Photoionization of the Be isoelectronic sequence: total cross sections

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Abstract
The photoionization of the four-electron beryllium-like isoelectronic series from the neutral to Fe\textsuperscript{22+} has been studied for ground 1S and metastable 3P initial states. The wavefunctions of the final-state (target) ions were built using the CIV3 code. Both nonrelativistic LS-coupling \textit{R}-matrix and relativistic Breit–Pauli (BP) \textit{R}-matrix methods were used to calculate the cross sections in the photon-energy range between the first ionization threshold and the 1s\textsuperscript{2}4f\textsubscript{7/2} threshold for each ion. Our total cross sections compare well with experiment which is available for Be, B\textsuperscript{+}, C\textsuperscript{+2}, N\textsuperscript{+3} and O\textsuperscript{+4}. The agreement between the present work and previous calculations is discussed in detail. The importance of relativistic effects is seen by the comparison between the LS and the BP results.

(Some figures in this article are in colour only in the electronic version)

1. Introduction
Since the universe is composed primarily of ions, the study of ions is of significance in astrophysics. Photoionization and the inverse process, electron–ion recombination, are important for the investigation of astrophysical, and other, plasmas. The Be-like four-electron closed-shell systems are particularly stable, which adds to their astrophysical importance. From the point of view of basic physics, the photoionization of ions is of interest as a fundamental process of nature. Furthermore, calculational technology has advanced to the point that it is possible to do extremely accurate calculations for systems with only four electrons. In addition, advances in target preparation and light source technology have led to a number of recent measurements of the photoionization of this isoelectronic sequence. Thus, the theoretical study of the photoionization of the Be-like isoelectronic sequence is rather timely as an adjunct to experiment and to assess the physics of the process.

The multiconfiguration Hartree–Fock (MCHF) method \cite{1} and its relativistic counterpart, the multiconfiguration Dirac–Fock (MCDF) method \cite{2}, are used extensively in calculating the discrete wavefunctions and discrete spectral properties of atomic systems. While MCHF and MCDF work with numerical orbitals, a similar method embodied in the CIV3 \cite{3} code obtains equivalent results using expansions of analytical orbitals with adjustable parameters. These are the primary methodologies employed to calculate the wavefunctions of the discrete initial state and final ionic state in the calculation of the photoionization of atomic systems. To obtain the final-state continuum wavefunction, and the dipole matrix elements and the photoionization cross sections, state-of-the-art methods include the random-phase approximation with exchange (RPAE) \cite{4, 5}, the relativistic random-phase approximation (RRPA) \cite{6}, many-body perturbation theory (MBPT) \cite{6}, multi-channel quantum defect theory (MQDT) \cite{8} and the \textit{R}-matrix method \cite{9, 10}.

For astrophysical modelling, however, data from the Opacity Project \cite{11} and the Iron Project \cite{12}, which are based on the Opacity Project \textit{R}-matrix method, nonrelativistic and relativistic respectively, provide a majority of the data for light atoms and ions, and most of these data result from nonrelativistic Opacity Project calculations.

On the experimental side, the past decade has seen an explosion of absolute cross section measurements of photoionization owing to the availability of intense light sources such as the Advanced Light Source (ALS) in the USA, ASTRID in Denmark, the Photon Factory in Japan and SuperACO in France. The merged-beam technique has been used in most measurements since the intensity of third-generation light sources has made this method practical \cite{13}. 
In the present work, photoionization cross sections of 14 members of the Be isoelectronic series are calculated using the relativistic Breit–Pauli $R$-matrix (BPRM) method [14]. In particular, the systems included in this investigation are \( \text{Be, B}^+, \text{C}^{+2}, \text{N}^{+3}, \text{O}^{+4}, \text{Ne}^{46}, \text{Mg}^{48}, \text{Si}^{+10}, \text{S}^{+12}, \text{Ar}^{+14}, \text{Ca}^{+16}, \text{Ti}^{+18}, \text{Cr}^{+20}, \) and \( \text{Fe}^{+22}; \) the choice of ions was dictated by the existence of experimental data and the astrophysical abundance which favours the even-Z systems. We report the ground-state and metastable-state cross sections and comment on their general behaviour along the sequence. The study also provides data for astrophysical models which are both complete and whose accuracy is assessable via comparison with experiments and other calculations. Extant experimental measurements include \( \text{Be}^{15, 16}, \text{B}^+^{17}, \text{C}^{+2}{18}, \text{N}^{+3}{19, 20} \) and \( \text{O}^{+4} {21}. \) Previous calculations include, in addition to Opacity Project [11, 22], work on \( \text{Be}^{23, 24}, \text{B}^+{25, 26}, \text{C}^{+2}{27–29}, \text{N}^{+3}{30} \) and \( \text{O}^{+4} {31}. \) Note that in the experimental results for the various ions, the target ion beams are often mixtures of the ground state \( 1s^22s2p^3 \) and metastable state \( 1s^22p^43P_0,1,2. \) Thus, in order to compare with experiment, calculations of both ground and metastable states are required, and the resulting cross sections are combined to match the composition of the experimental beams. In practice, however, the experimental fractions are often unknown and they are obtained by varying the fractions of the calculated cross sections to obtain optimal agreement with experiment. In addition, calculations using the nonrelativistic \((LS\text{-coupling})\) \( R \)-matrix method [9, 10], in each case, are also performed in an effort to assess the importance of relativistic interactions along the sequence.

In section 2, a brief description of \( R \)-matrix theory and the details of the calculation are presented. Section 3 reports the total cross sections resulting from our calculation, along with available experiments and other calculations. Comparisons and comments are also given here. Section 4 presents the conclusions.

2. Theory and method of calculation

The nonrelativistic \((LS\text{-coupling})\) photoionization processes given by

\[
1s^22s^2(1S^0) + h\nu \rightarrow [1s^2nl + e^-(kl')] \ell(1P^0)
\]

for ground-state photoionization and by

\[
1s^22s2p(3P^0) + h\nu \rightarrow [1s^2nl + e^-(kl')] \ell(3s^0, 3p^0, 3d^0)
\]

for metastable-state photoionization are considered in this work. In the relativistic case, the corresponding transitions are given by

\[
1s^22s^2(1S^0) + h\nu \rightarrow [1s^2nl + e^-(kl')] \ell(1P^0)
\]

and

\[
1s^22s2p(3P_0,1,2) + h\nu
\]

\[
\rightarrow [1s^2nl + e^-(kl')] \ell(3s^0, 3p_0,1,2, 3d_1,2,3)
\]

in \( LS\)J terms. However, in our Breit–Pauli calculations, the selection rule specifies only \( 0^0 \rightarrow 1^0 \) for ground state and \( 0^0 \rightarrow 1^e, 1^o \rightarrow (0^e, 1^e, 2^e) \) and \( 2^0 \rightarrow (1^e, 2^e, 3^e) \) for metastable-state transitions, where all these \( J\pi \) symmetries contain the contributions from all the possible \( LS \) terms. To construct the wavefunctions, we optimize the Slater-type orbitals, \( \phi_{\text{slat}} \), first discussed in [33]. We take the 1s and 2s orbitals from HF calculation by Weiss [34] and by Clementi and Roetti [35] and optimize other orbitals up to 4f with the CIV3 code [3]. In \( R \)-matrix theory [9, 10], the system consists of \( N + 1 \) electrons; the final state is the \( N \)-electron final state of the ion (known as a target state for historical reasons) plus a photoelectron. The \( N \)-electron configurations \( \phi_i \) are antisymmetric combinations of the one-electron orbitals. Using these configurations as a basis set, we diagonalize the \( N \)-electron Hamiltonian \( H(S) \) for each \( LS \) term to get target states, \( \Phi_j \), the final states of the ion minus the photoelectron. Of course, in an exact calculation, there must be an infinite number of configurations to complete the basis set, but we include only the ones that we believe to be the most important from a physical point of view. In the present work, nine configurations are employed: \( 1s^22s, 1s^22p, 1s^23s, 1s^23p, 1s^23d, 1s^24s, 1s^24p, 1s^24d \) and \( 1s^24f\). This list was dictated by the need to include all channels which can be open in the energy range considered herein; it also includes the \( 1s^24f\) channels which remain closed. Furthermore, some test calculations with the inclusion of some of the \( 1s^25l \) channels showed these to be quite unimportant in the photon energy range up to the first \( 1s^24f\) threshold. In the relativistic \((BP)\) calculation, relativistic corrections are added to the Hamiltonian and the expansion of target states is specified by \( LSJ \) terms. The resulting target state energies, shown in table 1 for four of our Li-like target (final state) ions, are compared with NIST values [36]. The agreement, an indication of the accuracy of the \( N \)-electron wavefunctions, is seen to be excellent. Note that the lack of spin–orbit splitting in the table for neutral Be reflects the fact that the splitting is so small that it shows up only in the fourth decimal place, and the table gives the energies only to three places.

\( R \)-matrix theory divides configuration space into an inner and an outer region, separated by a spherical shell of radius \( r_o \) centred at the nucleus. In the inner region, all \( N+1 \) electrons are treated on an equal footing and all exchange effects are considered. The \( (N+1)\)-electron wavefunction for the symmetry \( SL\pi \) (and \( J \) in the BP calculation) is given by

\[
\psi_k^{SL\pi} = A \sum_{ij} c_{ijk} \Phi_i \left(S_L^i; x_1, x_2, \ldots, x_N, \hat{r}_{N+1}\right) \frac{F_j(r_{N+1})}{r_{N+1}} + \sum_j d_{jk} \chi_j^{SL\pi}
\]

where \( \Phi_i \) are the target state wavefunctions coupled with the angular and spin parts of the photoelectron, \( A \) is the antisymmetry operator, \( F_j \) are the continuum wavefunctions of the photoelectron and \( \chi_j \) are the \( (N+1)\)-electron bound state wavefunctions. The summation over \( ij \) of the first term is over all open channels of \( \Phi_i \) and over all continuum electron orbitals \( F_j \) to give the \( SL\pi \) symmetry. The summation over \( j \) of the second term is over all \( (N+1)\)-electron bound states to ensure the completeness of the basis. In the outer region, the system is simplified as a two-body system where the photoelectron is in a long-range multipole field. The wavefunction in this
energies are relative to the $1s^22s^2$ ground-state energy.

Table 1. Energy levels (in Rydbergs) in the present work and in NIST data [34] for the Li-like target ions Be$^+$, Ne$^{17}$, S$^{13}$, and Fe$^{23}$. All energies are relative to the $1s^22s^2$ ground-state energy.

| Ion   | Present | NIST       | Ion   | Present | NIST       |
|-------|---------|------------|-------|---------|------------|
| Be$^+$ Z = 4 | 2p$^2$P$^0_{1/2}$ | 0.293 0.291 | 1.176 1.168 | 2.053 2.045 | 3.602 3.572 |
|       | 2p$^2$P$^3/2$   | 0.293 0.291 | 1.191 1.183 | 2.189 2.182 | 4.745 4.745 |
|       | 3s$^2$S$^1/2$   | 0.799 0.804 | 10.018 10.023 | 29.345 29.344 | 84.508 84.497 |
|       | 3p$^2$P$^0_{1/2}$ | 0.876 0.879 | 10.338 10.341 | 29.911 29.908 | 85.515 85.460 |
|       | 3p$^2$P$^3/2$   | 0.876 0.879 | 10.342 10.346 | 29.951 29.949 | 85.844 85.815 |
|       | 3d$^2$D$^1/2$   | 0.888 0.894 | 10.450 10.457 | 30.163 30.156 | 86.234 86.197 |
|       | 3d$^2$D$^3/2$   | 0.888 0.894 | 10.451 10.455 | 30.175 30.169 | 86.343 86.321 |
|       | 4s$^2$S$^1/2$   | 1.047 1.052 | 13.386 13.392 | 39.368 39.364 | 113.627 113.584 |
|       | 4p$^2$P$^0_{1/2}$ | 1.077 1.082 | 13.517 13.522 | 39.599 39.594 | 114.020 113.989 |
|       | 4p$^2$P$^3/2$   | 1.077 1.082 | 13.519 13.524 | 39.616 39.612 | 114.156 114.135 |
|       | 4d$^2$D$^1/2$   | 1.082 1.088 | 13.563 13.570 | 39.703 39.700 | 114.319 114.266 |
|       | 4d$^2$D$^3/2$   | 1.082 1.088 | 13.564 13.570 | 39.708 39.706 | 114.365 114.320 |
|       | 4f$^2$F$^1/2$   | 1.083 1.088 | 13.565 13.573 | 39.713 39.710 | 114.374 114.342 |
|       | 4f$^2$F$^3/2$   | 1.083 1.088 | 13.566 13.573 | 39.715 39.712 | 114.397 114.379 |

Table 2. Binding energies (in Rydbergs) of all 1s$^2$2s$^2$ ground-state ions in the present work and in NIST data [34].

| Ion   | Present | NIST       | Ion   | Present | NIST       |
|-------|---------|------------|-------|---------|------------|
| Be Z = 4 | 0.682 0.685 | Si$^{10}$ Z = 14 | 35.008 35.012 |
| B$^+$ Z = 5 | 1.844 1.849 | S$^{12}$ Z = 16 | 47.942 47.930 |
| C$^{12}$ Z = 6 | 3.514 3.520 | Ar$^{14}$ Z = 18 | 62.920 62.897 |
| N$^{13}$ Z = 7 | 5.688 5.694 | Cs$^{16}$ Z = 20 | 79.957 79.900 |
| O$^{14}$ Z = 8 | 8.365 8.371 | Ti$^{18}$ Z = 22 | 99.069 98.960 |
| Ne$^{16}$ Z = 10 | 15.228 15.234 | Cr$^{20}$ Z = 24 | 120.276 120.100 |
| Mg$^{16}$ Z = 12 | 24.107 24.100 | Fe$^{22}$ Z = 26 | 143.601 143.953 |

Table 3. Binding energies (in Rydbergs) of all 1s$^2$2s2p$^3$P$^0$ metastable ions in the present work and in NIST data [34].

| Ion   | Present | NIST       | Ion   | Present | NIST       |
|-------|---------|------------|-------|---------|------------|
| Be Z = 4 | 0.482 0.485 | Si$^{10}$ Z = 14 | 33.456 33.464 |
| B$^+$ Z = 5 | 1.502 1.509 | S$^{12}$ Z = 16 | 46.122 46.115 |
| C$^{12}$ Z = 6 | 3.034 3.042 | Ar$^{14}$ Z = 18 | 60.831 60.813 |
| N$^{13}$ Z = 7 | 5.072 5.082 | Ca$^{16}$ Z = 20 | 77.598 77.546 |
| O$^{14}$ Z = 8 | 7.614 7.625 | Ti$^{18}$ Z = 22 | 96.436 96.334 |
| Ne$^{16}$ Z = 10 | 14.209 14.220 | Cr$^{20}$ Z = 24 | 117.365 117.202 |
| Mg$^{16}$ Z = 12 | 22.821 22.820 | Fe$^{22}$ Z = 26 | 140.411 140.760 |

The region is given by

$$\Psi_{\text{LS}} = \sum_{ij} \epsilon_{ij} \Phi_i \left( S_i L_i; x_1, x_2, \ldots, x_N, \tilde{\xi}_{N+1} \right) \frac{F_j(r_{N+1})}{r_{N+1}}, \tag{6}$$

Note that there is no exchange term between the photoelectron and any other electron in this outer region. Then enforcing continuity at the boundary, we get the wavefunctions in both regions with the R-matrix as a connection between the parts. The Breit–Pauli version includes the relativistic corrections to the Hamiltonian to improve the accuracy in dealing with heavier ions.

When the initial wavefunction and the final wavefunction (for some specific total energy) are known, the photoionization cross section $\sigma$ is calculated by using the electric dipole approximation to evaluate the transition matrix.

Both initial and final states use the same set of orbitals optimized in CIV3. Since these orbitals are optimized for the target states, this might cause some problem in constructing the $(N+1)$-electron initial state. As seen in table 2, where ground initial state binding energies of all ions in our calculations are compared with NIST values [36], this is only a problem (and a slight one) at the very high end of the sequence, and similarly in table 3 for the metastable initial state binding energies. Increasing the basis set to take care of this problem simply shifts the ground-state energy, thereby shifting the whole cross section in energy, with essentially no effect on the dipole matrix elements. This is owing to the use of the orbitals optimized for the three-electron final states to expand the initial four-electron wavefunction. Such an increase in the basis set, simply to obviate an overall energy shift, was not considered to be worthwhile.
3. Results and discussion

3.1. Cross sections

The total photoionization cross sections, calculated using the BPRM, along the Be-like isoelectronic sequence for the $^1S_0$ ground state are shown in figure 1 and for the $^3P_0$ metastable state shown in figure 2 over the photon energy range (in Rydbergs) from the lowest ionization threshold up to 4f threshold. Actually, there are three metastable levels, $^3P_0$, $^3P_1$ and $^3P_2$, and their cross sections are almost identical. Thus, rather than showing each of them, figure 2 shows a statistical average of the three cross sections. Since the agreement of length and velocity gauges in our calculations is excellent (within a few per cent, at worst), all of our calculated cross sections are shown only in length gauge; it is of importance to emphasize that the agreement between length and velocity is a necessary condition for accuracy of calculated photoionization cross sections. Some general features of the evolution of these ground- and metastable-state cross sections are noted.

The resonances dominating the threshold region of each of the cross sections are the 2p$^n$s and 2p$^n$d autoionizing states. At higher energies are the manifolds of resonances converging to the $n = 3$ and the $n = 4$ states of the final state ions. It is interesting to note that the cross sections for the ground and metastable states are qualitatively similar, despite the fact that they are of differing parities, thereby connecting to opposite parity continua, and of different spin-multiplicity, so they connect to continua of different spin-multiplicity.

The area under the cross section curves, in Mb-Ryd, divided by 8.07 is the total oscillator strength over that energy region [37]; owing to the well-known sum rule [37], the total oscillator strength from the outer shell is 2 which is the number of outer-shell electrons. This sum includes the discrete oscillator strengths for the excitations below the ionization threshold, and these are large, e.g. in neutral Be, the 2s$\rightarrow$2p transition has an oscillator strength of 1.36 [38]. It is found, from the present results, that the oscillator strength from the first threshold to the 1s4f$^7\frac{1}{2}$ threshold is approximately 0.4 and is about the same for all Z considered and for
both initial states. Then, since the energy scale increases roughly as $Z^2$ (the hydrogenic energy scaling), it is evident that the cross sections must decrease as $1/Z^2$ to preserve the oscillator strength; the data figures 1 and 2 observe this scaling exactly.

The energy separations between $nl$ and $nl'$, on the other hand, do not increase as $Z^2$ along the isoelectronic sequence; they increase, but only roughly as $Z$. For example, the interval between 2s and 2p thresholds is 0.293 Ryd in Be ($Z = 4$), which is about 27% of the range from 2s threshold to 4f threshold. This percentage is down to 8.8% in Ne$^{16}$ ($Z = 10$), 5.5% in S$^{12}$ and 4.1% in Fe$^{22}$. Of course in the $Z \to \infty$, hydrogenic, limit levels of the same principal quantum number are degenerate (nonrelativistically) asymptotically, so a different energy dependence is expected. In any case, owing to the differences in the dependences of the thresholds of differing $n$ and $l$ along the isoelectronic sequence, the overlapping of resonances converging to a threshold having the same principal quantum is considerably altered as a function of $Z$. Of course, with increasing $Z$, spin–orbit effects, which increase as $Z^4$, become important so the situation for the higher-$Z$ ions is rather more complicated.

The width of a resonance indicates the strength of the Coulomb matrix element of the quasi-discrete resonance state with the final continuum state. The resonance widths increase slowly with $Z$ while the energy range grows with $Z^2$ as described above; actually, in the hydrogenic limit, the resonance widths are independent of $Z$ [39]. As a total effect, the widths of the resonances relative to the energy range decrease with increasing $Z$, making $\sigma(E)$ a smoother function and the resonance structures less important in the sense that less of the energy range is resonant and more is nonresonant background cross section. Thus, in the heavier ions, the background cross section can be fit more easily by a simple function without too much disturbance by the resonances. At the lower end of the sequence, owing to the extent of the resonance widths, this is more problematic. Furthermore, the widths also decrease relative to the energy separation of the resonances, with increasing $Z$, strongly affecting the resulting cross section in the resonance region.

Figure 2. As figure 1 but for the 1s$^2$2s2p$^3$P$^0$ metastable state. The cross section shown is a statistical average of the three individual $^3P_j$ cross sections.
There is clearly a wealth of information concerning the evolution of the resonances along the isoelectronic sequence, but the details will be presented in a separate paper.

3.2. Comparison with experiment

3.2.1. Be. For the neutral Be atom two experiments in separate energy ranges have been reported, both performed at the University of Wisconsin Synchrotron Radiation Center (SRC). Wehlitz et al [15] measured the ground-state cross section from the ionization threshold at 9.3227 eV to the 2p threshold at 13.277 eV with energy step (ΔE) 20 meV below, 5 meV beyond, 12.60 eV and monochromator bandpass of 12 meV, which we take as the full width at half maximum (FWHM) when convoluting our theoretical cross section calculated with energy step ΔE = 68 μeV. Figure 3 shows the present BPRM and nonrelativistic LS R-matrix cross sections along with the experimental results from 9.2 eV to 13.3 eV. From the comparison of the BPRM and LS results it is clear that relativistic effects in the photoionization of neutral beryllium are negligible. The present theoretical results show excellent agreement with experiment below about 12.5 eV, but the experimental peaks seem to be truncated, compared to theory, at higher energy. It is evident, however, that the positions of the resonances are in excellent agreement over the whole range. We can think of no explanation for the lower resonances in the series being more accurate than the higher members, so this could be an experimental problem.

In the higher energy range, near 3s and 3p thresholds, SRC measurements were made by Olalde-Velasco et al [16] with energy step 15 meV from 16 eV to 19.5 eV and 5 meV beyond 19.5 eV. With our energy step ΔE = 68 μeV, we convolute our result with FWHM = 27.5 meV and FWHM = 7.5 meV, below and beyond 19.5 eV respectively, to compare with experiment. BPRM and nonrelativistic cross sections as well as the measurement are shown in figure 4. Just as in the lower energy range, the difference between BPRM and nonrelativistic results is negligible. The overall background cross section in the calculation is about 0.6 Mb higher than the measurement, and there is a 0.1 eV energy shift between calculation and measurement.

3.2.2. B⁺. The B⁺ calculation is compared with the measurement by Schippers et al [17] at Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory (LBNL). The measurement was done with ΔE = 4 meV from 22.50 eV to 31.26 eV, whereas our calculation was performed with ΔE = 13.6 μeV. In the calculation, we assume that the initial beam has 71% 1S̄0 ground-state ions and 29% 3P̄1 metastable-state ions [17]. The calculations and the measurement are shown in figure 5. Both calculations are convoluted with FWHM = 25 meV. Below the ground-state ionization threshold at 25.091 eV (calculated result), the cross section is generated from metastable-state photoionization only. The theoretical threshold for the metastable state is 20.44 eV in the present calculation, which the experiment could not identify because the photon flux was too low. The difference between the BPRM result and the nonrelativistic result is clearly due to the splitting of the resonances in this region. BPRM clearly shows the peaks that are missing in the nonrelativistic cross section. The BPRM result matches the measurement well except for an overall energy shift of about 0.05 eV.

3.2.3. C²⁺. In the C²⁺ ion, the experiment was conducted by Müller et al [18] at ALS. It was done with ΔE = 4 meV from
Figure 4. Photoionization cross section of the ground-state Be from 16 eV to 21.5 eV: (a) present BPRM result (BP), (b) present nonrelativistic result (NR), (c) experiment (Exp) [16]. Both theoretical cross sections were calculated with energy step $\Delta E = 68 \mu eV$, and convoluted with FWHM = 5 meV to match experiment.

Figure 5. Photoionization cross section of B+ from 22.5 eV to 31.25 eV. The theoretical results are a weighted sum of ground-state (71%) and metastable $^3P_0$ state (29%) cross sections [17]: (a) present BPRM result (BP), (b) present nonrelativistic result (NR), (c) previous BPRM result [17] multiplied by 1.05 (BP) [17]), (d) experiment (Exp) [17]. Both present results were calculated with energy step $\Delta E = 13.6 \mu eV$ and convoluted with FWHM = 25 meV to match experiment. The previous BPRM result was convoluted in the same manner, and the ground and metastable state results were shifted by –22 meV and 4 meV, respectively, to match the measurement.

40.84 eV to 56.98 eV. We assume that 60% of the ions were in the $^1S_0$ ground state and 40% in the $^3P^o$ metastable state in the initial ion beam: specifically, 30% $^3P_0^o$ and 5% each of $^3P_1^o$ and $^3P_2^o$ [18]. The calculations used an energy step size $\Delta E = 12.2 \mu eV$ and are convoluted with FWHM = 30 meV. As shown in figure 6, similar to the B+ case, the splitting is the biggest difference between the two calculations. Compared with the experiment, the experimental threshold energies 41.39 eV and 47.89 eV are higher than the present values 41.28 eV and 47.81 eV for the metastable state and the ground state respectively. The theoretical background cross section is a bit higher than experimental cross section near the 2p3/2
threshold of \( ^1S_0 \) ground state at 55.8987 eV. Other than that, our BPRM result matches the experiment well in all resonance positions and widths.

### 3.2.4. N\(^{+3}\)

Experimental work on N\(^{+3}\) ions was performed by Bizau \textit{et al} [19] at ASTRID at the University of Aarhus. They obtained the cross section with \( \Delta E = 100 \) meV in the range 63.00–90.00 eV. In our calculation, we used \( \Delta E = 13.6 \) \( \mu \)eV and convoluted the result with FWHM = 230 meV. The fractions of \( ^1S_0 \) ground state and \( ^3P \) metastable state are assumed to be 65\% and 35\% respectively [19]; in the absence of any more detailed information on the excited initial states, we assumed that the three metastable states were populated statistically. In figure 7, it is seen that the difference between BPRM and the nonrelativistic results is that the peak heights and strengths in the metastable region below 79 eV are larger in the BPRM case. This is likely because the inclusion of relativistic effects in the BPRM calculation opens photoionization channels that are forbidden in the nonrelativistic \( LS \) case, thereby increasing the resonance oscillator strengths. Comparing our BPRM calculation with experiment, we find that in the low-energy range where only the metastable state contributes, the background agrees well but the resonances are slightly weaker than experiment, but much closer than the nonrelativistic results. In the higher-energy range where ground-state photoionization dominates, the experimental cross section is very noisy and it is difficult to pick out the higher resonances, but the first few show reasonable agreement. The nonresonant background cross sections are in good agreement in the lower energy region where only the metastables contribute, but theory is a bit higher than experiment at the higher energies where ground-state photoionization dominates.

In addition, there has been some recent high-resolution experimental work in very narrow energy ranges reported [20]: the region of the metastable thresholds, and the region of the 2p5p resonances. Apart from a small energy shift, our calculations, convoluted with the experimental resolution (not shown), show excellent agreement.

### 3.2.5. O\(^{+4}\)

The measured cross section was obtained by Champeaux \textit{et al} [21] at SuperACO at LURE in France with \( \Delta E = 56.4 \) meV in the range from 99.60 eV to 129.75 eV. In the calculation, we had an energy step size \( \Delta E = 13.6 \) \( \mu \)eV and it was convoluted with the experimental FWHM = 250 meV. The experiment reported fractions of 50\% \( ^1S_0 \) ground-state ions and 50\% \( ^3P \) metastable-state ions in the beam; since no breakdown of the metastable part of the beam was reported, we assumed a statistical distribution as in the N\(^{+3}\) case, discussed above. Similar to N\(^{+3}\) ions, in figure 8 the BPRM cross section shows stronger resonances than those in the nonrelativistic one in the region of the spectrum due to metastable photoionization only. The reason is presumably the same as that in the N\(^{+3}\) case, discussed above. Similar to N\(^{+3}\) ions, in figure 8 the BPRM cross section shows stronger resonances than those in the nonrelativistic one in the region of the spectrum due to metastable photoionization only. The reason is presumably the same as that in the N\(^{+3}\) case, the comparison between our calculation and the experiment is also similar to the N\(^{+3}\) case. The background and resonance positions match well with experiment in the metastable region, but it is much harder to read the resonance information in the ground-state region in the experiment.

### 3.3. Comparison with other calculations

The details of Opacity Project (OP) were described by Seaton [11]; the photoionization of Be-like ions was studied by Tully...
Figure 7. Photoionization cross section of N^3+ from 65 eV to 90 eV. The theoretical results are a weighted sum of ground-state (65%) and metastable-state (35%) cross sections [19]; it was assumed that the metastable fractions were statistical. Shown are (a) present BPRM result (BP), (b) present nonrelativistic result (NR) and (c) experiment (Exp) [19]. Both present results were calculated with energy step $\Delta E = 13.6 \mu eV$ and convoluted with FWHM = 230 meV to match experiment.

Figure 8. Photoionization cross section of O^4+ from 95 eV to 130 eV. The theoretical results are a weighted sum of ground-state (50%) and metastable-state (50%) cross sections [21]; it was assumed that the metastable fractions were statistical. Shown are (a) present BPRM result (BP), (b) present nonrelativistic result (NR) and (c) experiment (Exp) [21]. Both present results were calculated with energy step $\Delta E = 13.6 \mu eV$ and convoluted with FWHM = 250 meV to match experiment.

et al [22]. OP includes atomic data of 15 isoelectronic ions up to Fe^{22+} based on the nonrelativistic $R$-matrix calculation. To give a flavour of the comparison of the OP results with the present BPRM data, and how it changes along the isoelectronic sequence, the comparisons for Be, Ne^{6+}, Ar^{14+} and Fe^{22+} are shown in figures 9–12 respectively for both ground and metastable states; our BPRM results are the statistical average of the three $^3P_0$ metastable states. For Be, figure 9, the ground-state comparison shows that the OP ground-state threshold energy is a bit lower than the BPRM result and, thus, lower than the experimental (NIST) value, by about 0.1 eV. For the metastable state, the OP threshold is too low by considerably more than that. Consequently, the OP metastable cross section at threshold is about 10% too high. In addition,
careful comparison reveals that the OP resonances are at somewhat different energies than the present BPRM results. Since the latter are in good agreement with experiment, as detailed above, it is evident that the OP calculation is lacking in this respect as well. Furthermore, the OP calculations employed a smaller basis set than was used in the present calculations, so many of the higher resonances are absent. Most important, however, is that the energy mesh used in the OP calculation is seen to be much too coarse to correctly reproduce the resonances in both ground and metastable states. This results in much of the resonance oscillator strength being absent from the OP cross sections, as seen in figure 9.

For Ne$^{6+}$, shown in figure 10, the comparison is qualitatively similar, but the discrepancies are quantitatively greater, owing to the fact that relativistic interactions are more important in Ne$^{6+}$ than in neutral Be; for Ne$^{6+}$, the OP thresholds are too low by several eV and the 2p thresholds are
seen to be even worse, especially for the ground state. Further, owing to the energy step size, the higher $2pnl$ resonances are absent from the OP results.

Going up to Ar$^{14}$, figure 11, the comparison is seen to be dramatically worse. The OP thresholds are off by of the order of 20 eV. In addition, the resonances are almost unobservable; and those that are seen are at rather incorrect energies. Only the OP background, nonresonant cross section is reasonably good in this case. However, we note that the OP background cross section is not significantly better than the results of a central-field Hartree–Slater (HS) calculation which gives a threshold value of the ground-state cross section of about 0.11 Mb [40], in good agreement with these results.

For Fe$^{22}$, figure 12, the comparison is similar to the Ar$^{14}$ case, but even further apart. The OP thresholds are so far off that the whole OP resonance region converging to 2p ranges from 137 Ryd to 142 Ryd, but it ranges from 143 Ryd to 148 Ryd in the present work, and there is no overlap between
these regions between the two calculations. The OP thresholds are off by ~100 eV! Again, the OP background cross section is reasonably accurate, but so is the simple HS result of the compilation of [40].

Several photoionization calculations of lower members of the isoelectronic sequence, Be [23, 24], B+ [25, 26] and C++ [27, 28], have been calculated for both ground and metastable states using a variational R-matrix method (VRM) [41]. In these calculations, the 1s2 core is replaced by an effective potential which is optimized by comparison of binding energies with experiment, and the wavefunctions of the two outer electrons are solved by the Schrödinger equation. The basic differences between this method and the present calculation are that the variational R-matrix calculations are nonrelativistic while ours include relativistic effects and also, that the method is semi-empirical, based on optimizing the potential due to inner-shell electrons to fit experimental energies, while ours is purely ab initio. In figures 13–15 comparisons of the present BPRM photoionization cross sections with the variational R-matrix results are shown for Be, B+ and C++ ions, respectively; all cross sections presented are in length gauge since the length and velocity results essentially coincide in both calculations. Our cross sections are generally in good agreement with the variational R-matrix results, but there are a few differences in all three cases. First, both our 1S00 ground-state and 3P0 metastable-state ionization thresholds are lower than the variational R-matrix values. Second, the inclusion of relativistic effects opens more ionization channels, which cause splitting of some of the resonances, as seen in the figures. Third, there are differences in the shapes of the resonances at the beginning of some Rydberg series. For example, in figure 13, the thin resonance near 11.8 eV is seen to have a different shape in the two calculations which amounts to almost a vertical flip, and a similar flip occurs around 23.2 eV in B+. This means that in the analysis of the Beutler–Fano profile of resonance, the v value has opposite sign in the two calculations, which implies either the discrete or the continuum final state at the corresponding energy has a phase difference between the calculations.

There have also been calculations of the photoionization of C++ [29, 30], N++ [30] and O+++ [31] using orbitals obtained with the SUPERSTRUCTURE code [42] and nonrelativistic R-matrix to calculate the cross sections, except for C++ where a relativistic calculation was also done. Figures 16–18 show the comparison of our BPRM cross sections with the previous nonrelativistic results [30, 31] for both ground and metastable states of C++, N++ and O+++ ions, respectively. The general features of the cross sections, such as the ionization thresholds, resonance positions and widths, match pretty well. As seen in these figures, however, the main difference between their calculations and ours is the splitting of resonances due to relativistic effects. Looking at the comparison of ground-state photoionization of O+++ (figure 18), it appears that there is more structure in the results of [31] in the 14.5–16 Rydberg energy region than in the present calculation. This occurs because the calculations of [31] are nonrelativistic; the addition of relativistic interactions spreads the oscillator strength (which is conserved) over many smaller structures in the present results. Note further that the comparison of their results with our nonrelativistic cross sections (not shown) show excellent agreement, thereby indicating that these earlier calculations include the important physics, except for the relativistic effects. To emphasize this point, note that using the same methods for discrete states, but with a BPRM formulation for the continuum
Figure 14. As figure 13 for B⁺; the VRM results are from [25] and [26] for ground and metastable states, respectively.

Figure 15. As figure 13 for C⁴⁺; the VRM results are from [27] and [28] for ground and metastable states, respectively.

states, the relativistic photoionization calculation for C⁴⁺ was performed [29] and included both ground and metastable states [43]; the comparison with the present BPRM results is shown in figure 19, where excellent overall agreement is seen, both as to resonance positions and background nonresonant cross sections. Some small differences are seen in the amplitudes and shapes of the very narrow resonances. Also, for the ground-state cross section, the peaks of the [29] higher resonances of the major series are erratic, while our results are not. We attribute this to a lack of sufficient density of energy points in the neighbourhood of these resonance peaks in [29]. A similar BPRM calculation [31] for O⁺ has been performed (not shown) and the agreement with the present calculation is similar to that of the C⁴⁺ comparison exhibited in figure 19.

BPRM calculations of the photoionization of B⁺ [17], C⁴⁺ [18] and N⁴⁺ [20] using the same discrete orbital methodology as used in the present paper have also been reported. For the B⁺ and C⁴⁺ cases, the results for the experimental admixture of ground and metastable states, suitably convoluted with the experimental width, are shown in figures 5 and 6 respectively. As can be seen, they are almost identical to the present BPRM results. This is hardly surprising since the two calculations used essentially the same target states, although somewhat
3.4. Comparison between LS-coupling and BP calculations

To pinpoint the influence of relativistic effects, calculations have been performed at both the LS-coupling and Breit–Pauli (BP) levels, using exactly the same radial basis set and radial wavefunctions; this procedure ensures that any differences in the cross sections resulting from the two levels of calculation are due solely to relativistic effects. For the first five members of the sequence, both the LS-coupling and BP calculations are shown in figures 3–8. In this low-$Z$ part of the isoelectronic
sequence, it was seen that there were only small differences between LS and BP results; of importance, however, is that in every case, the relativistic result is closer to experiment. Owing to the experimental resolution that our theoretical results have been convoluted with, it is difficult from these figures to make any statement about how the importance of relativistic effects changes with increasing Z. However, looking at our unconvoluted results (not shown), it is clear that relativity becomes more important with increasing Z.

To explore this further, the comparison for Ne$^{+6}$ is shown in figure 20 with no convolution for both ground- and metastable-state cross sections; the metastable BP result presented is a statistical average of the cross sections of the three $^3P^o_j$ metastable states. While the background cross sections are the same, in both cases, the resonances are seen to differ in position, size and shape, particularly for the excited state. As an example, for the ground-state resonance at about 19.15 Ryd, the nonrelativistic position is about 0.04 Ryd (0.54 eV) lower than the BP location, which is caused by the relativistic shift of the ground-state energy plus the shift of the threshold energies of the final states of the ion. Further, for the photoionization of the initial excited metastable states, there is a marked difference in the size and shape of the resonances between LS and BP results that is not evident.
for ground-state photoionization. This is seen in figure 20 in the 21.2 Ryd photon energy region where a large narrow nonrelativistic resonance is ‘surrounded’ by a number of smaller relativistic resonances. This disagreement occurs primarily because the three relativistic metastable states have differing threshold energies which results in the resonances being located at somewhat different energies. Thus, in a statistical average, instead of a single resonance, as in the \( L_S \) case, there are three resonances ‘sharing’ the oscillator strength which is more or less preserved.

As \( Z \) increases further, the energy shifts are expected to grow larger, and, looking at the comparison for \( S^{+12} \), shown in figure 21, this is true. Here, shifts in thresholds and resonances of about 0.2 Ryd (2.7 eV) are evident. And, for \( Fe^{+22} \), shown in figure 22, shifts of thresholds and resonances as large as 1.6 Ryd, more than 20 eV, are noted. And for both \( S^{+12} \) and \( Fe^{+22} \) the discrepancies of the resonances for the excited state are evident, just as in the \( Ne^{+6} \) case discussed above. Furthermore, while only three of the higher members of the isoelectronic sequence are shown in detail, there is nothing special about those particular ions; the above discussion applies to all of the higher members of the sequence. In any case, it is clear that relativistic shifts become more and more important with increasing \( Z \).

The scale of the plots of figures 20–22 is such that the splitting of resonances is not seen. However, they are certainly there, and the splitting increases with \( Z \) also. The very small splitting of resonances for \( B^+ \) and \( C^{+2} \), seen in figures 5 and 6 respectively, is of the order of 100 meV. At the other end of the scale, for \( Fe^{+22} \), the splittings of the resonances can be as large as of the order of 10 eV. Also not evident from the plots is that the overlapping of resonance series is rather different in the \( L_S \) and BP cases, at the higher \( Z \). Thus, relativistic effects play an important role in perturbing the resonance positions, splitting them into doublets, and changing the overlaps among resonance series converging to different states of the final-state ion. The details of the resonances, and how they change as a function of \( Z \), will be reported and analysed in a separate paper.

4. Conclusions

From the comparison of our calculated cross sections for the ground and metastable states of a number of members of the Be isoelectronic sequence with experiment (where available) and previous calculations, we find that the relativistic Breit–Pauli \( R \)-matrix methodology, along with an extensive high-quality set of discrete orbitals to represent the final ionic (target) states and the initial states, provides an extremely accurate description of the photoionization process in the four-electron system. This is further confirmed by the excellent agreement between length and velocity gauges (within a few per cent), and by the excellent agreement of the initial state binding energies and target state excitation energies with the NIST data compilation, presented in tables 1–3.
In our study, it has been found that the overall magnitudes of the cross sections decrease with Z, which is necessary to satisfy the oscillator strength sum rule [37]. Inclusion of relativistic effects is found to be of importance to achieve high accuracy even at the lowest values of Z, owing to the splittings and shifts of the resonances engendered by these relativistic effects. And, since relativistic effects in energies increase as $Z^2$, while electrostatic energies increase as $Z^3$, these effects become much more important at higher Z; for Fe$^{28}$, for example, relativistic resonance energy shifts of close to 100 eV were found. And for the excited states, relativistic effects were even more important because the single nonrelativistic 3Po state is split into three states, 3Po, 3Pz, and 3Pz, each with a different threshold energy. Further, it is important to note that these conclusions should be quite general and not restricted just to the four-electron Be-like systems studied in detail here.

Many of the cross sections were seen to exhibit large numbers of very narrow resonances. Thus, to calculate cross sections which include all of the oscillator strength, the calculational energy mesh must be dense enough to include the maxima of these resonances. Furthermore, as seen in some of the comparisons of theoretical cross sections, some of the reported results contain the proper physics but are still inaccurate owing to the failure to include enough points in the energy mesh.

The results presented in this paper concern only the gross characteristics of the total cross sections. Clearly there is a wealth of information on the partial cross sections, cross sections for producing the various states of the three-electron final state ion. In addition, there are many series of autoionizing resonances converging to the various 1s2nl thresholds which have not yet been described or analysed, including overlapping of series converging to states of different principal quantum number, and how the resonances and the overlaps evolve as a function of Z. These issues shall be dealt with in future publications.

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