A GENERAL PROGRAM FOR COMPUTING MATRIX ELEMENTS IN ATOMIC STRUCTURE WITH NON-ORTHOGONAL ORBITALS

Oleg Zatsarinny

Institute of Electron Physics, Uzhgorod 294016, Ukraine

In many atomic processes involving inner atomic shells, the relaxation of electron orbitals plays the important role. The relaxation can be most efficiently included into consideration by using the non-orthogonal orbitals for the initial and final state. This requires the evaluating of the matrix elements of various operators with respect to the non-orthogonal one-particle orbitals. Initially, these matrix elements can be expressed as weighted sums of relevant radial integrals, possibly multiplied by overlap integrals. The program computes all the arising coefficients of the radial integrals and the corresponding overlap factors.

The calculations follow the method based on the representation of configuration wave functions through the Slater determinants [1], using the combination of the vector coupling and fractional parentage methods. The program, therefore, can also be used for obtaining the corresponding vector-coupling coefficients. Then the coefficients of the radial integrals and their overlap factors are obtained from integration over all spin and angular coordinates for the separate Slater functions that is much more simple task. Integration over the radial coordinates is defined either as unity, zero, or as expression for radial integrals. Due to the additional task of finding the determinant expansion, the method used is more laborious than those based on the Racah techniques [2,3] and widely used now for calculating the matrix elements with orthogonal orbitals. On the other hand, the present technique admits a simple extension to the case of non-orthogonal orbitals by the most general way. Besides, considerable reduction of calculations has been achieved by using the tables of vector coupling coefficients for the individual subshells.

Any number of s, p, or d electrons are allowed in a shell, but no more than two electrons or two holes in any shell of higher orbital angular momentum. In principle, the program admits the simple extension to the case of any f-subshell, but this requires the use of very large auxiliary file (about 2 Mbytes) for the corresponding vector coupling coefficients. *LS*-coupling is used, but its extension to *jj*-coupling is straightforward. Any amount of non-orthogonality between the orbitals may be presented leading to overlap integrals for the matrix elements.

The operators included in the present version of the program are the one- and two-particle electrostatic interaction along with the one-particle tensor operator and simple overlap. Matrix elements of these operators provide the basis for studying the formation or decay of the inner-shell vacancies. It has long been recognized that consideration of non-orthogonality leads to a more correct structure for interaction matrix elements and has great importance for the accurate determination of radiative decay or autoionization. A comprehensive review of application of the non-orthogonal orbitals to atoms has been recently given by Kupliauskiene [4].

1. E. U. Condon and G. H. Shortley, The theory of atomic spectra (1935).
2. U. Fano // Phys. Rev. A, 1965, v.140, p.67.
3. A. Hibbert and C. Froese Fischer // Comput. Phys. Commun. , 1991, v.64, p.417.
4. A. Kupliauskiene // Lithunian Journal of Physics, 1995, v.35, p.113.