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On the accuracy of valence–shell computations for heavy and super–heavy elements

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Abstract. Recent atomic computations on the (super–) heavy elements have raised the expectation that their low–lying excitation and ionization energies can be calculated with an accuracy of a few hundredth of an eV and, hence, that such computations might help in the identification of new lines. For most many–electron atoms, however, the higher–order relativistic and quantum electrodynamical (QED) effects are included so far only in a rather approximate form. Using different model computations for the neutral and weakly ionized ytterbium ($Z = 70$) and nobelium atoms ($Z = 102$), it is shown here that QED effects alone may lead to an uncertainty of 20–50 meV for the excitation energies of all super–heavy elements, and that even for highly–correlated wave functions the theoretical predictions are presently not more accurate than about 0.1 eV. Moreover, in order to support forthcoming spectroscopic measurements on the elements beyond $Z = 100$, detailed computations have been carried out for the two low–lying ${}^1\mathrm{S}_0 - {}^{1,3}\mathrm{P}^{\,o}_1$ excitation energies of nobelium by using systematically enlarged multiconfiguration Dirac–Fock wave functions.

PACS. 31.25.-v Electron correlation calculations for atoms and molecules – 32.70.Cs Oscillator strengths, lifetimes, transition moments

1 Introduction

Studies on the transuranium elements have attracted a alot of interest during the last two decades, both by experiment and theory. Apart from curiosity and the great ambition of discovering new isotopes, these investigations aimed for a better understanding of the electronic structure in strong (nuclear) fields as well as for insights into the chemical binding in Nature. For a long time, moreover, many experiments on the transuranium elements implied the hope that they might help for obtaining *stable islands* at the 'heavy side' of the nuclear chart or, at least, for predicting the properties of yet–undiscovered isotopes.

Because of the short lifetimes of most super–heavy isotopes (which are occasionally only of the order of milliseconds), however, experiments in the transuranium region are difficult and hard to perform without theoretical support. In a number of earlier computations [1,2], therefore, the aim was to predict the ground–state configurations and ionization potentials for all elements up to $Z = 172$ and, hence, to establish the chemical order in the periodic table. But although these computations certainly helped with a first chemical classification of the (super–) heavy elements, they were by far not accurate enough for spectroscopy, neither for predicting the level structures of the atoms nor their excitation or decay properties. In fact, more than two further decades were needed before atomic spectroscopy eventually arrived at $Z = 100$ by using a two–step resonant ionization of the fermium isotope ^{255}Fm [3]. Based on detailed computations for the low–lying resonances, and including the analysis of the absorption rates, two fermium resonances at 25099.8 cm^{-1} and 25111.8 cm^{-1} could be identified experimentally and have raised the hope that such low–lying resonances will be observed also for other heavy elements in the near future.

Over the years, meanwhile, various computations have become available which predict the ground–state and the low–lying levels for most heavy elements with nuclear charges up to $Z = 118$ and beyond. Making use of different refinements in describing the electronic correlations and having now a rich experience with the light and medium–range elements, the quality of these computations has been improved considerably. For the element E 111 (eka–gold), for example, Eliav and coworkers [4] found that — in contrast to the lighter group–11 elements — the ground state is formed by the $6d^9 7s^2\ {}^2\mathrm{D}_{5/2}$ level (instead of the $6d^{10} 7s\ {}^2\mathrm{S}_{1/2}$ as for the other coinage metals). From the comparison with the homologous element gold, these authors then estimated the excitation energies to an accuracy of a few hundredth of an eV ~ 300 cm^{-1} while the accuracy of the (theoretical) 10.6 eV ionization potential was assigned accurate to 0.1–0.2 eV. In all of these previous computations, however, quantum electrodynamical (QED) corrections were neglected, at least in the calculation of the excitation energies, in line with the common experience that QED hardly

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plays a role for the optical spectra of most elements, at least from a computational point of view. Therefore, it has been only recently that self–energy (SE) shifts were considered separately by Labzowsky and coworkers [5,6] and by Sapirstein and Cheng [7] for a single outer ns electron ($n \leq 8$) within a local potential approximation and were found to reduce the electron affinity of, for instance, eka–radon ($Z = 118$) by about 6 meV or, equivalently, almost 10% of the total affinity.

In this contribution, it is argued here that the (occasionally supposed) accuracy of a few hundredth of an eV for the excitation energies of the super–heavy elements is too optimistic, in particular, if the computations are based on the standard treatment of the Breit interaction and QED corrections for the neutral and weakly–ionized atoms. To this end, I will show that the uncertainties in the (ab–initio) prediction of the low–lying excitation energies arise not only from neglected correlation contributions but also from QED shifts in the total energies of the (super–) heavy elements. Although the theory of QED is now being accepted as the foundation for all atomic (and molecular) computations, there is — up to the present — no computational procedure in sight which would be feasible to incorporate the self–energy or vacuum polarization into the electronic structure calculations beyond, say, a screened hydrogenic or local–potential model. This is true especially for all (complex) atoms and ions except, perhaps, for those with just a very few electrons such as the helium– or lithium–like ions [8]. By comparing the level energies and shifts from various simple model computations, it is then concluded that the ab–initio predictions on the excitation energies, which are required for the forthcoming experiments with nobelium or lawrencium, are likely not more accurate than about 0.1 eV $\gtrsim$ 800 cm^{-1}. A sufficient realistic estimate of the theoretical accuracies is however required in order to support the experiments on the level structure of the super–heavy elements [9] and to ensure a proper experimental set–up for these observations. Overall, of course, a critical test on the 'quality of the present–day predictions' will become possible only if a (large) number of levels are predicted and — later on — confirmed or discarded by experiments [3].

To support a presently prepared experiment [9] with atomic nobelium ($Z = 102$), detailed computations have been carried out for the two lowest $^{1,3}P_1$ odd–parity resonances. Performing similar computations also for the homologous element ytterbium ($Z = 70$), our predictions are estimated to be accurate within about 1200 cm^{-1}, although further core–polarization and core–core correlations will be needed in the future in order to confirm these results. In the following section, the current (computational) models are first discussed in view of their capabilities and limitations in predicting the low–lying level structure of heavy atoms. Apart from the treatment of the electron–electron correlations, this includes in particular the uncertainty estimates due to the higher–order relativistic and self–energy shifts on the excitation energies. Section 3 later explains and compares the result for nobelium and its homologous element ytterbium. Finally, a few conclusions on the present–day accuracy of ab–initio predictions are drawn in Section 4.

2 Computational background

Not much needs to be said here about the demands and difficulties in carrying out atomic calculations for the heavy and super–heavy elements. Apart from the (very) strong relativistic and QED effects, these investigations have often been hampered by the large number of 'overlapping configurations' which enforces one to go up to the limits of what is computational feasible at the time. As recently shown by Zhou and Fischer [10], for example, a spectroscopically acceptable agreement with the observed $^2\mathrm{D}_{3/2}$–$^2\mathrm{P}^o_{1/2,3/2}$ fine structure in lutetium ($Z = 71$) could be obtained only by including core–polarization and core–core correlations to a rather huge extent. On the other hand, however, it should be noted also that, for the super–heavy elements $Z \geq 100$, only the low–lying excitations seems to be accessible by experiment in the near future.

At present, there are two methods available which are useful for studying the super–heavy elements. Apart from the multi–configuration Dirac–Fock (MCDF) method, the relativistic Coupled–Cluster (RCC) method has been found useful to provide very accurate results. This method allows in particular the incorporation of the Breit interaction self–consistently, a computational feature which has not been fully realized in the available MCDF codes. So far, however, most RCC computations were restricted to rather simple shell structures (with not more than two electrons or holes outside of closed shells otherwise) while, at least at the first glance, the MCDF method is known to be more flexible with regard to the shell structure and the computation of excitation and decay rates. Below, therefore, we make use of the MCDF method, in which an atomic state is approximated by a superposition of configuration state functions (CSF) of the same symmetry

$$\psi_\alpha(PJM) = \sum_{r=1}^{n_c} c_r(\alpha)\ |\gamma_r PJM\rangle \qquad (1)$$

and is optimized on the basis of the (many–electron) Dirac–Coulomb Hamiltonian [11]. Since the basic elements of the MCDF method have been presented at various places [12,13], here we give only a brief account of the theory. The major difference in the computations often concerns the number of CSF, n_c, in equation (1) which reflects the extent to which electron correlations are taken into account. Wave function expansions (1) of several ten or even hundred thousand CSF can nowadays be applied with the hope of obtaining a sufficiently accurate description of the excitation energies and transition properties. In Grasp92 [11], moreover, the CSF are constructed from antisymmetrized products of a common set of orthonormal orbitals, represented on some numerical mesh. Further relativistic corrections to the electron–electron interaction are added later in a second step by diagonalizing the Dirac–Coulomb–Breit Hamiltonian matrix. A critical point is the incorporation of the QED contributions into the level structure which, for the different models and structure codes available, may lead to rather different estimates. For the prediction of the low–lying resonances, of course, only the differences in the QED shifts are needed with sufficient accuracy and are 'tested' eventually by means of optical spectroscopy.

For complex atoms, so far, all the QED estimates are known to be built on *effective one–particle approximations* in which the two dominant contributions, the self–energy (SE) of the electrons and their vacuum polarization (VP), are treated independently. For heavy systems, both contributions are comparable in their size with the (relativistic) Breit interaction among the electrons and have been investigated in detail especially for the inner–shell electrons. In lowest order, the vacuum polarization can be taken into account by means of the local Uehling potential [14] and, hence, has been incorporated into relativistic structure calculations for many years now.

The computation of the self–energy, in contrast, requires (even in lowest order in αZ) a much larger effort. In the past, therefore, all estimates on the self–energy shifts were based on the hydrogen–like ions, a computational scheme which was extended only recently to effective potentials as obtained from Hartree–Fock (–Slater) computations of the ground–states [5]. But although such a one–particle picture obviously avoids the need of introducing intermediate states for the electrons between the emission and absorption of virtual photons in the QED framework, it provides independent shifts for the various electrons and, thus, does not allow the incorporation of correlation and relaxation effects on the SE. In such an approximation, moreover, there is no response of the wave function included, i.e. no self–consistent evaluation of the Lamb shift. The effects of the correlation and relaxation on the SE can be estimated in lowest order and are expected to be small, by analogy to the self–consistent incorporation of the Breit interaction.

In estimating the total SE shifts for the many–electron level energies, therefore, the principal source of uncertainty arises from the scaling of the one–electron SE shifts and how these contributions are included in the computations. In practice, rather different methods have been applied in the literature to scale up the self–energy data from the hydrogenic computations for the multi–electron atoms and ions. In GRASP92 [11], for instance, an *effective* nuclear charge Z_{eff} is determined from the mean radius $\bar{r}$ of the various orbitals and is used for the interpolation of the hydrogen–like results, independent of the actual shape of the orbital functions in the presence of the other electrons. The total self–energy shift is then taken as the sum of the one–particle contributions for the $K-$ and $L-$shell electrons, and by using a n^{-3} scaling rule for all further $s-$ and $p-$electrons in shells with larger principal quantum numbers.

An alternative method for estimating the one–particle SE in many–electron atoms has been suggested by Kim [15] which is based on the experience, that the dominant part of the self–energy *arises inside or very close to the nucleus*, say, within a sphere of 40–60 fm. In this method, the self–energy is obtained by multiplying the hydrogen–like SE shift for a point nucleus with the corresponding charge ratio (inside such a sphere) as obtained from the many–electron computations. For hydrogen–like ions with a point nucleus, tabulations of the electron SE have been listed by Mohr [16] for the $1s$, $2s$, and $2p$ orbitals and by Mohr and Kim [17] for ns, np, and nd ($n = 3, 4, 5$) orbitals. Although the use of a point nucleus (for the calculation of the charge ratios) has the advantage that the wave functions and, hence, the charge portion inside of a given sphere can be computed from analytic formulas, it represents another source of uncertainty and might be better replaced with finite–nucleus values in the future. For most medium and heavy atoms and ions, however, Kim's method was found to provide very reasonable results for the SE estimates of the inner shells, even though not much experience is yet available for the valence shells of heavy systems. For large wave function expansions, in addition, this method is fast and has been found more stable than the determination of the SE contributions via an effective charge.

As mentioned before, all models for estimating the SE in many–electron atoms have been tested mainly for the inner–shell electrons (or holes), for which the shifts in the transition wavelength can be compared — typically at the few–% level — with spectroscopically available X–ray data from multiple and highly–charged ions. Until now, however, it not yet clear how these models and their estimates can be applied to the valence shells and, in particular, to the low–lying excitations of the neutral or weakly ionized atoms. For an accurate prediction of the optical energies, namely, the SE shifts of the valence shells must first be combined with the changes in their effective occupation numbers, including contributions from both, the core–core and core–valence correlations. Up to the present, therefore, the QED shifts on the valence–shell excitations remain rather uncertain and might be used better as an 'estimate' of the uncertainties in the computations. In the next section, the SE shifts of a single $7s$ or $7p$ valence–shell electron is considered both, for the binding energies in the No^+ isoelectronic sequence and the low–lying excitation energies of atomic nobelium.

3 Results and discussions

Missing correlations effects are usually the main source of uncertainty in predicting the energies and excitation cross sections for the low–lying resonances. This is true, in particular, if an electronic excitation is associated with a change in the total spin (i.e. for the so–called 'spin–flip' or intercombination transitions). For most atoms and ions, however, these uncertainties can be controlled reasonably well by applying systematically enlarged MCDF or RCC computations. For light and medium elements (without open $d-$ and $f-$shells), both of these methods have been found accurate for the low–lying excitations to about

0.05 eV $\simeq$ 400 cm^{-1} in a number of case studies. A similar relative uncertainty of 1–3 % for the excitation energies has been obtained also for several multiple–charged ions [13,18,19], where the absolute deviations between the theoretical values and experiment are however larger owing to the increase of the effective charge $Z_{\rm eff}$.

Unfortunately, a rather different situation occurs for most heavy and super–heavy atoms with open $d-$ and $f-$shells (or with such closed or empty shells nearby in energy), for which the theoretical fine–structure splittings may differ from experiment by 30% and more [10]. While these deviations from experiment are often caused by missing core–core and core–valence excitations, they also arise due to the truncation of the virtual space. By increasing the maximum orbital angular momentum from f to h, for example, Zhou and Froese Fischer [10] found for the ^{2}D$-^2$P$^{\,o}$ excitations of atomic lawrencium ($Z = 103$) that the g orbitals contribute significantly to the level splitting, while the h orbitals appears to be unimportant. This behaviour can be understood from the fact that the g orbitals have a direct dipole coupling to the $4f$ core orbitals of the actinides, whereas the h orbitals are connected only via higher–order interactions. Because of the increased importance of dynamic correlation for the heavy elements, however, many of the earlier (MCDF) computations are not very realible since neither the g orbitals nor a sufficiently large radial basis set were taken into account for the wave functions in these studies. In estimating the uncertainties of atomic computations, moreover, one should bear in mind that the (numerical) convergence of the excitation energies with respect to the size of the wave function expansion is certainly a necessary but by far not a sufficient criterion. From the comparison for lutetium, for instance, it can be seen that the theoretical ^{2}D$_{3/2}-^2$P$^{\,o}_{1/2}$ excitation energies differs from experiment by 300 cm^{-1} in the RCC calculations [24] and by about 50 cm^{-1} in very extensive MCDF computations [10], and that even larger deviations have to be expected if nothing is known in advance from experiment as for atomic nobelium or lawrencium.

Besides the electron–electron correlations, of course, the QED treatment cause the next largest uncertainty in the theoretical energies for the (super–) heavy elements. To indicate the size of the self–energy, Figure 1 displays the SE shift of a single $7s_{\,1/2}$ and $7p_{\,1/2,3/2}$ electron for the (alkali–like) $5f^{\,14}6s^26p^67s \quad {}^2S_{1/2}$ and $5f^{\,14}6s^26p^67p \quad {}^2P_{1/2,3/2}$ levels, respectively. In this figure, Kim's method [15] together with the SE shifts by Mohr and Kim [17] and the Relci program [20,21] have been applied in order to estimate the self–energy in the No$^+$ isoelectronic sequence for Z = 101, ..., 112. In fact, the increase in the SE shifts is very similar to the computations by Labzowsky and co–workers for the coinage and alkali metals [5], who started from an effective one–particle potential as obtained from Dirac–Fock(–Slater) wave functions. For comparison, moreover, Figure 2 displays the (analogue) $6s$ and $6p$ SE shifts for the homologous Yb$^+$ sequence in the range Z = 69, ..., 80. Note the different energy scale on this figure which confirms the *empirical rule* from above, that QED effects are negligible for the valence–shell computations of the stable isotopes. They are important however for the super–heavy elements with, say, $Z \geq 100$ and occur — of course — even if the presently available codes do not support very accurate estimates on the self–energy. The latter is seen in Figure 3 which shows the SE of the $7s$ valence shell from three different models as suggested and utilized in the literature. Apart from Kim's model from above [20], this figure displays the data as obtained by the Grasp92 [11] program as well as those due to the extrapolation formula by Klarsfeld and Maquet [23].

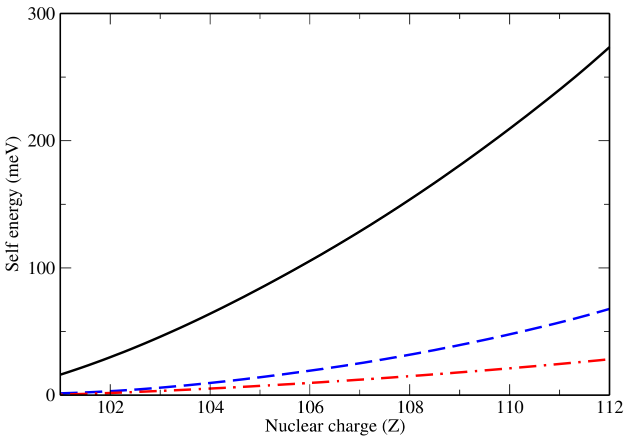

Fig. 1. Self–energy estimates (in meV) for the $7l_j$ valence–shell electrons in the No$^+$ isoelectronic sequence as obtained for the [Rn] $5f^{\,14}7l$ levels by using the Relci program [20]; $7s_{\,1/2}$ (—), $7p_{\,1/2}$ (– – –), and $7p_{\,3/2}$ (– · – · –).

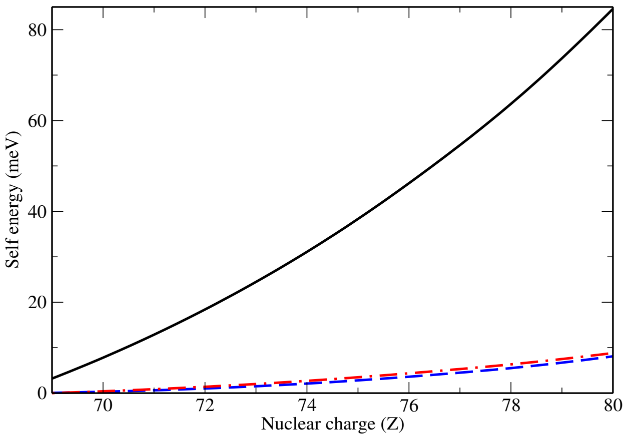

Fig. 2. Self–energy estimates (in meV) for the $6l$ valence–shell electrons in the Yb$^+$ isoelectronic sequence. The same as in Figure 1 but for the homologous [Xe] $4f^{\,14}6l$ levels; $6s$ (—), $6p_{1/2}$ (– – –), and $6p_{3/2}$ (– · – · –).

Figures 1–3 display the self–energy shifts for a single ns or np (n = 6 or 7) valence electron outside of otherwise closed shells. For deriving the excitation energies, of course, only the differences in the total QED shifts are relevant and must be obtained from a summation over the occupation numbers of the subshells. Apart from the missing response of the QED effects back onto the representation of the wave functions, hereby the main

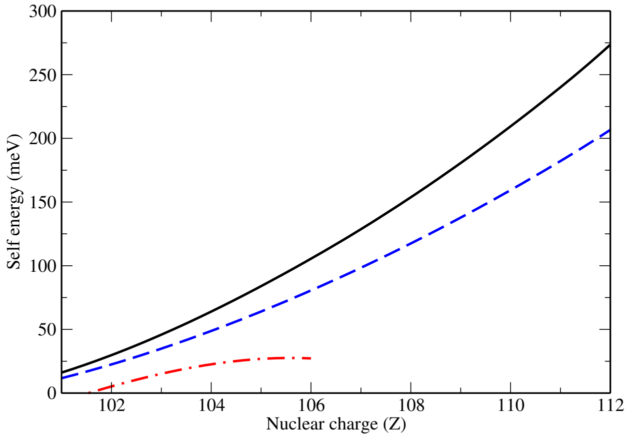

Fig. 3. Comparison of the $7s$ self–energy estimate (in meV) from different approximations; Relci [20] (—), Klarsfeld [23] (– – –), Grasp92 [11] (– · – · –).

uncertainty is due the one–particle model which implies a cancellation of the core contributions to the self–energy to better than 10 ppm. Including the Breit interaction, the total (higher–order) 'relativistic shifts' on the excitation energies may have different signs owing to the relative importance of the different effects for a particular level. This is demonstrated, for instance, in Table 1 for the higher–order relativistic and QED corrections to the total Dirac–Coulomb energy for the 7 lowest levels of ytterbium ($n = 6$) and nobelium ($n = 7$) with total angular momenta $J = 0, 1, 2$. For the sake of simplicity, however, only a medium–size wave function expansion has been applied in this table, including the configurations $(n-2)f^{\,14}ns^2$, $(n-2)f^{\,14}nsnp$, $(n-2)f^{\,13}ns^2nd$, $(n-2)f^{\,14}ns(n-1)d$, $(n-2)f^{\,13}ns^2np$, $(n-2)f^{\,13}ns(n-1)d^2$, and $(n-2)f^{\,13}nsnp(n-1)d$, respectively. To emphasize the importance of the various corrections, here we do not list the total shifts explicitly (which are larger by 3–5 orders of magnitudes) but just display the 'size' of the various contributions in eV.

From the viewpoint of atomic spectroscopy on the super–heavy elements, nobelium and lawrencium are at present the two most prominent candidates. For noblium, in fact, a first experiment is currently prepared at the GSI in Darmstadt in order to determine the low–lying resonances between about 20 000 and 30 000 cm^{-1}, using resonance ionization spectroscopy [9]. Since nobelium (and all elements beyond) have to be produced *on–line* in nuclear collisions, however, the success of such experiments depends vitally on the quality of the theoretical predictions, from which the search for new lines starts. In addition to the excitation energies, then the absorption rates are also of direct interest in order to support the classification of the level symmetries. In nobelium, the experiments commence from the ^{1}S$_0$ ground state and will therefore allow excitations predominantly into the odd–parity $J = 1$ levels, such as the two $7s7p\;\; ^{1,3}\mathrm{P}^o_1$ levels. As expected (and easily confirmed by means of the corresponding $6s6p\;\; ^{1,3}\mathrm{P}^o_1$ levels of the homologous element ytterbium), large–scale computations are required to come to an agreement with experiment that is at least reasonable.

Therefore, in order to provide the current preparation of the nobelium experiment with a first prediction, detailed computations have been carried out for the two $7s7p\;\; ^{1,3}\mathrm{P}^o_1$ resonances of atomic nobelium, including virtual excitations within an increasing set of valence shells. Besides rather simple calculation with just single, double and triple excitations from the $\{5f, 7s, 7p\}$ subshells into $\{5f, 6d, 7s, 7p\}$ (Model I), excitation were allowed also for the $6p$ core orbitals and by including singles and doubles from $\{5f, 6p, 7s, 7p\}$ into the $\{5f, 6p, 6d, 7s, 7p, 8s, 8p, 8d, 8f, 8g\}$ subshells, starting from the two $5f^{\,14}6p^{\,6}7s^2$ and $5f^{\,14}6p^{\,6}7s7p$ reference configurations. As the $8l$ orbitals are all *correlation orbitals*, the principal quantum number $n = \;8$ has no particular meaning and has been used simply to indicate the additional 'layer' of one–electron functions in the representation of the atomic states. The latter model (II) gives rise to 1536 CSF for the ^{1}S$_0$ ground state and already 28 035 CSF for the $^{1,3}\mathrm{P}^o_1$ excited levels, respectively. Including all the contributions from above, the finally obtained excitation energies are displayed in Table 2 below. Similar computations for ytterbium (with all the principal quantum numbers reduced by one, such as in $\{4f, 5p, 6s, 6p\}$, but with otherwise the same size of the wave function expansion) have shown these excitation energies to be accurate within 1200 cm^{-1} and the $^1\mathrm{P}^o_1$–$^3\mathrm{P}^o_1$ splitting even within 700 cm^{-1}. For ytterbium, the deviation from tables [22] mainly arise from missing correlations since, here, the higher–order relativistic and QED shifts are still negligible [cf. Tab. 1]. Therefore, the hope is that a similar accuracy applies also for nobelium, even though a slightly larger uncertainty might be assumed in this case owing to the radiative corrections as discussed above. To further improve the computations, we presently investigate the possibilities to enlarge the wave function expansions in order to incorporate also triple excitations as well as core–polarization effects, comparable with Zhou's recent study for lawrencium [10].

4 Conclusions

To draw attention to the present–day accuracy of the valence–shell calculations for the heavy and super–heavy elements, different computational models for estimating the higher–order relativistic and QED corrections have been analyzed. Detailed computations were performed, in particular, for the two $nsnp\;\; ^{1,3}\mathrm{P}^o_1$ resonances of nobelium ($n = 7$) and its homologous element ytterbium ($n = 6$), as well as along the No$^+$ and Yb$^+$ isoelectronic sequences. For the low–lying excitation energies of these atoms, the self–energy shifts are obtained by using a standard implementation within the Relci program [20] for the ns and np electrons. From the analysis of these computations, it is found that — although a number of large–scale computations have been reported even for elements with $Z > 110$ during the last decade — the accuracy of today's atomic calculations for the low–lying excitation

Table 1. Relativistic and QED contributions (in meV) to the low–lying excitation energies from the $(n-2)f^{14}ns^2\ {}^1\mathrm{S}_0$ ground–state for ytterbium ($n = 6$) and nobelium ($n = 7$). These contributions are obtained by taking the difference of the level shifts from to the various effects. The 'size' of the total shifts is also indicated.

	Level	${}^{2S+1}\mathrm{L}_J$	vacuum polariz.	self–energy	2nd order Breit	total shift
Yb	$4f^{14}6s6p$	${}^3\mathrm{P}_0$	1.4	2.1	–4.2	–0.7
	$4f^{14}6s6p$	${}^3\mathrm{P}_1$	1.4	2.1	–4.9	–1.4
	$4f^{14}6s6p$	${}^3\mathrm{P}_2$	1.5	2.2	–6.7	–3.0
	$4f^{14}6s5d$	${}^3\mathrm{D}_1$	1.4	2.6	–1.7	2.3
	$4f^{14}6s5d$	${}^3\mathrm{D}_2$	1.4	2.6	–2.8	1.2
	$4f^{14}6s6p$	${}^1\mathrm{P}_1$	1.4	2.2	–7.9	–4.3
	$4f^{14}6s5d$	${}^1\mathrm{D}_2$	1.5	2.2	–3.3	0.4
	Level shift (in eV)		∼50	∼250	∼400	
No	$5f^{14}7s7p$	${}^3\mathrm{P}_0$	6.6	18.2	–13.2	11.6
	$5f^{14}7s7p$	${}^3\mathrm{P}_1$	6.7	18.3	–15.0	10.8
	$5f^{14}7s7p$	${}^3\mathrm{P}_2$	7.2	18.9	–20.3	5.8
	$5f^{14}7s6d$	${}^3\mathrm{D}_1$	7.3	19.4	–10.8	15.9
	$5f^{14}7s6d$	${}^3\mathrm{D}_2$	7.3	19.5	–13.0	13.8
	$5f^{14}7s7p$	${}^1\mathrm{P}_1$	7.0	16.5	–23.6	–0.1
	$5f^{14}7s6d$	${}^1\mathrm{D}_2$	7.3	17.0	–14.2	10.1
	Level shift (in eV)		∼500	∼1300	∼1500	

Table 2. Excitation energies of the two ${}^{1,3}\mathrm{P}^o_1$ levels of atomic nobelium with respect to its $5f^{14}7s^2\ {}^1\mathrm{S}_0$ ground state. Computations have been carried out in two different models as briefly explained in the text.

	Level	${}^{2S+1}\mathrm{L}_J$	Excitation energy (eV)	
			Model I	Model II
No	$5f^{14}7s7p$	${}^3\mathrm{P}_1$	2.34	2.60
	$5f^{14}7s7p$	${}^1\mathrm{P}_1$	3.49	3.36

energies is likely not better than 0.1 eV or even less. A good deal of further computational and experimental data will be needed in order to finally arrive at the accuracy of a few hundredth of an eV ∼ 300 cm^{-1} for the low–lying resonances [4,25]. Since the higher–order relativistic and QED corrections increase rapidly with the nuclear charge, rather sizeable QED shifts to the optical transitions may arise for all elements beyond $Z = 100$. From the viewpoint of atomic spectroscopy, therefore, it seems more desirable for our present understanding of the electronic structure in strong nuclear fields if, instead in going towards heavier and heavier elements for which no spectroscopic studies will be available in the near future, reliable predictions are made and compared with experiment for the neutral and weakly ionized atoms with $Z \approx 100$.

Depending on the shell structure of the atoms and the particular resonance under consideration, predictions on the excitation energies and properties are still a challenge for modern atomic theory. As discussed above, the QED shifts to the valence–shell excitations are no longer negligible even for closed–shell structures, such as the $7s^2\ {}^1\mathrm{S}_0$ ground state of nobelium, if one aims for an accuracy of the theoretical prediction of about 0.1 eV ∼ 800 cm^{-1}. In fact, these QED estimates are the main limitations today in carrying out precise structure calculations for the super–heavy elements. Since, for the valence–shell electrons, these estimates are presently not more accurate than about 50%, there is a clear need for more rigorous computations of the SE contributions. From the experience with the light and medium elements for treating the (many–electron) interactions beyond the Dirac Hamiltonian its unlikely that a simple scaling of the higher–order relativistic and QED will work for the low–lying resonances, or for their excitation or decay rates. Up to the present, the interplay of these effects is not well enough understood. It is anticipate, therefore, that precise measurements on the super–heavy elements will yield new challenges and will hopefully stimulate a consistent many–particle theory for the (super–) heavy elements.

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