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Two-photon detachment of electrons from halogen negative ions

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Abstract. Absolute two-photon detachment cross sections and photoelectron angular distributions are calculated for halogen negative ions within lowest-order perturbation theory. The outer np ground-state wavefunctions are determined using the Dyson equation method. The *ab initio* correlation potential is scaled by introduction of a free parameter. We choose it to ensure that the np wavefunctions have a proper asymptotic behaviour $P(r) \propto \exp(-\kappa r)$, corresponding to correct (experimental) binding energies $E_b = \hbar^2\kappa^2/2m$. The latter is crucial for obtaining correct absolute values of the multiphoton cross sections (Gribakin and Kuchiev 1997 *Phys. Rev.* A **55** 3760). Comparisons with previous calculations and experimental data are performed.

1. Introduction

Halogen negative ions have been the subject of experimental and theoretical multiphoton detachment studies for over 30 years (Hall *et al* 1965, Robinson and Geltman 1967). Apart from the negative hydrogen ion which has traditionally received a lot of attention, especially from theorists, they are definitely the most studied negative ions. Nevertheless, there are very few firmly established results on the absolute values of the cross sections and photoelectron angular distributions in multiphoton processes. A number of experimental works report the cross sections and angular asymmetry parameters measured in two-photon detachment at selected photon energies in F^- and Cl^- (Trainham *et al* 1987, Blondel *et al* 1989, 1992, Kwon *et al* 1989, Davidson *et al* 1992, Sturrus *et al* 1992, Blondel and Delsart 1993). For heavier halogen ions, Br^- and I^-, the experimental data are scarce (Hall *et al* 1965, Blondel *et al* 1992, Blondel and Delsart 1993).

On the theoretical side, there were pioneering two-photon detachment calculations by Robinson and Geltman (1967) performed using a model potential approach, and a number of other perturbation-theory calculations employing the Hartree–Fock (HF) approximation for the ionic ground state, and either plane or HF waves for the photoelectron in the continuum (Crance 1987a, b, 1988). The latter were applied to study n-photon detachment cross sections and photoelectron angular distributions from halogen negative ions for n up to 5. Jiang and Starace (1988) used a transition-matrix approach and examined the contribution of the lowest-order correlation processes in the two-photon detachment from Cl^-. They showed that the role

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of correlations is small just above the threshold and increases slightly with the photon energy up to about 20%, compared with the HF result. Later on Pan *et al* (1990) and Pan and Starace (1991) performed similar calculations of the two-photon detachment cross section and angular distribution for F^-. Using first-order perturbation theory in electron interaction they included more correlation corrections and estimated the contribution of the many-electron effects at 10–20% in the cross sections, but almost negligible in the angular distribution asymmetry parameters. More recently, van der Hart (1996) used the R-matrix Floquet theory to calculate multiphoton detachment from F^- and Cl^-. He found a discrepancy with the results of the transition-matrix approach in F^- and Cl^- within about 30%.

In the above works, except that of Robinson and Geltman, the halogen ion ground state was described either in the HF or in a few-state configuration-interaction approximation. Consequently, the binding energy of the outer electron, as obtained from the calculation, was never in good agreement with the experimental electron affinity, and experimental energy values were used in the calculations of the multiphoton amplitudes and cross sections. On the other hand, the asymptotic behaviour of the ground-state wavefunction in these calculations remained incorrect. This may seem to have introduced only a small error in the calculation, since the bound-state wavefunction in the asymptotic region is small. However, as shown in the adiabatic theory of multiphoton detachment from negative ions (Gribakin and Kuchiev 1997a, b), the asymptotic behaviour of the bound-state wavefunction is crucial for obtaining correct absolute values of the probabilities of multiphoton processes. This theory based on the Keldysh approach (Keldysh 1964) shows that the electron escape from the atomic system in a low-frequency laser field takes place at large distances,

$$r \sim 1/\sqrt{\omega} \sim \sqrt{2n}/\kappa \gg 1 \tag{1}$$

where ω is the photon frequency, κ is related to the initial bound-state energy, $E_0 = -\kappa^2/2$, and n is the number of quanta absorbed (atomic units are used throughout). Accordingly, the multiphoton detachment rates are basically determined by the long-range asymptotic behaviour of the bound-state wavefunction, namely by parameters A and κ of the corresponding radial wavefunction $R(r) \simeq Ar^{-1}\mathrm{e}^{-\kappa r}$. This result is obtained using the length form of interaction with the laser field, which emphasizes large distances and proves to be the most convenient for multiphoton processes.

The analytical adiabatic approach is valid for *multiphoton* detachment processes, i.e. strictly speaking, for $n \gg 1$. However, the calculations for H^- and halogen negative ions indicate (Gribakin and Kuchiev 1997a, Kuchiev and Ostrovsky 1998) that the analytical formulae should give reasonable answers even for $n = 2$. To verify these conclusions we performed direct numerical calculations of the two-photon detachment cross section of the fluorine F^- negative ion (Gribakin *et al* 1998) within the lowest order of perturbation theory and compared the results obtained with different ground-state wavefunctions. We demonstrated explicitly the sensitivity of the cross sections to the asymptotic behaviour of the bound-state wavefunction and showed that the true cross section could be substantially higher than was previously believed, based on calculations with the HF 2p wavefunction.

In our previous work (Gribakin *et al* 1998) the asymptotically correct 2p wavefunction was obtained using a model potential chosen to reproduce the experimental value of the 2p-electron energy. Such a model potential approach is not free from ambiguities related to the choice of the potential. The aim of the present work is to perform more accurate calculations of the two-photon detachment from negative halogen ions using correct np wavefunctions obtained within the many-body Dyson equation method (see, e.g., Chernysheva *et al* 1988). Thereby we account for the ground-state correlation effects. Because of the role of the asymptotic part of the ground-state wavefunction, this is the single most important correlation effect in

multiphoton detachment from negative ions, as far as absolute values of the cross sections are concerned. This fact distinguishes this problem from single-photon processes, where other correlation effects are essential. The strong effect of the asymptotic behaviour of the ground-state wavefunction on the magnitude of multiphoton cross sections was observed earlier by Liu *et al* (1992). They performed an adiabatic hyperspherical calculation of two-photon detachment from H^- and noticed that an adjustment of the ground-state potential which led to a small 3.4% increase of κ resulted in a 25% decrease in the two-photon cross section. Neither the *R*-matrix calculations (van der Hart 1996) nor the correlation calculations within the perturbation theory (Pan *et al* 1990) use asymptotically correct wavefunctions. Ground-state correlations taken into account in those works do not lead to the correct asymptotic behaviour of wavefunctions obtained. As for the other correlation effects, Pan *et al* (1990) and Pan and Starace (1991) have estimated that their contribution is small, and we do not consider these correlations in our paper.

It is important to note that the above-mentioned calculations show that the effect of correlations is small only when the length form of the dipole operator is used. When the calculations are performed using the velocity form the effect of correlations looks much greater. Therefore, from the results of Pan *et al* (1990) and Pan and Starace (1991) one can deduce that the length form should generally be more reliable. The same conclusion follows from the adiabatic theory (Gribakin and Kuchiev 1997a, b) which demonstrates that large separations play a crucial role in multiphoton processes, and hence the length form for the dipole operator is more robust.

In what follows we briefly outline the method of calculation (section 2). A discussion of our results and comparisons with other calculations and experimental data are presented in section 3.

2. Method of calculation

2.1. Two-photon detachment

The total cross section of two-photon detachment of an electron from an atomic system by a linearly polarized light of frequency ω is

$$\sigma = \sum_{l_f L} \sigma_{l_f L} = \frac{16\pi^3}{c^2}\omega^2 \sum_{l_f L} \left|A_{l_f L}(\omega)\right|^2 \tag{2}$$

where $\sigma_{l_f L}$ is the partial cross section for the final-state photoelectron orbital momentum l_f and total orbital momentum L, and the continuous-spectrum wavefunction of the photoelectron in the matrix element $A_{l_f L}(\omega)$ is normalized to the δ-function of energy. For the detachment of the outer np electron from the negative halogen ion $n\mathrm{p}^6\ {}^1\mathrm{S}$ the final state can be either ${}^1\mathrm{S}$ ($L = 0$, $l_f = 1$) or ${}^1\mathrm{D}$ ($L = 2$, $l_f = 1,\ 3$). In the lowest second order the two-photon amplitude $A_{l_f L}(\omega)$ is determined by the following equations:

$$A_{l_f L}(\omega) = \sqrt{2L+1} \begin{pmatrix} 1 & 1 & L \\ 0 & 0 & 0 \end{pmatrix} \sum_l (-1)^l \begin{Bmatrix} 1 & 1 & L \\ l_f & l_0 & l \end{Bmatrix} M_{l_f l}(\omega) \tag{3}$$

$$M_{l_f l}(\omega) = \sum_\nu \frac{\langle \varepsilon_f l_f \| \hat{d} \| \nu l \rangle \langle \nu l \| \hat{d} \| n_0 l_0 \rangle}{E_0 + \omega - E_\nu + \mathrm{i}0} \tag{4}$$

where νl is the intermediate electron state with the orbital momentum l after absorbing the first photon ($l = 0, 2$ for the halogens) and $n_0 l_0$ is the initial bound state. The reduced dipole matrix elements are defined in the usual way, for example, in the length form,

$$\langle \nu l \| \hat{d} \| n_0 l_0 \rangle = (-1)^{l_>} \sqrt{l_>} \int P_{\nu l}(r)\, P_{n_0 l_0}(r) r \, \mathrm{d}r \tag{5}$$

where $l_> = \max\{l, l_0\}$ and P's are the radial wavefunctions.

The photoelectron angular distribution is given by the differential cross section

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} = \frac{\sigma}{4\pi} \sum_{j=0}^{2} \beta_{2j}(\omega) P_{2j}(\cos\theta) \tag{6}$$

where θ is measured with respect to the light polarization axis, and the asymmetry parameters β_{2j} are determined in terms of the two-photon transition amplitudes $A_{l_f L}$ and scattering phases of the photoelectron δ_{l_f}:

$$\beta_{2j} = \frac{16\pi^3\omega^2}{c^2\sigma}(4j+1)\,\mathrm{Re}\Bigg[\sum_{l'_f L' l''_f L''} (-1)^{l_0+L'+L''} (-\mathrm{i})^{l'_f+l''_f} \exp[\mathrm{i}(\delta_{l'_f} - \delta_{l''_f})] \sqrt{[l'_f][L'][l''_f][L'']} \times \begin{pmatrix} l'_f & 2j & l''_f \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} L' & 2j & L'' \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} L' & L'' & 2j \\ l''_f & l'_f & l_0 \end{Bmatrix} A_{l'_f L'} A^*_{l''_f L''} \Bigg] \tag{7}$$

where $[l] \equiv 2l + 1$ and $\beta_0 = 1$, so that the photoelectron angular distribution after two-photon detachment is characterized by β_2 and β_4.

The wavefunctions of the intermediate (νl) and final ($\varepsilon_f l_f$) states of the photoelectron are calculated in the HF field of the frozen neutral atom residue $n\mathrm{p}^5$. The photoelectron is coupled to the core to form the total spin $S = 0$ and angular momenta $L = 1$ for the intermediate s and d states ($l = 0, 2$), $L = 0, 2$ for the final-state p wave ($l_f = 1$), and $L = 2$ for the final-state f wave ($l_f = 3$). The intermediate state continua are discretized and represented by a 70-state momentum mesh with constant spacing Δk.

2.2. Ground-state wavefunction

If one describes the initial state $n_0 l_0$ in the HF approximation, the asymptotic behaviour of the corresponding radial wavefunction is incorrect. Namely, it is characterized by κ corresponding to the HF binding energy, rather than the exact (experimental) one. For example, in F^- the HF value is $\kappa = 0.6$, whereas the true one is $\kappa = 0.5$. As discussed in the introduction, it is very important to use asymptotically correct bound-state wavefunctions. In our previous paper we corrected the 2p wavefunction by solving the HF equations for the F^- ground state with a small additional repulsive potential of the form $V(r) = \alpha/[2(r^2 + a^2)^2]$, where the parameters α and a were chosen to ensure that the calculated energy was equal to the experimental value. Our choice $\alpha = 1$ and $a = 0.61$ ensured $\kappa = 0.5$, and produced the asymptotic parameter $A = 0.86$, close to the value recommended by Radtsig and Smirnov (1986).

In this work we refine the bound-state wavefunction using atomic many-body theory methods. The latter enable one to obtain a quasi-particle orbital which describes the bound electron in a many-body system from the Dyson equation (see, e.g., Chernysheva *et al* (1988), Gribakin *et al* (1990), where it is applied to calculations of negative ions)

$$\hat{H}^{(0)}\phi_E(\boldsymbol{r}) + \int \Sigma_E(\boldsymbol{r}, \boldsymbol{r}')\phi_E(\boldsymbol{r}')\,\mathrm{d}\boldsymbol{r}' = E\phi_E(\boldsymbol{r}). \tag{8}$$

Here $H^{(0)}$ is the single-particle HF Hamiltonian and Σ_E is the self-energy of the single-particle Green's function. This energy-dependent non-local operator plays the role of a correlation potential, and, if known exactly, produces exact bound-state energies from equation (8). The Dyson equation yields the correct binding energy and provides the best single-particle orbital of the initial state, which incorporates certain many-body effects, namely, the ground-state correlations. In most applications Σ_E is calculated perturbatively, and the lowest second-order contribution usually gives a considerable improvement on the HF results.

Within the second order in the electron Coulomb interaction V the matrix element of Σ_E between some single-electron states a and b looks like

$$\langle a|\Sigma_E|b\rangle = \sum_{\nu_1,\nu_2,n_1} \frac{\langle an_1|V|\nu_1\nu_2\rangle(\langle\nu_2\nu_1|V|n_1b\rangle - \langle\nu_1\nu_2|V|n_1b\rangle)}{E - E_{\nu_1} - E_{\nu_2} + E_{n_1} + \mathrm{i}0} + \sum_{\nu_1,n_1,n_2} \frac{\langle a\nu_1|V|n_1n_2\rangle(\langle n_2n_1|V|\nu_1b\rangle - \langle n_1n_2|V|\nu_1b\rangle)}{E - E_{n_1} - E_{n_2} + E_{\nu_1} - \mathrm{i}0} \tag{9}$$

where the sums run over occupied states n_1 and n_2, and excited states ν_1 and ν_2, and the second terms in parentheses are exchange contributions. The lowest-order correction to the energy of the orbital a is given by $\langle a|\Sigma_E|a\rangle$ calculated with $E = E_a$.

For all halogen negative ions the HF binding energies of the outer np subshell are greater than the corresponding experimental electron affinities. Hence, the correlation correction to the energy must be positive, which means a repulsive correlation potential. Indeed, our numerical calculations show that Σ_E is dominated by the direct contribution in the second sum in equation (9) (first term in parentheses). For $E \approx E_{n\mathrm{p}}$ the sum over the occupied states is basically given by $n_1 = n_2 = n\mathrm{p}$ (in many-body theory language this means that both holes are in the outer np subshell). It is obvious then that this contribution has $E_{\nu_1} - E_{n\mathrm{p}} > 0$ in the denominator, and with a squared matrix element (for $a = b = n\mathrm{p}$) in the numerator, it is explicitly positive.

It also follows from our calculations that Σ_E calculated in the second-order approximation overestimates the correlation correction. Therefore, to obtain best ground-state orbitals for multiphoton detachment calculations we introduce a free parameter η before the (dominant) direct term in the second sum of equation (9). This parameter is then chosen to reproduce experimental values of the np energies from the Dyson equation. The Dyson orbitals thus obtained have correct asymptotic behaviour and yield correct values of both κ and A. This procedure effectively takes into account the contribution of higher-order perturbation theory terms in Σ_E. It was used earlier in many-body calculations of neutral atoms and negative ions (see, e.g., Dzuba *et al* 1983, Dzuba and Gribakin 1997). Moreover, using different values of η we can effectively simulate the fine-structure splitting, and obtain the wavefunctions for both fine-structure components of the $n\mathrm{p}^6$ subshell, the upper $n\mathrm{p}_{3/2}$ and lower $n\mathrm{p}_{1/2}$, corresponding to the different binding energies. For heavier halogen negative ions (Br and I) the splitting between them becomes quite significant, and we account for different asymptotic behaviour of the corresponding radial wavefunctions in calculations of multiphoton processes. Since we use Σ_E from equation (9) in this semiempirical way, only the contributions of dominant monopole and dipole atomic excitations are included in the sums.

The two-photon amplitudes $M_{l_f l}$ (4) are calculated by direct summation over the intermediate states. It involves accurate evaluation of the free–free dipole matrix elements, and special attention is paid to pole- and δ-type singularities of the integrand (Korol 1994, 1997).

3. Results

3.1. Fluorine

The main difference between the present calculation and our previous work (Gribakin *et al* 1998) is in the initial-state 2p wavefunction. The self-consistent HF calculation of the F^- ground state yields the 2p-electron energy $E_{2p}^{HF} = -0.362$ Ryd, which is much lower than its true value equal to the negative of the experimental electron affinity of F: $E_{2p}^{exp} = -0.250$ Ryd (Hotop and Lineberger 1986). In the previous work we used a model potential which reproduced the experimental energy, and yielded a 2p wavefunction with the asymptotic parameters $A = 0.86$ and $\kappa = 0.5$ (cf $A = 0.94$ and $\kappa = 0.6$ for the HF wavefunction).

In the present work we obtain the 2p wavefunction from the Dyson equation (8). When Σ_E is calculated within the second order, equation (9), the 2p energy equal to -0.187 Ryd is obtained. Thus, the second-order approximation overestimates the strength of the polarization potential. When a scaling factor $\eta = 0.67$ is introduced in the way outlined in section 2.2, we reproduce the experimental energy for the 2p electron, and obtain the Dyson orbital of the 2p subshell. This 2p wavefunction is quite close to the HF one inside the atom, whereas for $r > 2$ au it goes higher than the HF solution. Its asymptotic behaviour is characterized by $\kappa = 0.5$ and $A = 0.64$. The latter value of A together with our best asymptotic parameters of the np orbitals of the other ions are presented in table 1, where they are compared with values recommended by Radtsig and Smirnov (1986) and Nikitin and Smirnov (1988). The latter were obtained by matching the HF wavefunctions with those possessing correct asymptotic behaviour.

Table 1. Asymptotic parameters of the np orbitals of the halogen negative ions.

Ion	Orbital	κ[a]	A[b]	A[c]	A[d]
F^-	2p[e]	0.500	0.64	0.84	0.7
Cl^-	3p[e]	0.516	1.355	1.34	1.3
Br^-	$4p_{3/2}$	0.497	1.53	1.49	1.4
Br^-	$4p_{1/2}$	0.530	1.60	—	—
I^-	$5p_{3/2}$	0.474	1.808	1.9	1.8
I^-	$5p_{1/2}$	0.542	2.587	—	—

[a] Obtained using experimental binding energies.
[b] Obtained from the our solutions of the Dyson equation.
[c] Radtsig and Smirnov (1986).
[d] Nikitin and Smirnov (1988).
[e] We neglect the fine-structure splitting for F^- and Cl^-.

The results of calculations of the two-photon detachment cross section and photoelectron angular distribution in F^- are presented in figures 1 and 2. Our results obtained using the HF 2p orbital (the HF two-photon threshold is at $\omega = 0.181$ Ryd) are about 10% higher than the similar dipole length lowest-order HF results of Pan *et al* (1990). A possible source of this discrepancy was discussed in our previous paper (Gribakin *et al* 1998), where we proposed that it could be associated with the fact that Pan *et al* (1990) used the Roothaan HF expansion of the bound state.

When we use the experimental energy of the 2p electron together with the HF wavefunctions the magnitude of the two-photon cross section changes very little, as seen earlier by Pan *et al* (1990) for both HF and correlated results (dotted curve in figure 1). The

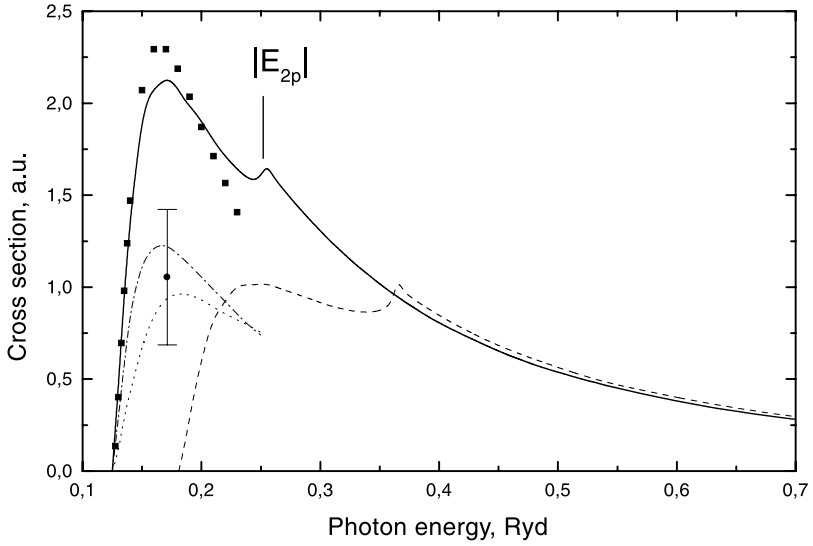

Figure 1. Two-photon detachment cross sections of F^-. Present calculations: – – –, HF wavefunctions of the 2p, intermediate and final states; ——, the same with the 2p wavefunction from the Dyson equation. Other results: · · · · · ·, calculations by Pan *et al* (1990) with correlations and experimental binding energies; — · —, *R*-matrix Floquet method by van der Hart (1996); ■, model calculations by Robinson and Geltman (1967); ●, experiment (Kwon *et al* 1989).

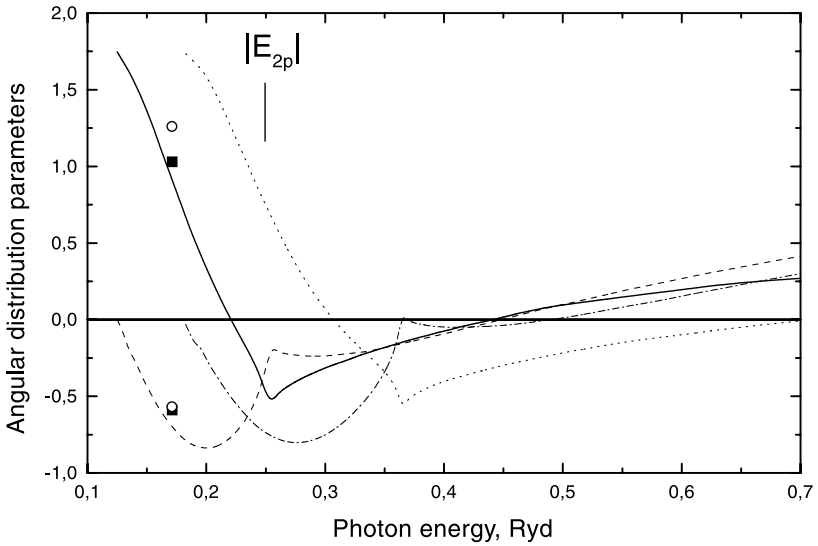

Figure 2. Photoelectron angular distribution parameters for F^-. · · · · · ·, the HF β_2 parameter; — · —, the HF β_4 parameter; ——, β_2 parameter with the Dyson 2p wavefunction; – – –, β_4 parameter with the Dyson 2p wavefunction. ■, experiment (Blondel and Delsart 1993); ○, correlated length results by Pan and Starace (1991).

HF results of Crance (1987a) are close to the above. The cross section of van der Hart (1996) obtained within the *R*-matrix Floquet approach is 30% higher (chain curve in figure 1) with a maximum of $\sigma = 1.25$ au at $\omega = 0.166$ Ryd.

However, when we use the 2p wavefunction with the correct asymptotic behaviour from the Dyson equation, the photodetachment cross section increases by a factor of ~ 2†. This cross section is shown by the full curve in figure 1, and we consider this to be our best evaluation of the cross section for F^-. The cusp on the curve at the single-photon threshold is a Wigner threshold effect. It is a consequence of the abrupt threshold dependence $\sigma \propto \sqrt{\omega - |E_0|}$ of the s-wave single-photon detachment channel, which opens at this energy.

The only other work that has used an asymptotically correct 2p wavefunction was the model potential calculation of Robinson and Geltman (1967), which produced a cross section twice as great as those of Crance, Pan *et al* and van der Hart. The results of Robinson and Geltman (full squares in figure 1) are much closer to our results in comparison with all others.

Thus, we see that in *multiphoton* processes the error introduced by using a bound-state wavefunction with an incorrect asymptotic behaviour could be much greater then other effects of electron correlations estimated by Pan *et al* (1990) at 10–20%. Of course, the difference between the experimental and HF energies is also a correlation effect. It influences the result via the asymptotic behaviour of the ground-state wavefunction, and we see that this is the most important correlation effect in multiphoton detachment. The use of the asymptotically correct 2p wavefunction changes the cross section by a factor of two, which is much greater than other correlation effects. In spite of this, the experimental cross section, as measured by Kwon *et al* (1989), favours the results of Pan *et al* and van der Hart (figure 1), and the lowest-order results obtained with the HF 2p wavefunction (figure 2 of Gribakin *et al* 1998). Since the asymptotic behaviour of the wavefunction should affect any multiphoton detachment calculation, the discrepancy between our present result and the experimental data could be resolved by future experiments. Of course, new correlated calculations which use asymptotically correct ground-state wavefunctions could also clarify the issue.

The angular asymmetry parameters β_2 and β_4 calculated using the Dyson 2p-state wavefunction are shown in figure 2. They reveal an interesting dependence on the photon energy with sign changes and cusps at the single-photon detachment threshold. Figure 2 also presents the experimental points of Blondel and Delsart (1993) obtained at $\omega = 0.171$ Ryd, and the correlated dipole length results of Pan and Starace (1991) at the same energy. The asymmetry parameters (7) are relative quantities, and they are much less sensitive to the shape of the ground-state wavefunction, or the binding energy. Thus, figure 2 shows that the angular asymmetry parameters obtained with the correct Dyson 2p wavefunction would be matched closely by the HF ones if we rescaled the photon energies. Theoretically this observation is supported by the adiabatic theory (Gribakin and Kuchiev 1997b) where the asymmetry of the photoelectron angular distribution depends on the ratio of the photoelectron energy to the binding energy. Accordingly, the results of different calculations of β are much closer than those for the photodetachment cross sections. For example, our present results are practically equal to those obtained in the model 2p wavefunction calculation below 0.22 Ryd (Gribakin *et al* 1998). There we also showed that the results from the analytical adiabatic theory (Gribakin and Kuchiev 1997b) are in good agreement with the numerical results from other approaches, including the plane-wave approximation, especially for β_4. It appears that this parameter is on the whole less sensitive to the details of the calculation, because it is simply proportional to the amplitude of f-wave emission, and there are no interference terms in expression (7) for β_4. The experimental values of $\beta_{2,4}$ for F^- obtained in the earlier work of Blondel *et al* (1992) are close to those of Blondel and Delsart (1993). This is why F^- serves as a good benchmark for angular asymmetry calculations. Figure 2 shows

† With the model 2p wavefunction, which had a larger value of A, the cross section was about three times larger than the HF results (Gribakin *et al* 1998). As follows from the adiabatic theory (Gribakin and Kuchiev 1997a, b), for a given κ the n-photon cross section is proportional to A^2.

that our present calculations with the Dyson 2p wavefunction are in good agreement with experiment.

3.2. Chlorine

The HF calculations of the Cl^- ground state gives $E_{3p}^{HF} = -0.301$ Ryd for the 3p-electron energy, while the experimental value derived from the electron affinity of Cl is $E_{3p}^{exp} = -0.2657$ Ryd (Hotop and Lineberger 1985). The spin–orbit splitting in Cl^- is still small, since the energies of the $3p_{3/2}$ and $3p_{1/2}$ states differ by less than 0.008 Ryd (Radtsig and Smirnov 1986), and we ignore it here.

When Σ_E includes the monopole and dipole terms, equation (8) yields the 3p binding energy of 0.22 Ryd. To obtain the 3p wavefunction with the experimental 3p energy we solve equation (8) using Σ_E with the scaling factor $\eta = 0.842$, introduced as outlined in section 2.2. The corresponding asymptotic parameters are listed in table 1.

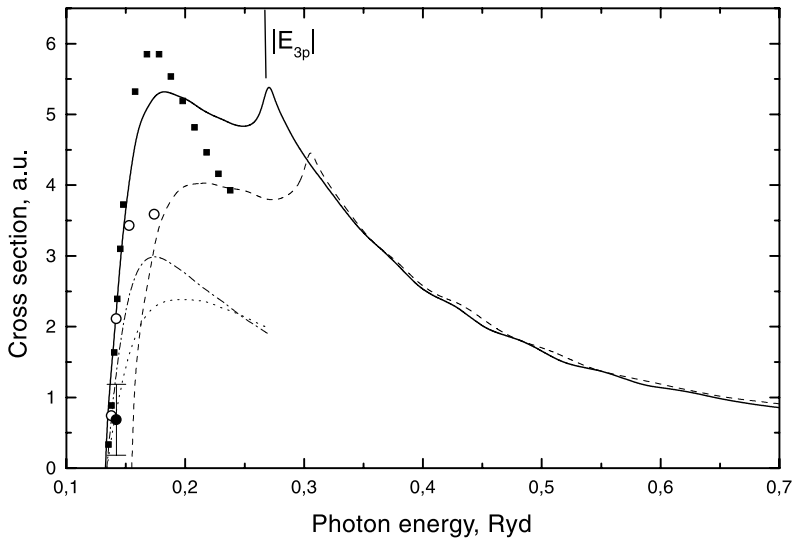

Figure 3. Two-photon detachment cross sections of Cl^-. Present calculations: – – –, HF wavefunctions of the 3p, intermediate and final states; ——, same with the 3p wavefunction from the Dyson equation. Other results: · · · · · ·, calculations by Jiang and Starace (1988); — · —, *R*-matrix Floquet method by van der Hart (1996); ○, HF calculations by Crance (1987b); ■, model calculations by Robinson and Geltman (1967); ●, experiment (Trainham *et al* 1987).

The two-photon detachment cross sections we have obtained for the negative chlorine ion are plotted in figure 3 together with the results of other calculations (Robinson and Geltman 1967, Crance 1987b, Jiang and Starace 1988, van der Hart 1996). Note that our HF cross section is significantly higher than the results obtained by Jiang and Starace (1988) and van der Hart (1996) (dotted and chain curves in figure 3, respectively), but agrees better with the HF cross section calculated by Crance (1987) (open circles) and is lower than the cross sections obtained within the plane-wave approximation (Crance 1987, Sturrus *et al* 1992).

The total detachment cross section calculated with the Dyson 3p wavefunction is 30% higher at the maximum than the HF one, but above the single-electron threshold it agrees quite well with the HF results. The maximal value of the cross section is closer to the model calculations by Robinson and Geltman (1967) (full squares in figure 3), who used

an asymptotically correct wavefunction from a model-potential calculation. However, the latter calculation reveals a rapid decrease of the cross section beyond the maximum. The experimental cross section obtained by Trainham *et al* (1987) at $\omega = 0.142$ Ryd is lower than all the calculations. Measurements of absolute values of multiphoton cross sections are very difficult due to inhomogeneity of the laser beam and the finite rise time of the laser pulse (Blondel 1995). The ponderomotive shift can also affect the measurements, especially in the near-threshold region. We believe that our calculation gives the best estimate of the two-photon detachment cross section for Cl^-. Discrepancies with other theories could be resolved if asymptotically correct ground-state wavefunctions are used in them.

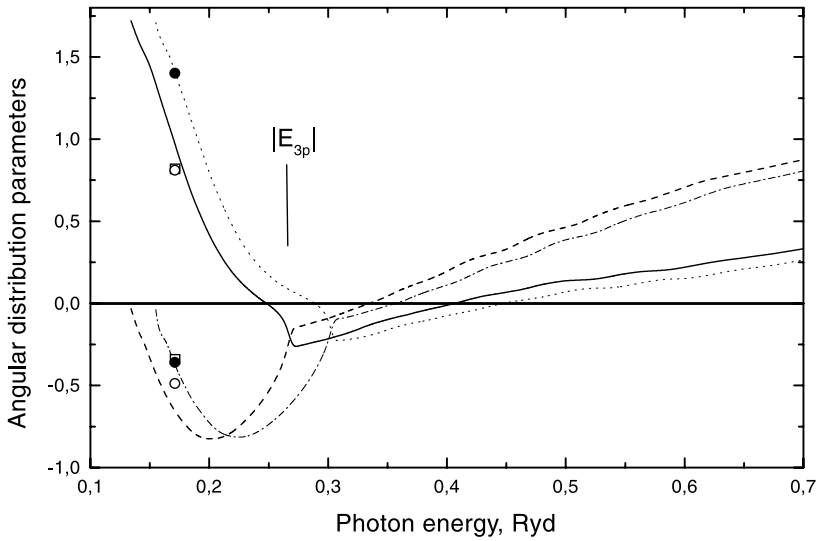

Figure 4. Photoelectron angular distribution parameters for Cl^-. ·····, the HF β_2 parameter; —·—, the HF β_4 parameter; ——, β_2 parameter with the Dyson 2p wavefunction; – – –, β_4 parameter with the Dyson 2p wavefunction. □, experiment (Blondel *et al* 1992); ● and ○, calculations in the plane-wave approximation and with the first Born correction, respectively (Blondel *et al* 1992).

The angular distribution parameters are shown in figure 4. In general, the parameters β_2 and β_4 behave similarly to those in negative fluorine, going through sign changes and cusps at the single-electron threshold. Also presented are the experimental data and the results of two calculations done within the plane-wave approximation and with the first Born correction at $\omega = 0.171$ Ryd (Blondel *et al* 1992). The first Born results are closer to our calculations with the correct (Dyson) ground-state wavefunction, where the interaction between the photoelectron and the atomic residue is included in all orders through the HF wavefunctions of the photoelectron. Comparison with the experimental data of Blondel *et al* (1992) looks inconclusive. In the subsequent measurement Blondel and Delsart (1993) confirmed the accuracy of the original data for F^-, but found that the β values for I^- in Blondel *et al* (1992) were affected by a spurious background. Thus, it appears that for heavier halogens the data are probably not as reliable as for fluorine (Blondel 1997).

3.3. Bromine

The binding energy of the 4p state in Br^- obtained in the HF approximation is equal to 0.2787 Ryd, which is less than those for F^- and Cl^-. On the other hand, the spin–orbit splitting

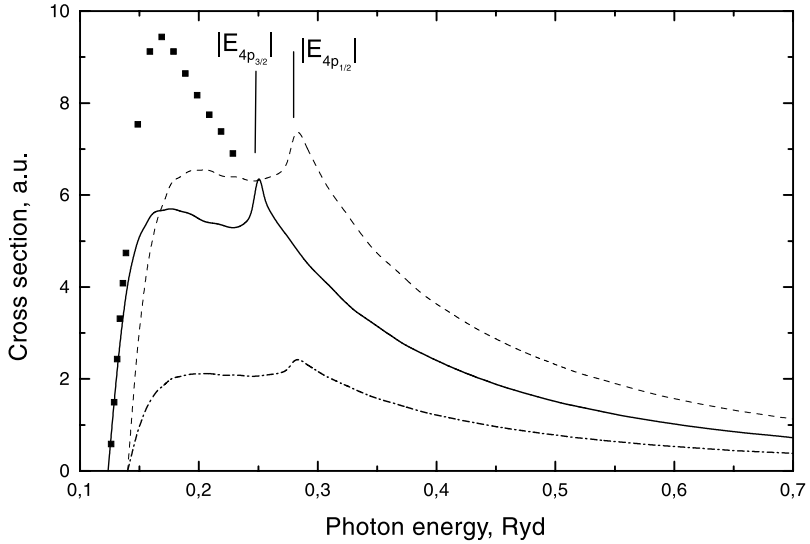

Figure 5. Two-photon detachment cross sections of Br^-. – – –, HF wavefunctions of the 4p, intermediate and final states; ——, same with the $4p_{3/2}$ wavefunction from the Dyson equation; — · —, same with the correct $4p_{1/2}$ wavefunction; ■, model calculations by Robinson and Geltman (1967).

of the 4p orbital for Br^-, 0.034 Ryd (Radtsig and Smirnov 1986), is four times greater than that in the negative chlorine ion. Besides this, the experimental data on the two-photon detachment from Br^- (Blondel *et al* 1992) were obtained separately for the two final fine-structure states of the atom, $4p_{3/2}$ and $4p_{1/2}$. Therefore, we use different ground-state wavefunctions for the $4p_{3/2}$ and $4p_{1/2}$ states.

To obtain the $4p_{3/2}$ radial wavefunction we solve equation (8) with $\eta = 0.865$ in Σ_E, and obtain the eigenvalue $E_{4p} = -0.247$ Ryd, equal to the experimental energy of the $4p_{3/2}$ state (Hotop and Lineberger 1985). The experimental energy of the $4p_{1/2}$ state, -0.281 Ryd† is very close to the HF 4p energy, and we simply use the corresponding HF wavefunction for the $4p_{1/2}$ orbital. The two wavefunctions thus obtained have the following asymptotic parameters: $A = 1.53$ and $\kappa = 0.497$ au for $4p_{3/2}$, and $A = 1.60$ and $\kappa = 0.530$ au for $4p_{1/2}$. The wavefunctions of the intermediate and final states are calculated in the frozen HF field of neutral atom residue, and we use the same sets to calculate the two-photon amplitudes (3) and (4) for both $4p_{3/2}$ and $4p_{1/2}$ states. After the electron detachment from these states the neutral Br is left in either of the two fine-structure states $^2P_{3/2}$ or $^2P_{1/2}$. The corresponding total and differential cross sections are evaluated from the equations, which account for the number of electrons in the $j = \frac{3}{2}$ or $\frac{1}{2}$ sublevel of the np subshell:

$$\sigma^{(j)}(\omega) = \frac{2j+1}{2(2l+1)}\sigma(\omega) \tag{10}$$

$$\frac{\mathrm{d}\sigma^{(j)}}{\mathrm{d}\Omega} = \frac{2j+1}{2(2l+1)}\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} \tag{11}$$

where σ and $\mathrm{d}\sigma/\mathrm{d}\Omega$ are defined by equations (2) and (6), and $l = 1$ for the halogen ions.

The results for the cross sections and angular distribution parameters are presented in

† It is equal to the negative of the sum of the electron affinity and the fine-structure splitting of the 4p subshell in Br.

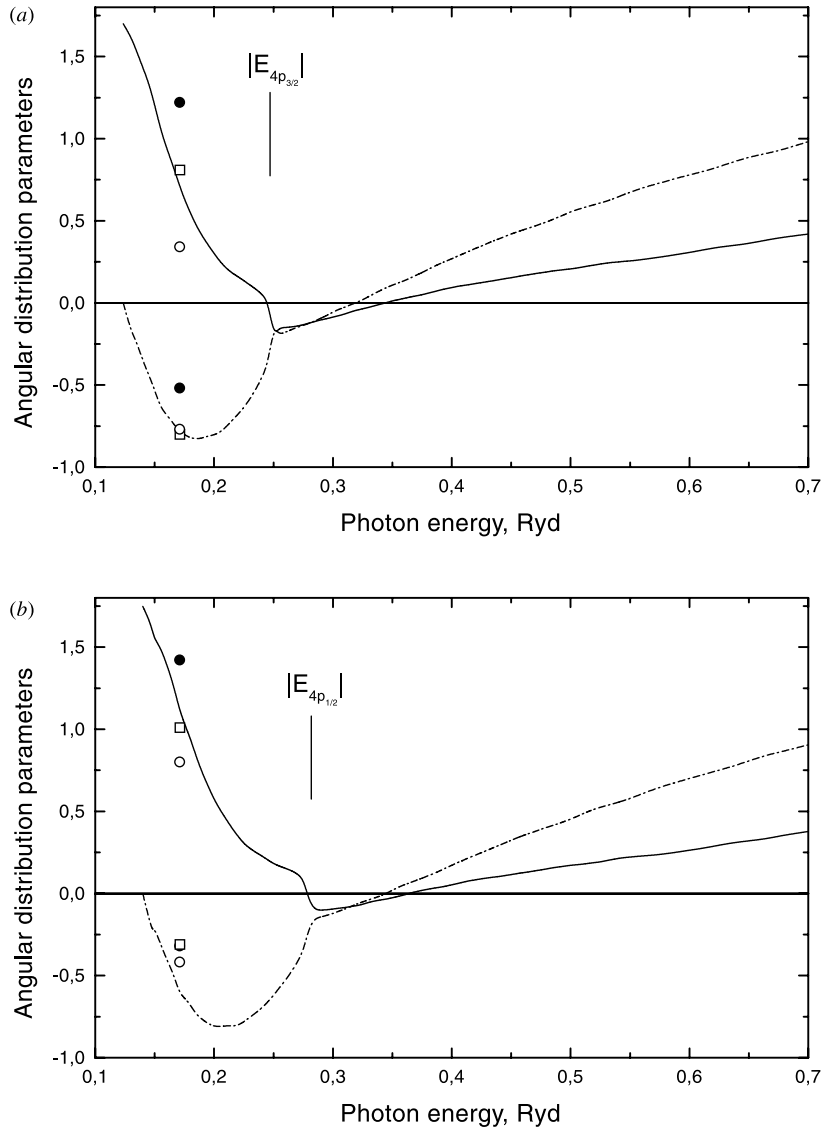

Figure 6. Photoelectron angular distribution parameters for Br^-. (*a*) β_2 (——) and β_4 (— · —) parameters for the $4p_{3/2}$ state. □, experiment (Blondel *et al* 1992); ● and ○, calculations in the plane-wave approximation and with the first Born correction, respectively (Blondel *et al* 1992). (*b*) The same for the β_2 and β_4 parameters for the $4p_{1/2}$ state.

figures 5 and 6. The partial $4p_{3/2}$ and $4p_{1/2}$ detachment cross sections have similar shapes with the cusps shifted by the spin–orbit splitting energy. We would like to emphasize that the ratio of the maxima of these partial cross sections deviates from the statistical value of 2 : 1. The reason is that the $4p_{3/2}$ and $4p_{1/2}$ wavefunctions have a different asymptotic behaviour due to the different binding energies. As we discussed above, this difference is enhanced in multiphoton processes, which clearly favour the more loosely bound state.

We have not found any experimental values of the two-photon detachment cross section in Br^-, so in figure 5 we compare our results with the calculations of Robinson and Geltman

(1967) and Crance (1988). In the calculation of Robinson and Geltman the fine-structure splitting was not taken into account. This means that they used the same wavefunction and energy for both sublevels (basically, a $4p_{3/2}$ one, since it corresponds to the experimental electron affinity). On the other hand, in the HF calculation the wavefunction is practically identical to that of the stronger bound $4p_{1/2}$ orbital. This is why our total cross section, obtained as a sum $\sigma^{(3/2)} + \sigma^{(1/2)}$, goes between the Robinson and Geltman and HF curves. The plane-wave approximation cross section of Crance (1988) has a much higher maximum than all of the results presented in the figure.

As regards the photoelectron angular distribution, the asymmetry parameters for the $4p_{3/2}$ and $4p_{1/2}$ sublevels have similar dependences on the photon energy (see figure 6). They also follow the general trends observed for F^- and Cl^-. The experimental data points of Blondel *et al* (1992) obtained at $\omega = 0.171$ Ryd agree well with our calculations, except for the β_4 parameter in the $4p_{1/2}$ detachment channel. The present calculation demonstrates better agreement with experiment than the plane-wave approximation, or that which includes the first Born correction (Blondel *et al* 1992).

3.4. Iodine

The two-photon detachment calculations for I^- are performed in the same way as for Br^-. The experimental energies of the $5p_{3/2}$ and $5p_{1/2}$ fine-structure sublevels in I^- are -0.2248 and -0.2941 Ryd, respectively (Hotop and Lineberger 1985, Radtsig and Smirnov 1986). The HF approximation yields $E_{5p}^{HF} = -0.2583$ Ryd. The Dyson orbital of the $5p_{3/2}$ state is obtained using the coefficient $\eta = 0.823$ in Σ_E. It yields the experimental $5p_{3/2}$ state energy, and the wavefunction with asymptotic parameters $A = -1.808$ and $\kappa = 0.474$ au. The same calculations with $\eta = 0.008$ reproduce the experimental $5p_{1/2}$ energy, and produce a wavefunction with $A = -2.587$ and $\kappa = 0.542$ au. Using these ground-state wavefunctions

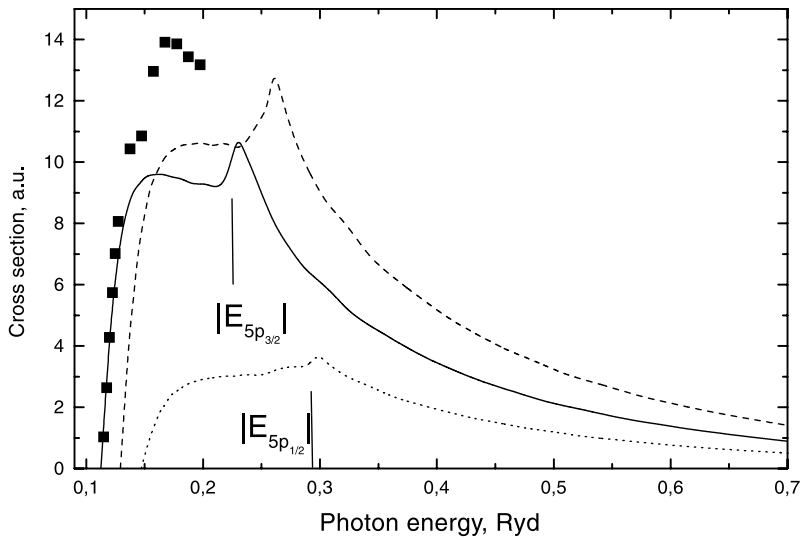

Figure 7. Two-photon detachment cross sections of I^-. – – –, HF wavefunctions of the 5p, intermediate and final states; ——, the same with the $5p_{3/2}$ wavefunction from the Dyson equation; · · · · · ·, the same with the $5p_{1/2}$ wavefunction from the Dyson equation; ■, model calculations by Robinson and Geltman (1967).

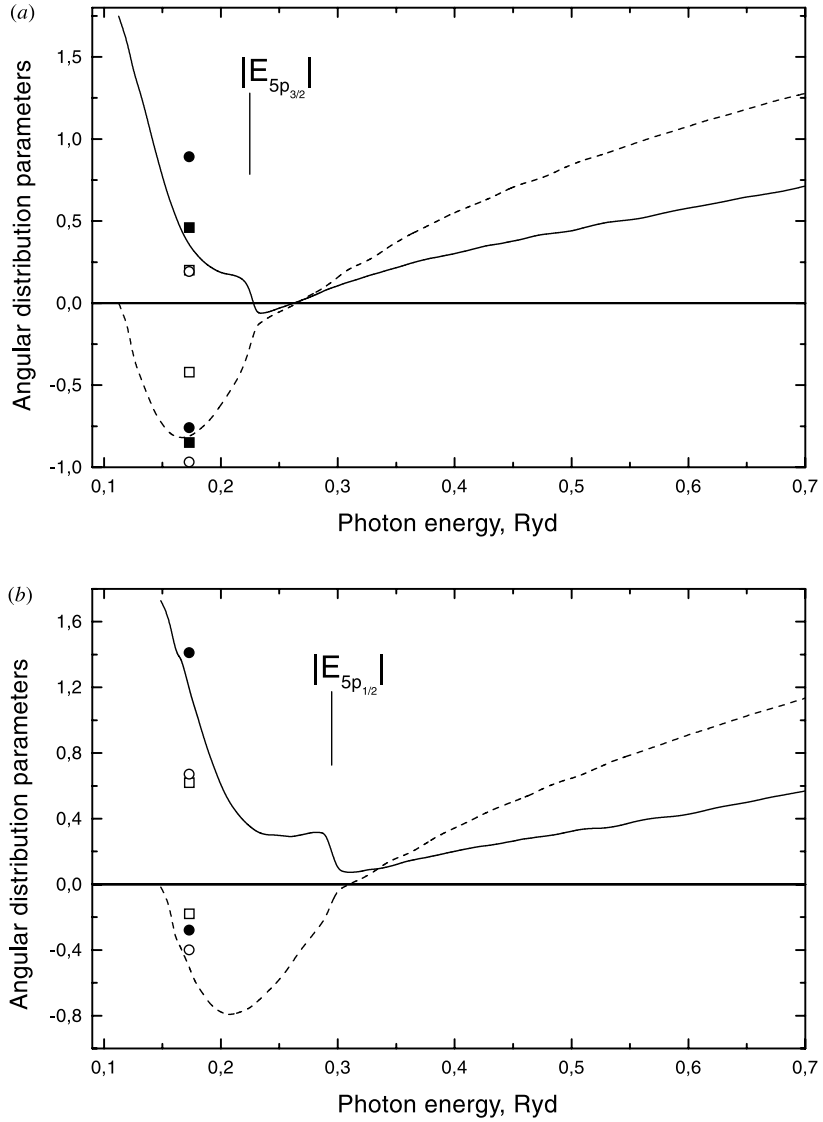

Figure 8. Photoelectron angular distribution parameters for I^-. (*a*) β_2 (——) and β_4 (– – –) parameters for the $5p_{3/2}$ state. □ and ■, experimental data of Blondel *et al* (1992) and Blondel and Delsart (1993), respectively; ● and ○, calculations in the plane-wave approximation and with the first Born correction, respectively (Blondel *et al* 1992). (*b*) The same for the β_2 and β_4 parameters for the $5p_{1/2}$ state.

together with the HF sets of the intermediate- and final-state wavefunctions, we calculate the two-photon detachment amplitudes (3) and (4) for the $5p_{3/2}$ and $5p_{1/2}$ electrons, and obtain the total and differential cross sections (10) and (11).

The cross sections are shown in figure 7. Due to a larger difference in the binding energies the effect of the non-statistical ratio between the maxima of the $\sigma^{(3/2)}$ and $\sigma^{(1/2)}$ cross sections is more pronounced here than in Br. In I^- their ratio in the region below the single-photon threshold is about 3 : 1 instead of the statistical value of 2 : 1. The HF threshold is located

between the two fine-structure thresholds. Nevertheless, the sum $\sigma^{(3/2)}+\sigma^{(1/2)}$ would rise above the HF curve. On the other hand, it would be close but still lower than the model-potential results of Robinson and Geltman (1967). The plane-wave calculations (Crance 1988) give an even higher cross section at the maximum.

The angular distribution parameters are presented in figure 8. For the $5p_{3/2}$ electron detachment from I^- there are two measurements at the photon energy of 0.171 Ryd (Blondel *et al* 1992, Blondel and Delsart 1993), and the more recent one shows a much better agreement with our calculations. If we speculate that the earlier measurement for the $5p_{1/2}$ fine-structure component was affected by the spurious background in a way similar to that seen in the $5p_{3/2}$ data, larger absolute values of $\beta_{2,4}$ could be expected for the $5p_{1/2}$ detachment measurements. This will bring them into better agreement with our calculated values (figure 8(*b*)). As for the β parameters calculated in the plane-wave approach and with the first Born correction, they show large scatter, similar to that seen in Cl and Br. It means that the potential between the photoelectron and the atom should be included non-perturbatively, at least at the HF level, as in the present calculation.

4. Concluding remarks

In the present paper we have performed direct numerical calculations of the two-photon detachment from the halogen negative ions. We paid special attention to the proper description of the initial ground-state wavefunction, namely, its correct asymptotic behaviour. The outer np ground-state orbitals of the negative ions were calculated from the many-body theory Dyson equation with the non-local correlation potential adjusted to reproduce experimental binding energies. Our calculations demonstrate explicitly that the use of asymptotically correct initial-state wavefunctions is very important for obtaining correct absolute values of the multiphoton detachment cross sections. This confirms the conclusion of the adiabatic theory (Gribakin and Kuchiev 1997a, b, Gribakin *et al* 1998) about the significance of large electron–atom separations in multiphoton processes.

For heavier halogen negative ions (Br and I) our calculations reveal substantial non-statistical branching of photodetachment into the $P^2_{3/2}$ and $P^2_{1/2}$ final atomic states. This effect is mainly a consequence of the different asymptotic behaviour of the corresponding outer negative ion orbitals $np_{3/2}$ and $np_{1/2}$. Our calculations predict the existence of prominent cusps in the two-photon detachment cross sections and angular asymmetry parameters at the single-photon detachment thresholds. The cross sections are in general close to those obtained by Robinson and Geltman (1967), who worked within a model-potential approach and used asymptotically correct bound-state wavefunctions. The photoelectron angular asymmetry parameters obtained in the present work give the best overall agreement with the measurements of Blondel *et al* (1992) and Blondel and Delsart (1993) at the photon energy of 0.171 Ryd.

Acknowledgments

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