Photoionization of $4d$ electrons in I^+ and I^{2+}

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It is demonstrated that by taking into account many-electron correlations within the framework of the generalized random-phase approximation with exchange, it becomes possible to describe within the experimental error the recently obtained data [Kjeldson *et al.* Phys. Rev. A **62**, 020702(R) (2000)] on the photoionization of iodine ions I^+ and I^{2+} near and above the $4d^{10}$-subshell threshold. Results are also presented for the single photoionization cross sections of the I^+ and I^{2+} ions.

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I. INTRODUCTION

Experimental data on the photoionization cross section of atomic iodine and its ions above the $4d$ threshold had long presented a problem for theory. In a number of experimental investigations the results showed a striking qualitative difference between the data on photoionization above the $4d$ threshold for atomic iodine and its ions [1–4] on one hand, and Xe [5] on the other. The difference was huge: the measured iodine photoionization cross sections, as a function of photon frequency ω, were found to be quite similar in shape to that of Xe, but a factor of three smaller. This result contradicted intuition and the results of several calculations [6,7], which led to the conclusion that for the intermediate and inner subshells, particularly well above their ionization thresholds, there should not be a prominent difference between Xe and its neighbor I. This view was supported by the oscillator strength sum rule that can be applied reasonably accurately to each individual subshell of a multielectron atom or ion. According to this sum rule [8,9], the area under the photoionization cross-section curve resulting from the ten $4d$ electrons in Xe and its ions Xe^+, Xe^{2+} on one hand, and I and its ions I^+, I^{2+}, I^- on the other, must be approximately the same.

On the basis of these qualitative arguments, calculations of $4d$ photoionization cross sections of I, I^-, I^{2+} that included significant electron-electron correlation using the random-phase approximation with exchange (RPAE) were performed, along with a careful analysis of the possible contributions of other, non-RPAE corrections [10]. It was concluded that the difference between the results of calculations and experimental data [2–4] could be explained only by the inaccuracy of the latter. Stimulated by this theoretical result [10], absolute measurements of the photoionization cross section of I^+ and I^{2+} [1] confirmed the main points of [10], demonstrating that the earlier experimental data required renormalization. However, the latest experimental data [1] shows some deviation from the RPAE results of [10]; the experimental cross section maximum, in the region dominated by $4d$-electron photoionization, is about 10% smaller than the RPAE result and shifted to higher energy by ~1 Ry. It is here demonstrated that by taking into account core relaxation, in addition to multielectron correlations, within the framework of the generalized random-phase approximation with exchange (GRPAE), good agreement is achieved between the results of the recent absolute measurements [1] and theory for the photoionization cross sections of I^+ and I^{2+} in the energy region dominated by $4d$ ionization.

II. BRIEF REVIEW OF THEORY

A detailed description of RPAE calculations is given in [9,11]. Briefly, the photoionization amplitude, within the RPAE, is given by [11]

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

Here $n\ell$ represents the principal and angular momentum quantum numbers for the initial state of the ejected electron, i.e., of the hole, ε, $\ell\pm 1$ the final state, $\nu''\equiv n''(\varepsilon'')$, $\ell'' = \ell'\pm 1$, and $\nu'\equiv\varepsilon'(n')$, ℓ' refer to the intermediate electron and hole Hartree-Fock (HF) states, and $D(\omega)$ and $d(\omega)$ are the RPAE and HF dipole photoionization amplitudes, respectively. The summation (integration) in Eq. (1) is performed over occupied ($\leq F$) and vacant ($>F$) one-electron states, which are determined by their energies (or principal quantum number) $\varepsilon'(n')$ and angular momentum ℓ' and the limit of $\delta \to 0$ is assumed. In Eq. (1), n_ν denotes the Fermi-step function, $n_\nu = 1$ for $\nu \leqslant F$ and $n_\nu = 0$ for $\nu > F$, E_ν are the HF energies. All single-electron states are calculated within the HF approximation.

However, somewhat different zeroth-order HF wave functions for the states of I^+ and I^{2+}, respectively, were used. For the case of I^+, in the open-shell RPAE, term dependence is very important for *outer*-shell excitation and ionization in the vicinity of the outer-shell thresholds. But, in the energy region above the $4d$ threshold, where photoionization from the filled $4d^{10}$ subshell dominates, the outer-shell cross sections are small and insensitive to the term dependence (exchange effects are small well-above threshold), and outer-shell multiplet structure does not significantly influence the $4d$ photoabsorption. Therefore, in case of I^+ ($[\mathrm{Kr}]4d^{10}5s^2 5p^4$), the term-averaged HF wave functions [12] associated with the following transitions $4d^{10} \to 4d^9\, n(\varepsilon)f,\ n(\varepsilon)p;\ 5p^4 \to 5p^3\, n(\varepsilon)d,\ n(\varepsilon)s;\ 5s^2 \to 5s\, n(\varepsilon)p$ have been used. Note that the excited states are calculated using the *same* core orbitals as in the initial state, i.e., core relaxation is not included in the RPAE method. Note also that the use of term-averaged HF wave functions leads to some small disagreement between cross sections obtained with the length and velocity forms of dipole operator. Therefore, the final partial and total RPAE photoabsorption cross sections presented have been averaged over the results of the two different forms of the operator.

The I^{2+} ion possesses a half-filled $5p$ subshell; therefore, it is convenient to use the spin-polarized version of the HF (SPHF) [13] in this case for the zeroth order ground and excited wave functions. Within SPHF framework, the outer-shell structure of I^{2+} is given by $[\mathrm{Kr}]4d^5\uparrow 4d^5\downarrow 5s\uparrow 5s\downarrow 5p^3\uparrow$, where the arrows represent electron-spin projections. The convenience of this methodology arises from the additional spin-polarized levels that behave as filled subshells, so that the ordinary methods of many-body theory can be applied without additional approximations [11,14]. In addition, the equality of length and velocity cross sections is preserved within this formulation. In our spin-polarized RPAE calculations, we have included the interaction between eight channels: $4d\uparrow\downarrow \to n(\varepsilon)f\uparrow\downarrow,\ n(\varepsilon)p\uparrow\downarrow;\ 5s\uparrow\downarrow \to n(\varepsilon)p\uparrow\downarrow;\ 5p\uparrow \to n(\varepsilon)d\uparrow,\ n(\varepsilon)s\uparrow$, and all of the zeroth order wave functions, ground and excited state, have been calculated using SPHF with no core relaxation

To make the calculations more accurate, the RPAE formulation is generalized to the GRPAE that introduces two important alterations into the RPAE, Eq. (1). First, the vacancy states are calculated by solving the (term-averaged or spin-polarized) HF equations in the presence of the vacancy itself, i.e., the final-state core orbitals are modified to take into account the existence of this vacancy. Thus, core relaxation is introduced and the excited orbitals are calculated in the field of these core-relaxed orbitals. Second is that instead of the HF occupied level energies E_v $(v \leqslant F)$ corresponding improved theoretical or even experimental ionization potentials are used. As it has been shown earlier [15], the use of

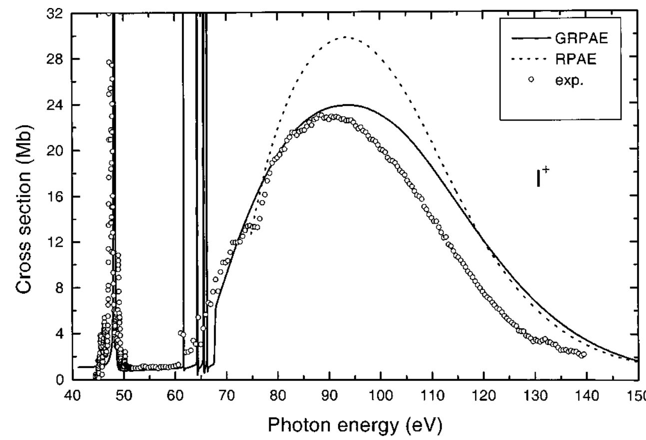

FIG. 1. Photoabsorption cross section of I^+. The solid line is the present GRPAE result, the dashed line is the RPAE result [14], and the open circles are experiment [1].

corrected energies in GRPAE calculations leads to better agreement between results obtained with length and velocity forms of a dipole operator.

The ions considered in this paper have open shells. Therefore, the application of the GRPAE equations to them is little bit more complex than in closed-shell systems. But these complications are the essentially same for the GRPAE and RPAE and have been discussed in detail [10,11]. In addition, since reliable experimental ionization thresholds are lacking for the inner shells under consideration here, theory is required to obtain values more accurate than HF. More accurate $4d$ threshold energies could be approximated by assuming that the difference between the experimental value of the $4d$ ionization threshold for I and its ions and the HF values are the same as for neutral Xe, a difference of about 7 eV. More accurately, the $4d$ ionization potentials can be obtained by adding to the experimental [1] excitation energy of the $4d \to 5p$ resonance, the calculated HF $5p$ ionization for I^+ and I^{2+}. These estimates give the following values for the $4d$ threshold energies: $|E_{4d}| \approx 67$ eV for I^+ and $|E_{4d}| \approx 82$ eV for I^{2+}, and these energies have been used in the GRPAE calculations.

III. RESULTS AND DISCUSSION

The total photoabsorption cross sections are obtained as a sum of all partial cross sections. The RPAE and GRPAE results for I^+ and I^{2+} ions in the range of 40–170 eV are shown in Figs. 1 and 2, respectively; also presented are the experimental data [1]. Note that for I^+ RPAE results are presented only above $4d$ ionization threshold, since our aim is to emphasize the effect of relaxation in the continuous spectrum. The RPAE $4d$ maxima are closer to threshold and higher then the GRPAE results. This is because the relaxed GRPAE orbitals are more compact, thus screening the nucleus more efficiently so that the field ‘‘seen’’ by the photoelectron is weaker in the GRPAE case, and more energy is required for the *f*-wave photoelectron to overcome the centrifugal barrier. The GRPAE maxima are, therefore, further out (in energy), broader, and since the areas under the cross-

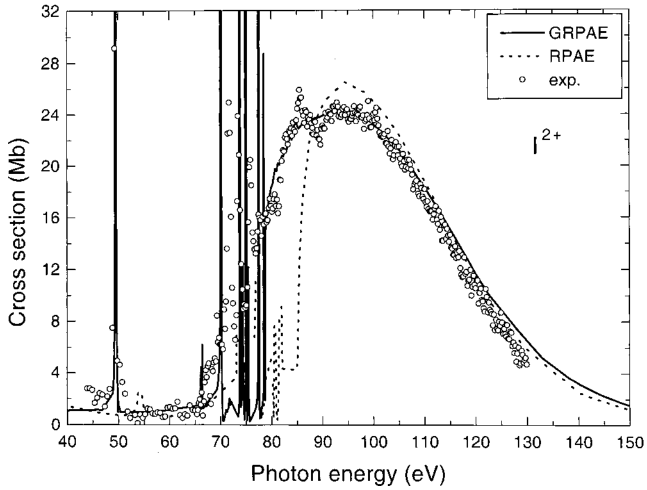

FIG. 2. Photoabsorption cross section of I^{2+}. The solid line is the present GRPAE result, the dashed line is the RPAE result [14], and the open circles are experiment [1].

section curves are constant, the GRPAE maxima are lower as well. As seen, the agreement between the GRPAE and experiment is much better, in fact well within the quoted 15% experimental error [1]. The first resonances about 48–49 eV, in Figs. 1 and 2, are the $4d\rightarrow 5p$ excitations. The other resonances just below the 4d thresholds are the various excitations from 4d to nf and np states. However, it should be noted that the fine structure of discrete levels and their oscillator strengths are reproduced by the GRPAE only qualitatively. This is understandable because the discrete transitions excitation energy and wave functions are not determined self-consistently (see [15]), i.e., by solving the HF equations for an atom or ion with an inner vacancy and an excited discrete electron. Although in the GRPAE equations we take into account electron correlation not only between 4d shell but also the effect upon them from outer 5s and 5p shells, the role of the latter in the considered ω region proved to be unimportant. The use of the more exact energies in the GRPAE calculations principally moves the maxima a bit, without materially altering their shapes; it is the core-relaxation introduced into GRPAE, that is, primarily responsible for the calculations being more accurate, as discussed above. Furthermore, note that, although we have presented to *average* of length and velocity cross sections, the difference between them, in both RPAE and GRPAE calculations, was never more than 2–3%, so this is a nonissue.

In Figs. 3 and 4 we present the GRPAE single-electron ionization cross section for I^+ and I^{2+}, respectively. Ionization of 4d electrons leads to double ionization, in each case, because the vacancy is filled virtually 100% of the time by an Auger process. Only photoionization of the outer, 5s and 5p, electrons lead to appreciable single ionization. And as it is has been recently shown for Xe^+ photoionization [16], the outer-shell cross sections near 4d threshold are strongly affected by the interchannel coupling interaction with the 4d photoionization channels. As a result, the single-ionization cross sections acquire rather strong maxima, owing to interchannel coupling, rather similar to the case of Xe^+ photoionization [14]. In this case these maxima presented in Figs. 3 and 4 are only very weakly modified by relaxation effects, as might be expected for maxima resulting from interchannel interactions of such widely separated channels. Most importantly, however, the calculated single-ionization cross sections agree quite well with the corresponding experimental data [1], which indicates that all of the important physics is included in the calculations.

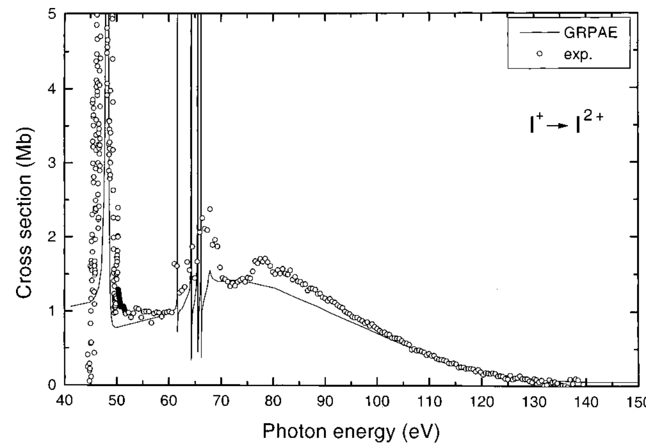

FIG. 3. Single photoionization cross section of I^+ leading to I^{2+}: the sum of the 5s and 5p cross sections. The solid line is the present GRPAE and the open circles are experiment [1].

IV. FINAL REMARKS

We have presented results of the GRPAE calculations of the photoabsorption cross section for I^+ and I^{2+} in the vicinity of and above the 4d ionization thresholds. Good agreement with recent absolute experimental data [1] was found; the introduction of relaxation and more accurate threshold energies brought the previous RPAE results [10] into agreement. In addition, single-ionization cross sections for these ions were calculated and good agreement with ex-

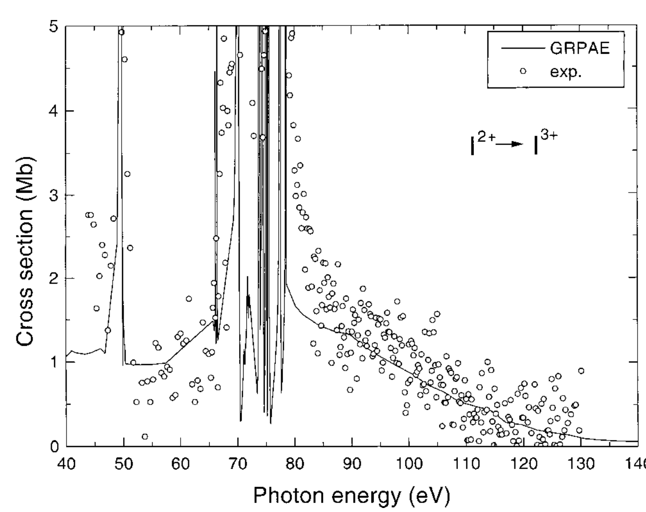

FIG. 4. Single photoionization cross section of I^{2+} leading to I^{3+}: the sum of the 5s and 5p cross sections. The solid line is the present GRPAE and the open circles are experiment [1].

periment [1] was found here too. The single-ionization cross sections, the sum of the $5s$ and $5p$ cross sections were found to be dominated by interchannel coupling interactions with the $4d$ channels; relaxation was found to be rather unimportant. The good agreement with experiment strongly suggests that the theoretical methodology employed in these calculations includes all of the important physical interactions for these photoionization processes.

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