

Two-channel relativistic random-phase approximation applied to the photoionisation of helium- and beryllium-like ions[†]

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Abstract. Atomic photoionisation cross sections including both relativistic and correlation effects for the helium and beryllium isoelectronic sequences are calculated in a two-channel relativistic random-phase approximation (RRPA). By studying the relativistic E1 transition along the sequence, the coupling between the low-energy photoelectron and the core electron (electrons) is found to deviate from relativistic jj coupling even for high Z elements. The deviation of the sum of dipole oscillator strength from the non-relativistic Thomas-Reiche-Kuhn rule is also investigated.

1. Introduction

Atomic photoionisation has been studied over the years along two distinct lines. For low photon energies in the ultraviolet and in the soft x-ray region, photoionisation occurs primarily from the outer shells of atoms. Low-energy cross sections are calculated in the electric-dipole approximation, with wavefunctions determined according to non-relativistic many-electron theory (Fano and Cooper 1968, Starace 1978). The limitation of the non-relativistic model in predicting accurate photoionisation cross sections is often attributed to the inadequacy of approximate many-electron wavefunctions. At higher photon energies, the photoeffect is dominated by the photoionisation of inner-shell electrons. In this case, when photon wavelengths are small and the electric-dipole approximation is inappropriate, the contribution from higher electric and magnetic multipoles must be included (Pratt *et al* 1973, Scofield 1973). Furthermore, electronic wavefunctions must be calculated in the Dirac-Breit formulation because of the relativistic velocities of the inner electrons. Correlation effects, however, are generally believed to be very small, so relativistic calculations are done in the single-particle approximation.

In the last few years, it has become obvious that the distinction between high- and low-energy regions is no longer possible. High-precision photoelectron spectroscopy for heavy atoms reveals the importance of relativistic effects in the photoionisation of

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outer-shell electrons, in addition to the well-understood importance of electron correlation for such systems. Recent experiments on the branching ratios of cross sections for different atomic subshells (Wuilleumier *et al* 1977, Samson *et al* 1975) and a recent measurement of the asymmetry parameter β (Dehmer and Dill 1976, Torop *et al* 1976) indicate that the finer details of low-energy photoionisation experiments cannot be understood without including both relativity and correlation in the theory. Furthermore, the need for accurate photoionisation cross sections of highly charged ions in the study of energy balance and electron transfer in astrophysical and laboratory thermonuclear plasmas illustrates the importance of a relativistic theory of photoionisation including correlations.

Existing relativistic theories for photoionisation are formulated in the independent-electron approximation (Pratt *et al* 1973, Scofield 1973, Walker and Waber 1973). To include electron correlation in the relativistic wavefunctions, the conventional configuration interaction method can be used for bound states (Desclaux 1975). For continuum wavefunctions, however, a different method is required.

In a recent communication (Johnson and Lin 1977), we outlined a relativistic random-phase approximation (RRPA) for atomic photoionisation in which relativistic effects and the electronic correlation are both included. The theory was applied to the calculation of the photoionisation cross sections and asymmetry parameter β for He and Be atoms to test the RRPA procedures for simple systems where detailed non-relativistic calculations were already available. Comparison with non-relativistic results indeed shows that relativistic effects are very small for these two systems; however, relativistic effects are expected to be of increasing importance for higher members of the isoelectronic sequences. In this paper we apply the two-channel RRPA theory to the calculation of the photoionisation cross sections and other quantities of the helium and beryllium isoelectronic sequences; deviations from non-relativistic predictions with respect to nuclear charge and photoelectron energies are investigated systematically. In addition, the deviation of the electric-dipole oscillator strength sum from the non-relativistic Thomas-Reiche-Kuhn (TRK) sum rule is studied for the helium isoelectronic sequence.

2. Results and discussions

A detailed N -channel RRPA theory for photoionisation will be given elsewhere. In the present paper, we study photoionisation of He- and Be-like ions from their ground states within the relativistic E1 approximation. For He-like ions, this approximation leads to final states $(1s_{1/2}\epsilon p_{1/2})$ and $(1s_{1/2}\epsilon p_{3/2})$ with $J = 1$ and odd parity, where ϵ is the photoelectron energy. These two states are degenerate; they are uncoupled in the asymptotic region or when the residual Coulomb interaction between the photoelectron and the core electron is neglected. If this residual interaction is included, then a two-channel theory is required for photoionisation.

We have applied the two-channel RRPA theory to the calculation of the photoionisation cross sections and other related quantities for the He and Be isoelectronic sequences. The results are presented in the following subsections.

2.1. Threshold photoionisation cross sections

According to a non-relativistic hydrogenic calculation (Bethe and Salpeter 1957) the

oscillator strength for K-shell photoionisation is

$$\frac{df}{dE} = \frac{2^8}{3} \frac{I_K^3}{\omega^4} \frac{\exp(-4\nu \cot^{-1} \nu)}{1 - \exp(-2\pi\nu)} \quad (1)$$

where all the quantities are given in atomic units, $I_K = \frac{1}{2}Z^2$ is the K-shell ionisation energy, ω is the photon energy and ν is defined by $\omega = \frac{1}{2}Z^2(1 + \nu^{-2})$, where Z is the nuclear charge. At the threshold,

$$(df/dE)_{th} = \frac{256}{3} e^{-4} / I_K \quad (2)$$

or

$$I_K(df/dE)_{th} = 1.563. \quad (3)$$

Notice that the result (3) is independent of any *single* effective charge used for the hydrogenic potential. Deviation of $I_K(df/dE)_{th}$ for helium-like ions can be attributed to the non-hydrogenic nature of the potential for the low- Z elements and to relativistic effects for the high- Z elements. In table 1, we show I_K and $(df/dE)_{th}$ extrapolated from the two-channel RRPA calculation and the value $I_K(df/dE)_{th}$ for several helium-like ions. The threshold values of df/dE obtained from the non-relativistic Z expansion of Dalgarno and Parkinson (1967) for some of these ions are also shown for comparison. It is interesting to note that the RRPA values are higher than the Z -expansion values for low- Z elements because the two theories include different amounts of electron-electron correlation. For high- Z ions, the RRPA values become smaller since the K-shell orbitals shrink as a result of relativity. The value of $I_K(df/dE)_{th}$ is greater than the corresponding non-relativistic hydrogenic value for low- Z but smaller for high- Z elements.

Table 1. Oscillator strengths of helium-like ions at their respective ionisation thresholds. The figure in parentheses gives the power of ten by which the value should be multiplied.

Element	$I_K(\text{au})$	$(df/dE)_{th}$		$I_K(df/dE)_{th}$	
		RRPA ^a	Z expansion ^b	RRPA	NR ^c
Li ⁺	2.7926	0.645	0.644	1.80	1.563
Be ²⁺	5.6682	0.320	0.316	1.81	
C ⁴⁺	14.423	0.121	0.119	1.75	
O ⁶⁺	27.188	0.630(-1)	0.620(-1)	1.71	
Ne ⁸⁺	43.972	0.381(-1)	0.386(-1)	1.68	
Ca ¹⁸⁺	188.65	0.854(-2)	0.874(-2)	1.60	
Zn ²⁸⁺	436.61	0.359(-2)	0.377(-2)	1.57	
Mo ⁴⁰⁺	876.71	0.176(-2)		1.54	
Ag ⁴⁵⁺	1108.5	0.133(-2)		1.47	
Xe ⁵²⁺	1483.8	0.974(-3)		1.45	
W ⁷²⁺	2921.2	0.478(-3)		1.40	
Pb ⁸⁰⁺	3673.2	0.368(-3)		1.35	
U ⁹⁰⁺	4790.3	0.269(-3)		1.21	

^a Extrapolated from df/dE calculated at finite photoelectron energies.

^b From the Z expansion results of Dalgarno and Parkinson (1967).

^c Non-relativistic hydrogenic results.

The threshold oscillator strengths given in table 1 corresponds to the non-relativistic 1P channel. There is also a corresponding 3P channel contribution which will be discussed in § 2.4.

2.2. *E1 photoionisation cross sections for He-like ions*

In table 2, we present oscillator strengths for several He-like ions. The oscillator strengths are normalised to the threshold values given in table 1; the photoelectron energies are normalised to the K-shell ionisation energies which are also given in table 1. For elements with $Z < 10$, we present oscillator strengths for photon energies in the range $I_K < \omega < 10I_K$. For higher- Z elements, we present the values only for $I_K < \omega < 4I_K$ since the higher electric- and magnetic-multipole terms also become important for these systems. Our values serve to show how the E1 oscillator strengths vary along the isoelectronic sequence. The smooth variation in table 2 allows interpolation.

2.3. β parameter for the angular distribution of photoelectrons of He-like ions

According to non-relativistic theory, the β parameter for all He-like ions has the numerical value two. In table 3, we show the deviation of β from its non-relativistic value (the calculated RRPA values are smaller than two) for several higher- Z elements in the lower photoelectron energy region (in units of K-shell ionisation energies of the ions). Deviation from two is not significant until $Z \sim 42$ for a photoelectron energy of $E = 4I_K$, or $Z \approx 74$ for a photoelectron energy of $E = 0.5I_K$.

2.4. *Relativistic electric-dipole oscillator strength sum rule for He-like ions*

According to the non-relativistic Thomas-Reiche-Kuhn sum rule, the total electric-dipole oscillator strength summed over discrete states and integrated over continuum states is equal to the number of electrons. It has been shown that this is not valid in relativistic quantum mechanics (Levinger *et al* 1957, Payne and Levinger 1956). Deviations are attributed to the increase of electron mass due to its kinetic energy. In the calculations of Payne and Levinger (1956), contributions of all electric and magnetic multipoles to the oscillator strength are included; they obtain a value of 0.8 for hydrogenic ions with $Z = 82$. In table 4, we list the electric-dipole oscillator strength sum for helium-like ions and the contributions from both discrete and continuum states.

Several important features of the RRPA theory make the study of the sum rule possible. The non-relativistic RPA theory satisfies the TRK sum rule and furthermore the dipole oscillator strength evaluated using both velocity and length forms are identical (Amusia and Cheropkov 1975). Relativistically, it is possible to show that the RRPA theory is gauge invariant (Lin 1977) and that the corresponding length and velocity forms give identical oscillator strengths (Johnson and Lin 1976). Thus, the deviation of the dipole oscillator strength from the number of electrons is just that due to relativistic effects.

To obtain the electric-dipole sum, we calculate the discrete oscillator strengths for transitions $(1s^2)^1S_0 \rightarrow (1snp)^{1,3}P_1$ for $n = 2-8$. The contribution of higher- n states is evaluated by an extrapolation using quantum defects. The continuum oscillator strength is evaluated numerically to an energy point such that the total contribution from the higher-energy portion is less than 0.005. The sum of oscillator strengths on the higher-energy side is assumed to follow the high-energy behaviour of equation (1).

Table 2. dI/dE of helium-like ions in the relativistic dipole approximation, normalised to their respective threshold value $(dI/dE)_{th}$. The photoelectron energy is given in units of ionisation potential I_K to show the smoothness of the Z dependence. The figure in parentheses gives the power of ten by which the values should be multiplied.

E	Li^+	Be^{2+}	C^{4+}	O^{6+}	Ne^{8+}	Ca^{18+}	Zn^{28+}	Mo^{40+}	W^{72+}	Pb^{80+}	U^{90+}
0.05	0.919	0.901	0.894	0.887	0.885	0.882	0.882	0.871	0.871	0.870	0.869
0.1	0.844	0.813	0.799	0.790	0.790	0.781	0.779	0.767	0.762	0.760	0.756
0.15	0.774	0.736	0.717	0.707	0.704	0.694	0.691	0.681	0.670	0.667	0.663
0.2	0.710	0.668	0.646	0.634	0.631	0.620	0.616	0.602	0.591	0.587	0.584
0.25	0.651	0.607	0.583	0.572	0.569	0.555	0.551	0.539	0.526	0.520	0.515
0.4	0.508	0.464	0.438	0.426	0.422	0.408	0.403	0.392	0.373	0.368	0.364
0.6	0.373	0.334	0.310	0.299	0.295	0.283	0.277	0.267	0.247	0.243	0.239
0.8	0.280	0.247	0.227	0.218	0.214	0.203	0.198	0.190	0.171	0.167	0.164
1.0	0.215	0.188	0.171	0.164	0.160	0.151	0.146	0.139	0.122	0.119	0.116
1.5	0.121	0.103	0.923(-1)	0.876(-1)	0.859(-1)	0.792(-1)	0.759(-1)	0.705(-1)	0.589(-1)	0.566(-1)	0.559(-1)
2.0	0.763(-1)	0.626(-1)	0.549(-1)	0.519(-1)	0.509(-1)	0.464(-1)	0.438(-1)	0.399(-1)	0.319(-1)	0.309(-1)	0.299(-1)
4.0	0.177(-1)	0.144(-1)	0.124(-1)	0.115(-1)	0.112(-1)	0.982(-2)	0.887(-2)	0.756(-2)	0.543(-2)	0.503(-2)	0.455(-2)
7.5	0.367(-2)	0.283(-2)	0.246(-2)	0.227(-2)	0.218(-2)	0.111(-2)	0.102(-2)	0.922(-3)			
10.0	0.165(-2)	0.156(-2)	0.111(-2)	0.102(-2)	0.922(-2)						

Table 3. Deviation of the β parameter from the non-relativistic value of two for He-like ions as a function of photoelectron energy E in units of the ionisation potential I_K . The β parameter is given by $2 - \gamma$, where γ is the entry in the table. The figure in parentheses gives the power of ten by which the value should be multiplied.

Element	E					
	0.1	0.3	0.5	1.0	2.0	4.0
Ne ⁸⁺	1.5(-5)	1.8(-5)	2.5(-5)	4.1(-5)	9.4(-5)	2.5(-4)
Ca ¹⁸⁺	2.9(-4)	4.0(-4)	5.1(-4)	8.7(-4)	1.8(-3)	4.8(-3)
Zn ²⁸⁺	1.6(-3)	2.1(-3)	2.8(-3)	4.7(-3)	9.8(-3)	2.6(-2)
Mo ⁴⁰⁺	6.7(-3)	9.2(-3)	1.2(-2)	1.9(-2)	4.1(-2)	0.10
Xe ⁵²⁺	1.9(-2)	2.6(-2)	3.3(-2)	5.5(-2)	0.11	0.27
W ⁷²⁺	7.7(-2)	9.9(-2)	0.12	0.20	0.39	0.77
Pb ⁸⁰⁺	0.12	0.16	0.20	0.31	0.55	0.99
U ⁹⁰⁺	0.20	0.26	0.32	0.49	0.79	1.21

This is known to be slightly inaccurate but the overall error introduced using this approximation is not expected to be large since the integrated oscillator strength from the high-energy portion is small. In table 4, we notice that the dipole sum evaluated using this numerical method is quite accurate for $Z < 10$, the small deviation of the sum from two for these low- Z elements is due to the numerical accuracy; however, for higher- Z elements, the deviation from two can be attributed to relativity.

2.5. $E1$ photoionisation cross sections of beryllium-like ions

In table 5, we list threshold electric-dipole oscillator strengths for some low- Z elements of the beryllium isoelectronic sequence and the normalised values at higher energies. Relativistic effects are less important because the velocity of the 2s electrons is smaller. Our calculation includes the inter-shell interaction between 1s and 2s electrons.

Table 4. Total dipole oscillator strength sum for helium-like ions. Contribution from discrete and continuum states (including singlets and triplets) and the total sum are given to show the deviation from the non-relativistic Thomas-Reiche-Kuhn sum rule.

Element	Discrete		Continuum		Sum
	¹ P	(³ P)	¹ P	(³ P)	
Li ⁺	0.667		1.330		1.997
Be ²⁺	0.797		1.201		1.999
C ⁴⁺	0.919		1.080		1.999
O ⁶⁺	0.975		1.021		1.996
Ne ⁸⁺	1.007	(0.00056)	0.987		1.994
Ca ¹⁸⁺	1.030	(0.0295)	0.903		1.963
Zn ³⁸⁺	0.912	(0.147)	0.859		1.918
Mo ⁴⁰⁺	0.772	(0.264)	0.808	(0.005)	1.849
Ag ⁴⁵⁺	0.746	(0.294)	0.778	(0.008)	1.825
Xe ⁵²⁺	0.687	(0.307)	0.770	(0.009)	1.773
W ⁷²⁺	0.582	(0.312)	0.674	(0.025)	1.593
Pb ⁸⁰⁺	0.539	(0.303)	0.637	(0.038)	1.517
U ⁹⁰⁺	0.482	(0.286)	0.602	(0.048)	1.418

Table 5. Relativistic electric-dipole oscillator strengths of the beryllium sequence. The first row gives the extrapolated 2s threshold oscillator strength. The other entries are the normalised (with respect to the threshold value) oscillator strengths for photoelectron energies in units of the 2s ionisation threshold. The figure in parentheses gives the power of ten by which the value should be multiplied.

E	B^+	C^{2+}	O^{4+}	Ne^{6+}	Ca^{16+}	Zn^{26+}
$(df/dE)_{th}$	0.556	0.411	0.203	0.119	0.238(-1)	0.100(-1)
0.05	0.971	0.943	0.930	0.915	0.893	0.859
0.1	0.942	0.888	0.865	0.839	0.806	0.769
0.15	0.912	0.837	0.805	0.774	0.738	0.702
0.2	0.881	0.789	0.748	0.717	0.678	0.644
0.25	0.851	0.744	0.696	0.665	0.624	0.592
0.4	0.754	0.626	0.567	0.537	0.494	0.467
0.6	0.638	0.504	0.442	0.414	0.375	0.350
0.8	0.539	0.411	0.351	0.326	0.290	0.271
1.0	0.459	0.340	0.285	0.263	0.230	0.214
1.5	0.316	0.223	0.179	0.164	0.139	0.128
2.0	0.226	0.154	0.121	0.109	0.905(-1)	0.829(-1)
4.0	0.813(-1)	0.514(-1)	0.384(-1)	0.330(-1)	0.237(-1)	0.232(-1)
7.5	0.256(-1)	0.145(-1)	0.105(-1)	0.880(-2)	0.647(-2)	0.562(-2)
10.0	0.134(-1)	0.767(-2)	0.520(-2)	0.446(-2)	0.319(-2)	0.273(-2)

2.6. Electron-ion angular-momentum coupling in RRP

In the previous paragraphs we have labelled the final excitation channels using the jj coupling convention. For comparison with non-relativistic photoionisation calculations it is more convenient to express the amplitudes in an LS basis rather than the jj basis used here. In figure 1 we show the fraction of triplet to singlet excitation

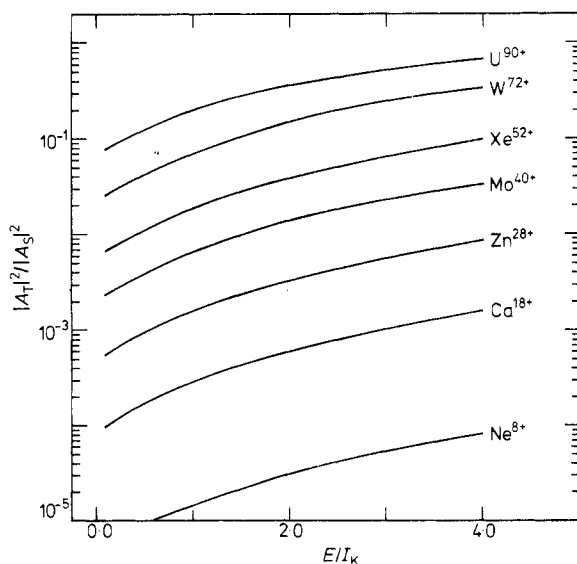


Figure 1. Fraction of triplet to singlet cross sections for helium-like ions as a function of photoelectron energy in units of the ionisation potential I_K .

probability for $1s \rightarrow p$ transitions in the He sequence and in figure 2 we give the same ratio for $2s \rightarrow p$ transitions in the Be sequence. This ratio, which is one measure of the importance of relativity for high- Z ions, remains small for all but the highest members of the sequence and then is most significant when continuum electron relativistic effects are large at high electron energies.

These observations are in marked contrast to the corresponding bound-state studies (Kim and Desclaux 1976, Johnson *et al* 1976) where the electron-ion coupling was found to be almost purely jj for $Z > 40$. To explain the connection between our results and the bound-state studies we note that the continuum counterparts of the bound eigenstates are the eigenstates of the scattering matrix S .

In bound-state cases only one of these eigenstates is excited depending on the energy; however above the ionisation threshold all eigenstates are simultaneously

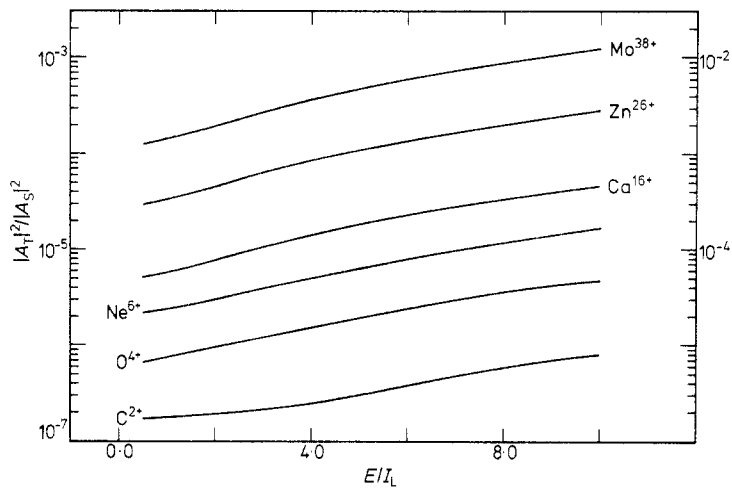


Figure 2. Fraction of triplet to singlet cross sections for beryllium-like ions as a function of photoelectron energies E in units of the ionisation potential I_L . The scale on the left refers to the ions of C, O and N while the scale on the right refers to Ca, Zn and Mo.

Table 6. Angular-momentum coupling studies for Mo^{38+} . The excitation probability into eigenstates of S and into LS states is given at different energies to illustrate the approximate LS coupling of the excited ion. The decomposition of the individual eigenstates of S into jj states is also listed to illustrate the approximate jj coupling of the eigenstates. Energies are in units of the L-shell ionisation potential I_L .

E/I_L	State 1	State 2	1P_1	3P_1	Eigenstate 1		Eigenstate 2	
					$s_{1/2}p_{1/2}$	$s_{1/2}p_{3/2}$	$s_{1/2}p_{1/2}$	$s_{1/2}p_{3/2}$
0.5	0.9029	0.0971	0.9988	0.0012	0.2880	0.9576	0.9576	-0.2880
1.0	0.8806	0.1194	0.9986	0.0014	0.2464	0.9692	0.9692	-0.2464
2.0	0.8471	0.1529	0.9981	0.0019	0.1885	0.9821	0.9821	-0.1885
4.0	0.7906	0.2094	0.9962	0.0038	0.1057	0.9944	0.9944	-0.1057
7.5	0.7263	0.2737	0.9919	0.0081	0.0518	0.9987	0.9987	-0.0518
10.0	0.7163	0.2837	0.9879	0.0121	0.0354	0.9994	0.9994	-0.0354

excited. To make comparisons of angular-coupling schemes with relativistic bound-state studies we must examine the angular-momentum content of the individual eigenstates of S . We find that these individual eigenstates are jj coupled at moderately high Z , in harmony with the bound-state studies, whereas the overall excitation amplitude which is a mixture of these eigenstates is LS coupled.

These points are illustrated in table 6 where the excitation amplitude of Mo^{+38} $2s \rightarrow \epsilon p$ is analysed as a function of energy. In columns 2–5 of table 6 we give the excitation probabilities for the eigenstates of S and for LS states. The ratio of column 4 to column 5 is the fraction plotted for Mo^{38+} in figure 2. In the last four columns we give the eigenstates of S in terms of jj states to illustrate that these eigenstates are indeed jj coupled even though the entire amplitude is almost purely LS coupled.

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