Abstract. Possibilities of the new quasirelativistic approach designed for \textit{ab initio} calculations of spectral characteristics of highly charged ions and heavy atoms are briefly described and illustrated with an example of a study of spectral characteristics of gallium-like Molybdenum and Tungsten.

1. Brief description of the method

Within the quasirelativistic approach the main relativistic effects are taken into account already in obtaining the radial orbitals. Nevertheless the orbitals remain one component and independent on $j$. Some peculiarities of the well-known quasirelativistic approximation by R. D. Cowan, described in the monograph [1] and references therein, caused a demand of creating this different approach.

The general form of the quasirelativistic Hartree-Fock (QRHF) equations used by us is described in [2]. Taking into account the corrections for $p$ electrons presented in paper [3] brings about the quasirelativistic equations of the following form:

$$
\left\{ \frac{d^2}{dr^2} - \frac{l(l+1)}{r^2} - V(nl \mid r) - \epsilon_{nl} \right\} P(nl \mid r) - X(nl \mid r) + \frac{\alpha^2}{4} \frac{D(nl \mid r)P(nl \mid r)}{1 - \frac{\alpha^2}{4} (\epsilon_{nl} + V(nl \mid r))} = 0.
$$

Here $X(nl \mid r)$ denotes the exchange part of the potential, and $V(nl \mid r)$ - the direct part of it including an interaction of an electron with a nucleus $U(r)$ and with other electrons $V(nl \mid r) = U(r) + Y(nl \mid r)$. The contact interaction with a nucleus is denoted $D(nl \mid r)$ and the last term describes the mass dependence on the velocity.

The main distinctions between the approach under investigation and the well-known computer code by R. D. Cowan [1] are the following:

- No statistical potentials are used. There are only conventional self-consistent field direct $V(nl \mid r)$ and exchange $X(nl \mid r)$ potentials in QRHF.
- The finite size of the nucleus is taken into account in the determination of the potential $U(r)$ while solving the quasirelativistic equations [4].
- The mass-velocity term splits into two parts – the direct potential and the exchange one.
- The contact interaction term contains only the nucleus potential $U(r)$ derivative in the numerator. No two-electron potentials are included in the numerator.
Only the direct part of the potential \( V(nl|r) \) is included into the denominator of the contact interaction with a nucleus term.

The contact interaction with a nucleus is taken into account not only for \( s \)-electrons, but also for \( p \)-electrons with some additional corrections made [3]:

\[
D(nl | r) = \left( \delta(l,0) + \frac{1}{3} \delta(l,1) \right) \frac{1}{dr} \left[ \frac{d}{dr} - \frac{1}{r} \left( \alpha^2 Z^2 \delta(l,1) \left( -\frac{37}{30} - \frac{5}{9n} + \frac{2}{3n^2} \right) + 1 \right) \right].
\]

(2)

The electron contact interaction may be taken into account when calculating the potential functions forming \( V(nl|r) \) and \( X(nl|r) \) [2].

Exploitable radial orbitals (RO) are already quasirelativistic; therefore the energy operator matrix must be calculated with account of the relativistic corrections as it is done within Breit-Pauli (BP) approach. The integral describing the one-electron part of the energy operator independent on the total momentum of an electron \( j \) can be written down from the equation (1). The one-electron part of the spin-orbit interaction integral is described as follows [3]:

\[
\eta_{QR}(nl) = \frac{\alpha^2}{8} \int_{0}^{\infty} \frac{dU(r)}{dr} \frac{1}{r} \frac{d}{dr} \frac{1}{1 - \frac{\alpha^2}{4} (V_{nl} + V(r))} dr.
\]

(3)

Remaining relativistic interactions of the BP approach are two-electron ones. Taking account of these interactions in the case of quasirelativistic ROs is not different from the case of the conventional non-relativistic functions.

The transformed radial orbitals with the variable parameters (TRO) are used in this work to describe the virtual excitations in the configuration interaction (CI) approach. This method for the non-relativistic functions was developed in [5] and successfully applied to take into account the correlation effects in many calculations. TRO is obtained from the RO of the investigated configuration \( K_0 \) using the following transforming function:

\[
P_{TRO}(nl | r) = N \left[ \int f(k, m, A, B) P(nl_0 | r) \sum_{n' < n} P(n'l | r) P(n'l | r) f(k, m, A, B) P(nl_0 | r) dr \right].
\]

(4)

Here \( N \) is a normalization factor. The first term in the parentheses represents the transformation itself and the second one ensures the orthogonality of the radial orbitals. In the present work the exponential transformation is used:

\[
f(k, m, A, B) = r^k \left( 1 + A r^m \right) \exp(-Br); \quad k = l_0 - l - l + 2, ..., l_0 - l + 6; \quad m = 0, 2, 4, 6; \quad A, B > 0.
\]

(5)

The parameters \( k \) and \( m \) can only be integers with a step equal to 2. This is because the quasirelativistic RO in the vicinity of the origin expand in powers of \( r \) only of one parity depending on the value of \( l \) [4]. The criterion in determining the optimal values of integer parameters \( k \) and \( m \) and real parameters \( A \) and \( B \) is the maximum of the averaged energy correction, expressed in the second order of perturbation theory. More detailed description of the method used one can find in [6].

2. Results and discussion

The spectral characteristics of highly charged ions were obtained employing the quasirelativistic RO for the calculation of the multiconfiguration energy operator matrix within the BP approach (QR+CI). The calculations executed within the described approach were reduplicated by analogical calculations based on the usual non-relativistic radial orbitals (HF+CI). All procedures of TRO obtaining, admixed configurations and their term selection, and others were the same in both calculations. The procedures have been described elsewhere for HF+CI case (see for example [7]). It allows one to evaluate the advantages and new possibilities in using the quasirelativistic RO against the conventional non-relativistic RO when one performs the CI calculation using transformed radial orbitals in the same way. The solution of Hartree-Fock equations and calculations of the angular parts of matrix elements
were performed by the codes from the known program complex [8]. All other calculations were completed using our own computer programs.

The energy spectra, the probabilities of the electric dipole transitions and the radiation lifetimes were calculated for nine configurations: 4s^24p, 4s4p^2, 4p_1^1, 4s^24d, 4s4p4d, 4p_2^1, 4s^24f, 4s4p4f and 4s4d^2 of Mo^{+11} and W^{+43} ions. A part of the results for Mo^{+11} with experimental data available is presented in Table 1. As seen from the table, the deviations from the experimental energy values are several times smaller within QR+CI approach than those of HF+CI. The mean square deviations presented at the end of the table confirm this fact. It is necessary to mention that the level characteristics presented in the first column of the table correspond to the experimental data from [9]. At the same time in the case of two pairs of close lying levels displayed in bold both theoretical calculations reveal opposite positions of the mentioned terms when the maximum expansion coefficients of the multiterm function are used for classification. The comparison of the lifetimes presented in two last columns shows, that in this case switching from the non-relativistic RO to the quasirelativistic ones does not have significant influence on the values.

**Table 1. Spectral characteristics of Mo^{+11}**

| Term          | Energy levels (cm\(^{-1}\)) | Lifetimes (ns) |
|---------------|------------------------------|----------------|
|               | Exp. [9] | HF+CI | QR+CI | HF+CI | QR+CI |
| 4s^2 4p^2 (^3P) 0.5 | 28464 | 25100 | 26700 | - | - |
| 4s^2 4p^2 (^3P) 1.5 | 211589 | 206100 | 209900 | 32.80 | 30.50 |
| 4s^2 4p^2 (^3P) 2.5 | 224236 | 217700 | 222000 | 6.56 | 5.99 |
| 4s^2 4p^2 (^3P) 3.0 | 269162 | 263400 | 268400 | 0.3050 | 0.3150 |
| 4s^2 4p^2 (^3F) 0.5 | 297054 | 295700 | 299900 | 0.0351 | 0.0346 |
| 4s^2 4p^2 (^3F) 0.5 | 325519 | 321200 | 326900 | 0.0329 | 0.0332 |
| 4s^2 4d^2 (^3D) 1.5 | 424004 | 425600 | 426800 | 0.0126 | 0.0126 |
| 4s^2 4d^2 (^3D) 2.5 | 428285 | 429700 | 430900 | 0.0143 | 0.0146 |
| 4p_1^1 3D 1.5 | 493598 | 488100 | 494500 | 0.0374 | 0.0388 |
| 4p_1^1 3S 1.5 | 507733 | 499700 | 507000 | 0.0464 | 0.0451 |
| 4p_1^1 3D 2.5 | 510263 | 502700 | 510000 | 0.1080 | 0.1100 |
| 4p_1^1 3P 0.5 | 546449 | 540700 | 548400 | 0.0460 | 0.0464 |
| 4p_1^1 3P 1.5 | 559781 | 550900 | 559500 | 0.0461 | 0.0466 |

In Table 2 the characteristics of E1 transitions from the excited states to the levels of ^3P term of the ground configuration 4s^24p of W^{+43} ion are presented. The data for E2 and M1 transitions within the ground configuration are shown in the last row. They are compared with the results of the calculations introduced in paper [10] performed within Dirac-Fock approach using GRASP (GR) code and with the wavelength measurement results in Tokamak (Tok) plasma from the same paper. As seen from the table the application of HF+CI approach leads to rather significant inaccuracies of wavelengths. It is quite explicable as the usual BP approach is not intended to perform calculations for ions charged so highly. Application of the quasirelativistic RO in analogous calculations increases essentially the accuracy of the results. Though in this case the obtained QR+CI wavelengths are inferior to the pure relativistic results, the deviations are quite acceptable. The oscillator strengths (gf) obtained within
two approaches are in rather good agreement. At the same time the emission transition probabilities (A) differ essentially. It is due to the strong dependence of the probabilities on the accuracy of the transition energy calculations, which are described much better within QR+CI approach.

Table 2. Characteristics of the transitions to the levels of the ground configuration 4s^24p of W^{43} ion.

| J_{final} | LS_{initial} | λ (Å) | gf | A (s^-1) |
|-----------|--------------|------|----|----------|
|           |              | HF+CI  | QR+CI | GR[10] | Tok.[10] | HF+CI  | QR+CI | HF+CI  | QR+CI  |
| 0.5       | 4d \, ^2D_{1,5} | 51.62 | 47.12 | 47.60 | 47.91 | 1.55 | 1.72 | 9.71×10^{11} | 1.29×10^{12} |
| 0.5       | 4s4p \, ^2P_{0,5} | 67.96 | 59.30 | 60.20 | 60.63 | 0.758 | 0.764 | 5.48×10^{11} | 7.24×10^{11} |
| 0.5       | 4s4p \, ^2D_{1,5} | 68.84 | 59.98 | 61.19 | 61.14 | 0.816 | 0.801 | 2.87×10^{11} | 3.71×10^{11} |
| 0.5       | 4s4p \, ^2P_{0,5} | 133.22 | 125.76 | 128.99 | 128.24 | 0.151 | 0.157 | 2.84×10^{10} | 3.30×10^{10} |
| 1.5       | 4s4p \, ^2D_{2,5} | 140.80 | 133.51 | 136.82 | 135.34 | 0.268 | 0.254 | 1.50×10^{10} | 1.59×10^{10} |
| 0.5       | 4p \, ^2P_{1,5} | 155.00 | 122.38 | 125.87 | 126.39 | 1.38×10^{-6} | 2.46×10^{-6} | 9.55×10^{4} | 2.74×10^{5} |
| E2        |               | 3.48×10^{-5} | 4.41×10^{-5} | 2.41×10^{6} | 4.90×10^{6} |

The presented examples reveal that application of the quasirelativistic RO within CI approach allows one to increase significantly the accuracy of the obtained results and essentially broadens the framework of the BP approximation.

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