Ostlund, *Modern Quantum Chemistry.*

Let us start with molecular spin orbitals, $\chi(\mathbf{x})$, which describe the motion of a single electron as a function of spatial coordinates *and* a spin coordinate, denoted collectively by $\mathbf{x}$, where $\mathbf{x} = \{x, y, z, \omega\}$ or $\mathbf{x} = \{r, \theta, \phi, \omega\}$, with ω being a formal "spin coordinate" used by Szabo and Ostlund. Typically, a spin orbital is written as a product of a spatial part times a spin function (usually just α or β), i.e., $\chi(\mathbf{x}) = \phi(\mathbf{r})\alpha(\omega)$ or $\chi(\mathbf{x}) = \phi(\mathbf{r})\beta(\omega)$, where $\phi(\mathbf{r})$ is a spatial orbital that depends only on the spatial coordinates such as $\mathbf{r} = \{x, y, z\}$ or $\mathbf{r} = \{r, \theta, \phi\}$.

There are two standard notations for integrals in terms of molecular spin orbitals, denoted "physicists' notation" and "chemists' notation." The physicists' notation lists all complex-conjugate functions to the left, and then non-complex-conjugate functions to the right. For two-electron integrals, within a pair of complex-conjugate functions (or non-complex-conjugate functions), the orbital for electron 1 would be listed first, followed by the orbital for electron 2. In chemists' notation, by contrast, one lists the functions for electron 1 on the left, followed by functions for electron 2 on the right. Within each pair, one lists the complex-conjugate functions first, followed by the non-complex-conjugate functions.

The one-electron integrals are the easiest. One-electron integrals over spin orbitals in physicist's notation are defined as

$$\langle i|h|j\rangle = \int d\mathbf{x}_1 \chi_i^*(\mathbf{x}_1)\hat{h}(\mathbf{r}_1)\chi_j(\mathbf{x}_1) \tag{1}$$

where the one-electron Hamiltonian operator $\hat{h}(\mathbf{r}_1)$ is defined as

$$\hat{h}(\mathbf{r}_1) = -\frac{1}{2}\nabla_1^2 - \sum_A \frac{Z_A}{r_{1A}} \tag{2}$$

It is immediately obvious that

$$\langle i|h|j\rangle = \langle j|h|i\rangle^*. \tag{3}$$

Szabo and Ostlund use square brackets to distinguish spin-orbital integrals in chemists' notation from those in physicists' notation as given above. For the case of one-electron integrals, there is in fact no distinction between physicists' notation and chemists' notation, and so the chemists' notation one-electron spin-orbital integral,

$$[i|h|j] = \int d\mathbf{x}_1 \chi_i^*(\mathbf{x}_1)\hat{h}(\mathbf{r}_1)\chi_j(\mathbf{x}_1) \tag{4}$$

is identical to the physicists' notation $\langle i|h|j\rangle$. Thus we also know that

$$[i|h|j] = [j|h|i]^*. \tag{5}$$

If the orbitals are real, then

$$\langle i|h|j\rangle = \langle j|h|i\rangle \tag{6}$$

$$[i|h|j] = [j|h|i] \tag{7}$$

If spin is integrated out, we are left with integrals in terms of spatial orbitals only. It is customary to denote integrals over spatial orbitals by parentheses, i.e.,

$$(i|h|j) = \int d\mathbf{r}_1 \phi_i^*(\mathbf{r}_1)\hat{h}(\mathbf{r}_1)\phi_j(\mathbf{r}_1). \tag{8}$$

Note again that there is no actual distinction between physicists' and chemists' notation for one-electron spatial orbital integrals. The above permutational symmetries hold for spatial orbital one-electron integrals also, namely,

$$(i|h|j) = (j|h|i)^* \tag{9}$$

for complex orbitals, and

$$(i|h|j) = (j|h|i) \tag{10}$$

for real orbitals.

Permutational symmetries in the two-electron integrals are somewhat more interesting. The two-electron integral in physicists' notation is

$$\langle ij|kl\rangle = \int d\mathbf{x}_1 d\mathbf{x}_2 \chi_i^*(\mathbf{x}_1)\chi_j^*(\mathbf{x}_2)\frac{1}{r_{12}}\chi_k(\mathbf{x}_1)\chi_l(\mathbf{x}_2) \tag{11}$$

while in chemists' notation it is written

$$[ij|kl] = \int d\mathbf{x}_1 d\mathbf{x}_2 \chi_i^*(\mathbf{x}_1)\chi_j(\mathbf{x}_1)\frac{1}{r_{12}}\chi_k^*(\mathbf{x}_2)\chi_l(\mathbf{x}_2) \tag{12}$$

Clearly the integral is unchanged if the dummy indices of integration are permuted. This leads to the symmetry

$$\langle ij|kl\rangle = \langle ji|lk\rangle \tag{13}$$

Furthermore, the complex conjugate of the integral is

$$\langle ij|kl\rangle = \langle kl|ij\rangle^* \tag{14}$$

Combining these two symmetries leads to one further equality, namely

$$\langle ij|kl\rangle = \langle lk|ji\rangle^* \tag{15}$$

Therefore, in the general case we have

$$\langle ij|kl\rangle = \langle ji|lk\rangle = \langle kl|ij\rangle^* = \langle lk|ji\rangle^* \tag{16}$$

or

$$[ij|kl] = [kl|ij] = [ji|lk]^* = [lk|ji]^* \tag{17}$$

For the case of real orbitals, we can clearly remove the complex conjugations in the equations above, leading to a four-fold permutational symmetry in the two-electron integrals. However, an additional symmetry arises if the orbitals are real: in that case, the same integral is obtained if i and k (or j and l) are swapped in $\langle ij|kl\rangle$. It is trivial to verify that this leads to an overall eightfold permutational symmetry,

$$\begin{gathered} \langle ij|kl\rangle = \langle ji|lk\rangle = \langle kl|ij\rangle = \langle lk|ji\rangle = \\ \langle kj|il\rangle = \langle li|jk\rangle = \langle il|kj\rangle = \langle jk|li\rangle \end{gathered} \tag{18}$$

or

$$\begin{gathered} [ij|kl] = [kl|ij] = [ji|lk] = [lk|ji] = \\ [ji|kl] = [lk|ij] = [ij|lk] = [kl|ji] \end{gathered} \tag{19}$$

Finally, it is worthwhile to consider the permutational symmetries in the antisymmetrized two-electron integral, $\langle ij||kl\rangle$, defined as

$$\begin{aligned} \langle ij||kl\rangle &= \langle ij|kl\rangle - \langle ij|lk\rangle & (20)\\ &= [ik|jl] - [il|jk] & (21) \end{aligned}$$

In the general case, the permutational symmetries are

$$\begin{gathered} \langle ij||kl\rangle = \langle ji||lk\rangle = \langle kl||ij\rangle^* = \langle lk||ji\rangle^* = \\ -\langle ij||lk\rangle = -\langle ji||kl\rangle = -\langle lk||ij\rangle^* = -\langle kl||ji\rangle^* \end{gathered} \tag{22}$$

One consequence of these relationships is that

$$\langle ii||jk\rangle = \langle ij||kk\rangle = 0 \tag{23}$$

If we integrate out spin, we are left again with integrals over spatial orbitals $\phi(\mathbf{r})$. Most frequently, two-electron integrals over spatial orbitals are written in chemists' notation as,

$$(ij|kl) = \int d\mathbf{r}_1 d\mathbf{r}_2 \phi_i^*(\mathbf{x}_1)\phi_j(\mathbf{x}_1)\frac{1}{r_{12}}\phi_k^*(\mathbf{x}_2)\phi_l(\mathbf{x}_2) \tag{24}$$

These integrals have the same permutational symmetries as the two-electron integrals over spin orbitals in chemists' notation, namely,

$$(ij|kl) = (kl|ij) = (ji|lk)^* = (lk|ji)^* \tag{25}$$

for complex orbitals, and

$$(ij|kl) = (kl|ij) = (ji|lk) = (lk|ji) = (ji|kl) = (lk|ij) = (ij|lk) = (kl|ji) \tag{26}$$

for real orbitals.