Role of ionization–excitation processes in the cross section for direct ionization of heavy atomic ions by electron impact

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Role of ionization-excitation processes in the cross section for direct ionization of heavy atomic ions by electron impact

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The contribution to the ionization cross section of ionization-excitation processes by electron impact is usually negligibly small for low- and medium-Z elements. We demonstrate here, however, that for heavy atomic ions with the outermost shell being nd (n = 4, 5) the ionization-excitation processes play an evident role in the ionization cross section. For the 4s2p2d10 ground level of Gd15+, the ionization-excitation cross section due to the excitation of levels in the 4s2p2d4f configuration is comparable to the direct 4p and 4s ionization cross sections of (4s2p2d10)1/2 and (4s4p2d10)1/2. The total ionization cross section will be underestimated by 15% without including the contribution from ionization-excitation processes. This is a general conclusion for heavy atomic ions, which is verified by taking Pd-like ions of Sn4+, Ba10+, Nd14+, Tb17+, Yb24+, and W28+ as examples. The role of ionization-excitation processes can be understood from the overlapping of the wave functions between the 4d and 4f orbitals.

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I. INTRODUCTION

Apart from its fundamental importance, the electron impact ionization (EII) cross section has practical applications in plasma modeling in both astrophysical and laboratory plasmas [1–3]. Most EII researches have focused on the light-and medium-Z elements, as reviewed by Mattioli et al. [4] and Dere [5] for elements from hydrogen to germanium. In contrast, relatively fewer publications have reported the EII cross section of heavy elements such as gadolinium (Z = 64) and terbium (Z = 65) [14–17]. In the area of magnetic confinement fusion, EUV lithography at 13.5 nm, which is produced by even multiple autoionizations [8–11]. It is a troublesome task to track the Auger and radiative decay pathways.

There are direct and indirect ionization channels for EII processes. As the atomic number increases, the contribution from the indirect processes becomes more and more important. Mattioli et al. [4] pointed out that previously proposed EII cross sections are often underestimated due to the neglect of indirect processes for medium-Z elements. For heavy ions, such an underestimation becomes even more pronounced, as demonstrated here.

In this work, we investigate the role of ionization-excitation processes in the cross section for direct ionization of heavy atomic ions by electron impact, taking Pd-like ions as examples. Ionization with simultaneous excitation is significantly more correlated, and hence its contribution to the ionization cross section is usually small compared with that of direct ionization processes [31,32]. Our results show, however, that the ionization cross section can be underestimated by about 15% if one neglect the contributions of ionization-excitation processes for heavy ions.

II. THEORETICAL METHOD

The calculation of the level-to-level ionization cross section was carried out using a fine-structure level distorted wave approximation implemented by the Flexible Atomic Code (FAC) developed by Gu [33]. The direct ionization cross section from an initial state $\psi_i$ to a final state $\psi_f$ can be expressed as

$$d\sigma_{ii}(E_0, \varepsilon) d\varepsilon = \frac{2\pi}{k_i^2 g_i} \sum_{k_i, k_f} (2J_T + 1)\left| \langle \psi_i|k_i,J_T\rangle \right|^2$$

$$\times \sum_{p \neq q} \frac{1}{R_{pq}} |\langle \psi_f|k_f,J_T\rangle |^2,$$

where $k_i$ and $k_f$ are the initial and final states, $J_T$ is the total angular momentum, $R_{pq}$ is the rotational constant of the system, and $\varepsilon$ is the electron kinetic energy. The contribution to the excitation of levels in the 4s2p2d4f configuration is comparable to the direct 4p and 4s ionization cross sections of (4s2p2d10)1/2 and (4s4p2d10)1/2. The total ionization cross section will be underestimated by 15% without including the contribution from ionization-excitation processes. This is a general conclusion for heavy atomic ions, which is verified by taking Pd-like ions of Sn4+, Ba10+, Nd14+, Tb17+, Yb24+, and W28+ as examples. The role of ionization-excitation processes can be understood from the overlapping of the wave functions between the 4d and 4f orbitals.

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where $\epsilon_0$ and $k_i$ are the energy and kinetic momentum of the incident electron; $e$ is the energy of the ejected electron; $\kappa_i$ is the statistical weight of the initial state; $k_{f1}$ and $k_{f2}$ are the relativistic angular quantum numbers of the incident, scattered, and ejected electrons; $J_T$ is the total angular momentum when the target state is coupled to the continuum orbital; and $M_T$ is the projection of the total angular momentum. The energy reservation holds for the process, i.e., $\epsilon_0 = I + \epsilon_1 + e$, where $\epsilon_1$ is the energy of scattered electron and $I$ is the ionization potential from the initial state $\psi_i$ to the final state $\psi_f$. The wave function $\psi_i$ is represented by a linear combination of configuration state functions (CSFs), which are antisymmetric sums of the products of $N$ one-electron Dirac spinors [8,33]. The wave function $\psi_f$ is similarly obtained with one less bound electron. To solve the Dirac spinors of $\psi_i$ and $\psi_f$, local central potentials, which include the contribution from the nuclear charge and electron-electron interaction of the $N$ and $N - 1$ electron systems, are used. The detailed expression of the local central potential of the respective ion can be found in Gu [33]. The wave functions of the continuum orbitals are obtained by solving the Dirac equations with the same central potential as the bound orbitals. The ionization cross section from $\psi_i$ to $\psi_f$ is obtained from

$$
\sigma_d(\epsilon_0) = \int_0^{2\pi} \frac{d\theta}{d\epsilon} \frac{d\epsilon_0}{d\epsilon} d\epsilon.
$$

The energy conservation relation means that the total energy of the scattered and ejected electrons is fixed but the energy of any one electron can be varied from zero to the maximum, $\epsilon_0 - I$. Thus we set an upper limit ($\epsilon_0 - I)/2$ in the integration to avoid a double counting of the continuum states.

Specifically, we investigate the ionization cross section of heavy ions from the threshold to 4000 eV, taking Pd-like ions as examples. The ground configuration of Pd-like ions is [Ni]4s$^2$4p$^6$4d$^{10}$. Here [Ni] means a Ni-like electron structure; that is, the orbitals of 1s, 2s, 2p, 3s, 3p, and 3d are fully occupied. The direct ionization of electrons from these orbitals will result in higher ionization stages rather than single ionization. The direct ionization processes of Pd-like ions are shown schematically as

$$
e + 4s^24p^44d^{10} \to \begin{cases} 4s^24p^64d^9 + 2e, \\
4s^24p^54d^{10} + 2e, \\
4s^24p^64d^{10} + 2e. \end{cases}
$$

They include the direct ionization of 4d, 4p, and 4s electrons. However, they do not include contributions from ionization-excitation processes. To include them, we should further consider the following processes:

$$
e + 4s^24p^64d^{10} \to \begin{cases} 4s^24p^64d^9n + 2e, \\
4s^24p^54d^9n + 2e, \\
4s^24p^64d^9n + 2e. \end{cases}
$$

These processes refer to direct ionization of 4d, 4p, and 4s electrons with simultaneous excitation of a 4d electron to a higher orbital $n$. In principle, simultaneous excitation of a 4p or 4s electron is also possible, but the cross section from these processes is very small, and thus we do not consider them here.

The total ionization cross section is a summation of processes included in Eqs. (3) and (4).

### III. RESULTS AND DISCUSSION

We first investigate the detailed level-to-level ionization cross section for Pd-like Gd$^{16+}$. The first ionization potentials (IPs) of Gd$^{16+}$ and Gd$^{19+}$ are calculated to be 559.1 and 595.4 eV, respectively. To the best of our knowledge, there are no experimental data for IPs of Gd$^{16+}$ and Gd$^{19+}$ ions [34]. Rodrigues et al. [35] calculated these values to be 565.0 and 601.0 eV in the Dirac-Fock approximation, which is about 6 eV higher than our results. The difference is because the electron correlations were neglected in the calculations of Rodrigues et al. [35]. To verify it, we also calculated these data using the Dirac-Fock approximation, and the results are 564.2 and 600.0 eV, which are in good agreement with those of Rodrigues et al. [35]. According to our calculation, the ionization thresholds are 559.1, 687.1, and 802.5 eV for direct ionization of the 4d, 4p, and 4s subshell electrons of Gd$^{18+}$, respectively. Ionization of 3d, 3p, and 3s electrons will result in double ionization. The thresholds for direct ionization and ionization-excitation processes relevant to our discussion are given in Table I. There are too many ionization-excitation channels, and a few that have relatively larger cross sections are given. By inspecting Table I, we know that the direct ionization of the 4d, 4p, and 4s electrons of Gd$^{16+}$ produces Gd$^{19+}$ since the IP of these orbitals is less than the summation of the IPs of Gd$^{16+}$ and Gd$^{19+}$. Also the ionization excitation to configurations of 4s$^2$4p$^4$4d$^4$4f and 4s$^2$4p$^4$4d$^4$4f produces Gd$^{17+}$. These two configurations are the most dominant channels of ionization-excitation processes.

Figure 1 shows the direct ionization and ionization-excitation cross section (in units of 1 Mb = $10^{-18}$ cm$^2$) from the 4s$^2$4p$^6$4d$^{10}$ ground level of Gd$^{18+}$ to the levels given in Table I. The cross sections corresponding to 1–2, 1–3, 1–4, 1–8, and 1–10 represent the direct ionization of 4d, 4p, and 4s electrons, while the others denote the ionization-excitation cross sections. Obviously, the direct ionization cross section

<table>
<thead>
<tr>
<th>No.</th>
<th>Level</th>
<th>IP(eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(4s$^2$4p$^6$4d$^{10}$)$_0$</td>
<td>0.0</td>
</tr>
<tr>
<td>2</td>
<td>(4s$^2$4p$^4$4d$^9$)$_{3/2}$</td>
<td>559.09</td>
</tr>
<tr>
<td>3</td>
<td>(4s$^2$4p$^4$4d$^9$)$_{1/2}$</td>
<td>565.89</td>
</tr>
<tr>
<td>4</td>
<td>(4s$^2$4p$^5$4d$^{10}$)$_{3/2}$</td>
<td>687.11</td>
</tr>
<tr>
<td>5</td>
<td>4s$^2$4p$^4$4d$^{10}$(4d$^2$)$^{3/2}$</td>
<td>707.55</td>
</tr>
<tr>
<td>6</td>
<td>4s$^2$4p$^4$4d$^{10}$(4d$^2$)$^{1/2}$</td>
<td>718.45</td>
</tr>
<tr>
<td>7</td>
<td>4s$^2$4p$^4$4d$^{10}$(4d$^2$)$^{1/2}$</td>
<td>721.32</td>
</tr>
<tr>
<td>8</td>
<td>(4s$^2$4p$^4$4d$^9$)$_{1/2}$</td>
<td>748.48</td>
</tr>
<tr>
<td>9</td>
<td>4s$^2$4p$^4$4d$^{10}$(4d$^2$)$^{1/2}$</td>
<td>761.04</td>
</tr>
<tr>
<td>10</td>
<td>(4s$^2$4p$^4$4d$^9$)$_{1/2}$</td>
<td>802.48</td>
</tr>
<tr>
<td>11</td>
<td>4s$^2$4p$^4$4d$^{10}$(4d$^2$)$^{1/2}$</td>
<td>898.12</td>
</tr>
</tbody>
</table>
Excitation processes can more clearly be seen in Fig. 2, which shows the ionization cross section. The physical effects due to ionization-excitation processes cannot be neglected in the calculation of the single-ionization cross sections comparable to those of direct ionization. Such a conclusion shows that the ionization-excitation cross sections are usually smaller than that from direct single ionization. Here we see that some channels of ionization excitation have a cross section with and without contributions from the ionization-excitation processes. Without the contribution of the ionization-excitation processes, the cross section will be underestimated by a few percent to 15% (for Gd$^{18+}$). Toward lower ionized ions from barely ionized Sn$^{4+}$ to highly ionized W$^{28+}$, the fraction of underestimation is stabilized to be the same value of about 12% for Nd$^{14+}$, Ba$^{10+}$, and Sn$^{4+}$. This value is nearly constant for all Pd-like ions from Sn$^{4+}$ to Gd$^{18+}$, independent of specific ions. Toward the direction of increasing ionization stages from Gd$^{18+}$, the fraction of underestimation is 9%, 5%, and 5% for Tb$^{19+}$, Yb$^{24+}$, and W$^{28+}$, respectively. This value decreases from 15% for Gd$^{18+}$ to 9% for Tb$^{19+}$ and then stabilizes to 5% for a wide range of Pd-like ions. The dominant ionization-excitation channels are levels belonging to the configuration of $4s^24p^4d^4f$.

Ionization-excitation processes are, in general, much weaker than those of the pure direct ionization for light- and medium-Z elements. Bellm et al. [36,37] experimentally measured the differential ionization-excitation cross-section ratios for the $n = 2–4$ states of He$^+$ relative to the direct ionization cross section is underestimated by 9.5% at the incident electron energy of 1000 eV. Such an underestimation is increased to 12.5% at 1500 eV and then basically reaches a consistent value of about 15%. The dominant channels of the ionization-excitation processes originate from levels of the $4s^24p^4d^4f$ and $4s^24p^54d^4f$ configurations. The contribution from the $4s^24p^54d^4f$ configuration is, in general, larger, than that of $4s^24p^4d^4f$.

![FIG. 1. (Color online) Level-to-level direct ionization and ionization-excitation cross section (1 Mb = $10^{-18}$ cm$^2$) of the 4s$^24p^6d^{10}$ ground level of Gd$^{18+}$. The numbers for each line are defined in Table I. The lines corresponding to 1–5, 1–6, 1–7, 1–9, and 1–11 represent the ionization-excitation cross section.](image1)

![FIG. 2. (Color online) Ionization cross section of the ground level of Gd$^{18+}$ with and without contributions from the ionization-excitation processes.](image2)
ionization of He by electron impact, and their results confirmed this conclusion. They further demonstrated that second-order approximation is necessary in their hybrid distorted-wave and convergent R-matrix approach. Thus the use of the first Born approximation of Eq. (1) might lead to inaccuracy in the convergent approximation is necessary in their hybrid distorted-wave and this conclusion. They further demonstrated that second-order ionization of He by electron impact, and their results confirmed this conclusion by using a fine-structure-level distorted-wave approximation on a fictitious mean configuration with fractional occupation numbers, representing the average electron cloud of the configurations included above. To adequately describe the initial and final states of electron impact processes, we have included extensive electron correlations including single and double excitations from the respective ground configuration. The electron correlation is vital for obtaining an accurate EII cross section, and its effects have been demonstrated in research fields such as the radiative opacity of hot, dense, high-Z plasmas [38–40]. By inspecting Fig. 4, one can know the reason why the ionization-excitation processes have evident contributions to the total ionization cross section from the viewpoint of the radial wave function. For the barely charged ion of Sn$^4+$ [Fig. 4(a)], there is a definite overlapping between the radial wave functions of 4d and nf ($n = 4, 5$). This means that the transition matrix element of $\langle 4d|\frac{1}{r_{4d-4f}}|nf \rangle$ ($n = 4, 5$) in Eq. (1) is large. With the increase of the atomic number (Gd$^{18+}$ and W$^{28+}$), the wave function of 4f tends to be inward compared with that of the 4d orbital. The 4f orbital shows collapse characteristics. From the radial wave functions of 4d and 4f, we can understand the basic feature of ionization-excitation processes. In fact, this is a general phenomenon for heavy ions with outmost subshells of 4d and 5d.

IV. CONCLUSION

The detailed level-to-level ionization cross section of the 4s$^2$4p$^6$4d$^{10}$ ground level of Gd$^{18+}$ is investigated theoretically by using a fine-structure-level distorted-wave approximation from the threshold to 4000 eV. The ionization-excitation cross section due to excitation of levels in the 4s$^2$4p$^6$4d$^4$4f configuration is comparable to the direct ionization cross sections of (4s$^2$4p$^6$4d$^{10}$)$_{1/2}$ and (4s$^2$4p$^6$4d$^{10}$)$_{1/2}$. If the contribution from these ionization-excitation channels is neglected, the total ionization cross section can be underestimated by a few percent to about 15%. For heavy atomic ions, this is a general phenomenon. We demonstrate this conclusion by investigating the ionization-excitation cross section of Pd-like ions of Sn$^{4+}$, Ba$^{10+}$, Nd$^{14+}$, Tb$^{19+}$, Yb$^{24+}$, and W$^{28+}$. For the barely charged ion Sn$^{4+}$, there is definite overlapping between
the wave functions of the 4\textit{d} and \textit{n}f (\textit{n} = 4, 5) orbitals. With the increase of the atomic number, the 4\textit{f} orbital moves inward and collapses, which results in a considerable overlap of 4\textit{d} and 4\textit{f} electrons.

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