

Article

Cowan Code: 50 Years of Growing Impact on Atomic Physics

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Abstract: The famous Cowan’s book, “The Theory of Atomic Structure and Spectra”, published in 1981, and his suite of computer codes based on it, continue to be highly influential in atomic physics and many other research areas. As of September 2018, there have been more than 5000 citations to Cowan’s book and codes, and each year adds about 150 citations to this list. The present work briefly describes what these codes do and why they are responsible for most of the current progress in the analyses of atomic spectra. Various modifications of these codes, including my own, will also be described.

Keywords: Cowan code; atomic structure; energy levels; transition probabilities; semiempirical parametric calculations

1. Introduction

Although Cowan’s classic book [1] was published in 1981, the early versions of his computer codes that are generally referred to this book were fully developed as early as in 1968 [2], which accounts for the 50-year period mentioned in the title of the present paper. The program package usually called “the Cowan code” consists of four separate codes. Some parts of this package were developed even earlier [3,4].

When I received an invitation to make a talk at the 11th International Conference on Atomic and Molecular Data and their Applications (ICAMDATA-2018), Robert Duane Cowan was still alive (see Figure 1). He died on 26 July 2018 in a hospice in Albuquerque at an age of 98. The main facts of his biography can be found in an obituary available online [5]. The present article is a transcript of my talk given on 13 November 2018 at Cambridge, Massachusetts.



Figure 1. Robert Duane Cowan (24 November 1919–26 July 2018).

2. Impact of Cowan’s Book and Computer Codes

According to the citation index of the Institute for Scientific Information (ISI) Web of Science database [6], there have been more than 5000 citations of Cowan’s book [1] and the codes based on it. The citing articles cover a wide range of 58 research categories, ranging from optics, atomic physics, solid state physics, astronomy, and chemistry to nuclear physics (see Figure 2). Figure 3 shows the dynamics of these citations from 1981 to 2017. Since 1990, there have been about 150 new citations to Cowan’s work every year. This shows that Cowan’s legacy continues to have a great influence on science.

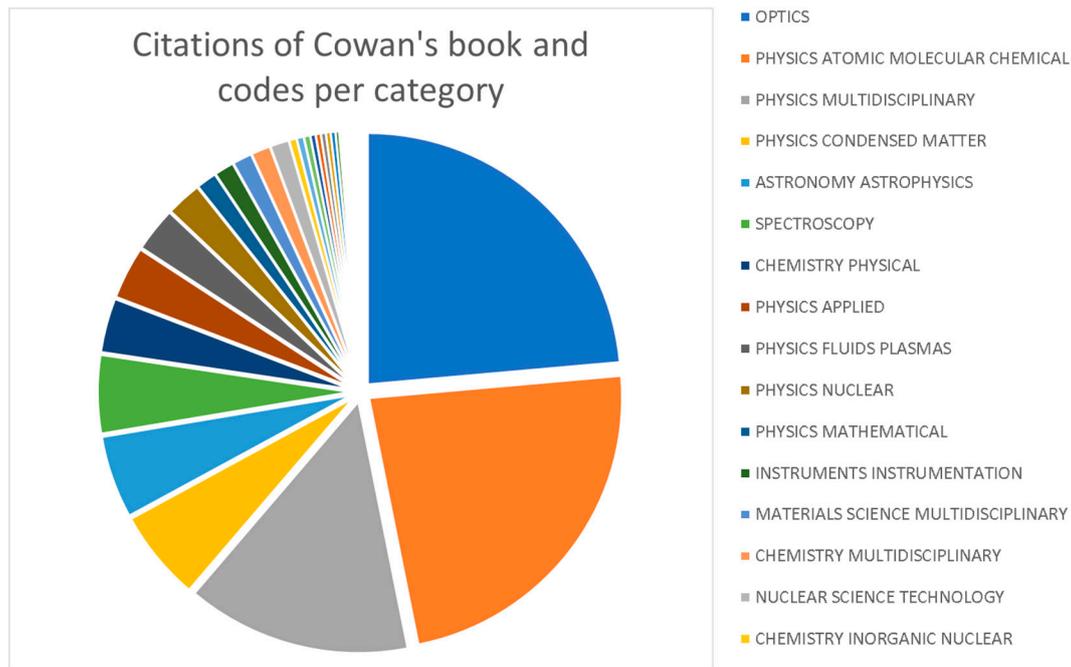


Figure 2. Distribution of 5026 citations to Cowan’s book [1] and the computer codes based on it, per research category (per Cited Reference Search of Web of Science [6]).

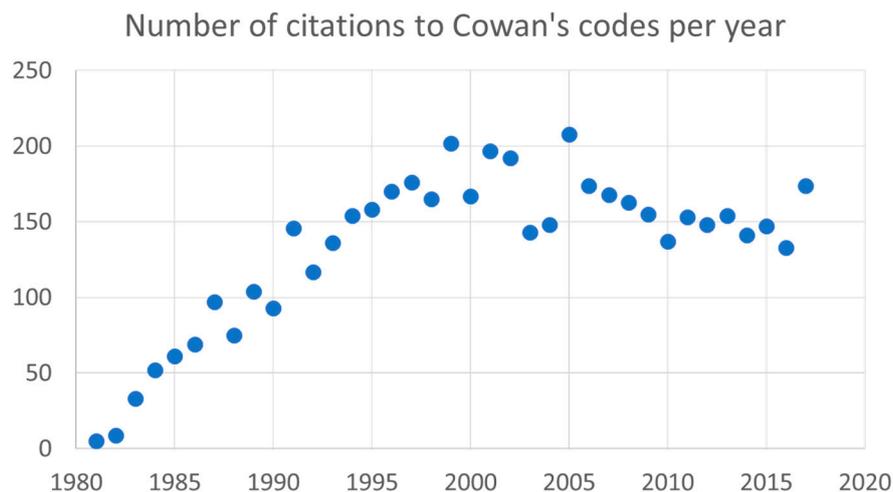


Figure 3. Number of citations to Cowan’s book [1] and computer codes based on it per year (per the same source as Figure 2).

In the following sections, I will try to explain why Cowan’s book and codes are so important to modern atomic physics. I will briefly describe the predecessors of Cowan’s codes, explain what those

codes do, enumerate other existing atomic physics codes, including various versions of Cowan's codes, point out some known problems in these codes, and outline the needs for future development.

3. What Cowan's Codes Do

The package of Cowan's codes consists of four Fortran programs. The names of these programs are made of Cowan's initials, 'RC', followed by a code letter. Some code names are followed by a part or version number. The codes are intended to be run in sequence, and each program produces output files that are simultaneously input files for the next code in the chain.

The calculations start with the code RCN, which calculates single-configuration radial wavefunctions for a spherically symmetrized atom via the Hartree–Fock method. Next, RCN2 calculates the radial integrals (Slater parameters), including the configuration interactions (all terminology is described in [1]). Then, RCG, which is the main code of the package, computes the angular matrix elements of the Hamiltonian, and by diagonalizing it, computes the energy levels, transition wavelengths, and radiative rates for the electric-dipole (E1), magnetic-dipole (M1), and electric-quadrupole (E2) transitions. RCG can also compute autoionization rates and plane-wave Born excitation cross-sections for electronic collisions. Finally, RCE does a least-squares fitting of atomic energy levels (i.e., adjusts the Slater parameters to fit experimental levels). The adjusted Slater parameters can be transferred to the input file of RCG. Then, re-running RCG produces much more accurate transition rates. The extent of improvement depends on the quality of the least squares fit and can be as large as orders of magnitude for some transitions. However, one can rarely expect the accuracy of the calculated transition rates to be better than 20% for the strongest transitions, due to the limitations of the method. No general estimate of uncertainties can be made. These uncertainties must be analyzed by comparisons with other data and evaluated for each calculation.

4. Cowan's Predecessors

Before Cowan's codes were developed, the basic theory was already known, and there were other computer codes developed in early 1960s. The most well-known of them was the suite of the so-called French codes (AGENAC, ASSAC, DIAGAC, and GRAMAC). They were created in Laboratoire Aimé Cotton in Orsay near Paris. In these acronyms, the last two letters "AC" stand for "Aimé Cotton." The French codes did most of the same things as Cowan's in similar steps:

- Compute the wavefunctions.
- Compute the Slater parameters. It was possible to also compute parameters of additional interactions, such as hyperfine. The user had to construct the input files from the output of the previous code in a laborious semi-manual procedure.
- Assemble the Hamiltonian matrix (extremely tenuous semi-manual task). It was flexible, allowing for introduction of additional interactions.
- Diagonalize the Hamiltonian.
- Use the output of the diagonalization to compute the atomic structure. Calculation of transition rates was not included in the codes. The users had to build their own code extensions to do that.
- Use a least-squares fitting code to adjust the Slater parameters.

All steps involved the difficult manual work of constructing the input files and parsing the output files, which made computations very inefficient. However, the ability of calculating hyperfine structure, isotope shifts, and effects of other interactions (such as external electric and magnetic fields or weak interactions neglected in Cowan's codes) made the French suite of codes indispensable. It is quite unfortunate that these codes no longer exist. The source codes have never been published. The same is true for Cowan's suite of codes. However, Cowan's codes have been preserved in the Los Alamos National Laboratory, where he worked, and are available online (see Section 7).

A copy of the manual for the French suite of code still exists in the archives of the Atomic Spectroscopy Group of the National Institute of Standards and Technology (NIST). The first page of this manual is shown in Figure 4.

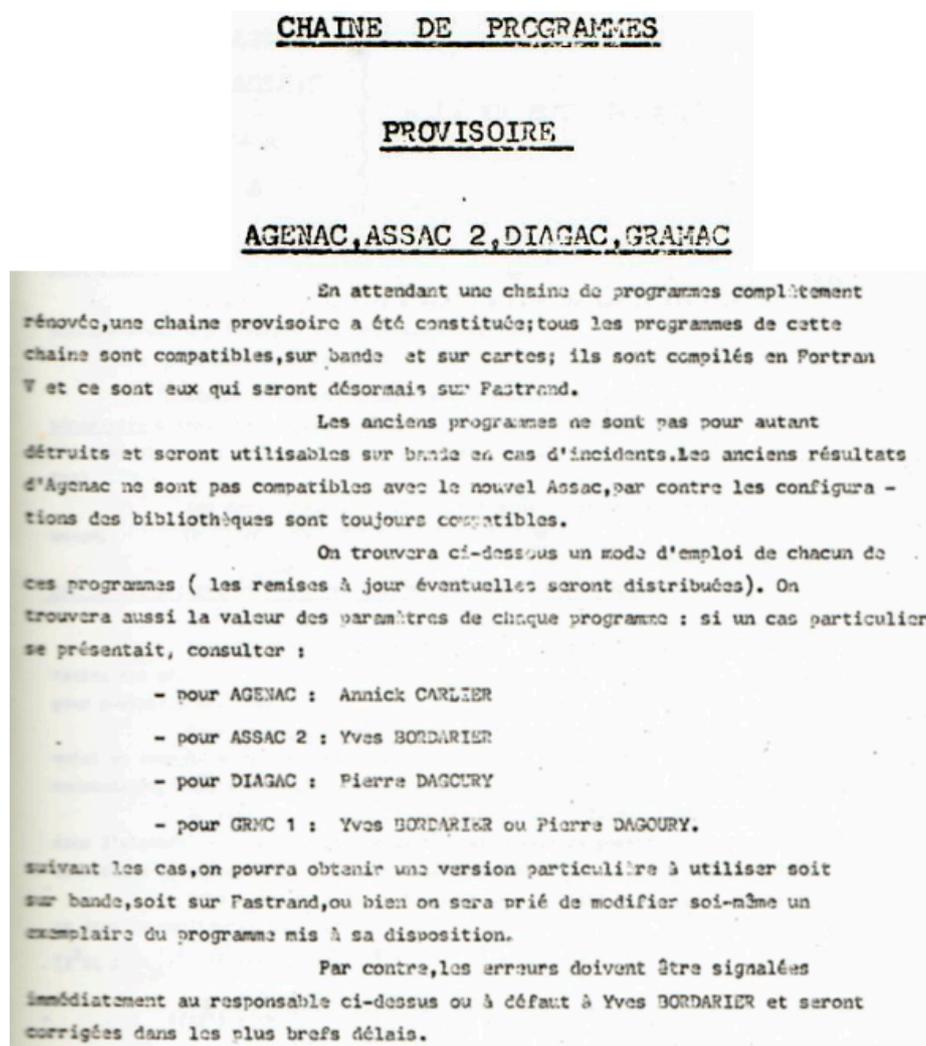


Figure 4. The first page of the manual for the French suite of atomic codes.

Very little is known about the authors of these codes. Yves Bordarier (1930–2014) was a brilliant theoretician. His Ph.D. thesis was devoted to the procedures of summation for Wigner's $6j$ -symbols. His solutions found applications not only in atomic physics, but also in crystallography. In collaboration with other well-known atomic physicists, such as J. Blaise, B. R. Judd, M. Klapisch, and G. G. Gluck, he published three papers on the hyperfine structure of Tm [7] and Eu [8], and on isotope shifts and the electronic structure of Os atoms [9]. Annick Carlier also worked on the interpretation of electronic structure and isotope shifts in lanthanide atoms, such as Sm [10]. Little is known about Pierre Dagoury. He was a computer engineer and worked in the Aimé Cotton Lab for only a short time. These people were brilliant scientists. The codes they created in this early time of computer technology allowed successful analyses of such complex lanthanide spectra that even today are extremely difficult to analyze.

5. The Workflow of Cowan's Suite of Codes

Most of the calculational procedures of Cowan's codes look similar to those of the French suite:

- Specify the atomic configurations and code options in two input files.
- Run RCN (produces input for RCN2).
- Run RCN2 (produces input for RCG).
- Run RCG (cringe at the results, as they are rather inaccurate). This produces the input for RCE and outputs nicely formatted transition data.
- Run RCE. To fit experimental levels, edit an input file and rerun RCE.
- Use utility codes to transfer fitted parameters to the RCG input file.
- Re-run RCG and smile! The results are now very accurate.

One difference from the French suite is that all the tasks are automated (although manual intervention, such as changing the program options, is still allowed), except for the least-squares fitting (LSF) with RCE. Running the LSF still involves a lot of manual work and requires much expertise acquired by trial and error. There is no strict methodology for it; some even call it ‘black magic’ [11]. However, some general recipes do exist, and by knowing them, the analysis of an atomic spectrum with Cowan’s codes takes from a few hours to a few weeks, depending on the complexity of the problem. This is much more efficient than working with the French codes, which typically required years for an analysis of one spectrum. The downside of Cowan’s codes is their limited flexibility, where they do not allow for the analysis of hyperfine structure and isotope shifts.

Another important difference is the ability of Cowan’s codes to calculate transition probabilities. This enables comparisons between predicted and experimental intensities of spectral lines, which increases the reliability of line identifications and sometimes allows a unique choice between multiple possible level assignments. In the case of Tm II, investigated by Wyart [12], such comparisons led to the revision of previous wrongly assigned quantum numbers J of many energy levels.

In the calculational workflow shown above, the statement about the improvement of accuracy by the LSF is, of course, only qualitative. The quality of the fit depends crucially on the inclusion of important interacting configurations in the calculation, as well as the choice of free and constrained parameters. While the accuracy of the fitted and predicted energies can be assessed easily in a straightforward way (by comparison of calculated and experimental levels), uncertainties of the predicted transition rates are much more difficult to estimate. The methodology for such estimation has been developed at NIST and is described in my review [13].

6. Why are Cowan’s Codes So Important?

From the point of view of modern atomic physics, Cowan’s codes are rather primitive. They use the non-relativistic Hartree–Fock method, with only some of the relativistic effects accounted for as perturbations. Moreover, the radial wavefunctions are computed in a hydrogenic single-configuration approximation, and they are frozen in calculations of configuration interactions. That is why Cowan’s method is usually called a superposition of configurations, rather than a multiconfiguration calculation. The latter, unlike Cowan’s RCN, varies the radial wavefunctions of each basis configuration in the self-consistent field calculation. Nowadays, a number of much more sophisticated multiconfiguration codes exist:

- MCHF [14], CIV3 [15], ... (non-relativistic with relativistic corrections)
- MCDHF [16], MCDFGME [17], FAC [18], MR-MP [19], ... (relativistic)

A more extensive, although still incomplete, list of modern ab initio codes can be found in Section 9.2. These ab initio codes can provide better accuracy, but only for a limited number of spectra, such as those isoelectronic to H, He, Ne, Ar, Kr, K, Rb, Cs, F, Cl, Br, Be, Mg, and Ca (to some extent), those isoelectronic to B, Al, Ga, C, Si, Ge, N, P, As, O, S, Se, Ni, Pd, Pt, Cu, Ag, and Au (to a much lesser extent), and only for a limited number of low-excitation levels. However, for nd - and nf -transition elements, these codes are equally or even less accurate than Cowan’s code. For heavy elements such as lanthanides and actinides, they even fail to reproduce the experimentally known

ground states (meaning that they predict incorrect levels or configurations to be the lowest ones in energy). This reflects the fact that ab initio multiconfiguration methods cannot handle atomic systems where electron-correlation effects (i.e., configuration interactions, CIs) are large and numerous. This problem is illustrated in Figure 5, depicting a Grotrian diagram of the Fe II spectrum [20]. Strong CIs occur between closely-lying levels of the same parity and the same J values. One can see that as the energies approach the ionization limit, the density of levels belonging to various Rydberg series crossing each other increases, leading to an increasing number of strong configuration interactions.

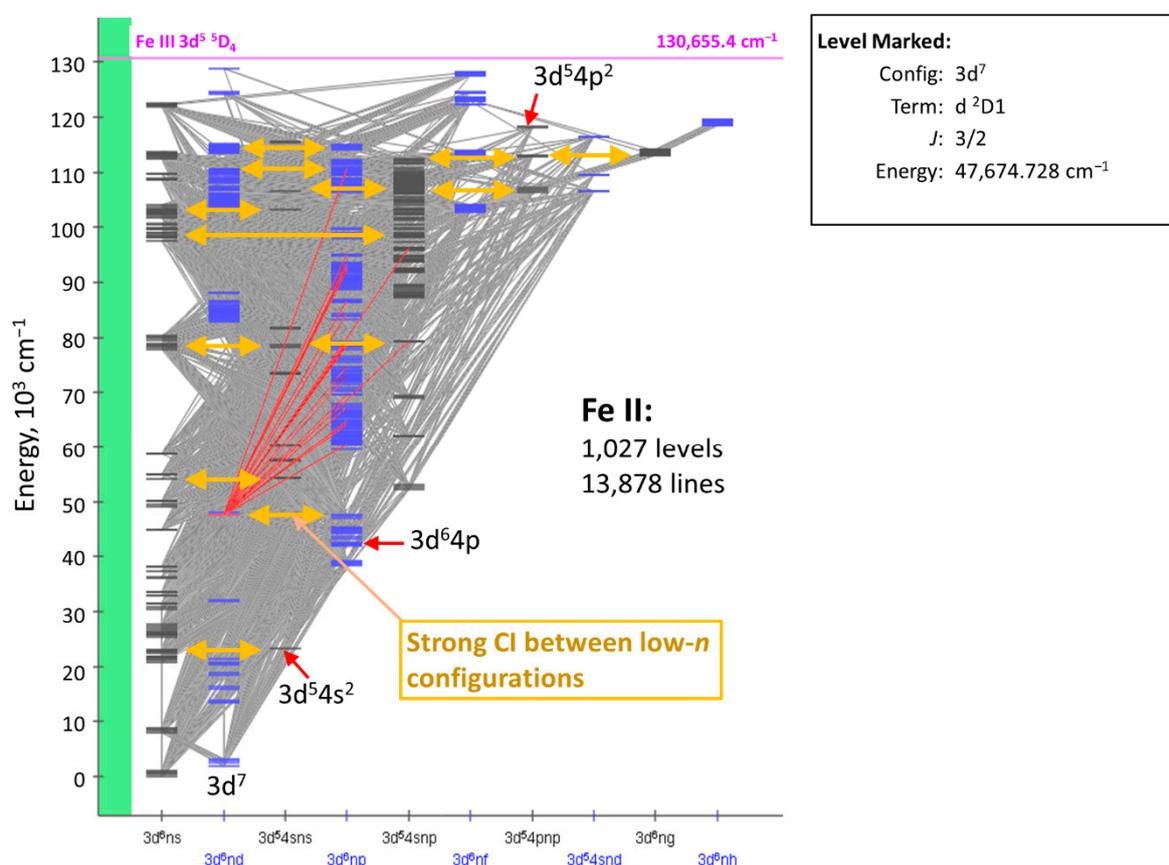


Figure 5. Grotrian diagram of the Fe II spectrum [20]. The yellow horizontal double-arrows indicate strong configuration interactions.

An exact account of the CI effects requires a precise determination of level energies. One should recall that the multiconfiguration methods try to achieve it via the addition of a large number of virtual excitations to high-lying configurations. Thus, the precise determination of positions of highly-excited Rydberg levels requires a huge number of configurations, growing exponentially with increasing excitation energy. Even for such a moderately heavy atom as Fe, the dimension of the required matrices becomes unmanageably large (even for supercomputers) for levels that are higher than about half of the ionization energy, i.e., for most of experimentally known levels. For heavier atoms, such as lanthanides and actinides, the number of interacting Rydberg series is much greater, and the energy region riddled by strong CI effects descends to the vicinity of the ground level, making the entire energy structure unmanageable for computation with multiconfiguration methods.

On the other hand, with Cowan's codes, the LSF of all levels, with a standard deviation $<100 \text{ cm}^{-1}$, can be accomplished in one week, reproducing all strong line intensities and predicting unknown levels with a similar accuracy. Thus, for the spectra of transition elements, including lanthanides and actinides, analysis using LSF with Cowan's codes remains the only working tool for the past few decades and is expected to remain such for a few more decades.

7. Versions of Cowan's Codes

The latest mainstream version of Cowan's code package is presently distributed by Cormac McGuinness at the University of Dublin, Ireland [21]. This package contains Cowan's original source codes and documentation in addition to installation routines written for Linux operating systems.

My version, originally developed for Windows-based personal computers, had branched from the mainstream version circa 1989 and has mutated quite substantially since then. It is now distributed from a NIST website [22]. This package also includes the source codes and documentation, as well as several utility codes. It will be described in more detail in the next section.

There are also many other private or proprietary versions of Cowan's codes. The ones I am aware of are listed below:

- P. Quinet's version with core polarization (private) [23].

The only codes modified in this version are RCN and RCN2.

- R. L. Kurucz's version (private).

Branched from mainstream circa 1970. Designed for very large configuration sets and uses large workstations. The famous Kurucz's Atoms collection of computed atomic line lists [24] was produced with these codes.

- J. Ruczkowski, M. Elantkowska, and J. Dembczyński's version (private) [25].

Incorporates LSF of transition matrix elements in addition to Slater integrals.

- Los Alamos CATS (Cowan ATomic Structure) code (proprietary) [26].

Parallelized, with dynamic memory allocation, for a large computer cluster. This version does not have an LSF code.

8. My Version of Cowan's Codes

I started using Cowan's codes in 1981, when I worked at the Institute of Spectroscopy in Troitsk, Russia. The only available computer that could run this code was a Russian adaptation of PDP-11. Cowan's original codes were adapted for it by Dr. Dmitri S. Viktorov. One peculiar feature of that computer was that its processor held upper-case Cyrillic character symbols in the memory region that was originally intended to contain lower-case Latin letters. Thus, no lower-case Latin letters were available in this system, and all source codes and input/output files had to be converted to upper case. This is the historical reason for upper-case characters appearing in the source codes and some of the input files of my version of Cowan's codes.

I started changing the code near 1989. My starting point was a version modified (after Viktorov) by Yu. Ralchenko to produce level designations using seniority quantum numbers instead of the Nielson and Koster indexes used in Cowan's original RCG code. Since then, I have ported these codes to several different compilers working under Microsoft Windows, VAX-VMS, and several versions of Unix, including Linux and MacOS. Versions prior to 1994 did not have any major differences from the mainstream. In 1994–1995, when I was a guest researcher at NIST, I tried to calculate the spectra of some lanthanide atoms and found that the space needed to store the temporary files required by RCG exceeds the capacity of hard drives typically available then in personal computers. To alleviate the problem, it was necessary to compress the sparse matrices stored in those temporary files. The implementation of this compression was the first major change I made to the codes. At about the same time, Craig Sansonetti and I independently discovered an overflow bug in the term-sorting routine of RCG, which led to the first major bug fix that I made. Since then, I have made a large number of calculations in all isoelectronic sequences from H I to Ds I (hydrogen to darmstadtium), which inevitably revealed numerous other bugs that were lying dormant in the codes.

Besides fixing the bugs, in 1999, I made a drastic modification to the LSF code RCE. In Cowan's original implementation, the input file for RCE is created by RCG and consists of several sections that have no information about eigenvector compositions of energy levels, which makes the association of theoretical and experimental levels a time-consuming and error-prone work. Furthermore, the association of theoretical and experimental levels between the LSF iterations could be made using only two options: Sorting of eigenvalues in increasing order of energies in each J -parity group or sorting by calculated Landé factors. Both options perform poorly, making the iterations unstable. In my version, a different algorithm, based on eigenvector recognition [13] was implemented. This implementation includes an alternative input file for RCE, which is created by RCE itself on its first run. This file has a much easier-to-use layout, where each eigenvalue is accompanied by its eigenvector, which can easily be identified with experimental level classifications, and each Slater parameter is immediately followed by its controlling options. Working with this file made the LSF process much more efficient and the convergence of the iterations more stable.

Additionally, my version of Cowan's code package contains a number of utility codes for various manipulations of the input/output files. The most widely used are the following:

- 'printout': Converts the RCE output to nicely formatted tables of energy levels (including the intermediate quantum numbers omitted in Cowan's original output) and LSF parameters.
- 'conv_out': Converts the RCG output to nicely formatted tables of levels and lines. This code can also create input files for the visual line-identification code IDEN2 [27].
- 'update11': Transfers fitted LSF parameters from the RCE output to the RCG input file, re-runs RCG, and runs 'printout'.
- 'reorder_ing11': Converts the RCG input file to change the order of shell summation.

Instructions for the usage of all these codes are given in the writeup provided with the package and are also available from the codes (they are printed if the codes are executed without parameters).

It should be noted that codes similar to IDEN2 [27], mentioned above, which allow handling and visualizing a great amount of calculated data from Cowan's code together with experimental data, mainly account for the progress in increasing the speed of spectral analyses of complex spectra in the last few decades.

9. Other Codes with Similar or Better Capabilities

9.1. Semiempirical Codes with Parametric Fitting

A powerful orthogonal operators code was developed by Raassen and Uylings [28] in the Zeeman Laboratory, Amsterdam, Netherlands. It implements the concept of orthogonal operators, described by Hansen et al. [11]. Although this code is similar to Cowan's, in that it uses a non-relativistic approximation with relativistic corrections accounted as perturbations, it additionally accounts for small second-order interactions, which are omitted in Cowan's codes. The methodology of orthogonal operators is qualitatively very different from Cowan's parametric calculations. Its capabilities are illustrated in Table 1, which is an abbreviated version of Table 1 by van het Hof et al. [29] (the original table contains also references to the analyses of each spectrum).

Table 1 shows in bold font the standard deviation σ obtained in the LSF for each investigated spectrum of $3d^n4s$ configurations. This parameter indicates the accuracy with which experimentally unknown levels can be predicted by LSF. It can be seen that in all cases, σ is of the order of 1 cm^{-1} , or even smaller. This is really a spectroscopic accuracy for these spectra, and it is two orders of magnitude smaller than the uncertainty achievable with Cowan-code LSF.

The power of the orthogonal operators method was recently demonstrated by the successful analyses of the Re III and Os III spectra by Azarov and Gayasov [30] and Azarov et al. [31]. The last previous attempt to analyze these spectra was made in 1993 by Wyart et al. [32], who deemed it hopeless, despite the large astronomical interest in these spectra.

Table 1. Survey of the $3d^n4s$ configurations investigated using orthogonal operators.

Conf.:	3d4s	3d ² 4s	3d ³ 4s	3d ⁴ 4s	3d ⁵ 4s	3d ⁶ 4s	3d ⁷ 4s	3d ⁸ 4s	3d ⁹ 4s
N_c :	4	16	38	63	74	63	38	16	4
N_0 :	5	17	30	42	42	42	30	17	5
Spectrum:	Ti III	V III	Cr III	Mn III	Fe III	Co III	Ni III	Cu III	Zn III
N_e :	4	16	37	54	65	58	38	16	4
σ [cm^{-1}]:	0	0.4	0.6	1.4	0.8	1.8	0.7	0.6	0
Spectrum:	V IV	Cr IV	Mn IV	Fe IV	Co IV	Ni IV	Cu IV	Zn IV	Ga IV
N_e :	4	16	17	62	59	51	37	16	4
σ [cm^{-1}]:	0	0.2	1.0	1.0	1.2	1.8	0.7	0.7	0
Spectrum:	Cr V	Mn V	Fe V	Co V	Ni V	Cu V	Zn V	Ga V	Ge V
N_e :	4	16	36	57	68	47	37	15	4
σ [cm^{-1}]:	0	0.4	0.4	1	0.7	1.4	0.9	0.5	0
Spectrum:	Mn VI	Fe VI	Co VI	Ni VI					As VI
N_e :	4	15	36	57					4
σ [cm^{-1}]:	0	0.3	0.6	1.2					0

N_c : Total number of levels in the configuration. N_0 : Total number of parameters used in the least-squares fitting (LSF). Some of these parameters were fixed at the calculated values. N_e : Number of established levels in the configuration.

The method of orthogonal operators was developed in the Zeeman Laboratory over the course of several decades. Dismantling of the atomic spectroscopy research group in 1999 had put an unfortunate stop to this development. Since then, Ton Raassen worked in the Institute for Space Research of the Space Research Organization of the Netherlands (SRON), while Peter Uylings was teaching physics courses at the University of Amsterdam. After their official retirement this year, Raassen and Uylings have announced that they are returning to atomic physics research and renewing the development of the orthogonal operators code [33].

Up until now, the orthogonal operators formalism has been implemented only for the d^n , $d^n l$, $d^n l_1 l_2$, and f^2 configurations. For other configurations with partially filled f shells, the theory is yet to be developed.

There exist other atomic codes capable of making the LSF with similar or better accuracy than Cowan's codes. One such code is that of Ruczkowski, Elantkowska, and Dembczyński [25], which is a modification of Cowan's codes, incorporating LSF of transition matrix elements in addition to Slater integrals.

Another important extension of Cowan's method was developed by J.-F. Wyart at the Aimé Cotton Laboratory in Orsay, France. It is called a generalized least-squares fit (GLS) and is based on the empirical fact that the Slater parameters behave smoothly along sequences of spectra that are similar in some sense. For example, Blaise et al. [34] employed the GLS method to analyze the $5f^n$ and $5f^n 7s$ configurations in a sequence of the first spectra of actinides having different occupation numbers n . In this sequence, the Slater parameters P_k were found to vary smoothly as a function of n :

$$P_k = A(P_k) + (n - 7)B(P_k) + (n - 7)^2 C(P_k), \quad (1)$$

where empirical constants A , B , and C can be found by adding a set of equations similar to Equation (1) to the equations expressing the deviations of calculated levels from experimental ones and solving this extended system of equations in a least-squares procedure.

Similarly, Wyart et al. [35] expressed the smooth variation of Slater parameters along the platinum isoelectronic sequence Au II–Bi VI as

$$P_k = A(P_k) + B(P_k)Z_c + C(P_k)/[Z_c + D(P_k)], \quad (2)$$

where Z_c is the core charge. They used Equation (2) in the GLS. Introducing equations similar to Equations (1) and (2) in the least-squares fit of several spectra makes the fitting more stable and

dependable, since it reduces the ratio of the number of free parameters to the number of experimentally known energy levels.

The GLS code was written by J.-F. Wyart as an extension to the French codes described earlier (it makes use of the output from DIAGAC and GRAMAC). This code has not been used since the mid-1990s and is effectively dead nowadays, as the French codes went out of use. However, its basic concepts are fairly simple, and it should not be very difficult to rewrite this code for modern computer platforms, to which Cowan's codes have already been ported.

9.2. Other Ab Initio Codes

As mentioned in Section 6, there exist a number of powerful ab initio codes that are similarly or more accurate than Cowan's code (in its ab initio or scaled Hartree–Fock modes). The list below enumerates the most widely known of these codes:

- Non-relativistic codes with relativistic corrections:
 - C. Froese Fischer et al.: ATSP2K (MCHF) [14]
 - A. Hibbert: CIV3 [15]
 - W. Eissner et al.: SUPERSTRUCTURE [36]
 - P. Bogdanovich et al.: Quasirelativistic Hartree–Fock (CI; unpublished; see, e.g., [37])
- Relativistic codes:
 - I. Grant, C. Froese Fischer, P. Jönsson et al.: GRASP2K (MCDHF) [16,38]
 - M. F. Gu: FAC (MCDF, MBPT) [18]
 - J.P. Desclaux, P. Indelicato: MCDFGME [17]
 - Y. Ishikawa: Møller–Plesset many-body perturbation theory (MR-MP; unpublished; see, e.g., [19])
 - W.R. Johnson, U. I. Safronova, M.S. Safronova: RMBPT (unpublished, see, e.g., [39])
 - M.S. Safronova et al.: RMBPT (all-order; unpublished); see, e.g., [40]
 - E. Eliav, U. Kaldor: Coupled-Cluster (unpublished, see, e.g., [41])
 - V.A. Dzuba, W.R. Johnson: SD Coupled-Cluster (unpublished, see, e.g., [42])
 - I.M. Savukov: parametric CI+MBPT (unpublished, see, e.g., [43])

Some of the codes listed above possess limited options for semiempirical parametric fitting, for example, the CIV3 code [15], which allows for a semiempirical adjustment of the diagonal elements of the Hamiltonian matrix, roughly equivalent to the adjustment of the configuration average energies in Cowan's LSF. The SUPERSTRUCTURE code [36] allows for the adjustment of the λ parameters of the radial wavefunctions. Savukov's CI+MBPT (configuration interaction plus many-body perturbation theory) method [43] also includes some free parameters that can be optimized by a least-squares fitting of experimental energy levels. However, I am not aware of any publicly available implementation of these semiempirical fitting procedures.

10. Known Problems in Cowan's Codes

One of the recently found problems in Cowan's codes is related to CIs between configurations forming a Rydberg series [44]. Brillouin's theorem [1] requires the direct CI integrals of rank zero of such configurations to be exactly zero. The problem arises because of the method used in Cowan's codes to identify a Rydberg series. In Cowan's implementation, it was thought that the Rydberg electron is always in the last occupied shell specified in the input file for RCN. However, it is not always possible to arrange the input file in this way. Moreover, most users do not even know about this rule and specify electronic shells using a standard ordering of the nl shells, with the principal (n) and orbital (l) quantum numbers increasing from left to right. The following example gives two

possible layouts of the RCN input file for calculating the odd-parity configuration complex ($1s^2 2p + 1s^2 3p + 1s^2 4p + 3p 5p^2 + 4p 5p^2$) in neutral lithium:

```
(a)
3      1Li I s22p      1s2 5p0 2p
3      1Li I s23p      1s2 5p0 3p
3      1Li I s24p      1s2 5p0 4p
3      1Li I 5p23p     1s0 5p2 3p
3      1Li I 5p24p     1s0 5p2 4p

(b)
3      1Li I s22p      1s2 2p
3      1Li I s23p      1s2 2p0 3p
3      1Li I s24p      1s2 2p0 3p0 4p
3      1Li I 5p23p     1s0 2p0 3p 4p0 5p2
3      1Li I 5p24p     1s0 2p0 3p0 4p 5p2
```

Both layouts are allowed by RCN and produce the same values for all single-configuration Slater parameters. However, the CI parameters are (incorrectly) calculated to be different for the last two configurations. Since these configurations differ by only the principal quantum number of one electron (3p or 4p), they are Rydberg configurations by definition. Layout (a) correctly produces the CI integral $R_d^0(5p3p,5p4p) = 0$. However, layout (b) results in the corresponding CI integral $R_d^0(3p5p,4p5p) \neq 0$, which is incorrect. The “bug fix” suggested in the erratum of reference [44] solves the problem only partially, where it provides the solution to the problem occurring in most commonly encountered cases, but not in such as given in the above example.

Other known problems are related to the transformation between different coupling schemes:

- No transformation to jj and jK coupling is available for shells with equivalent electrons. Such shells are always represented in LS coupling.
- Recoupling to a non-standard order of shell summation is not exact in the presence of CI.

A workaround exists for both these problems, where one may use the ‘Coupling’ code designed by G. Gaigalas as part of a future version of the GRASP2K package [45]. This code can recouple any set of eigenvectors, including those produced by Cowan’s code, to virtually any possible coupling scheme, including variations in the order of summation of shells.

11. Summary and Outlook

The failure of modern ab initio atomic theory methods to reproduce experimentally observed energy structures of complex heavy atoms and ions indicates that semiempirical analysis with parametric fitting (LSF) will remain the main tool for the theoretical interpretation of complex spectra, such as lanthanides and actinides. Cowan’s codes remain the most universal tool in such analyses. However, these codes have many limitations. To overcome them, new LSF codes are needed that can better account for the relativistic and second-order effects, such as spin-spin and spin-orbit interactions. In particular, the orthogonal operators method needs to be extended to spectra with open f shells. As of today, no fully relativistic atomic codes exist that are capable of comprehensive parametric fitting. The development of such codes would be most welcome. Finally, codes for the parametric fitting of hyperfine structures and isotope shifts, some of which exist for private use, should be published and made available. These developments are needed to address the long-standing deficiency in experimental analyses of atomic spectra illustrated in the triangular diagram in Figure 6.

As seen in Figure 6, no experimental data exist for most spectra of atoms heavier than molybdenum with core charges $Z_c > 5$. Many of these unknown spectra are becoming of urgent interest for new applications, such as for atomic clocks on heavy multicharged ions [46], extreme ultraviolet lithography for the production of next-generation semiconductor circuits [47], and inertial fusion [48]. The

development of accurate semiempirical atomic codes is of vital importance for the analysis of such spectra.

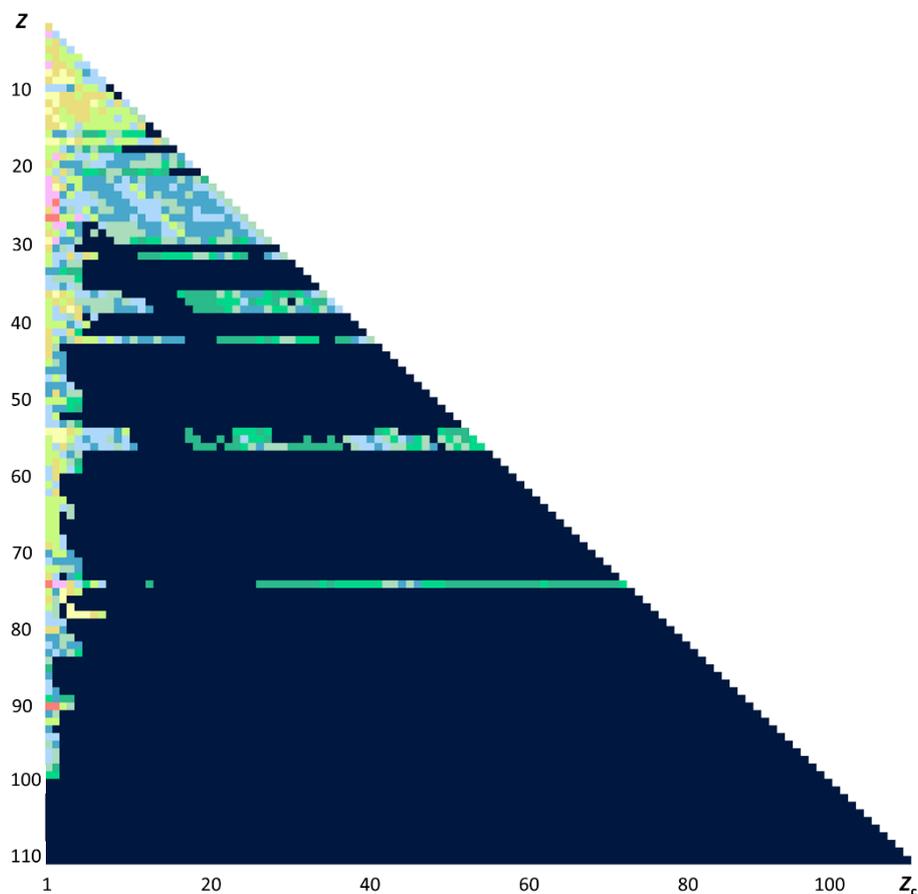


Figure 6. The Lines Holdings from the NIST Atomic Spectra Database [20]. Each square represents an ion with atomic number Z and core charge Z_c (e.g., $Z_c = 1$ represents neutral atoms, $Z_c = 2$ represents singly ionized, etc.). The color of the squares represents the amount of experimental data on the spectrum. The brighter the color, the more data are available. A black color represents that no data are available for a given spectrum.

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References

1. Cowan, R.D. *The Theory of Atomic Structure and Spectra*; University of California Press: Berkeley, CA, USA, 1981.
2. Cowan, R.D. Theoretical Calculation of Atomic Spectra Using Digital Computers. *J. Opt. Soc. Am.* **1968**, *58*, 808–818. [[CrossRef](#)]
3. Cowan, R.D. Atomic Self-Consistent-Field Calculations Using Statistical Approximations for Exchange and Correlation. *Phys. Rev.* **1967**, *163*, 54–61. [[CrossRef](#)]
4. Cowan, R.D.; Andrew, K.L. Coupling Considerations in Two-Electron Spectra. *J. Opt. Soc. Am.* **1965**, *55*, 502–516. [[CrossRef](#)]
5. Clark, C.A. Obituary: Robert Duane Cowan 26 July 2018. Available online: <https://ladailypost.com/content/obituary-robert-duane-cowan-july-26-2018> (accessed on 9 October 2018).
6. Web of Science, Originally Produced by the Institute for Scientific Information (ISI), Now Maintained by Clarivate Analytics. Available online: <http://isiknowledge.com/> (accessed on 10 September 2018).

7. Bordarier, Y.; Vetter, R.; Blaise, J. Étude des structures hyperfines des raies d'arc de ^{169}Tm . *J. Phys.* **1963**, *24*, 1107–1112. [[CrossRef](#)]
8. Bordarier, Y.; Judd, B.R.; Klapisch, M. Hyperfine Structure of Eu I. *Proc. R. Soc. Lond. Ser. A* **1965**, *289*, 81–96.
9. Gluck, G.G.; Bordarier, Y.; Bauche, J.; van Kleef, T.A.M. Déplacement isotopique, calculs théoriques et structure des termes dans le spectre d'arc de l'osmium. *Physica* **1964**, *30*, 2068–2104. [[CrossRef](#)]
10. Carlier, A.; Blaise, J.; Schweighofer, M.-G. Étude des configurations impaires $4f^6 6s 6p$ et $4f^5 5d 6s^2$ de Sm I. *J. Phys.* **1968**, *29*, 729–738. [[CrossRef](#)]
11. Hansen, J.E.; Uylings, P.H.M.; Raassen, A.J.J. Parametric Fitting with Orthogonal Operators. *Phys. Scr.* **1988**, *37*, 664–672. [[CrossRef](#)]
12. Wyart, J.-F. On the Interpretation of Complex Atomic Spectra by Means of the Parametric Racah-Slater Method and Cowan Codes. *Can. J. Phys.* **2011**, *89*, 451–456. [[CrossRef](#)]
13. Kramida, A. Critical Evaluation of Data on Atomic Energy Levels, Wavelengths, and Transition Probabilities. *Fusion Sci. Technol.* **2013**, *63*, 313–323. [[CrossRef](#)]
14. Froese Fischer, C.; Tachiev, G.; Gaigalas, G.; Godefroid, M.R. An MCHF Atomic-Structure Package for Large-Scale Calculations. *Comput. Phys. Commun.* **2007**, *176*, 559–579. [[CrossRef](#)]
15. Hibbert, A. CIV3—A General Program to Calculate Configuration Interaction Wave Functions and Electric-Dipole Oscillator Strengths. *Comput. Phys. Commun.* **1975**, *9*, 141–172. [[CrossRef](#)]
16. Jönsson, P.; Gaigalas, G.; Bieroń, J.; Froese Fischer, C.; Grant, I.P. New Version: GRASP2K Relativistic Atomic Structure Package. *Comput. Phys. Commun.* **2013**, *184*, 2197–2203. [[CrossRef](#)]
17. Desclaux, J.P.; Indelicato, P. *Multiconfiguration Dirac-Fock with General Matrix Elements*; Laboratoire Kastler Brossel: Paris, France, 2017; Available online: http://dirac.spectro.jussieu.fr/mcdf/mcdf_code/mcdfgme_accueil.html (accessed on 1 July 2019).
18. Gu, M.F. The Flexible Atomic Code. *Can. J. Phys.* **2008**, *86*, 675–689.
19. Vilkas, M.J.; Koc, K.; Ishikawa, Y. Relativistic Multireference Møller-Plesset Perturbation Theory Based on Multiconfigurational Dirac-Fock Reference Functions. *Chem. Phys. Lett.* **1998**, *296*, 68–76. [[CrossRef](#)]
20. Kramida, A.; Ralchenko, Y.; Reader, J.; NIST ASD Team. *NIST Atomic Spectra Database (Ver. 5.6.1)*; National Institute of Standards and Technology: Gaithersburg, MD, USA, 2018. Available online: <https://physics.nist.gov/asd> (accessed on 1 July 2019).
21. McGuinness, C.; Robert, D. *Cowan's Atomic Structure Code*; Trinity College, University of Dublin: Dublin, Ireland, 2007; Available online: <https://www.tcd.ie/Physics/people/Cormac.McGuinness/Cowan/> (accessed on 1 July 2019).
22. Kramida, A. *A Suite of Atomic Structure Codes Originally Developed by RD Cowan Adapted for Windows-Based Personal Computers*; National Institute of Standards and Technology: Gaithersburg, MD, USA, 2018. [[CrossRef](#)]
23. Quinet, P.; Palmeri, P.; Biémont, E. On the use of the Cowan's code for atomic structure calculations in singly ionized lanthanides. *J. Quant. Spectrosc. Radiat. Transf.* **1999**, *62*, 625–646. [[CrossRef](#)]
24. Kurucz, R.L. *Atoms*; Harvard University: Cambridge, MA, USA, 2017; Available online: <http://kurucz.harvard.edu/atoms.html> (accessed on 1 July 2019).
25. Ruczkowski, J.; Elantkowska, M.; Dembczyński, J. An Alternative Method for Determination of Oscillator Strengths: The Example of Sc II. *J. Quant. Spectrosc. Radiat. Transf.* **2014**, *145*, 20–42. [[CrossRef](#)]
26. Abdallah, J., Jr.; Clark, R.E.H.; Cowan, R.D. *Theoretical Atomic Physics Code Development I. CATS: Cowan Atomic Structure Code*; Report LA-11436-M; Los Alamos National Lab: Los Alamos, NM, USA, 1988; Volume I, p. 31. Available online: <https://fas.org/sgp/othergov/doe/lanl/docs3/00323386.pdf> (accessed on 1 July 2019).
27. Azarov, V.I.; Kramida, A.; Vokhmentsev, M.Y. IDEN2—A Program for Visual Identification of Spectral Lines and Energy Levels in Optical Spectra of Atoms and Simple Molecules. *Comput. Phys. Commun.* **2018**, *225*, 149–153. [[CrossRef](#)]
28. Raassen, A.J.J.; Uylings, P.H.M. The Use of Complete Sets of Orthogonal Operators in Spectroscopic Studies. *Phys. Scr.* **1996**, *65*, 84–87. [[CrossRef](#)]
29. van het Hof, G.J.; Raassen, A.J.J.; Uylings, P.H.M. Parametric Description of $3d^N 4s$ Configurations using Orthogonal Operators. *Phys. Scr.* **1991**, *44*, 343–350.
30. Azarov, V.I.; Gayasov, R.R. The Third Spectrum of Rhenium (Re III): Analysis of the $(5d^5 + 5d^4 6s) - (5d^4 6p + 5d^3 6s 6p)$ Transition Array. *At. Data Nucl. Data Tables* **2018**, *122*, 306–344. [[CrossRef](#)]

31. Azarov, V.I.; Tchang-Brillet, W.-Ü.L.; Gayasov, R.R. Analysis of the Spectrum of the $(5d^6+5d^56s)-(5d^56p+5d^46s6p)$ Transitions of Two Times Ionized Osmium (Os III). *At. Data Nucl. Data Tables* **2018**, *122*, 345–377. [[CrossRef](#)]
32. Wyart, J.-F.; Raassen, A.J.J.; Uylings, P.H.M.; Joshi, Y.N. Spectra of High-Z Ions of Stellar Interest. A Theoretical Study of $(d + s)^8$ Mixed Configurations in 5d- and 4d-Elements. *Phys. Scr.* **1993**, *47*, 59–64. [[CrossRef](#)]
33. Uylings, P.H.M.; (University of Amsterdam). Private communication, 2018.
34. Blaise, J.; Wyart, J.-F.; Conway, J.G.; Worden, E.F. Generalized Parametric Study of $5f^N$ and $5f^N7s$ Configurations. *Phys. Scr.* **1980**, *22*, 224–230. [[CrossRef](#)]
35. Wyart, J.-F.; Raassen, A.J.J.; Joshi, Y.N.; Uylings, P.H.M. The $5d^96p-5d^9(6d+7s)$ Transitions in the Isoelectronic Sequence Au II-Bi VI. *J. Phys. II* **1992**, *2*, 895–912. [[CrossRef](#)]
36. Eissner, W.; Jones, M.; Nussbaumer, H. Techniques for the Calculation of Atomic Structures and Radiative Data Including Relativistic Corrections. *Comput. Phys. Commun.* **1974**, *8*, 270–306. [[CrossRef](#)]
37. Bogdanovich, P.; Rancova, O. Quasirelativistic Hartree-Fock Equations Consistent with Breit-Pauli Approach. *Phys. Rev.* **2006**, *74*, 052501. [[CrossRef](#)]
38. Froese Fischer, C.; Gaigalas, G.; Jönsson, P.; Bieroń, J. GRASP2018—A Fortran 95 version of the General Relativistic Atomic Structure Package. *Comput. Phys. Commun.* **2019**, *237*, 184–187. [[CrossRef](#)]
39. Safronova, M.S.; Johnson, W.R.; Safronova, U.I. Relativistic Many-Body Calculations of the Energies of $n = 2$ States for the Berylliumlike Isoelectronic Sequence. *Phys. Rev.* **1996**, *53*, 4036–4053. [[CrossRef](#)]
40. Safronova, U.I.; Safronova, M.S.; Kozlov, M.G. Relativistic All-Order Calculations of In I and Sn II Atomic Properties. *Phys. Rev.* **2007**, *76*, 022501. [[CrossRef](#)]
41. Eliav, E.; Kaldor, U.; Ishikawa, Y. Ionization Potentials and Excitation Energies of the Alkali-Metal Atoms by the Relativistic Coupled-Cluster Method. *Phys. Rev. A* **1994**, *50*, 1121–1128. [[CrossRef](#)] [[PubMed](#)]
42. Dzuba, V.A.; Johnson, W.R. Coupled-Cluster Single-Double Calculations of the Relativistic Energy Shifts in C IV, Na I, Mg II, Al III, Si IV, Ca II, and Zn II. *Phys. Rev. A* **2007**, *76*, 062510. [[CrossRef](#)]
43. Savukov, I.M. Parametric CI+MBPT Calculations of Th I Energies and g -Factors for Even States. *J. Phys. B* **2007**, *50*, 165001. [[CrossRef](#)]
44. Kramida, A. Configuration Interactions of Class 11: An Error in Cowan's Atomic Structure Theory. *Comput. Phys. Commun.* **2017**, *215*, 47–48, *Erratum* **2018**, *232*, 266–267. [[CrossRef](#)]
45. Gaigalas, G. Coupling: The program for searching optimal coupling scheme in atomic theory. *Submitted to Comput. Phys. Commun.* **2019**.
46. Safronova, M.S.; Dzuba, V.A.; Flambaum, V.V.; Safronova, U.I.; Porsev, S.G.; Kozlov, M.G. Highly Charged Ions for Atomic Clocks, Quantum Information, and Search for α variation. *Phys. Rev. Lett.* **2014**, *113*, 030801. [[CrossRef](#)]
47. Banine, V.Y.; Koshelev, K.N.; Swinkels, G.H.P.M. Physical Processes in EUV Sources for Microlithography. *J. Phys. D* **2011**, *44*, 253001. [[CrossRef](#)]
48. Glenzer, S.H.; Fournier, K.B.; Wilson, B.G.; Lee, R.W.; Suter, L.J. Ionization Balance in Inertial Confinement Fusion Hohlräume. *Phys. Rev. Lett.* **2001**, *87*, 045002. [[CrossRef](#)] [[PubMed](#)]

