Breit and QED contributions in atomic structure calculations of tungsten ions

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Abstract
The Fac, Grasp2k, and Mcdfgme codes are compared in three case studies of the radiative transitions occurring in tungsten ions: (i) Ni1 and Ni2 lines in Ni-like tungsten, (ii) 3p_{3/2} - 3p_{1/2} fine splitting in Cl-like tungsten, and (iii) K\alpha_1 and K\alpha_2 lines in W VIII. Various approaches to including the Breit interaction term and QED corrections in atomic calculations are examined. Electron correlation effects are also investigated and compared to the Breit and QED contributions. The data presented here may be used to estimate theoretical uncertainties relevant to interpretation of high-resolution spectroscopic data.

Keywords: X-ray spectra; Multiconfiguration Dirac-Fock calculations; Line energies; Breit interaction; QED corrections

1. Introduction
The investigation of tungsten ions is of great importance in theoretical and applied atomic physics. Firstly, high-Z atoms such as tungsten, are used to probe relativistic and quantum-electrodynamics (QED) effects [1] and have been suggested as potential candidates for testing the time variation of the fine structure constant [2]. Secondly, tungsten is chosen as a plasma-facing material in large tokamaks, such as JET (Joint European Torus) and ITER (International Thermonuclear Experimental Reactor), and thus constitutes the majority of the impurity ions in the tokamak plasma. Therefore, spectroscopic studies of tungsten ions provide a diagnostic tool relevant to a wide range of electron temperatures [3, 4]. High-precision atomic calculations are required to interpretation of complex spectra of high-charged tungsten ions and they constitute the solid base for the farther benchmark modelling of the radiation emission from tokamak plasmas. Several codes are used to predict the atomic structure and transition probabilities of ions that are of interest in plasma research, such as Relac [5], the Cowan code [6], Hullac [7], Grasp [8] and Grasp2k [9, 10], Mcdfgme [11, 12], Rmbpt [13], and Fac [14]. Recently, two of these, Fac and Grasp2k, have become the most widely used codes. When comparing results obtained from Fac and Grasp2k calculations, it is crucial to know which theoretical contributions are included in the calculations and what may potentially produce discrepancies. Hence, the aim of this article is to discuss the differences in theoretical contributions taken into account by the Fac, Grasp2k, and Mcdfgme codes. The relative roles of the electron correlation contribution and the Breit and QED contributions is also examined.

Both the Grasp2k and the Mcdfgme codes use the Multi-Configuration Dirac-Hartree-Fock (MCDHF) approach. The methodology of MCDHF calculations has been presented in many papers; see, e.g., [15]. The Grasp (General-Purpose Relativistic Atomic Structure Program) code was developed by the Grant group at University of Oxford and recently improved by Froese Fischer, Jönsson, and collaborators in order to perform large-scale Configuration Interaction (CI) calculations. The Mcdfgme (Multi Configuration Dirac Fock and General Matrix Element) code was developed by Desclaux and Indelicato in France, and takes into account the Breit and QED corrections in a detailed way. The Fac (Flexible Atomic Code), utilising the modified multiconfigurational Dirac-Hartree-Fock-Slater (DHF) method, was developed by M. F. Gu at Stanford University for speed, multi-utility, and collisional-radiative modelling. The main difference between the DHF and DHFS methods is that DHFS approximates the non-local DHF exchange potential by a local potential. Since the DHFS method uses an approximate form of the electron-electron interaction potential, it is commonly considered to be less accurate than the more sophisticated MCDHF method. This assumption is examined in the present work. The main aim of the research presented here is to estimate the theoretical uncertainties relevant to the interpretation of high-resolution spectroscopic data.

2. Theoretical background
2.1. MCDHF methods
The methodology of MCDHF calculations performed in the present studies is similar to the one published earlier, in several papers (see, e.g., [11, 12, 15–18]). The effective Hamiltonian for an N-electron system is expressed by

$$\hat{H} = \sum_{i=1}^{N} \hat{h}_e(i) + \sum_{j=1}^{N} V_{ij}$$

(1)
| Contribution | \( [M_g]^{3}p^{6}3d^{10}_{J=0}^{(1S_{0})} \) | \( [M_g]^{3}p^{1}3p^{1}_{l=1}3d^{10}4d^{1}_{l=1}^{(3P_{1})} \) | \( [M_g]^{3}p^{1}3p^{1}_{l=1}3d^{10}4d^{1}_{l=1}^{(3P_{1})} \) | \( [M_g]^{3}p^{1}3p^{1}_{l=1}3d^{10}4d^{1}_{l=1}^{(3P_{1})} \) |
|--------------|----------------|----------------|----------------|----------------|
| **Dirac-Fock** | 2392.09 | 2392.05 | 2391.25 | 2366.90 | 2366.87 | 2365.96 |
| **Breit(\( \omega = 0 \)) + Rec.** | -4.95 | -4.97 | -4.64 | -4.23 | -4.28 | -3.93 |
| **Mag.** | -5.91 | -5.14 | 0.85 | 0.00 | 0.00 | 0.00 |
| **Ret. (\( \omega = 0 \))** | 0.93 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| **Recoil** | 0.38 | 0.39 | 0.40 | 0.40 | 0.40 | 0.40 |
| **Breit(\( \omega > 0 \))** | 0.38 | 0.39 | 0.40 | 0.40 | 0.40 | 0.40 |
| **VP** | -0.02 | -0.02 | -0.03 | -0.02 | -0.02 | -0.03 |
| **VP11 + 21** | -0.02 | -0.02 | -0.02 | -0.02 | -0.02 | -0.02 |
| **VP11 + 21 + 13** | -0.02 | -0.02 | -0.02 | -0.02 | -0.02 | -0.02 |
| **SE** | -0.38 | -0.48 | -0.39 | -0.41 | -0.51 | -0.40 |
| **Welt. mod.** | -0.39 | -0.40 | -0.40 | -0.40 | -0.40 | -0.40 |
| **QED h.o.** | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| **Total (Welt.)** | 2387.12 | 2386.96 | 2386.19 | 2362.62 | 2362.45 | 2361.61 |
| **Total (dens.)** | 2387.11 | 2387.11 | 2386.19 | 2362.62 | 2362.45 | 2361.61 |

\( \text{Ni1} (^3P_1 \rightarrow ^1S_0) \) and \( \text{Ni2} (^3P_1 \rightarrow ^1S_0) \) transitions in Ni-like tungsten ion (eV).
Table 2: Various theoretical contributions to the energy of $3p_{1/2} - 3p_{3/2}$ fine splitting in Cl-like tungsten (eV).

| Contribution | $3p_{3/2}$ | $3p_{1/2}$ | $3p_{1/2} - 3p_{3/2}$ |
|--------------|------------|------------|----------------------|
|              | Grasp2k + QEDmod | Grasp2k + QEDmod | MCDQME | FAC | Grasp2k | Grasp2k + QEDmod | MCDQME | FAC | Grasp2k | Grasp2k + QEDmod | MCDQME | FAC |
| Dirac-Fock   | -346399.48 | -346396.71 | -346379.23 | -346752.33 | -346749.55 | -346732.10 | 352.85 | 352.84 | 352.87 |
| Breit $(\omega = 0)$ + Rec. | 400.90 | 399.90 | 401.31 | 404.47 | 403.45 | 405.12 | -3.58 | -3.56 | -3.81 |
| Mag. Ret. $(\omega = 0)$ | 442.39 | -42.59 | 0.09 | 0.09 | 445.92 | -42.56 | -0.03 | 0.00 | 0.00 |
| Recoil | -9.02 | -8.98 | -8.47 | -8.43 | -5.55 | -5.55 | 0.11 | 0.10 | 0.10 |
| Breit $(\omega > 0)$ VP | -71.97 | -71.15 | -72.04 | -71.50 | -71.24 | -72.15 | -71.50 | -71.24 | -72.15 |
| VP11 | -71.97 | -71.15 | -72.04 | -71.50 | -71.24 | -72.15 | -71.50 | -71.24 | -72.15 |
| VP11 + 21 | -71.97 | -71.15 | -72.04 | -71.50 | -71.24 | -72.15 | -71.50 | -71.24 | -72.15 |
| SE | -71.97 | -71.15 | -72.04 | -71.50 | -71.24 | -72.15 | -71.50 | -71.24 | -72.15 |
| Welt. dens. mod. | 376.72 | 376.48 | 375.28 | 376.43 | 376.16 | 375.06 | 0.29 | 0.31 | 0.22 |
| QED h.o. | 382.41 | 382.08 | 0.32 | 0.32 | 0.31 | 0.00 | 0.00 | 0.00 | 0.00 |
| Total(Welt.) | -345702.86 | -345699.59 | -345674.67 | -346051.96 | -346048.73 | -346024.07 | 349.11 | 349.14 | 349.39 |
| Total(dens.) | -345697.17 | -345699.75 | -346048.87 | -346046.31 | 349.14 | 349.13 |

where $\omega = (\omega_z - \epsilon) / c$ is the frequency of one virtual photon exchanged and $\epsilon$ and $\omega_z$ are orbital energies of interacting electrons.

2.2. Breit interaction

The electron-electron interaction term is a sum of the Coulomb interaction term $V_{\text{Coul}}$ and the Breit interaction term $V_{\text{Breit}}$ in the Coulomb gauge is

\[ V_{\text{Coul}} = \frac{1}{r_{ij}} \]

\[ V_{\text{Breit}} = V_{\text{Coul}} + \psi \]

The Breit operator in the Coulomb gauge is

\[ \psi = \psi_1 + \psi_2 \]

where $\psi_1$ and $\psi_2$ are the angular components of the Dirac bispinors.

2.3. Breit–Hartree–Fock–Slater exchange potential

The main difference between the Dirac–Hartree–Fock method and the Dirac–Hartree–Fock–Slater method is that the Dirac–Hartree–Fock–Slater exchange potential is approximated by a local potential. The MDF code uses an approximate form of the local exchange potential [19–21].
where $V_{\text{magn}}$ is called magnetic (Gaunt) [22] part and $V_{\text{ret}}$ is called retardation part.

The three-frequency approximation to the full transverse Breit interaction, i.e. Eq. (7), is well suited for most computations of many-electron atomic systems since the explicit frequency-dependent form, because of remedying the lack of covariance of Dirac-Coulomb-Breit Hamiltonian and the differences of state energy by using frequency-independent and frequency-dependent Breit operator are usually small [11, 23, 24]. The Breit interaction can be included in two general ways: in the self-consistent field process, such as in MCD$\Phi$ME code [11, 25–27], or in perturbational approach, such as in GRASP/Grasp2k codes [8, 9].

2.3. QED corrections

The bound-state vacuum polarization (VP) contribution is related to the creation and annihilation of virtual electron-positron pairs in the field of the nucleus. It is a correction to the photon propagator. The first term of order $\alpha(Za)^2$ can be calculated as the expectation value of the Uehling potential. The Uehling potential in the case of finite nuclear size and spherical symmetric nuclear charge distribution $\rho(\vec{r})$ can be expressed as [28]:

$$U(\vec{r}) = \frac{2}{3} \frac{Za^2 \hbar^2}{mr} \int_0^{\infty} d^3r' \frac{r' \rho(r')}{(r + r')}$$

where the function $K_0(x)$ is defined as:

$$K_0(x) = \int_0^x dt e^{-t} \left( t + \frac{1}{2t} \right) \sqrt{t^2 - 1}$$

The higher-order terms have been given by Källén and Sabry [29] for order $\alpha^3(Za)$ and by Wichmann and Kroll [30, 31] for order $\alpha^2(Za)^2$.

Self-energy (SE) contribution arises from the interaction of the electron with its own radiation field. It is a correction to the electron propagator. For one-electron systems the most important (one-loop) self-energy term has been calculated exactly by Mohr [32–34] and expressed as:

$$\Delta E_{\text{se}} = \frac{\alpha(Za)^4}{\pi n} F_{\text{m}}(Za) m_e c^2$$

where $F_{\text{m}}(Za)$ is a slowly varying function of $Za$. For many-electron atomic systems the self-energy correction to the energy is changed by the electron screening. There are three general ways to estimate self-energy screening for atoms. The major differences between these approaches are for results of SE correction to the energy of $s$ subshells.

In the ‘Welton picture’ approach [12, 35, 36] the self-energy correction for $s$-type Dirac-Fock orbitals is scaled from exact hydrogenic results from the following relation:

$$(\Delta E_{\text{se}})^{\text{Welton}} = \frac{\langle s|V_{\text{magn}}(r)|s\rangle_{\text{DF}}}{\langle s|V_{\text{magn}}(r)|s\rangle_{\text{hyd}}}(\Delta E_{\text{se}})^{\text{hyd}}$$

where $V_{\text{magn}}(r)$ is a nuclear potential. This approach is implemented in Mcd$\Phi$Me code. Low et al. [37] created extension of Grasp2k package, that implements Welton picture approach to estimate SE screening into Grasp2k suite. The Grasp2k code natively approximates the screening coefficient by taking the ratio of the Dirac-Fock wavefunction density in a small region around the nucleus ($r < r', r' = 0.0219\alpha_0, \alpha_0$ – Bohr’s radius) to the equivalent density for a hydrogenic orbital, i.e. [37]

$$(\Delta E_{\text{se}})^{\text{Welton}} = \frac{\langle s|V_{\text{magn}}(r)|s\rangle_{\text{DF}}}{\langle s|V_{\text{magn}}(r)|s\rangle_{\text{hyd}}} (\Delta E_{\text{se}})^{\text{hyd}}$$

This approach is called ‘density approach’ further in the manuscript. Last years some modern approaches for the estimation of hydrogenic SE data to many-electron atoms have been presented, such as the model Lamb-shift operator [38–40] and the spectral representation (projection operator) of the Lamb shift [41]. Recently Shabaev et al. [40, 42] published Qedmo, a program for calculating the model Lamb-shift operator basing on numerical radial wavefunctions. In this paper the Grasp2k wavefunctions are used as a QEDmod input.

3. Results and discussion

3.1. Breit and QED contributions

In present work the Fac, Grasp2k, and Mcd$\Phi$Me codes are compared in three case studies of radiative transitions occurring in tungsten ions. The first case study is focused on radiative transitions among outer orbitals in highly ionised tungsten. The study of characteristic x-ray radiation emitted by highly ionized W atoms is of great importance for both theoretical and applied atomic physics, including fusion applications [1, 4, 43]. In the recent works of Rzadkiewicz et al. [44] and Kozioł and Rzadkiewicz [45], the energy levels of the ground and excited states of W$^{45+}$ and W$^{46+}$ ions and the wavelengths and transition probabilities of the $4d \rightarrow 3p$ transitions were calculated using the MCDHF Configuration Interaction (CI) method, but no deeper analysis of the Breit and QED contributions to the energy levels was performed. Hence, the N11 and N22 transitions in Ni-like (W$^{46+}$) tungsten were selected as the first case study. The initial levels of these transitions are $\left[\text{Mg}3p^2 3p^3 3d^{10} 4d^1_{3/2} j=1 \right] (1P_1)$ and $\left[\text{Mg}3p^2 3p^3 3d^{10} 4d^1_{5/2} j=1 \right] (1P_1)$ and the final level is $\left[\text{Mg}3p^2 3d^{10} \right] (1S_0)$. The N11 and N22 transitions are $1P_1 \rightarrow 1S_0$ and $1P_1 \rightarrow 1S_0$, respectively.

The second case study concerns the $3p_{1/2} \rightarrow 3p_{1/2}$ fine splitting in Cl-like (W$^{57+}$) tungsten. Recently, a Cl-like isoelectronic sequence was proposed as an electronic configuration...
Table 3: Various theoretical contributions to the energy of $1s^{-1}$, $2p_{1/2}^{-1}$, and $2p_{3/2}^{-1}$ hole states of W$^{7+}$ (eV) and energy of $K\alpha_{1,2}$ transitions.

| Contribution | $1s^{-1}$ | $2p_{1/2}^{-1}$ | $2p_{3/2}^{-1}$ |
|--------------|-----------|----------------|----------------|
|              | GRASP2k   | GRASP2k + QEDmod | MCDGME | FAC | GRASP2k | GRASP2k + QEDmod | MCDGME | FAC | GRASP2k | GRASP2k + QEDmod | MCDGME | FAC |
| Dirac-Fock   | -369478.91 | -369476.90 | -369453.39 | -427763.39 | -427760.56 | -427729.68 | -429115.93 | -429112.94 | -429082.02 |
| Breit($\omega = 0$) + Rec. | 234.57 | 234.29 | 234.08 | 425.12 | 424.64 | 425.46 | 440.54 | 439.40 | 441.22 |
| Mag.         | 270.66 | -36.43 | 0.06 | -9.05 | -9.08 | -7.24 | -7.26 |
| Ret.($\omega = 0$) | 0.06 | 0.10 | 0.10 | 0.10 | 0.10 | 0.10 | 0.10 | 0.10 | 0.10 |
| Recoil       | -4.95 | -5.00 | -9.05 | 0.10 | 0.10 | 0.10 | 0.10 | 0.10 | 0.10 |
| Breit($\omega > 0$) | 0.06 | 0.10 | 0.10 | 0.10 | 0.10 | 0.10 | 0.10 | 0.10 | 0.10 |
| VP           | -4.95 | -5.00 | -9.05 | 0.10 | 0.10 | 0.10 | 0.10 | 0.10 | 0.10 |
| VP11         | 232.51 | 231.23 | 228.50 | 379.95 | 377.50 | 375.58 | 378.85 | 376.07 | 374.49 |
| VP11+21     | 232.51 | 231.23 | 228.50 | 379.95 | 377.50 | 375.58 | 378.85 | 376.07 | 374.49 |
| VP11+21+13  | 232.51 | 231.23 | 228.50 | 379.95 | 377.50 | 375.58 | 378.85 | 376.07 | 374.49 |
| SE           | 232.51 | 231.23 | 228.50 | 379.95 | 377.50 | 375.58 | 378.85 | 376.07 | 374.49 |
| Welt. dens.  | 232.51 | 231.23 | 228.50 | 379.95 | 377.50 | 375.58 | 378.85 | 376.07 | 374.49 |
| mod.         | 230.35 | 377.68 | 376.39 | 376.39 | 376.39 | 376.39 | 376.39 | 376.39 | 376.39 |
| QED h.o.     | -369059.38 | -369058.44 | -369033.40 | -427039.28 | -427037.80 | -427000.63 | -428376.04 | -428375.32 | -428338.66 |
| Total(Welt.) | -369059.38 | -369058.44 | -369033.40 | -427039.28 | -427037.80 | -427000.63 | -428376.04 | -428375.32 | -428338.66 |
| Total(dens.) | -369059.38 | -369058.44 | -369033.40 | -427039.28 | -427037.80 | -427000.63 | -428376.04 | -428375.32 | -428338.66 |
| Total(mod.)  | -369059.84 | -427038.69 | -428375.63 | -428375.63 | -428375.63 | -428375.63 | -428375.63 | -428375.63 | -428375.63 |

| Contribution | $K\alpha_1$ | $K\alpha_2$ |
|--------------|------------|------------|
|              | GRASP2k | GRASP2k + QEDmod | MCDGME | FAC | GRASP2k | GRASP2k + QEDmod | MCDGME | FAC |
| Dirac-Fock   | 59637.02 | 59636.04 | 59628.63 | 58284.48 | 58283.65 | 58276.29 |
| Breit($\omega = 0$) + Rec. | -205.97 | -205.11 | -207.14 | -190.54 | -190.35 | -191.38 |
| Mag.         | -218.84 | -218.84 | -218.84 | -218.84 | -218.84 | -218.84 |
| Ret.($\omega = 0$) | 22.92 | 22.92 | 22.92 | 22.92 | 22.92 | 22.92 |
| Recoil       | -0.04 | -0.04 | -0.04 | -0.04 | -0.04 | -0.04 |
| Breit($\omega > 0$) | 4.08 | 4.08 | 4.08 | 4.08 | 4.08 | 4.08 |
| VP           | 29.42 | 29.42 | 29.42 | 29.42 | 29.42 | 29.42 |
| VP11         | 29.42 | 29.42 | 29.42 | 29.42 | 29.42 | 29.42 |
| VP11+21     | 29.42 | 29.42 | 29.42 | 29.42 | 29.42 | 29.42 |
| VP11+21+13  | 29.42 | 29.42 | 29.42 | 29.42 | 29.42 | 29.42 |
| SE           | -146.34 | -144.85 | -145.99 | -147.44 | -146.27 | -147.08 |
| Welt. dens.  | -148.96 | -150.06 | -150.06 | -150.06 | -150.06 | -150.06 |
| mod.         | -146.04 | -146.04 | -146.04 | -146.04 | -146.04 | -146.04 |
| QED h.o.     | 0.20 | 0.20 | 0.20 | 0.20 | 0.20 | 0.20 |
| Total(Welt.) | 59316.66 | 59316.88 | 59305.26 | 57979.90 | 57979.36 | 57967.23 |
| Total(dens.) | 59314.04 | 59314.04 | 59314.04 | 59314.04 | 59314.04 | 59314.04 |
| Total(mod.)  | 59315.79 | 59315.79 | 59315.79 | 59315.79 | 59315.79 | 59315.79 |
that could be used to accurately test current methods of computing the Breit and QED effects [46]. The $3p_{3/2} - 3p_{1/2}$ fine splitting in Cl-like tungsten has recently been investigated both experimentally [47] and theoretically [48–50].

The third case study is focused on core radiative transitions in stripped tungsten. The energy shifts of the $K\alpha_1$, $K\beta_1$, and $K\beta_2$ lines of stripped high-Z atoms have been suggested as being potentially relevant to diagnostics of high-energy-density laser-produced plasmas [51]. Hence, the $K\alpha_1 (1s^{-1} \rightarrow 2p_{3/2}^{-1})$ and $K\alpha_2 (1s^{-1} \rightarrow 2p_{1/2}^{-1})$ transitions in W$^{7+}$ were selected as the third case study. The W$^{7+}$ ion was selected because it has simple closed-shell valence electronic configurations and, as a result, there are only two transitions between initial and final states to be studied. The electronic configurations for the $1s^{-1}$, $2p_{1/2}^{-1}$, and $2p_{3/2}^{-1}$ hole states are then $1s_{1/2} 2s^2 2p^6 M^{18} N^{32} S^2 5p^6$, $1s^2 2s^2 2p_{1/2} 2p_{3/2}^2 M^{18} N^{32} S^2 5p^6$, and $1s^2 2s^2 2p_{1/2}^2 2p_{3/2}^2 M^{18} N^{32} S^2 5p^6$, respectively. Table 1 presents various theoretical contributions to the energies of the $[Mg]3p^3 3d^{10} 4d^1 (J = 1)$ and $[Mg]3p^3 3d^{10} (J = 0)$ states of the Ni-like W ion and the energies of the Ni1 and Ni2 transitions. Table 2 presents various theoretical contributions to the energy of the $3p_{3/2} - 3p_{1/2}$ fine splitting in a Cl-like tungsten ion. It has various theoretical contributions to the energies of $1s^{-1}$, $2p_{1/2}^{-1}$, and $2p_{3/2}^{-1}$ hole states of W$^{7+}$ and the $K\alpha_1$ and $K\alpha_2$ transitions. Relativistic and radiative effects are treated slightly differently in the different codes. The term 'Dirac-Fock' in the tables indicates that the energy shifts of the hole states of W$^{7+}$ and the $K\alpha_1$ and $K\alpha_2$ transitions to be studied. The electronic configurations for the $1s^{-1}$, $2p_{1/2}^{-1}$, and $2p_{3/2}^{-1}$ hole states are then $1s_{1/2} 2s^2 2p^6 M^{18} N^{32} S^2 5p^6$, $1s^2 2s^2 2p_{1/2} 2p_{3/2}^2 M^{18} N^{32} S^2 5p^6$, and $1s^2 2s^2 2p_{1/2}^2 2p_{3/2}^2 M^{18} N^{32} S^2 5p^6$, respectively.

As seen from Tables 1, 2, and 3, the absolute level energies calculated by the Fac code differ significantly from the energies calculated by the Grass2k and Mcdfome codes, by about 20–30 eV. However, the energies of the radiative transitions differ much less, about 1 eV in the case of the Ni1 and Ni2 lines and below 1 eV for the $3p_{3/2} - 3p_{1/2}$ fine splitting in W$^{57+}$. For the $K\alpha_1$ and $K\alpha_2$ transitions in W$^{7+}$, the Fac calculated numbers are smaller by about 10 eV than those obtained by the MCDHF codes. This difference is too large to estimate properly the outer-shell ionization level from K-shell x-ray lines shift [51]. It can be concluded that the Fac code is sufficiently accurate in cases where radiative transitions are linked to an electron jump within the valence shells (if high accuracy is not required), but is less accurate for transitions that are linked to inner-shell hole states.

Comparing the Breit contributions obtained from the Grass2k code (where the Breit term is treated perturbatively) and from the Mcdfome code (where Breit term is included in a variational SCF process) allows the so-called ‘variational effect’ to be estimated. The magnitude of this effect is about 1 eV (0.1–0.3%) in the cases studied here. However, it has been found that the variational effect is significantly reduced when active space is expanding [53, 54]. The frequency-dependent Breit term is about 2% of the frequency-independent one (having the opposite sign).

As mentioned above, three different approximations to estimate the SE corrections have been used: the Welton picture, the density approach, and the model Lamb-shift operator. For Grass2k calculations, it is possible to compare these models by using these same wavelfunctions. In the case of W$^{46+}$, the 'density' approach gives SE contributions to the energy levels that are significantly larger, by about 5 eV, than those of the other two approaches. However, this difference vanishes for the Ni1 and Ni2 transition energies. The case of the W$^{57+}$ ion is similar. For the $1s^{-1}$, $2p_{1/2}^{-1}$, and $2p_{3/2}^{-1}$ hole states of W$^{7+}$ the 'model operator' method gives SE contributions to the energy levels that are significantly smaller than those of the 'Welton picture', which, in turn are smaller than those of the 'density' approach.

3.2. Relative role of correlation contribution and Breit and QED contributions

It is interesting to compare the electron correlation contributions to the Breit and QED contributions in selected cases. For the Ni1 and Ni2 lines, the correlation contribution was studied extensively by Rzadkiewicz et al. [44] and Kozioł and Rzadkiewicz [45] using a MCDHF Configuration Interaction (CI) calculation. They pointed out that electron correlation effect ranges from -1.87 eV to -2.87 eV for the Ni1 line energy and from -1.05 eV to -2.45 eV for the Ni2 line energy, depending on the CI model used. The correlation effect is then larger by an order of magnitude than the frequency-dependent Breit term (omitted in the calculations in [44, 45] due to the inclusion of virtual orbitals within the CI procedure) and larger by more than an order of magnitude than the differences arising from the use of different QED models.

In the case of the $3p_{3/2} - 3p_{1/2}$ fine splitting in W$^{57+}$ the MCDHF-CI calculations were performed with the Grass2k code (see e.g. [44, 45] for details). The $1s, 2s$, and $2p$ subshells are inactive orbitals. All single (S) and double (D) substitutions from the $3s$ and $3p$ orbitals to the active spaces (AS) of virtual orbitals are allowed. The virtual orbital sets used were: AS1 = {3d,4s,4p,4d,4f}, AS2 = AS1 + {5s,5p,5d,5f,5g}, AS3
Table 4: The $3p_{1/2} - 3p_{3/2}$ fine splitting calculated for various CI active spaces.

| Active space | Energy (eV) | Wavelength (Å) |
|--------------|-------------|----------------|
| AS0          | 349.11      | 35.515         |
| AS1          | 347.26      | 35.703         |
| AS2          | 347.84      | 35.644         |
| AS3          | 347.62      | 35.666         |
| AS4          | 347.50      | 35.678         |
| AS5          | 347.49(1)   | 35.680(2)      |

Experiment:
Lennartsson et al. [47] 35.668(4)
Other theory:
Quinet [48] 35.633
Singh and Puri [50] 35.632
Aggarwal and Keenan [49] 35.686
Bilal et al. [46] 35.765

$\approx$ AS2 $\{6s,6p,6d,6f,6g\}$, AS4 $\{7s,7p,7d,7f,7g\}$, and AS5 $\approx$ AS4 $\{8s,8p,8d,8f,8g\}$. Table 4 collects the results of the $3p_{3/2} - 3p_{1/2}$ fine splitting calculated for various CI active spaces. The AS0 value is a number related to Gras2k calculations with the ‘Welton picture’ approach for estimating the SE contribution. For the final active space, AS5, the theoretical uncertainties are presented. They are related to convergence with the size of a basis set and estimated as an absolute value of difference between energy(wavelengths) calculated for AS4 and AS5 stages. The wavelengths for the AS3-AS5 approaches agree well with the experimental values from the work of Lennartsson et al. [47]. The correlation effect is about 1.62 eV, which is about three times larger than the frequency-dependent Breit term and the total QED effect.

Table 5: The $K_{α1}$ and $K_{α2}$ transition energy in W$^{7+}$ calculated for various CI active spaces. Theoretical uncertainties for ‘AS3 + Auger shift’ are related to convergence with the size of a basis set and to error of interpolation Auger shift corrections.

| Active space | $K_{α1}$ | $K_{α2}$ |
|--------------|----------|----------|
| AS0          | 59316.66 | 57979.90 |
| AS1          | 59315.82 | 57979.06 |
| AS2          | 59316.43 | 57979.60 |
| AS3 + Auger shift | 59318.77(30) | 57983.13(30) |

Experiment (neutral W):
Bearden [55] 59318.24 57981.7
Deslattes et al. [56] 59318.847(50) 57981.77(14)

Other theory (neutral W):
Deslattes et al. [56] 59318.8(17) 57981.9(19)

For the $K_{α1}$ and $K_{α2}$ transition energies in W$^{7+}$, MCDHF-CI calculations were performed to check correlation effects. The active space of occupied orbitals contains orbitals involved in radiative transitions (1s and 2p) and two the most outer subshells: 4f and 5p. All other occupied subshells are inactive core. All SD substitutions from the active space of occupied orbitals to the active spaces of virtual orbitals are allowed. The virtual orbital active spaces used were: AS1 $\approx$ $\{5d,5f,5g\}$, AS2 $\approx$ AS1 $+\{6s,6p,6d,6f,6g\}$, and AS3 $\approx$ AS2 $+\{7s,7p,7d,7f,7g\}$. The results of the $K_{α1}$ and $K_{α2}$ transition energies in W$^{7+}$, calculated with various CI active spaces, are shown in Table 5. It is evident that the correlation effects are small in this case. Similar order of magnitude for correlation effects were found for the $K_{α1,2}$ lines of Al and Si [57] and of Kr, Pb, U, Pu, Fm [58, 59]. Because inner-hole states are autoionising, the level energy shift due to the coupling between the two hole states and one excited electron, called Auger shift, must be included [56]. The Auger shift contribution to the $K_{α1}$ and $K_{α2}$ transition energies can be approximated through interpolation from the numbers given by Indelicato, Lindroth et al. [58–60]. The interpolated values for the Auger shift contribution are 2.14 eV and 3.33 eV for the $K_{α1}$ and $K_{α2}$ lines, respectively. Adding the Auger shift contributions to the MCDHF-CI values reduces the substantially discrepancy between theory and experiment for $K_{α1}$ line, however overestimate value for $K_{α2}$ line.

4. Conclusions

The interpretation of atomic observations by theory and the testing of computational predictions by experiment are interactive processes. In this paper the Fac, Gras2k, and MCDHF codes have been compared in selected case studies involving radiative transitions occurring in the tungsten ions W$^{7+}$, W$^{57+}$, and W$^{46+}$. Transitions involving electron jumps between outer or inner orbitals are both considered. Various approaches to including the Breit interaction term and QED corrections in atomic calculations have been examined and their contributions compared to those of electron correlations. In the case when transitions involve electron jumps between outer shells (the first and second cases in the present work) the frequency-dependent Breit contribution to transition energy is smaller few times than the electron correlation contribution. Then, ommiting the frequency-dependent Breit term is not a big mistake. In the case when transitions involve electron jumps between inner and outer shells (the third case in the present work) the frequency-dependent Breit contribution dominates over the electron correlation contribution. In this case also the differences between QED models may be bigger than correlation contribution. The presented data may be used to estimate theoretical uncertainties relevant to interpretation of high-resolution spectroscopic data.

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