Rapid Communications

Proposal of highly accurate tests of Breit and QED effects in the ground state $2p^5$ of the F-like isoelectronic sequence

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We propose that the ground term transition, $2p^5\,{}^2P_{3/2}$-${}^2P_{1/2}$, for ions in the F-like isoelectronic sequence could be used to accurately test current methods to compute Breit and quantum-electrodynamic (QED) effects. These systems are of interest since correlation is small due to what we will label Layzer quenching. Using the multiconfiguration Dirac-Hartee-Fock method, we investigate how correlation, Breit and QED corrections vary along the sequence and show that QED dominates over correlation already for $Z \approx 20$. We also investigate the behavior of different QED effects as a function of the nuclear charge and find that the self-energy dominates for the mid-Z range (40–80), but then decreases to change sign for $Z \approx 90$. For a few elements between $Z = 85$ and 90 the vacuum polarization is the leading term, while for higher Z the two QED contributions cancel. This opens up the possibility for these ions to carefully test the frequency-dependent transverse photon correction. The uncertainties of the treatment of the well-understood frequency-independent Breit correction and correlation are expected to be at least three orders of magnitude smaller than the QED and frequency-dependent transverse photon corrections for high Z. In this work we also compare and evaluate the results from three different methods to compute self-energies.

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When attempting to calculate accurate transition energies for ions, one is faced with essentially two competing challenges. First, the introduction of correlation, as a correction to our independent particle model, and second, the introduction of corrections due to relativistic and quantum-electrodynamic (QED) effects. These two are not only competing, but also present us with different types of challenges. Correlation is basically well understood and mainly requires large-scale calculations, especially to represent the dynamical correlation due to the "cusps," i.e., when the interelectronic distances approach zero [1]. Relativistic and QED effects are a challenge on a more basic level, since we are only able to represent them in our Hamiltonian in an approximate fashion. It is therefore important to find examples of systems where the correlation is small and can be included to a high degree of accuracy, which can serve as testing grounds for the relativistic and QED effects.

For many methods that deal with correlation, such as the multiconfiguration Dirac-Hartree-Fock (MCDHF) we are using in this Rapid Communication, an important concept is the Layzer complex [2,3]. This consists of all electron configurations with the same set of n-quantum numbers and parity. In the hydrogenic limit (when the nuclear charge $Z \to \infty$) all configurations belonging to the same complex will be degenerate and also exhibit large overlaps of their wave functions. However, this is not a single-configuration Layzer complex as it consists of one electron outside of a filled $2s$ subshell. [1]. If, on the other hand, we find cases where there is only one configuration in a Layzer complex, we can expect that correlation is smaller and less complicated to model. There are two types of systems when this happens. First, configurations with only one electron outside of closed shells (note, not subshells). Rigorous calculations of QED effects for what seems to be similar kinds of systems, for example the B-like isoelectronic sequence, are already available [4,5]. However, this is not a single-configuration Layzer complex as it consists of one electron outside of a filled $2s$ subshell. Among ground states the singly occupied valence subshell will then always have an ns electron (for $n = 1$–7). Unfortunately these ground configurations only have one level and no transitions can be observed. A more interesting case of this "Layzer quenching" of correlation is when there is a single hole in the outermost shell. Among ground configurations we will find three examples of such systems, namely, $2p^5$, $3d^9$, and $4f^{13}$. The two first examples are represented in F-like and Co-like ions, respectively. In the present work we are focusing on F-like and will discuss how these ions can be used to probe primarily Breit and QED effects.

As pointed out above, we need to model correlation as well as Breit and QED effects. Our method of choice is the MCDHF method [1], in the form of the GRASP2K package [6]. In this, correlation is included by expanding our atomic state function as a linear combination of configuration state functions (CSFs), $\Phi(\gamma_i J)$:

$$\Psi(\gamma J) = \sum_i c_i \Phi(\gamma_i J). \tag{1}$$

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The CSFs are antisymmetrized linear combinations of products of single-electron Dirac orbitals and are generated based on the restricted active space approach, which allows the electrons in the predefined multireference configurations to be excited to unoccupied or unfilled orbitals in an active set method [1]. This method has recently been applied to the atomic properties of monovalent [7] or single hole ions [8–10], giving results with spectroscopic accuracy. In the present case, the ground configuration $2p^5$ is the single member of the multireference set. Correlation is then taken into account by including all possible configurations that arise from single and double excitations from all the shells of the reference configuration to orbitals with $n \leqslant n_{\max}$ and $l \leqslant \min(n_{\max} - 1, 6)$. Due to the rate of convergence, we are using different values for different parts of the isoelectronic sequence, with principal quantum number $n_{\max} = 8$ for ions with $Z = 10$–32, $n_{\max} = 7$ for ions with $Z = 33$–62, and finally $n_{\max} = 6$ for ions with $Z > 62$. The transverse photon interaction is included in GRASP2K through a standard Hamiltonian (see [1], and references given therein), as a correction to order α^2 to the Dirac-Coulomb Hamiltonian included in the self-consistent-field part of the calculations:

$$H_{\mathrm{TP}} = -\sum_{k>j=1}^{N}\left[\frac{\alpha_j\alpha_k\cos(\omega_{jk}r_{jk}/c)}{r_{jk}} + (\alpha_j\cdot\nabla_j)(\alpha_k\cdot\nabla_k)\frac{\cos(\omega_{jk}r_{jk}/c)-1}{\omega_{jk}^2 r_{jk}}\right], \quad (2)$$

where ω_{jk} is the frequency of the exchanged, virtual photon. This reduces to the frequency-independent Breit interaction when $\omega_{jk} \to 0$, which we will label Breit(0). The remaining and frequency-dependent part we will label Breit(w). Breit(0) is the dominating correction to the Dirac-Coulomb results for all ions in the sequence and it is basically well understood how to include it in our calculations. This is not the case for the Breit(w) part, since the frequency only represents a physical property for spectroscopic orbitals, defined as orbitals occupied in the multireference set (in our case $1s$, $2s$, and $2p$). The Breit(w) is therefore worthwhile to monitor separately. We stress here that we only include Breit(w) within the single-configuration Dirac-Hartree-Fock approximation, since all other states includes correlation orbitals.

The QED corrections are included as self-energy (SE) and the screened vacuum polarization (VP). The contributions from SE are obtained from a screened hydrogenic approximation [1,11–14], for CSFs with principal quantum number $n \leqslant 4$ and can be expressed as

$$\Delta E_{\mathrm{SE}} = \left(\frac{\alpha}{\pi}\right)\frac{\alpha^2 Z^4}{n^3}F(nlj, Z\alpha), \quad (3)$$

where $F(nlj, Z\alpha)$ is weakly dependent on $Z\alpha$.

The screened VP correction is evaluated by Uehling model potentials [15] together with some higher order corrections. For details, see [1,6], and references given therein.

The size of different contributions to the fine structure of the $2p^5\,{}^2P$ for ions in the F-like isoelectronic sequence are shown in [16] and Fig. 1. We see that Breit(0) is the largest correction for all elements. Correlation contributes a few percent at the neutral end, but the relative contribution decreases fast with Z. It is also clear that the contribution from SE is larger than

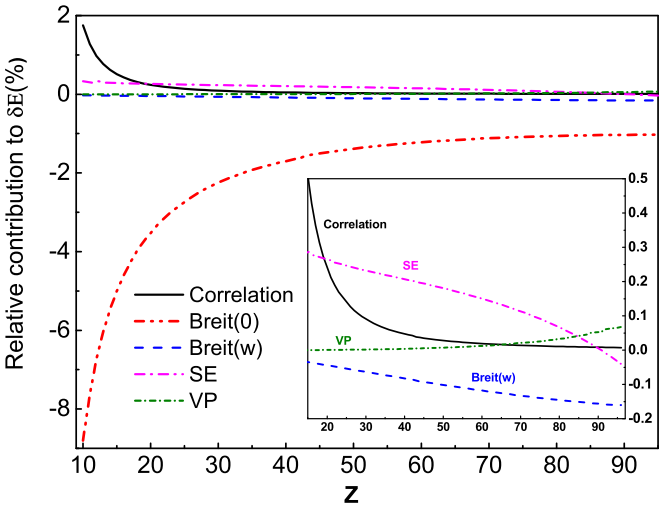

FIG. 1. Different contributions to the fine structure of the $2p^5\,{}^2P$ for ions in the F-like ions as a function of the nuclear charge Z. The different contributions are defined in the text. SE stands for self-energy and VP for vacuum polarization.

correlation already for nuclear charge, $Z \approx 20$, while also the VP correction passes correlation around $Z \approx 67$. Furthermore, the relative SE contribution is fairly constant for a large number of ions, but decreases and changes sign at $Z \approx 90$. This makes this sequence interesting to explore the Breit(w) and QED effects, since for midrange ions ($Z = 40$–80) SE dominates, but for $Z = 85$–90, the VP is predicted to be the largest effect. For $Z \geqslant 90$ the two effects cancel and QED is small. These ions are therefore an important testing ground for the frequency-dependent transverse photon effect, Breit(w). In Fig. 2 we give the relative difference between observed and computed results, with the experimental error bars. Note, we only use wavelengths from direct measurements of the $M1$ transition [17–25]. We can note that the original GRASP2K

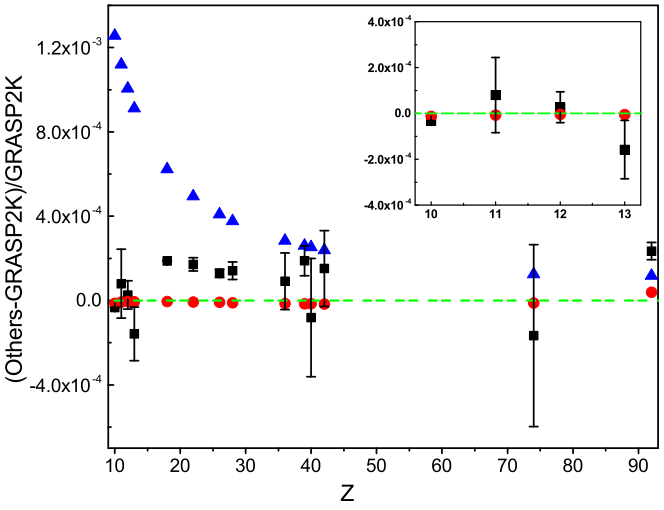

FIG. 2. Comparison of the fine-structure energy splitting of $2p^5\,{}^2P$ from the original GRASP2K calculations with the results of the other two calculations: Model QED (blue △), Welton (red ○), and also with the direct observations (black □) (see text). Note that the error bar for the Ar X case is given as the error of the transformation from air wavelength (see text).

TABLE I. Fine-structure energies, δE, (in cm^{-1}) for $2p^5\,{}^2P$ of F-like ions from direct measurements and our calculations. The notation for experimental values, e.g., 780.4240(11) implies 780.4240 ± 0.0011. Note that the error estimate for Ar^{9+} is from a measurement of an air wavelength. For the comparison here we need to convert to the vacuum value to find excitation energies. This could introduce larger uncertainties than the one stated here (see text).

		Experiment		Calculations δE		
Z	Ion	δE	Ref.	GRASP2K	Welton	Model QED
10	Ne^{+}	780.4240(11)	[17]	780.45	780.44	781.43
11	Na^{2+}	1366.5(2)	[18]	1366.44	1366.43	1367.97
12	Mg^{3+}	2228.8(1)	[18]	2228.76	2228.75	2231.00
13	Al^{4+}	3442.1(4)	[18]	3442.66	3442.64	3445.80
18	Ar^{9+}	18067.494(7)	[19]	18064.22	18064.02	18075.35
22	Ti^{13+}	47218.4(15)	[20]	47210.30	47209.96	47233.64
26	Fe^{17+}	102578.8(20)	[20]	102565.53	102564.62	102607.47
28	Ni^{19+}	143959(6)	[20]	143938.65	143937.17	143992.81
36	Kr^{27+}	446438(60)	[21]	446398.00	446390.78	446523.87
39	Y^{30+}	637751(45)	[22]	637630.72	637621.02	637796.52
40	Zr^{31+}	713520(200)	[23]	713579.63	713566.78	713758.12
42	Mo^{33+}	886305(160)	[23]	886172.81	886156.18	886382.65
74	W^{65+}	11202000(4839)	[24]	11203870	11203728	11205267
92	U^{83+}	31564817(1290)	[25]	31557409	31558633	31561114

calculations are very close to the experimental value for Ne II, giving us high confidence in our calculations of the dominant corrections, correlation and Breit(0), in the low-Z end of the sequence. Since the former contributes a few percent and the latter around 10%, while the relative difference to the experimental value is of the order of 10^{-5}, we can conclude that our calculations are correct to at least about one-tenth per thousand for these effects. For the high-Z end, the correlation contribution is less than 10^{-5} and Breit(0) contributes about 1%, so the maximum relative error of these are on the order of 10^{-6}, to be compared to QED effects and Breit(w) that contributes a few per thousand, i.e., three orders of magnitude larger than the uncertainties in our calculations of the major effects. The data points between Ne II and Ar X come from measurements made on astrophysical plasmas in the infrared spectral region. The Na III and Mg IV points imply a trend where the deviation is increasing toward the point for Ar X, but the Al V data point breaks the trend. Looking at the data points between $Z = 18$ and $Z = 42$ we see that the experimental energies are systematically higher than the original GRASP2K calculations and it is in this region that the QED self-energy dominates. There are unfortunately no measured results between $Z = 42$ and $Z = 74$, where the self-energy and frequency-dependent Breit are close to equal and opposite in size. The next accurate data point is for U, $Z = 92$, where the frequency-dependent Breit dominates. We compare computed and measured energies for the fine-structure splitting in Table I. It is clear that the reported experimental accuracy for midrange Z is not good enough to investigate the various contributions given in Fig. 1 and distinguish between different computation methods. Further experimental work for this and higher Z would therefore be important.

Finally, we have performed two more calculations using different ways to include the self-energy part of QED into the GRASP2K code. The first method, which we label as "Welton" [14], is based on Welton's concept of the electron self-energy and the latest available hydrogenic values are used, while the second one, the "Model QED" [26], is based on a model QED operator which includes both the local and nonlocal parts of the self-energy operator. The Welton method is basically in agreement with the standard inclusion of the self-energy in the GRASP2K code except for a small deviation for very high Z. The Model QED gives worse results for the lower end of the sequence, where it consistently overestimates the fine structure. It is true that the trend is improving for higher Z, but this choice of representation does not seem to be warranted in a general-purpose code such as GRASP2K.

The two experimental data points with highest claimed accuracy so far are for Ne II and Ar X. The Ne II fine structure is close to our calculated value and gives us confidence in our calculational procedures. The Ar X point is also very interesting as it shows a breakdown in the calculation even for fairly low Z. However, the way the data is presented in [19] could be questioned. In this publication the authors convert the calculated wavelength, which of course is a vacuum wavelength, to an air wavelength to compare with the measurement that is done in air. This is unfortunate, since the refractive index of air depends on a number of parameters, including temperature and humidity. For example, a 1° change in the air temperature will lead to a 5 mÅ change in the Ar X wavelength. This is more than two times the quoted uncertainty in [19] and calls into doubt the very narrow uncertainty estimates of these authors. In general, to defend these small uncertainties for a measured wavelength, it would be necessary to very carefully monitor the laboratory conditions and make the conversion to vacuum wavelengths accordingly. As an added complication it is necessary that the laboratory conditions are the same for observation of the line under consideration and the spectrometer calibration. The only method to reach the stated accuracy might therefore be to remeasure the wavelength in vacuum.

To conclude we should stress that we are not proposing tests of either QED or the frequency-dependent Breit interaction, only probing how various models of these interactions are incorporated into the GRASP2K computer package. We show

that different interactions are more or less dominating along the F-isoelectronic sequence and, that there is a notable discrepancy between the limited experimental data and our calculations. Why this occurs, we hope will be explained via further fundamental QED studies and additional experiment. The $M1$ spectral lines discussed here are strong if the transition rate of the $2p^5\,{}^2P_{1/2}$ level is fast compared to any collisional deexcitation rate, which is true for most ions in the sequence in an electron beam ion trap plasma. The difficulty with experiment is finding high-accuracy calibration lines. The uranium experiment [25] was serendipitously allotted with accurately known H- and He-like argon lines surrounding the F-like U $M1$ line. Hence this data point is accurate and already shows the above-mentioned discrepancy with all of our calculations. The $M1$ line has been observed in F-like sulfur [27] in an astrophysical plasma but unfortunately the spectrometer was not well enough calibrated to get a wavelength measurement of high accuracy. It is hoped that more cases like F-like U can be found. Through the agreement of our calculations with the very accurate fine-structure energy for Ne II [17] we have shown that electron correlation is not the cause of this discrepancy, as hypothesized through the Layzer quenching idea. We call for further work to understand and improve methods by which QED and frequency-dependent Breit are included in state-of-the-art atomic structure codes such as GRASP2K.

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