**E1-21: Computer generation of the formulae for Hamiltonian matrix elements in post Hartree-Fock photoionization calculations**

G Bandarage
(*Open Univ. of Sri Lanka, Nawala*)

Inner electron photoionization spectra of atoms and molecules exhibit satellites due to shake up processes, which involve the simultaneous excitation of outer electrons. They are multi-electron processes and even the simplest theoretical description must include electron correction effects which require the use of post Hartree-Fock wave functions.

In Configuration Interaction (CI) approximation the calculation of the observable properties, such as cross sections, requires the evaluation of the Hamiltonian matrix elements between a large number of Slater determinants.

A computer program to calculate the formulae for non-vanishing Hamiltonian matrix elements once the electronic configurations of the CI wave functions and the spin coupling scheme are specified was developed.

Due to large numbers, unlike in the case of Hartree-Fock wave functions, the formulae for such matrix elements cannot be deduced manually by inspecting the wave functions. An additional complication arises in photoionization due to the non-orthogonality of the ionizing electron orbital to the bound state molecular orbital. This makes the computer an indispensable tool in tackling the problem.

The computer program, written in FORTRAN 77, consists of 2 modules. One generates the terms in CI wave functions, based on the electronic configurations and the spin coupling scheme, and the other generates the formulae for the matrix elements. The latter is built up on the following facts:

* In general there are 13 different types of matrix elements.
* The formulae for the matrix elements between 2 Slater determinants can be obtained using Condon-Slater rules.
* The identity of a matrix element can be specified completely using 9 integers.
* The formula can then be specified with these integers and one complex number specifying their coefficient.

As an example a very simple case is considered. A 4-electron system with one electron being ionized (thus in a continuum orbital). The formulae for the Hamiltonian matrix elements for a CI wave function having 3 electronic configurations, is calculated in equal weights, represented in the input to the program as follows:

```
2,1,0,0,  0.577350269,1,
1,1,1,0,  0.577350269,1,
0,1,1,1,  0.577350269,2,
```

The first 4 integers represent the electronic occupation numbers of orbitals 1,2,3 and 4. The real number depicts the coefficient of each configuration in the CI wave function (which is normalized). The last integer gives the spin function associated with the term. A typical line of output is depicted below.

```
-0.288675D+00 0.000000D+00   5 5 1 2 1 1 1 1 2
```

Here the first 2 real numbers give the complex coefficient of this particular matrix element and the 9 integers identify the matrix element. In this problem there are 1540 non-vanishing matrix elements of which some are identical. The program adds these algebraically and lists unique ones with correct coefficients. There are 577 such entries.

A FORTRAN 77 computer program (which runs on a personal computer) which does algebraic manipulations to calculate the formulae for the non-vanishing Hamiltonian matrix elements between 2 CI wave functions, was developed.