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Photoionization of atomic iodine and its ions

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Calculations of the photoionization cross section for the atomic iodine atom and its ions I^- and I^{2+} using the random-phase approximation with exchange are performed in a broad photon energy range from 40 to 136 eV. A significant (factor of 3) difference between recent experimental data and our theoretical results is found in the region dominated by the giant resonance from the $4d$ subshells. Sum-rule analysis suggests that the experimental situation requires reexamination.

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In this paper we present theoretical results for the photoionization cross section of atomic I and its ions I^- and I^{2+}, calculated using the random-phase approximation with exchange (RPAE). The energy range considered goes from the first ionization threshold up to more than 150 eV, thus including the threshold of the $4d^{10}$ subshell. The study of atomic I is of interest since it is a neighbor of Xe in the periodic table, and the Xe photoionization cross section in this energy region is largely determined by multielectron correlations [1].

In addition, in recent measurements [2,3] the cross section for $4d^{10}$-subshell photoionization in atomic I [2] and its positive ions, I^+ and I^{2+} [3], were found to be smaller than in Xe by a factor of 3. The agreement of the $4d$ ionization results between I and I^+ argues for the reliability of the experimental data. However, from the proximity of atomic I to Xe in the periodic table, it is likely that the photoabsorption of intermediate and inner subshells of Xe and I, as well as that of their positive ions, should be almost the same. It has been known for some time that the photoabsorption cross sections of atoms with a closed $4d$ subshell, namely, Xe, Cs, and Ba, are dominated by a giant resonance positioned above the $4d$ threshold [1]. The cross sections for this $4d$-subshell ionization, in experiment and in theory, satisfy the one-electron dipole sum rule with reasonable accuracy, as do previous calculations for I [4,5] and I^- [6], which exhibited the same behavior: the presence of a huge $4d$ giant resonance, the cross section of which almost completely saturates the dipole sum rule.

Experimental photoelectron spectroscopy for I^- [7] found, on the contrary, that the $4d^{10}$ subshell photoionization cross section is smaller than Xe by a factor of about 3. It is in principle possible that this result could be caused by molecular effects, since the experiment was actually performed on CH_3I. But the giant resonance occurs at a high enough energy where molecular effects are likely to be relatively small.

Another conceivable mechanism for the reduction of the $4d$ cross section is the possibility of ionization of a $4d$ electron plus simultaneous excitation (or ionization) of an outer-shell electron. This can be looked at as inelastic scattering of the photoelectron emerging from the $4d^{10}$ subshell by the outer shells [8], which leads to excitation or ionization of the residual ion due to energy loss by the photoelectron. Those photoelectrons that lose some of their energy are shifted to another part of the photoelectron spectrum, thereby lowering the strength (cross section) of the main line. This decrease is found to be about 20–30 % in Xe and Ba [9–11]. Assuming that this effect is much stronger in I^- (or in molecular CH_3I) than in Xe, the experimental observation [7] could, in principal, be understood. However, there is no evidence for the large shift of photoelectron flux into ionization plus excitation channels in the experiment [7]. Furthermore, the details of this inelastic scattering of the photoelectron should be strongly dependent upon the details of the structure of the outer-shell electrons. But in the experimental study of the photoionization of $4d$ electrons of atomic iodine [2], the cross sections found were also about a factor of 3 smaller than the theoretical and the Xe cross sections. Recently new measurements on the ions I^+ and I^{2+} were reported [3]. Using a normalization procedure applied previously to obtain absolute cross sections [2], results that basically agree with the data for atomic I [2] were obtained. It is, however, almost impossible to imagine that the photoelectron's inelastic scattering, which contributes about 20–30 % in Xe, Cs, and Ba, is accidentally extraordinarily large not only for I^- but for I, I^+, and I^{2+}, also. To try to understand this discrepancy, then, calculations of the photoionization cross section of I^-, I, and I^{2+} were performed within the framework of the latest version of RPAE and its generalizations.

The negative ion I^- is a closed-shell system, whereas I and I^{2+} are open-shell systems. Therefore while I^- is a system to which ordinary RPAE [1] can be applied, I and I^{2+} require a generalization of RPAE. In this paper the iodine atom is considered using the RPAE generalization for open subshell atoms [12,13]. It is very difficult to apply this method to open shells with two or more vacancies in them. But for atoms with a half-filled subshell, another method was developed based on the following idea. According to Hund's rule, in the ground state of such an atom all electrons in the

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half-filled shell have the same spin direction. As a result, other subshells also become split into two levels, each being occupied by electrons having either the same spin direction as in the half-filled subshell or opposite to that. One can consider these atoms as being constructed of two kinds of different electrons, usually called ‘‘up’’ and ‘‘down’’ electrons. Then Hartree-Fock (HF) and RPAE methods, generalized to consider those two-component atoms, have been developed [1,14]. Such an approach is used here to calculate the I^{2+} photoionization cross section.

To consider I^{-}, the following system of RPAE equations for so-called reduced matrix elements was solved [1,6]:

$$\langle n\ell \| D(\omega) \| \varepsilon,\ell \pm 1\rangle = \langle n\ell \| d(\omega) \| \varepsilon,\ell \pm 1\rangle + \left(\sum_{\nu' \leqslant F, \nu'' > F} - \sum_{\nu' > F, \nu'' \leqslant F} \right) \frac{2}{3} \frac{\langle \nu'' \| D(\omega) \| \nu' \rangle \langle \nu'; n\ell \| U_1 \| \nu''; \varepsilon,\ell \pm 1\rangle}{[\omega - E_{\nu''} + E_{\nu'} + i\delta(1-2n_{\nu''})]}, \tag{1}$$

where $n\ell$ is the principal quantum number and angular momentum for the initial state of the ejected electron, i.e., of the hole, ε, $\ell \pm 1$ is its final state, and $\nu'' \equiv n''(\varepsilon'')$, $\ell'' = \ell' \pm 1$, $\nu' \equiv \varepsilon'(n'), \ell'$ determine the HF intermediate electron and hole states. The summation (integration) in Eq. (1) is performed over occupied ($\leqslant F$) and vacant ($> F$) one-electron states, which are determined by their energy (principal quantum number) $\varepsilon'(n')$ and angular momentum ℓ'. Here n_q denotes the Fermi step function $n_q = 1$ for $q \leqslant F$ and $n_q = 0$ for $q > F$. Equation (1) is obtained from the usual RPAE equations (1) in operator form

$$\hat{D} = \hat{d} + \hat{D}\hat{\chi}\hat{U}, \tag{2}$$

after transforming it by taking matrix elements and performing the integration over angular variables of the one-electron HF wave function analytically and summing over spin projections. Here $\hat{D}$ and $\hat{d}$ are the operators representing photoabsorption with creation of an electron-hole pair in the RPAE and HF approximations, respectively, $\hat{\chi}$ represents the propagation of an electron-hole pair in an intermediate state, and U is the (direct minus exchange) electron-hole Coulomb interaction.

The calculations for atomic I have been performed using the generalization of RPAE for open-shell atoms [12,13]. This method was successfully tested in performing calculations for the open subshell itself; e.g., $3p^5$ in Cl and $2p^4$ in O. Here our main interest is in the closed shell, namely the $4d^{10}$ in an open-shell atom. Photoionization in this case leads to a rather complicated final state having three open shells. To simplify the calculation, while retaining the essence of the RPAE correlations, an approximation is introduced: The angular momenta of the ionized shell $n\ell$ and the photoelectron $\varepsilon\ell_1$ are coupled to produce the state with the term ^1P as required by dipole selection rules, leading to $\ell_1 = \ell \pm 1 \geqslant 0$ only. This ^1P is then coupled to the orbital and spin angular momenta of the open shell, $(n_0\ell_0)^q(L_0S_0)$ ($q < 4\ell_0 + 2$ being the number of electrons in this shell) to give the total orbital and spin angular momentum of the final state L_fS_f. There are several possible values of L_fS_f; that leads to the appearance of many open channels in the photoionization of closed shells in an open-shell system. This approximation amounts to using the same exchange term between the ionized shell $n\ell$ and the photoelectron $\varepsilon\ell_1$ for all cases.

The dipole matrix element in the HF approximation is defined by

$$\langle \varepsilon\ell_1 L_f S_f \| d \| L_0 S_0 \rangle = \delta_{S_0 S_f} \sqrt{2S_0+1}\, W^{\ell L_0 S_0}_{\ell_1 L_f S_f} \langle \varepsilon\ell_1 \| d \| n\ell \rangle,$$
$$W^{\ell L_0 S_0}_{\ell_1 L_f S_f} = \sqrt{\frac{2(2L_f+1)}{3}}\,(-1)^{\ell + L_0 - L_f}, \tag{3}$$

with $\langle \varepsilon\ell_1 \| d \| n\ell \rangle$ being the reduced dipole amplitude in the HF approximation. Note that Eq. (3) differs from the definition (4) in [12] for the case of photoionization of the open shell by the factor $W^{\ell L_0 S_0}_{\ell_1 L_f S_f}$. Substituting the coefficients $C^{\ell L_0 S_0 1}_{L'S'\ell_0 LS}$, where LS is the orbital and spin angular momentum of the ionized subshell, by the corresponding $W^{\ell L_0 S_0}_{\ell_1 L_f S_f}$, the expression for the matrix element of the Coulomb interaction U is obtained, which is required in the RPAE equation (1).

In the case of half-filled shell atoms, one has to consider, instead of Eq. (2), a system of two equations forming the spin-polarized RPAE, which can be conveniently presented in a matrix form as [14]

$$\begin{pmatrix} D_{\uparrow} \\ D_{\downarrow} \end{pmatrix} = \begin{pmatrix} d_{\uparrow} \\ d_{\downarrow} \end{pmatrix} + (D_{\downarrow} D_{\uparrow}) \begin{pmatrix} \chi_{\uparrow\uparrow} & 0 \\ 0 & \chi_{\downarrow\downarrow} \end{pmatrix} \begin{pmatrix} U_{\uparrow\uparrow} & U_{\uparrow\downarrow} \\ U_{\downarrow\uparrow} & U_{\downarrow\downarrow} \end{pmatrix}, \tag{4}$$

where the arrow ↑ (↓) denotes the ‘‘up’’ (‘‘down’’) one-electron state. Their wave functions are found by solving a

TABLE I. Binding energies in rydbergs used in the calculations with the available experimental data in parentheses. The entries separated by a slash for I^{2+} are the result of *spin-polarized* Hartree-Fock calculations.

	I^{-}	I	I^{2+}
$5p$	0.258	0.806(0.768)	2.22
$5s$	1.11	1.64(1.55)	2.60/3.19
$4d$	4.22	4.80	6.25/6.28

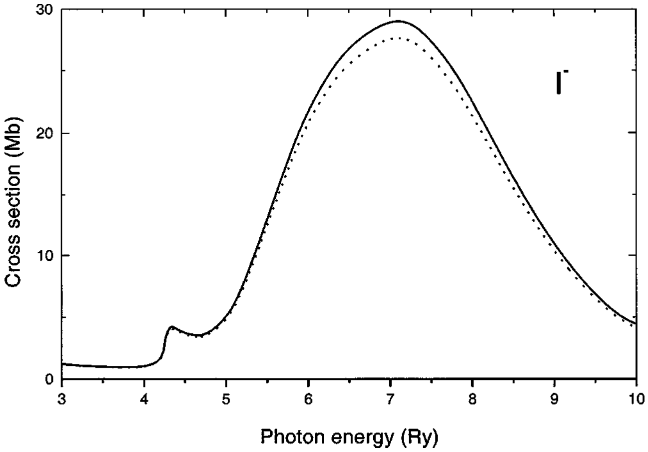

FIG. 1. Calculated photoabsorption cross section for I^- in length (dashed curve) and velocity (solid curve) formulations in the region of the $4d$ giant resonance.

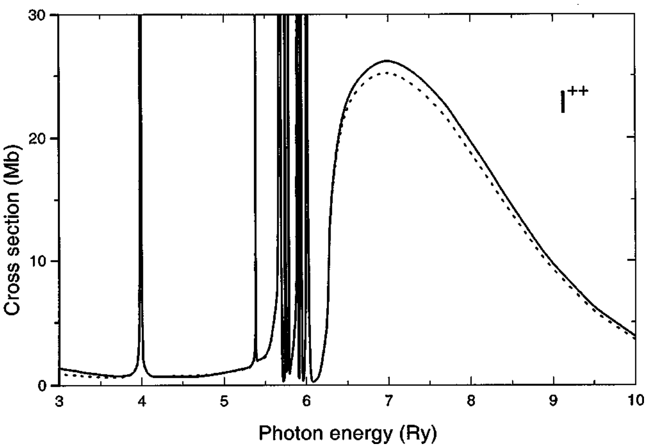

FIG. 3. Calculated photoabsorption cross section for I^{2+} in length (dashed curve) and velocity (solid curve) formulations in the region of the $4d$ giant resonance.

matrix HF equation, which is a generalization of the ordinary HF in which two kinds of electrons, up and down, are assumed. The integration over angular variables of the one-electron HF wave function can be performed in Eq. (4), leading to a system of equations for the reduced matrix elements similar to Eq. (1).

The general numerical procedure of solving the RPAE equation is essentially the same for closed, open, and half-filled shell atoms and goes on as described in [15]. Up to eight interacting channels (transitions) were taken into account. Hartree-Fock thresholds are employed in the calculations and are shown in Table I; unfortunately, experimental results are available only for I $5p$ and $5s$ [16], where the comparison shows reasonably good (5%) agreement.

The results of calculations presented in this paper are in accord with qualitative considerations and previous calculations [4–6], demonstrating that in I^-, I, and I^{2+} the absolute cross sections, in the energy range above the $4d$ thresholds, are dominated by powerful giant resonances, which are similar to each other in shape and strength. They almost completely saturate the sum rule, giving values not less than 8, as compared to 10, which is the total number of electrons in the $4d$ subshell. The calculated absolute cross sections are larger by a factor of 3–4 than the measured ones [2,3]. Noting the reliability of the theoretical results, their consistency, and the fact that they are obtained using methods that have led to a satisfactory description of many other experimental results, naturally lead to a suggestion that the experimental data [2,3] have an error, perhaps of a normalization nature.

Specifically, the calculated cross section for I^- is shown in Fig. 1. There is not much difference from the earlier calculated results [6], even though in the present calculation the simultaneous interactions among all five essential transitions, $5p \rightarrow \varepsilon s,d$, $5s \rightarrow \varepsilon p$, and $4d \rightarrow \varepsilon p,f$, were taken into account in the RPAE equations; previously, they were included only pairwise [6]. The results for atomic I are given in Fig. 2. The cross section is a sum of contributions from all allowed channels, ${}^2S$, ${}^2P$, and ${}^2D$ final states of the total system,

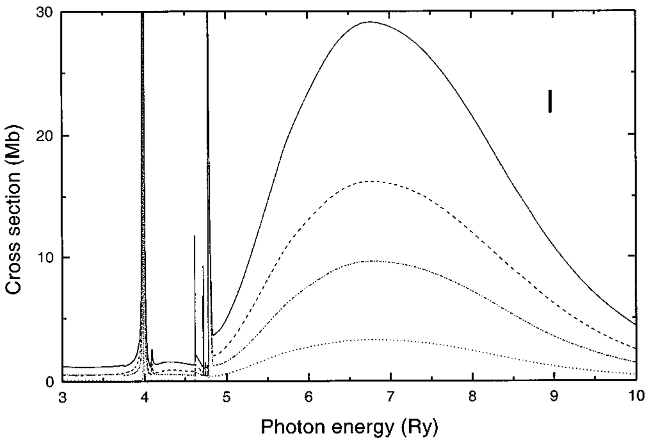

FIG. 2. Calculated total photoabsorption cross section (solid curve) for I in the length formulation in the region of the $4d$ giant resonance, along with the partial cross sections for ${}^2D$ (dashed curve), ${}^2P$ (dot-dashed curve), and ${}^2S$ (dotted curve) final channels, all in length formulation.

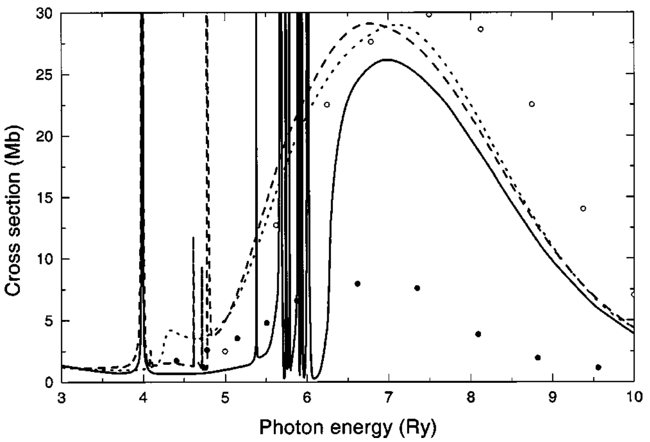

FIG. 4. Comparison of the calculated cross sections for I^- (dotted curve), atomic I (dashed curve), and I^+ (solid curve) in the region of the $4d$ giant resonances along with the experimental points for atomic I [2] (solid dots) and the previous theoretical results for I [4,5] (open dots).

residual ion plus photoelectron, which are connected to the initial ^2P state of atomic I via a dipole transition. The primary contribution to the total cross section comes from the $L=2$ channel with the giant resonance maximum of 17 Mb, followed by the $L=1$ channel with its maximum contribution of 10 Mb, while $L=0$ gives only 3 Mb at most. The maximum of the photoabsorption cross section is 30 Mb, just as it is in I^-, where the giant resonance is an almost perfectly symmetrical maximum. The results for I^{2+} are presented in Fig. 3. The number of transitions here is the greatest of the three cases, because each subshell splits into two ''up'' and ''down'' levels. Included in the calculations are $5p\rightarrow\varepsilon s$ (up), $5s\rightarrow\varepsilon p$ (up), $5s\rightarrow\varepsilon p$ (down), $4d\rightarrow\varepsilon p$ (up), $4d\rightarrow\varepsilon f$ (up), $4d\rightarrow\varepsilon p$ (down), and $4d\rightarrow\varepsilon f$ (down). The absolute cross section is a little bit smaller than in I; the giant resonance is asymmetric with its maximum being about 27 Mb. In addition, autoionizing resonances near the $4d$ threshold are quite strong.

To compare the cross sections of I^-, I, and I^{2+} with each other and with the experimental data on I [2], they are shown in Fig. 4. The close correspondence among the results of calculations, including the earlier calculation [4,5] that used an entirely different methodology, emphasizes the significant deviation from experiment, as pointed out earlier. It should also be mentioned that the maximum of the giant resonance in I^-, I and I^{2+} is positioned at almost the same energy, while the shape becomes increasingly asymmetric from I^- to I^{2+}. Also shown in Fig. 4 is the experimental result [2] for atomic I; the factor of 3 difference in magnitude between theory and experiment is clear.

In conclusion, most of the oscillator strength of the $4d^{10}$ subshell is thus missing and unaccounted for in the experimental results, and major differences from the situation in neighboring Xe are exhibited. It is, therefore, suggested that, as a matter of some urgency, the experimental situation in atomic iodine and its ions be revisited; there is either some new and unexpected physics to explore, or a major error in magnitude to correct.

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