Two-photon detachment of electrons from halogen negative ions

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Abstract. Absolute two-photon detachment cross sections and photoelectron angular distribution are calculated for halogen negative ions within lowest-order perturbation theory. The Dyson equation method is used to obtain the outer np ground-state wave functions with proper asymptotic behavior $P(r) \propto \exp(-\kappa r)$, 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.

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1. Introduction

Halogen negative ions have been subject of experimental and theoretical multiphoton detachment studies for over thirty years (Hall et al 1965, Robinson and Geltman 1967). Apart from the negative hydrogen ion which traditionally receives 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 five. 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 of correlations is small just above the threshold but increases with the photon energy and reaches 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 to 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 wave function in these calculations remained incorrect. This may seem
to have introduced only a small error in the calculation, since the bound-state wave
function in the asymptotic region is small. However, as shown in the adiabatic theory of
multiphoton detachment from negative ions (Gribakin and Kuchiev 1997a, 1997b), the
asymptotic behaviour of the bound-state wave function is crucial for obtaining correct
absolute values of the probabilities of multiphoton processes. This theory based on the
Keldysh approach (Keldysh 1964) approach shows that the electron escape from the
atomic system in a low-frequency laser field takes place at large distances,

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

where $\omega$ is the photon frequency, $\kappa$ 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 wave function, namely by parameters
$A$ and $\kappa$ of the corresponding radial wave function $R(r) \simeq Ar^{-1}e^{-\kappa r}$. This result is
obtained using the length form of interaction with the laser field, which 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
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 wave function and showed that the true cross section should be
substantially higher than it was previously believed, based on calculations with the
HF $2p$ wavefunction. Moreover, the use of the ground-state wavefunction with correct
asymptotic behaviour in multiphoton detachment calculations is often more important
than other effects of electron correlations.

In our previous work the asymptotically correct $2p$ wavefunction was obtained using
a model potential chosen to reproduce the experimental value of the $2p$-electron energy.
Of course, any model-potential approach is not free from ambiguities related to the
choice of the potential. The aim of present work is to perform more accurate calculations
of the two-photon detachment in negative halogen ions using correct $np$ wavefunctions
obtained within the many-body Dyson equation method (see, e.g. Chernysheva et al
1988). Section 2 briefly outlines the method of calculation. 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 $\omega$ is

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

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 is normalized to the $\delta$-function of energy. For the detachment of the outer np electron from the negative halogen ion $np^6 1S$ the final state can be either $1S$ ($L = 0$, $l_f = 1$) or $1D$ ($L = 2$, $l_f = 1, 3$). In the lowest 2nd order the two-photon amplitude $A_{l_f L}(\omega)$ is determined by the following equations

$$A_{l_f L}(\omega) = \sqrt{2L + 1} \left[ \begin{array}{ccc} 1 & 1 & L \\ 0 & 0 & 0 \end{array} \right] \sum_{L'} (-1)^{l_f} \left\{ \begin{array}{ccc} 1 & 1 & L' \\ l_f & l_0 & l \end{array} \right\} M_{l_f L}(\omega),$$

$$M_{l_f L}(\omega) = \sum_{\nu} \frac{\langle \nu l || \hat{d} || \nu l \rangle \langle \nu l || \hat{d} || n_0 l_0 \rangle}{E_0 + \omega - E_\nu + i0},$$

where $\nu l$ 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, e.g., in the length form,

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

where $l_\geq = \max\{l, l_0\}$ and $P$‘s are the radial wave functions.

The photoelectron angular distribution is given by the differential cross section

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

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

$$\beta_{2j} = \frac{16\pi^3 \omega^2}{c^2 \sigma} (4j + 1) \Re \left[ \sum_{L', L''} (-1)^{l_0 + L' + L''} (-i)^{l_f'} \exp \left[ i(\delta_{l_f'} - \delta_{l_f''}) \right] \sqrt{|L'| |L''| |L'|} \right] \times \left( \begin{array}{ccc} l_f' & 2j & l_f'' \\ 0 & 0 & 0 \end{array} \right) \left( \begin{array}{ccc} L' & 2j & L'' \\ 0 & 0 & 0 \end{array} \right) \left\{ \begin{array}{ccc} L' & L'' & 2j \\ l_f' & l_f'' & l_0 \end{array} \right\} A_{l_f', L'} A_{l_f'', L''},$$

where $[l] \equiv 2l + 1$ and $\beta_0 = 1$, so that the photoelectron angular distribution after two-photon detachment is characterized by $\beta_2$ and $\beta_4$. 
The wavefunctions of the intermediate ($\nu l$) and final ($\epsilon f$) states of the photoelectron are calculated in the HF field of the frozen neutral atom residue $np^5$. 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 $\Delta k$.

2.2. Ground-state wavefunction

If one describes the initial state $n_0l_0$ in the HF approximation, the asymptotic behaviour of the corresponding radial wavefunction is incorrect. Namely, it is characterized by $\kappa$ 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 we have shown (Gribakin et al 1998) is in fact much more important to have an asymptotically correct bound-state wavefunction $P_{n_0l_0}$ than to use correct initial state energy $E_0$ in equation (4). The need for an asymptotically correct wavefunction was also clearly illustrated by the adiabatic hyperspherical calculation of multiphoton detachment from $H^-$ by Liu et al (1992), where a 3.4% change of $\kappa$ resulted in a 25% change of the two-photon cross section. 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 $\alpha$ 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)

$$\hat{H}^{(0)}\phi_E(r) + \int \Sigma_E(r, r')\phi_E(r')dr' = E\phi_E(r)$$

Here $H^{(0)}$ is the single-particle HF Hamiltonian and $\Sigma_E$ 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). In most applications $\Sigma_E$ is calculated by means of perturbation-theory expansion, and the lowest second-order contribution usually gives a considerable improvement on the HF results. Note that in some sense the Dyson equation provides the best single-particle orbital of the initial state for photodetachment calculations. Because it is in fact a quasiparticle orbital, it incorporates certain many-body effects, namely, the ground-state correlations leading to the correct binding energy.
Within the second order in the electron Coulomb interaction $V$ the matrix element of $\Sigma_E$ between some single-electron states $a$ and $b$ looks like

$$
\langle a|\Sigma_E|b\rangle = \sum_{\nu_1,\nu_2,n_1} \frac{\langle n_1|V|\nu_1\nu_2\rangle(\langle \nu_2\nu_1|V|n_1b\rangle - \langle \nu_1\nu_2|V|n_1b\rangle)}{E - E_{\nu_1} - E_{\nu_2} + E_{n_1} + i0} 
+ \sum_{\nu_1,n_1,n_2} \frac{\langle n_1|V|n_1n_2\rangle(\langle n_2n_1|V|\nu_1b\rangle - \langle n_1n_2|V|\nu_1b\rangle)}{E - E_{n_1} - E_{n_2} + E_{\nu_1} - i0},
$$

(9)

where the sums run over occupied states $n_1$ and $n_2$, and excited states $\nu_1$ and $\nu_2$, and the second terms in parentheses are exchange contributions. The lowest-order correction to 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 $\Sigma_E$ is dominated by the direct contribution in the second sum in equation (9) (first term in parenthesis). For $E \approx E_{np}$ the sum over the occupied states is basically given by $n_1 = n_2 = np$ (in many-body theory language this means that both holes are the outer $np$ subshell). It is obvious then that this contribution has $E_{\nu_1} - E_{np} > 0$ in the denominator, and with a squared matrix element (for $a = b = np$) in the numerator, it is explicitly positive.

It also follows from our calculations that $\Sigma_E$ 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 $\eta$ 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. Moreover, using different values of $\eta$ we can effectively simulate the fine-structure splitting, and obtain the wavefunctions for both fine-structure components of the $np^6$ subshell, the upper $np_{3/2}$ and lower $np_{1/2}$, 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 $\Sigma_E$ from equation (9) in this semiempirical way, only the contributions of dominant monopole and dipole atomic excitations are included in the sums.

Note that the importance of large distances in multiphoton problems (Gribakin and Kuchiev 1997a, 1997b) supports the use of the length form of the photon dipole operator. This is in agreement with the results of Pan et al (1990) who showed that the two-photon detachment cross sections obtained with the dipole operator in the velocity form are much more sensitive to the shift of the photodetachment threshold and correlation corrections, while the length form results are much more robust.

The two-photon amplitudes $M_{l,\mu}$ (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 $\delta$-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, 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 $2p$ wave function 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 $\Sigma_E$ 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 Sec. 2.2, we reproduce the experimental energy for the $2p$ electron, and obtain an accurate 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 wave function with that possessing a correct asymptotic behaviour. Unlike the use of the Dyson equation with the many-body correlation potential (even if somewhat adjusted), this procedure is not free from ambiguities. They manifest in the differences between $A$ values from the two sources cited.

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. According to them electron correlation effects suppress the cross section in $F^-$ by about 20% at the maximum.

When we use the experimental energy of the $2p$ electron together with the HF
Table 1. Asymptotic parameters of the \( np \) orbitals of the halogen negative ions.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Orbital</th>
<th>( \kappa )</th>
<th>( A )</th>
<th>( A' )</th>
<th>( A'' )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( F^- )</td>
<td>( 2p_e )</td>
<td>0.500</td>
<td>0.64</td>
<td>0.84</td>
<td>0.7</td>
</tr>
<tr>
<td>( Cl^- )</td>
<td>( 3p_e )</td>
<td>0.516</td>
<td>1.355</td>
<td>1.34</td>
<td>1.3</td>
</tr>
<tr>
<td>( Br^- )</td>
<td>( 4p_{3/2} )</td>
<td>0.497</td>
<td>1.53</td>
<td>1.49</td>
<td>1.4</td>
</tr>
<tr>
<td>( Br^- )</td>
<td>( 4p_{1/2} )</td>
<td>0.530</td>
<td>1.60</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>( I^- )</td>
<td>( 5p_{3/2} )</td>
<td>0.474</td>
<td>1.808</td>
<td>1.9</td>
<td>1.8</td>
</tr>
<tr>
<td>( I^- )</td>
<td>( 4p_{1/2} )</td>
<td>0.542</td>
<td>2.587</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

\( a \) Obtained using experimental binding energies.
\( b \) Obtained from 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 \( Cl^- \).

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 line in figure 1). The 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 (dash-dotted line in figure 1) with a maximum of \( \sigma = 1.25 \text{ au} \) at \( \omega = 0.166 \text{ Ryd} \).

However, when we use the \( 2p \) wavefunction with the correct asymptotic behaviour from the Dyson equation, the photodetachment cross section increases about two times.†. This cross section is shown by solid line 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 used an asymptotically correct \( 2p \) wavefunction was the model potential calculation of Robinson and Geltman (1967), which produced a cross section two times greater than 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 the effects of electron correlations. Of course, the difference between the experimental and HF energies is also a manifestation of electron correlation effects. It influences the

† 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, 1997b), for a given \( \kappa \) the \( n \)-photon cross section is proportional to \( A^2 \).
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
and more, which is much greater than other correlation effects (Pan et al 1990). This
fact distinguishes this problem from the single-photon processes, where other correlation
effects are essential.

The angular asymmetry parameters $\beta_2$ and $\beta_4$ 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 the
results of different calculations are much closer for them than for the absolute values of
the photodetachment cross sections. Thus, our present results are practically equal to
those obtained in the model $2p$ wavefunction calculation (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 in $\beta_4$. 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 $\beta_4$. 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
that our present calculations with the Dyson $2p$ wavefunction is in good agreement with
experiment.

3.2. Chlorine

The HF calculations of the $\text{Cl}^-$ ground state gives $E_{3p}^{\text{HF}} = -0.301$ Ryd for the $3p$-
electron energy, while the experimental value derived from the electron affinity of Cl is
$E_{3p}^{\text{exp}} = -0.2657$ Ryd (Hotop and Lineberger 1985). The spin-orbit splitting in $\text{Cl}^-$ 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 $\Sigma_E$ 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 $\Sigma_E$ with the scaling factor $\eta = 0.842$, introduced as outlined in
Sec. 2.2. The corresponding asymptotic parameters are listed in Table 1.

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 dotted-dashed lines in figure 3, respectively), but agree better with the HF cross section calculated by Crance (1987) (open circles) and less than the cross sections obtained within 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 result obtained by Trainham et al (1987) at \( \omega = 0.142 \) Ryd is also shown.

The angular distribution parameters are shown in figure 4. In general the parameters \( \beta_2 \) and \( \beta_4 \) behave similarly to those in the 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 \( \beta \) values for I\(^-\) in Blondel et al 1992 where affected by a spurious background. It appears that in the case of heavier halogens, for the data obviously are not as reliable as in the fluorine case (Blondel 1997).

### 3.3. Bromine

The binding energy of the 4p state in Br\(^-\) obtained 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 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 \( \Sigma_E \), and obtain the eigenvalue \( E_{4p} = -0.247 \) Ryd, equal to the experimental energy of the
4p\textsubscript{3/2} state (Hotop and Lineberger 1985). The experimental energy of the 4p\textsubscript{1/2} state, \(-0.281\) Ryd\(^\dagger\) is very close to the HF 4p energy, and we simply use the corresponding HF wavefunction for the 4p\textsubscript{1/2} orbital. The two wavefunctions thus obtained have the following asymptotic parameters: \(A = 1.53\) and \(\kappa = 0.497\) au for 4p\textsubscript{3/2}, and \(A = 1.60\) and \(\kappa = 0.530\) au for 4p\textsubscript{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\textsubscript{3/2} and 4p\textsubscript{1/2} states. After the electron detachment from these states the neutral Br is left in either of the two fine-
structure states \(^2\)P\textsubscript{3/2} or \(^2\)P\textsubscript{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:

\[
\sigma^{(j)}(\omega) = \frac{2j + 1}{2(2l + 1)} \sigma(\omega)
\]

\[
\frac{d\sigma^{(j)}}{d\Omega} = \frac{2j + 1}{2(2l + 1)} \frac{d\sigma}{d\Omega}
\]

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

The results of cross section and angular distribution parameter calculations are presented in figures 5 and 6.

The partial 4p\textsubscript{3/2} and 4p\textsubscript{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 is not equal to the statistical 2 : 1. The reason is that because of the different binding energies the 4p\textsubscript{3/2} and 4p\textsubscript{1/2} wavefunctions have different asymptotic behaviour. 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 of was not taken into account. This means that they used the same wavefunction and energy for both sublevels (basically, a 4p\textsubscript{3/2} one, since it corresponds to the experimental electron affinity). On the other hand, in the HF calculation the wave function is practically identical to that of the stronger bound 4p\textsubscript{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.

\(^\dagger\) It is equal to the negative of the sum of the electron affinity and the fine-structure splitting of the 4p subshell in Br.
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 \(\beta_4\) parameter in the \(4p_{1/2}\) detachment channel. Our 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 calculation 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 \(-0.2248\) Ryd 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 \(\Sigma_F\). 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 \(\eta = 0.008\) reproduces the experimental \(5p_{1/2}\) energy, and produces a wavefunction with \(A = -2.587\) and \(\kappa = 0.542\) au. Using these ground-state wavefunctions together with the HF sets of the intermediate and final state HF 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 non-statistical ratio between the maxima of the \(\sigma_{3/2}\) and \(\sigma_{1/2}\) cross sections is even more noticeable here than in \(Br\). In \(I^-\) their ratio in the region below the single-photon threshold is about 3 : 1 instead of the statistical 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 in better agreement with our calculated values (figure 8 b). As for the \(\beta\) 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. Of course, for a more accurate description one will have to include correlation effects, e.g., the electron-atom polarization potential.

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. We have confirmed the understanding based on the adiabatic theory (Gribakin and Kuchiev 1997a, 1997b, Gribakin et al 1998) that using asymptotically correct initial state wavefunctions is especially important for the absolute values of the multiphoton detachment cross sections.

For heavier halogen negative ions (Br and I) our calculations reveal substantial non-statistical branching of photodetachment into the $P_{3/2}$ and $P_{1/2}$ 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 also predict the existence of prominent cusps in the two-photon detachment cross sections and angular asymmetry parameters at the single-photon detachment thresholds. Our cross sections are in general closer to those obtained by Robinson and Geltman (1967), who worked within a model-potential approach and used asymptotically correct bound-state wavefunctions. Our calculations of the photoelectron angular asymmetry parameters give best overall agreement with the measurements of Blondel et al (1992) and Blondel and Delsart (1993) at the photon energy of 0.171 Ryd.

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**Figure captions**

**Figure 1.** Two-photon detachment cross sections of $F^-$. Present calculations: - - - -, HF wavefunctions of the 2p, intermediate and final states; ——, 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 Hart (1996); ■, model calculations by Robinson and Geltman (1967); ●, experiment (Kwon et al 1989).
Figure 2. Photoelectron angular distribution parameters for F\(^{−}\). ·····, the HF $\beta_2$ parameter; ···, the HF $\beta_4$ parameter; ·····, $\beta_2$ parameter with the Dyson 2$p$ wavefunction; ·····, $\beta_4$ parameter with the Dyson 2$p$ wavefunction. ■, experiment (Blondel and Delsart 1993); ○, correlated length results by Pan and Starace (1991).
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 Hart (1996); ○, HF calculations by Crance (1987); ■, model calculations by Robinson and Geltman (1967); ●, experiment (Trainham et al 1987).
Figure 4. Photoelectron angular distribution parameters for Cl$^-$. ·····, the HF $\beta_2$ parameter; ····, the HF $\beta_4$ parameter; ·····, $\beta_2$ parameter with the Dyson $2p$ wavefunction; ·····, $\beta_4$ 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).
Figure 5. Two-photon detachment cross sections of Br−. - - - -, HF wavefunctions of the 4p, intermediate and final states; ——, same with the 4p3/2 wavefunction from the Dyson equation; — · —, same with the correct 4p1/2 wavefunction; ■, model calculations by Robinson and Geltman (1967).
Figure 6. Photoelectron angular distribution parameters for Br$. (a) $\beta_2$ (——) and $\beta_4$ (- - - -) parameters for 4$p_{3/2}$ state. $\square$, 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 $\beta_2$ and $\beta_4$ parameters for 4$p_{1/2}$ state.
Figure 7. Two-photon detachment cross sections of I⁻. - - - -, HF wavefunctions of the 5p, intermediate and final states; ——, same with the 5p₃/₂ wavefunction from the Dyson equation; — · —, same with the 5p₁/₂ wavefunction from the Dyson equation; ■, model calculations by Robinson and Geltman (1967).
Figure 8. Photoelectron angular distribution parameters for I⁻. (a) $\beta_2$ (——) and $\beta_4$ (-----) parameters for 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 $\beta_2$ and $\beta_4$ parameters for 5p$_{1/2}$ state.