

# Secondly Quantized Multi-Configurational Approach for Atomic Databases

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## 1 Introduction

Studies of the structure of atoms and ions (ultracold to relativistic included) as well as their two-body interactions with photons, electrons and other particles require accurate methods for the description of such objects.

In order to obtain accurate values of atomic quantities it is necessary to account for relativistic and correlation effects. Relativistic effects may be taken into account as Breit-Pauli corrections or in a fully relativistic approach. In both cases for complex atoms and ions, a considerable part of the effort must be devoted to integrations over spin-angular variables, occurring in the matrix elements of the operators under consideration.

Many existing codes for integrating are based on a scheme by Fano [1]. The integrations over spin-angular variables in this case constitute a considerable part of the problem, especially when atoms with many open shells are treated, and the operators are not trivial. In the papers of Gaigalas *et al.* [2],[3], an efficient approach for finding matrix elements of any one- and two-particle atomic operator between complex configurations is suggested. It is free of shortcomings of previous approaches. This approach allows one to generate fairly accurate databases of atomic parameters (Froese Fischer *et al.* [4],[5]).

Further development of the approaches by Gaigalas *et al.* [2],[3] for the spin-spin and spin-other-orbit relativistic corrections in the Breit-Pauli approximation is presented in this paper.

## 2 Matrix Elements Between Complex Configurations

According to the approach of Gaigalas *et al.* [3], a general expression of the submatrix element for any two-particle operator between functions with  $u$  open shells can be written as follows:

$$\begin{aligned}
 & (\psi_u^{bra}(LS) || G || \psi_u^{ket}(L'S')) = \\
 &= \sum_{n_i l_i, n_j l_j, n'_i l'_i, n'_j l'_j} (\psi_u^{bra}(LS) || \hat{G} (n_i l_i, n_j l_j, n'_i l'_i, n'_j l'_j) || \psi_u^{ket}(L'S')) = \\
 &= \sum_{n_i l_i, n_j l_j, n'_i l'_i, n'_j l'_j, \kappa_{12}, \sigma_{12}, \kappa'_{12}, \sigma'_{12}} \sum (-1)^\Delta \Theta' (n_i \lambda_i, n_j \lambda_j, n'_i \lambda'_i, n'_j \lambda'_j, \Xi) \times \\
 & \quad \times T (n_i \lambda_i, n_j \lambda_j, n'_i \lambda'_i, n'_j \lambda'_j, \Lambda^{bra}, \Lambda^{ket}, \Xi, \Gamma) \times \\
 & \quad \times R (\lambda_i, \lambda_j, \lambda'_i, \lambda'_j, \Lambda^{bra}, \Lambda^{ket}, \Gamma), \tag{1}
 \end{aligned}$$

where  $\Lambda^{bra} \equiv (L_i S_i, L_j S_j, L'_i S'_i, L'_j S'_j)^{bra}$  is the array of bra function shells' terms, and similarly for  $\Lambda^{ket}$  and  $\lambda \equiv ls$ .

Thus, to calculate the spin-angular part of a submatrix element of this type, one has to obtain:

1. The recoupling matrix  $R\left(\lambda_i, \lambda_j, \lambda'_i, \lambda'_j, \Lambda^{bra}, \Lambda^{ket}, \Gamma\right)$ , which has an analytical expression in terms of just 6j- and 9j-coefficients.
2. Submatrix elements  $T\left(n_i \lambda_i, n_j \lambda_j, n'_i \lambda'_i, n'_j \lambda'_j, \Lambda^{bra}, \Lambda^{ket}, \Xi, \Gamma\right)$  for tensorial products of creation/annihilation operators that act upon a particular electron shell. So, all the advantages of tensorial algebra and quasispin formalism (Rudzikas [6]) may be efficiently exploited in the process of their calculation.
3. The phase factor  $\Delta$ .
4.  $\Theta'\left(n_i \lambda_i, n_j \lambda_j, n'_i \lambda'_i, n'_j \lambda'_j, \Xi\right)$  which is proportional to the two-electron submatrix element of operator  $\hat{G}$ .

Further development of this approach for the spin-spin and spin-other-orbit relativistic corrections in the Breit-Pauli approximation is presented in the following section.

### 3 The Spin-Spin and Spin-Other-Orbit Operators

The *spin-spin* operator  $H^{ss}$  itself contains tensorial structure of two different types, summed over  $k$ :

$$H^{ss} \equiv \sum_k \left[ H_{ss}^{(k+1k-12,112)} + H_{ss}^{(k-1k+12,112)} \right]. \quad (2)$$

Their submatrix elements are:

$$\begin{aligned} & \left( n_i \lambda_i n_j \lambda_j \left\| H_{ss}^{(k+1k-12,112)} \right\| n_{i'} \lambda_{i'} n_{j'} \lambda_{j'} \right) = \frac{3}{\sqrt{5}} \sqrt{(2k+3)^{(5)}} \times \\ & \times \left( l_i \left\| C^{(k+1)} \right\| l_{i'} \right) \left( l_j \left\| C^{(k-1)} \right\| l_{j'} \right) N^{k-1} \left( n_i l_i n_j l_j, n_{i'} l_{i'} n_{j'} l_{j'} \right), \end{aligned} \quad (3)$$

$$\begin{aligned} & \left( n_i \lambda_i n_j \lambda_j \left\| H_{ss}^{(k-1k+12,112)} \right\| n_{i'} \lambda_{i'} n_{j'} \lambda_{j'} \right) = \frac{3}{\sqrt{5}} \sqrt{(2k+3)^{(5)}} \times \\ & \times \left( l_i \left\| C^{(k-1)} \right\| l_{i'} \right) \left( l_j \left\| C^{(k+1)} \right\| l_{j'} \right) N^{k-1} \left( n_j l_j n_i l_i, n_{j'} l_{j'} n_{i'} l_{i'} \right), \end{aligned} \quad (4)$$

where we use a shorthand notation  $(2k+3)^{(5)} \equiv (2k+3)(2k+2)(2k+1)(2k)(2k-1)$  and radial integral in (3), (4) is defined as in Glass and Hibbert [7]:

$$\begin{aligned} & N^k \left( n_i l_i n_j l_j, n_{i'} l_{i'} n_{j'} l_{j'} \right) = \\ & = \frac{\alpha^2}{4} \int_0^\infty \int_0^\infty P_i(r_1) P_j(r_2) \frac{r_2^k}{r_1^{k+3}} \epsilon(r_1 - r_2) P_{i'}(r_1) P_{j'}(r_2) dr_1 dr_2, \end{aligned} \quad (5)$$

where  $\epsilon(x)$  is a Heaviside step-function,

$$\epsilon(x) = \begin{cases} 1; & \text{for } x > 0, \\ 0; & \text{for } x \leq 0. \end{cases} \quad (6)$$

The *spin-other-orbit* operator  $H^{soo}$  itself contains tensorial structure of six different types, summed over  $k$ :

$$H^{sso} \equiv \sum_k \left[ H_{soo}^{(k-1k1,101)} + H_{soo}^{(k-1k1,011)} + H_{soo}^{(kk1,101)} + H_{soo}^{(kk1,011)} + H_{soo}^{(k+1k1,101)} + H_{soo}^{(k+1k1,011)} \right]. \quad (7)$$

Their submatrix elements are:

$$\begin{aligned} \left( n_i \lambda_i n_j \lambda_j \left\| H_{soo}^{(k-1k1, \sigma_1 \sigma_2 1)} \right\| n_{i'} \lambda_{i'} n_{j'} \lambda_{j'} \right) &= 2 \cdot (\sigma_1 + 2\sigma_2) \{ (2k-1)(2k+1) \times \\ &\times (l_i + l_{i'} - k + 1)(k - l_i + l_{i'}) (k + l_i - l_{i'}) (k + l_i + l_{i'} + 1) \}^{1/2} \times \\ &\times (k)^{-1/2} \left( l_i \left\| C^{(k)} \right\| l_{i'} \right) \left( l_j \left\| C^{(k)} \right\| l_{j'} \right) N^{k-2} (n_j l_j n_i l_i, n_{j'} l_{j'} n_{i'} l_{i'}), \end{aligned} \quad (8)$$

$$\begin{aligned} \left( n_i \lambda_i n_j \lambda_j \left\| H_{soo}^{(kk1, \sigma_1 \sigma_2 1)} \right\| n_{i'} \lambda_{i'} n_{j'} \lambda_{j'} \right) &= -2 \cdot (\sigma_1 + 2\sigma_2) (2k+1)^{1/2} \left( l_i \left\| C^{(k)} \right\| l_{i'} \right) \times \\ &\times \left( l_j \left\| C^{(k)} \right\| l_{j'} \right) \left\{ (k(k+1))^{-1/2} (l_i(l_i+1) - k(k+1) - l_{i'}(l_{i'}+1)) \times \right. \\ &\times \left. \left\{ (k+1) N^{k-2} (n_j l_j n_i l_i, n_{j'} l_{j'} n_{i'} l_{i'}) - k N^k (n_i l_i n_j l_j, n_{i'} l_{i'} n_{j'} l_{j'}) \right\} - \right. \\ &\left. - 2(k(k+1))^{1/2} V^{k-1} (n_i l_i n_j l_j, n_{i'} l_{i'} n_{j'} l_{j'}) \right\}, \end{aligned} \quad (9)$$

$$\begin{aligned} \left( n_i \lambda_i n_j \lambda_j \left\| H_{soo}^{(k+1k1, \sigma_1 \sigma_2 1)} \right\| n_{i'} \lambda_{i'} n_{j'} \lambda_{j'} \right) &= 2 \cdot (\sigma_1 + 2\sigma_2) \{ (2k+1)(2k+3) \times \\ &\times (l_i + l_{i'} - k)(k - l_i + l_{i'} + 1)(k + l_i - l_{i'} + 1)(k + l_i + l_{i'} + 2) \}^{1/2} \times \\ &\times (k+1)^{-1/2} \left( l_i \left\| C^{(k)} \right\| l_{i'} \right) \left( l_j \left\| C^{(k)} \right\| l_{j'} \right) N^k (n_i l_i n_j l_j, n_{i'} l_{i'} n_{j'} l_{j'}). \end{aligned} \quad (10)$$

The radial integrals in (8)-(10) are (see Glass and Hibbert [7]):

$$\begin{aligned} &V^k (n_i l_i n_j l_j, n_{i'} l_{i'} n_{j'} l_{j'}) = \\ &= \frac{\alpha^2}{4} \int_0^\infty \int_0^\infty P_i(r_1) P_j(r_2) \frac{r_1^{k-1}}{r_1^{k+2}} r_2 \frac{\partial}{\partial r_1} P_{i'}(r_1) P_{j'}(r_2) dr_1 dr_2. \end{aligned} \quad (11)$$

Now we have all we need (the operators for tensorial structure and their submatrix elements) for obtaining the value of a matrix element of these operators for any number of open shells in bra and ket functions. This lets us exploit all advantages of the approach by Gaigalas *et al.* [3].

The spin-spin and spin-other-orbit operators itself generally contain tensorial structure of several different types. Therefore the expression (1) must be used separately for each possible tensorial structure for performing spin-angular integrations according to [3]. Each type of tensorial structure is associated with a different type of recoupling matrix  $R(\lambda_i, \lambda_j, \lambda'_i, \lambda'_j, \Lambda^{bra}, \Lambda^{ket}, \Gamma)$  and with different matrix elements of standard tensorial quantities  $T(n_i \lambda_i, n_j \lambda_j, n'_i \lambda'_i, n'_j \lambda'_j, \Lambda^{bra}, \Lambda^{ket}, \Xi, \Gamma)$ .

## 4 Conclusions

The tensorial forms of the general secondly quantized spin-spin interaction operator (2) and spin-other-orbit interaction operator (7) and its submatrix elements ( for spin-spin interaction expressions (3), (4) and for spin-other-orbit expressions (8), (9) and (10)) are presented. In calculating its matrix elements between functions with  $u$  open shells this allows to exploit all the advantages of method by Gaigalas *et al.* [3]:

1. to obtain both diagonal and off-diagonal elements with respect to the configuration matrix elements in a unified approach,
2. to use in practical applications the tables of submatrix elements of standard quantities, which here are both the coordinate representation and the occupation number representation tensorial operators,
3. to apply the quasispin formalism for the occupation numbers parts and make use of it,
4. to make use of having recoupling matrices simpler than in other known approaches.

## References

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