Fully relativistic *R*-matrix study of the interaction between a slow electron and atomic iodine: Scattering and photodetachment

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An 11-state close-coupling calculation for the interaction between a slow electron and atomic iodine is carried out using the fully relativistic *R*-matrix method. The cross sections are presented for the photodetachment of a negative atomic iodine ion and for electron scattering by neutral atomic iodine from the threshold to 8 eV. The electron affinity for negative iodine is obtained as 2.958 eV. For the photodetachment process, we get fairly good agreement with experimental results for the distinct spin-orbit split between the $5p_{3/2}$ and $5p_{1/2}$ thresholds due to the relativistic effect as well as for the cross sections near the thresholds. The electron scattering cross sections display energy dependence similar to that for electron scattering by heavy rare-gas atoms, i.e., a Ramsauer-Townsend minimum well at a lower energy and a broad peak after the well.

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The photodetachment process of the negative iodine ion, as a good example to illustrate various electron correlation effects, has been focused on for decades. Early on, Robinson and Geltman [1] used a central-field model for both bound and free electron states to obtain the photodetachment cross section for the negative iodine ion. Radojević *et al.* [2] used the relativistic random-phase approximation (RRPA) to calculate the photodetachment of negative halogen ions F^-, Cl^-, Br^-, and I^- from threshold to about 100 eV. Based on the RRPA method also, Radojević and Kelly [3] calculated the photodetachment cross section of the negative iodine ion with relaxation effects included (RRPAR). Recently, Kutzner *et al.* [4] investigated the effects of core relaxation and polarization in the photodetachment process of I^- for $5p$, $4d$, and $4p$ subshells using the modification of the RRPA including relaxation and polarization effects (RRPARP). The relativistic effects, as reported in the review by Ivanov [5], are significant in the near-threshold region. In this region, experimental results are available from Mandl and Hyman [6], and Neiger [7]. In Mandl and Hyman's experiment, they observed an apparent peak in the cross section around 5.5 eV, which was thought to be an autodetachment state of I^-. To the best of our knowledge, however, no theoretical results proved that this peak is due to an autodetachment state. In order to clarify this discrepancy, further theoretical investigations in the near-threshold region with a different scheme are necessary. No theoretical study about electron scattering from atomic iodine was found in the literature so far. The relativistic effect is well known to be very important to study the dynamics of middle- and high-Z elements, as shown in some earlier theoretical studies [8–10]. In the present study, by using a fully relativistic close-coupling *R*-matrix approach, the photodetachment cross section from the threshold to 8 eV of I^- is calculated, and compared with the experimental results. The total and elastic electron scattering cross sections from atomic iodine are also given from the threshold to 8 eV.

The *R*-matrix method for electron-atom and photon-atom interactions has been discussed in great detail by Burke *et al.* [11]. The present calculations have been carried out by using the fully relativistic *R*-matrix code DARC [12–14]. We will just give an outline as follows. In an *R*-matrix calculation, the wave function of the $(N+1)$-electron system is given by

$$\Psi_k(X_1 \cdots X_{N+1}) = \hat{A} \sum_{ij} c_{ijk} \Phi_i(X_1 \cdots X_N \hat{r}_{N+1} \sigma_{N+1}) u_{ij}(r_{N+1}) + \sum_j d_{jk} \phi_j(X_1 \cdots X_{N+1}), \quad (1)$$

where $\hat{A}$ is the antisymmetrization operator to take into account the exchange effect between the target electrons and the free electron. X_i stands for the spatial (r_i) and the spin (σ_i) coordinates of the ith electron. The functions $u_{ij}(r)$ in the first sum construct the basis sets for the continuum wave functions of the free electron, and Φ_i is the coupling between the target wave function of a specific level $J_i\pi_i$ and the angular and spin parts of the free electron. The correlation functions ϕ_j in the second sum are formed from the same set of bound orbitals and must be included to compensate for the incompleteness of the continuum orbitals. They can also be used to compensate for the correlation effects not adequately considered because of the cutoff in the first sum. In the relativistic *R*-matrix calculations, the orbitals are obtained from the multiconfigurational Dirac-Fock code GRASP [15] by using an extended average level (EAL) optimizing process for the concerned energy levels included in the close-coupling method. The single-particle functions have the form

$$\varphi(r) = \frac{1}{r} \begin{pmatrix} P_{n\kappa}(r) \chi^m_{\kappa}(\theta, \phi) \\ iQ_{n\kappa}(r) \chi^m_{-\kappa}(\theta, \phi) \end{pmatrix}, \quad (2)$$

here $P_{n\kappa}(r)$ and $Q_{n\kappa}(r)$ are, respectively, the large and small component radial wave functions, and the functions $\chi^m_{\pm\kappa}(\theta, \phi)$ are two-component spinors made up of spherical harmonics and Clebsch-Gordan coefficients. The radial parts of the bound orbitals are input to the fully relativistic *R*-matrix code as numerical values on a suitable mesh of points.

In the present calculations, the iodine atom target

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TABLE I. Calculated relativistic energy levels (in eV) of the first 11 low-lying excited states of the iodine atom compared with experimental results [16].

Configuration	Term	J	Theor.	Expt.
$5p^5$	$^2P^o$	3/2	0.0	0.0000
		1/2	0.9395	0.9427
$5p^4 6s$	^4P	5/2	6.7875	6.7741
		3/2	7.7397	7.6652
		1/2	7.6293	7.5507
$5p^4 6s$	^2P	3/2	7.0363	6.9551
		1/2	7.9748	7.8347
$5p^4 6p$	$^4P^o$	5/2	8.0215	8.0479
$5p^4 6p$	$^4S^o$	3/2	8.0475	8.0583
$5p^4 6p$	$^4D^o$	5/2	8.1172	8.1394
$5p^4 6p$	$^4D^o$	7/2	8.1169	8.1426

wave functions are described by a closed core $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2$ and seven one-electron orbitals obtained by considering configuration interaction: $5p_{1/2}$, $5p_{3/2}$, $6s_{1/2}$, $6p_{1/2}$, $6p_{3/2}$, $5d_{3/2}$, and $5d_{5/2}$. In our work, we mainly want to clarify the photodetachment and scattering cross section for the $5p$ shell of iodine, i.e., the near-threshold structure, so only the $5p$ electrons are allowed to be excited to higher orbitals and at most three electrons are allowed to be excited at the same time. Under this situation, there are 2546 configurations in total. The first 11 lowest levels of the iodine atom are included in the close-coupling expansion of the relativistic R-matrix calculation. The calculated energy levels of the first 11 lowest states in the close-coupling expansion are shown in Table I along with the experimental results [16]. One can see that the theoretical results agree with the experimental results fairly well, and all the discrepancies are within 2%. The good agreement between the theoretical energy levels and the experimental result implies that the $5p$ valence electron correlation has been reasonably considered in our calculation. According to the biggest convergence radius of the single-electron orbital wave functions, R-matrix boundary was chosen to be 60 a.u. in our calculation to ensure that the wave function is completely wrapped within the R-matrix sphere.

The accuracy of both the initial and final states is quite essential for the description of the photodetachment process. The same set of bound electron orbitals is used for both the neutral atom and the negative ion, which are obtained with the EAL optimizing facility for the energy levels of the neutral target. This set of bound-state orbitals is usually not sufficient for the description of the loosely bound states of the negative ion. Nevertheless, this smaller extension of the one-electron orbitals is improved effectively by the algorithm of the R-matrix scheme for the bound states. This is achieved by connecting the wave functions of the $N+1$ electrons given by Eq. (1) inside the R-matrix sphere smoothly with an exponentially decaying wave function outside the sphere at the boundary. In the internal region, the continuum orbitals, obtained by solving the model single-channel scattering problem, are orthogonal both to themselves and to the bound orbitals. The bound orbitals plus the continuum orbitals then form a larger basis set of functions compared with the basis set for the N-electron target system over the internal region. The inclusion of the continuum orbitals for the $(N+1)$-electron system is also helpful for avoiding the possible overestimation of the coupling between the neutral and negative ion states when the same set of bound orbitals is used for both of them. An electron affinity of 2.958 eV for I^- $5p^6\ ^1S_0$ is obtained in the present relativistic close-coupling calculation. This bound energy is close to the experimental results 3.0591(1) eV obtained by Webster *et al.* [17] and 3.059 038(10) eV by Hanstorp and Gustafsson [18].

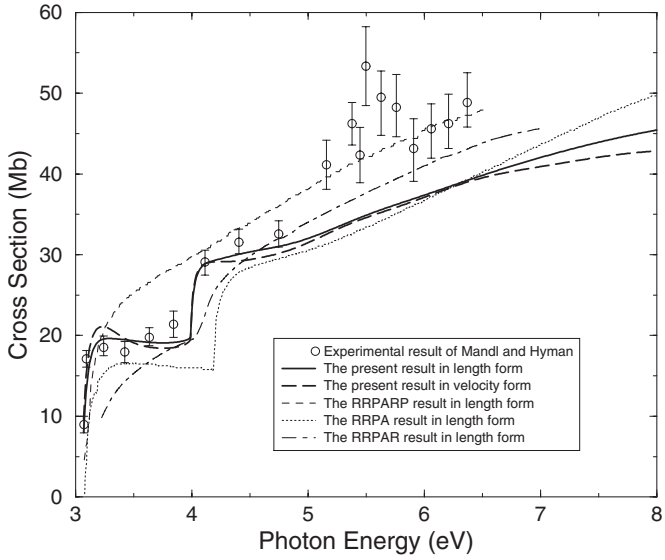

FIG. 1. Total photodetachment cross sections from $5p^6\ ^1S_0$ level of negative atomic iodine ion. Solid and long-dashed lines, present the length and velocity forms cross section; dotted line, RRPA result [2]; dot-dashed line, RRPAR result [3]; dashed line, RRPARP result [4]. Empty circles experimental data [6].

Figure 1 shows the photodetachment cross section of the negative atomic iodine ion from the threshold to 8 eV. The experimental data and some other theoretical results are also showed in the figure for comparison. Because of the confusion of too many lines, only the length form of the cross section of the other three theoretical results is plotted in the figure. One can see that the experimental data do not decisively favor any other results in this region. After moving our results 0.1 eV to higher photon energy to correct for the calculated photodetachment threshold, they agree with the experimental data perfectly from the threshold to 5 eV. The spin-orbit splitting between the $5p_{1/2}$ and $5p_{3/2}$ thresholds, about 0.9395 eV in our result, fits the experimental data of Mandl and Hyman [6] much better than the RRPA [2] and RRPAR result [3], which are 1.1176 and 1.1193 eV, respectively. There is no spin-orbit splitting structure in the RRPARP result. The length form and velocity form of the photodetachment cross section of our results fit each other quite well. The discrepancy between the theoretical results and experimental data appears after 5 eV. An apparent photon absorption structure was observed in the experiment near 5.5 eV and the experimental data around 5.5 eV are higher

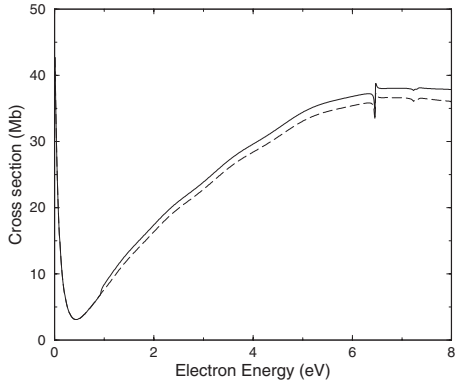

FIG. 2. Total and elastic electron scattering cross sections from atomic iodine. The solid line stands for the total cross section, and the long-dashed line for the elastic cross section.

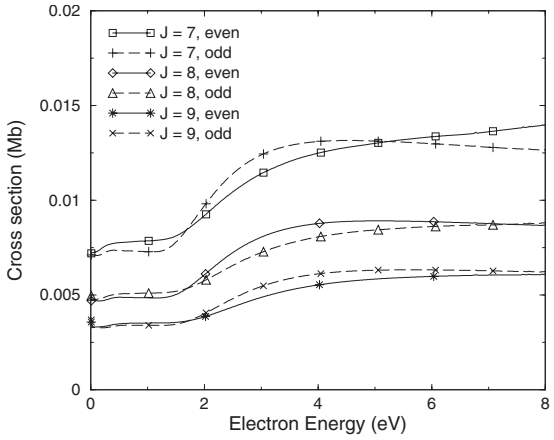

FIG. 3. The latter six partial wave cross sections from $J=7$ to 9. Lines with different symbols refer to different partial wave cross sections.

than the present, RRPA, and RRPAR results. Mandl and Hyman [6] proposed that this peak is due to the autodetachment state of the negative ion, which has odd parity and total angular momentum J equal to 1. In particular, the terms described by the LS-coupling notation $5s^2 5p^4(^3P)6s6p(^5P_1$ or $^5D_1)$ might have the lowest energy and thus account for the low-lying peak reported in the experiment. However, the states mentioned above are included automatically in our close-coupling calculation and no significant structures caused by these states were found there. No proof for this kind of resonance was found in other theoretical results, either. If this structure does not come from the photodetachment process of the negative atomic iodine ion but rather from some other process in the shock-heated vapors of CsI, the discrepancy between the theoretical and experimental results can then be understood. With regard to the theoretical results so far, a new experiment for the photodetachment of I^- near threshold is needed.

With the same atomic orbital wave functions, the electron scattering cross sections from atomic iodine below 8 eV are also calculated. The highest energy level of the included 11 target states is around 8 eV, so including these first 11 target states should be enough for the calculation to illustrate the near-threshold structure of the scattering process. In the present calculation, the partial wave cross sections up to $J=9$ are included. The final results are obtained by extrapolating the total cross section to higher J using the geometric series method described by Burgess *et al.* [19]. The total and elastic electron scattering cross sections from the atomic iodine are plotted in Fig 2. From Fig. 2 one can see that the elastic cross section makes the largest contribution to the total cross section. Near threshold, the cross section increases sharply with decrease of the electron energy. After a minimum near the electron energy of 0.4 eV, the cross section increases with increase of the electron energy. After 0.9395 eV, the first channel, i.e., the first excitation state $5p^5\,^2P^o_{3/2}$, opens and the inelastic cross sections contribute to the total cross section. There are some structures after 6 eV which arise from the higher-lying excited states. In order to check whether the 20 partial waves included are enough for the convergence of the partial wave expansion, Fig. 3 gives six latter partial wave cross sections from $J=7$ to 9. From Fig. 3 one can find that the higher the J value, the smaller is the cross section, and the sum of the latter six partial wave cross sections makes no more than a 0.2% contribution to the total cross section near 8 eV. For high incident electron energy, as discussed by Burgess and Sheorey [20], the geometric series method based on the Coulomb Bethe approximation used in the present DARC code might be less powerful. But in our calculation the electron energy is lower than 8 eV, so the method and results are reliable. We have also obtained the final cross sections without extrapolation; the results are about 0.05% lower than those with extrapolation. From the discussion above, the total cross section is convergent.

The first ten partial cross sections from $J=0$ to 4 are given in Figs. 4(a)–4(j), respectively. In Fig. 4(b), just at the first excitation threshold, a so-called cusp appears in the elastic cross section, arising from the interrelation of the cross sections of the various processes (the elastic cross section and excitation of all excited states allowed in a given energy). Drukarev [21] discussed the fact that, in the no channel coupling picture, for $l=0$, a long-range tail of the potential will lead the cross section to a deep minimum, the so-called Ramsauer-Townsend effect [22–24]. In our close-coupling calculation, in Fig. 4(a), for the final state with even parity and total angular momentum J equal to 0, the minimum of the cross section occurs at an electron energy about 0.165 eV. This accords with $5p^5\,^2P_{3/2}+kp$ scattering but not s-electron scattering. Three resonances are predicted in our calculation, which can be found from Figs. 4(a), 4(c), and 4(e), respectively. For the first one, we have analyzed and identified the resonance as the $5p^4(^3P)6s^2\,^3P_0$ resonance state with position at 7.235 eV and width of 0.05 eV. The second and third are the resonances for the $5p^4(^3P)6s^2\,^3P_1$ resonance state with position at 7.30 eV and width of 0.08 eV, and the $5p^4(^3P)6s^2\,^3P_2$ resonance state with position at 6.458 eV and width of 0.03 eV. Though there is no experimental result or other theoretical calculation to our knowledge, the position of the resonance states in our calculation is reasonable according to the energy level of atomic iodine.

In summary, we have carried out calculations on the pho-

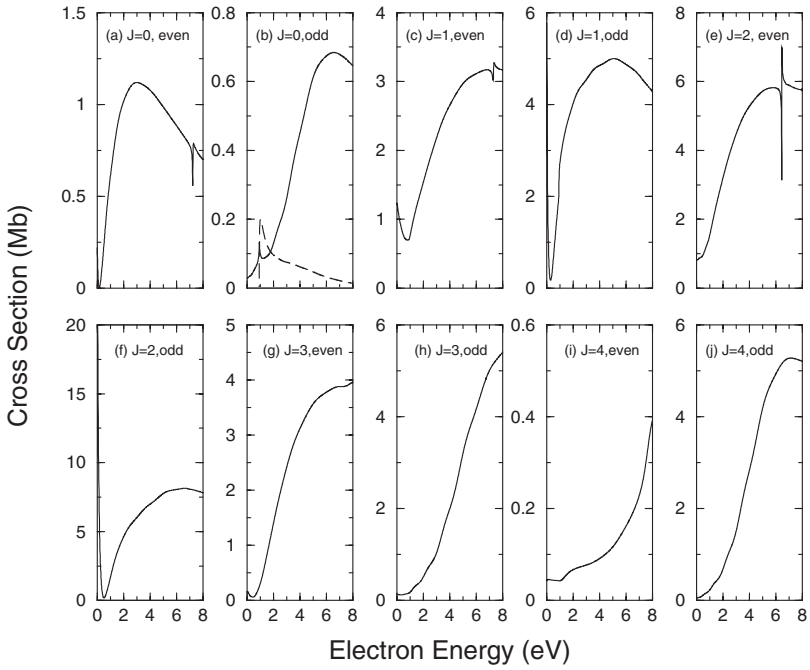

FIG. 4. The former ten partial cross sections from $J=0$ to 4 with even and odd parity. In (b), the solid line is the elastic cross section and the long-dashed lines are the inelastic cross sections of this partial wave.

todetachment of I^- ion and electron scattering from the atomic iodine by using a fully relativistic R-matrix method. Our photodetachment cross section shows a clear and precise spin-orbital splitting of the $5p^5\ ^2P_{3/2}$ and $5p^5\ ^2P_{1/2}$ states. As in other theoretical calculations, our result has not found significant contributions from the autodetachment states, which were thought to cause the pronounced photoabsorption around 5 eV in the experimental result [6]. The total and elastic cross sections from atomic iodine from the threshold to 8 eV are also calculated with the present fully relativistic R-matrix method. The elastic cross section makes the largest contribution to the total cross section, and the cross sections display similar features to that observed in electron scattering with heavy rare-gas and heavy alkaline-earth metal atoms. Several weak resonance states are predicted in the present calculation.

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