Assignment III

CH603

Reading two electron integrals

The aim of this assignment is to write a function to read the two electron integrals correctly from the file. The are stored in the file eri.dat and are provided in Mulliken notation over real AO basis functions:

$$(\mu\nu|\lambda\sigma) \equiv \int \phi_\mu^*(\mathbf{r}_1)\phi_\nu(\mathbf{r}_1)r_{12}^{-1}\phi_\lambda^*(\mathbf{r}_2)\phi_\sigma(\mathbf{r}_2)d\mathbf{r}_1 d\mathbf{r}_2$$

Hence, the integrals obey the eight-fold permutational symmetry relationships:

$$(\mu\nu|\lambda\sigma) = (\nu\mu|\lambda\sigma) = (\mu\nu|\sigma\lambda) = (\nu\mu|\sigma\lambda) = (\lambda\sigma|\mu\nu) = (\sigma\lambda|\mu\nu) = (\lambda\sigma|\nu\mu) = (\sigma\lambda|\nu\mu)$$

and only the permutationally unique integrals are provided in the file, with the restriction that, for each integral, the following relationships hold:

$$\mu \geq \nu, \qquad \lambda \geq \sigma, \qquad \text{and} \qquad \mu\nu \geq \lambda\sigma,$$

where

$$\mu\nu \equiv \mu(\mu+1)/2 + \nu \qquad \text{and} \qquad \lambda\sigma \equiv \lambda(\lambda+1)/2 + \sigma.$$

The function should return all the integrals (zero and non-zero) as four dimensional numpy array of dimension (nbasis,nbasis,nbasis,nbasis). Subsequently the four dimensional array should be printed in a file along with their indices. The sample code for printing is provided.

Hint 1: First one need to find out an unique compound index from the four indexes of the integrals. Remember, we are dealing with a symmetric matrix and we need to store them in an one dimensional array. Consider the lower triangle of an *n x n* symmetric matrix:

$$
\begin{bmatrix}
A_{00} & \cdots & \cdots & \cdots & \cdots \\
A_{10} & A_{11} & \cdots & \cdots & \cdots \\
A_{20} & A_{21} & A_{22} & \cdots & \cdots \\
\vdots & \vdots & \vdots & \ddots & \vdots \\
A_{n0} & A_{n1} & A_{n2} & \cdots & A_{nn}
\end{bmatrix}
$$

The total number of elements in the lower triangle is M = n(n+1)/2. We could store these in a one-dimensional array by ordering them

$$
\begin{bmatrix}
0 & \cdots & \cdots & \cdots & \cdots \\
1 & 2 & \cdots & \cdots & \cdots \\
3 & 4 & 5 & \cdots & \cdots \\
6 & 7 & 8 & 9 & \cdots \\
\vdots & \vdots & \vdots & \vdots & \ddots
\end{bmatrix}
$$

How do we translate row (*i*) and column (*j*) indices of the matrix to the position in the linear array (*ij*)?

$$
ij \equiv \begin{cases} i(i+1)/2 + j & \text{if} \quad i > j \\ \\ j(j+1)/2 + i & \text{if} \quad i < j \end{cases}
$$

Therefore, one can calculate the compound index using a standard if-else conditional statement:

Hint 2: The eight-fold permutational symmetry of the two-electron repulsion integrals can be viewed similarly. Only now they are a four dimensional array. The Mulliken-notation integrals are symmetric to permutations of the bra indices or of the ket indices. Hence, we can view the integral list as a symmetric "super-matrix" of the form:

$$\begin{bmatrix} (00|00) & \dots & \dots & \dots & \dots \\ (10|00) & (10|10) & \dots & \dots & \dots \\ (11|00) & (11|10) & (11|11) & \dots & \dots \\ (20|00) & (20|10) & (20|11) & (20|20) & \dots \\ \vdots & \vdots & \vdots & \vdots & \ddots \end{bmatrix}$$

Thus, just as for the two-dimensional case above, we only need to store the lower triangle of this matrix, and a one-dimensional array of length *M(M+1)/2* will do the trick. Given four AO indices, *i*, *j*, *k*, and *l* corresponding to the integral, (ij|kl), we can translate these into compound row (*ij*) and column (*kl*) indices using the expression above, as well as the final compound index:

$$ijkl \equiv \begin{cases} ij(ij+1)/2 + kl & \text{if} \quad ij > kl \\ \\ kl(kl+1)/2 + ij & \text{if} \quad ij < kl \end{cases}$$

Hint 3: First find out compound index for all the unique and non-zero integrals present in the eri.dat and store the compound index, together with the value of the integral.

Now open loops for i,j,k and l found the compound index, get the corresponding integral value and print it along with the i,j,k and l.

The code should be applicable for any arbitrary system provided no of basis functions (nbasis) are provided.