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, \( \chi(x) \), which describe the motion of a single electron as a function of spatial coordinates and a spin coordinate, denoted collectively by \( x \), where \( x = \{x, y, z, \omega\} \) or \( x = \{r, \theta, \phi, \omega\} \), with \( \omega \) 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 \( \alpha \) or \( \beta \)), i.e., \( \chi(x) = \phi(r)\alpha(\omega) \) or \( \chi(x) = \phi(r)\beta(\omega) \), where \( \phi(r) \) is a spatial orbital that depends only on the spatial coordinates such as \( r = \{x, y, z\} \) or \( r = \{r, \theta, \phi\} \).

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

\[
\langle i | h | j \rangle = \int d x_1 \chi_i^* (x_1) \hat{h}(r_1) \chi_j (x_1)
\]

where the one-electron Hamiltonian operator \( \hat{h}(r_1) \) is defined as

\[
\hat{h}(r_1) = -\frac{1}{2} \nabla_1^2 - \sum_A \frac{Z_A}{r_{1A}}
\]
It is immediately obvious that
\[ \langle i|h|j \rangle = \langle j|h|i \rangle^*. \] (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,
\[ [i|h|j] = \int d\mathbf{x}_1 \chi_i^*(\mathbf{x}_1)\hat{h}(\mathbf{r}_1)\chi_j(\mathbf{x}_1) \] (4)
is identical to the physicists’ notation \( \langle i|h|j \rangle \). Thus we also know that
\[ [i|h|j] = [j|h|i]^*. \] (5)

If the orbitals are real, then
\[ \langle i|h|j \rangle = \langle j|h|i \rangle \] (6)
\[ [i|h|j] = [j|h|i] \] (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.,
\[ (i|h|j) = \int d\mathbf{r}_1 \phi_i^*(\mathbf{r}_1)\hat{h}(\mathbf{r}_1)\phi_j(\mathbf{r}_1). \] (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,
\[ (i|h|j) = (j|h|i)^* \] (9)
for complex orbitals, and
\[ (i|h|j) = (j|h|i) \] (10)
for real orbitals.

Permutational symmetries in the two-electron integrals are somewhat more interesting. The two-electron integral in physicists’ notation is
\[ \langle ij|kl \rangle = \int d\mathbf{x}_1 d\mathbf{x}_2 \chi_i^*(\mathbf{x}_1)\chi_j^*(\mathbf{x}_2)\frac{1}{r_{12}}\chi_k(\mathbf{x}_1)\chi_l(\mathbf{x}_2) \] (11)
while in chemists’ notation it is written
\[ [ij|kl] = \int d\mathbf{x}_1 d\mathbf{x}_2 \chi_i^*(\mathbf{x}_1)\chi_j(\mathbf{x}_1)\frac{1}{r_{12}}\chi_k^*(\mathbf{x}_2)\chi_l(\mathbf{x}_2) \] (12)
Clearly the integral is unchanged if the dummy indices of integration are permuted. This leads to the symmetry

\[ \langle ij|kl \rangle = \langle ji|lk \rangle \] (13)

Furthermore, the complex conjugate of the integral is

\[ \langle ij|kl \rangle = \langle kl|ij \rangle^* \] (14)

Combining these two symmetries leads to one further equality, namely

\[ \langle ij|kl \rangle = \langle lk|ji \rangle^* \] (15)

Therefore, in the general case we have

\[ \langle ij|kl \rangle = \langle ji|lk \rangle = \langle kl|ij \rangle = \langle lk|ji \rangle \] (16)

or

\[ [ij|kl] = [kl|ij] = [ji|lk] = [lk|ji] \] (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,

\[ \langle ij|kl \rangle = \langle ji|lk \rangle = \langle kl|ij \rangle = \langle lk|ji \rangle \] (18)

or

\[ [ij|kl] = [kl|ij] = [ji|lk] = [lk|ji] \] (19)

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

\[ \langle ij||kl \rangle = \langle ij|kl \rangle - \langle ij|lk \rangle = [ik|jl] - [il|jk] \] (20)

In the general case, the permutational symmetries are

\[ \langle ij||kl \rangle = \langle ji||lk \rangle = \langle kl||ij \rangle^* = \langle lk||ji \rangle^* = -\langle ij||lk \rangle = -\langle ji||kl \rangle = \langle kl||ij \rangle^* = \langle lk||ji \rangle^* \] (22)
One consequence of these relationships is that

\[ \langle ii | jj \rangle = \langle ij | kk \rangle = 0 \]  \hspace{1cm} (23)

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

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

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

\[ (ij|kl) = (kl|ij) = (ji|lk)^* = (lk|ji)^* \]  \hspace{1cm} (25)

for complex orbitals, and

\[ (ij|kl) = (kl|ij) = (ji|lk) = (ij|lk) = (lk|ij) = (ij|lk) = (kl|ji) \]  \hspace{1cm} (26)

for real orbitals.