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Theoretical Studies on Expressions of Condensed-Phase Photoionization Cross Section*

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Abstract *A set of general expressions for photoionization cross sections of atoms or molecules embedded in a medium and a dielectric influence function are derived based on Maxwell's equations and the Beer–Lambert's law in this work. The applications are performed for the photoionization process of solid gold both in the Clausius–Mossotti (virtual cavity) model and the Glauber–Lewenstein (real cavity) model firstly. The results show that the present theoretical expressions of photoionization cross section can be used to describe the photoionization process of atoms in condensed matter properly.*

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1 Introduction

The study on the photoionization cross section and angular distribution of photoelectrons of isolated atoms and molecules (or in ideal gas) has always received much attention. Understanding these microscopic processes and the related microscopic properties is fundamental and important to many physical and chemical studies. Most of the experiments have been performed for isolated atoms, such as noble gas, where the influence of neighboring atoms can be neglected. However, on the other hand, as the development of molecular dynamics simulations, condensed matter physics, laser-driven fusion, and materials science, the evaluation and explanation of the influence of particle (atomic, molecular, etc.) interactions on photoionization cross sections has been one of the aims of condensed physics and atomic and molecular physics.[1] Therefore, understanding the response properties of bulk atoms, molecules, and the perturbations caused by environmental interactions is necessary in order to achieve an efficient procedure for, for example, designing optical molecular materials at microscopic level. Photoionization processes of atoms and molecules in a special condition, especially in high temperature, pressure or density, have been paid more and more attention by theorists and experimentalists.[2−4] The aim of the present work is to describe the photoionization cross sections of atoms and molecules in several conditions as the coupling between the macroscopic effects and the microscopic property such as photoionization cross sections of an isolated atom. It not only will open a new way to calculate the photoionization cross sections of atoms in condensed matter from macroscopic quantity, but also can be helpful to studying accurately the photoionization processes of clusters and condensed matter etc.

The famous expression for photoionization cross sections[5] of isolated atoms and molecules used in most theoretical studies is

$$\sigma_i(\omega) = \frac{4\pi\omega}{c}\zeta = \frac{4\pi\omega}{c}\,\mathrm{Im}\,(\alpha)\,, \tag{1}$$

where ζ is the imaginary part of polarizability $\alpha(\omega)(= \eta + \mathrm{i}\zeta)$. Equation (1) is usually invalid in describing the photoionization cross sections of atoms in condensed system. In order to reduce the complexity of the problems, some kinds of approximation method and pseudopotential have always been introduced into calculating the influence of atomic interactions on photoionization cross sections in condensed system in history. However, as the rapid increase of the computational power, these problems once set aside can now be attacked accurately and directly.[6] In another way, the photoionization cross section of atoms embedded in matter can be related to the polarizability of atoms and the classical quantities according to Lax's famous expression,[7]

$$\sigma(\omega) = \Big[\frac{n}{\epsilon}\Big(\frac{E_e}{E}\Big)^2\Big]\frac{8\pi^3\omega}{3c}I_{ba}(\omega)\,, \tag{2}$$

where $I_{ba}(\omega)$ represents the square of the matrix element of emission transition from the initial quantum state a to the final state b, ω is the photon energy, n and ϵ are the index of refraction and the dielectric constant respectively. The factor $(E_e/E)^2$ describes the fact that the emitted electron is located in the medium of which the effective field E_e may differ from the average macroscopic electric field E. Equation (2) is dependent not only on the properties of the system but also on the external electric field which is not the property of the system. This makes Eq. (2) very difficult to be calculated in theory. Hence, it is necessary to find a set of accurate and simple methods to solve these problems.

In the present work we have suggested a set of expressions for photoionization cross sections which couples the photoionization cross-sections of an isolated particle and most of the important influence of the macroscopic effects

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on the photoionization cross-sections. The present theoretical expression for photoionization cross-sections of condensed matter is based on experimental Beer–Lambert's law and Maxwell's equations without using any mathematical approximation and physical models. We also suggest that the influence of particle interactions of surroundings with the photionized particle on the photoionization cross sections can be easily investigated using the dielectric influence function (DIF). It is also proposed that a density turning point (DTP) of a photoionized system may be viewed as the critical point where the photoionization properties of atoms in solid system may have notable change. The interatomic interactions are considered using the well-known Clausius–Mossotti model[8] and Glauber–Lewenstein[9] model of dielectric constant in this study. The results show that the suggested method is reliable and would open a new way to calculate the photoionization cross-sections of atoms in condensed system.

2 Theory

Based on Beer–Lambert's law[10] and Maxwell's equations, one can obtain the following equations for a linear Kramers–Kronig dielectric:

$$\mu\Big(\epsilon + \mathrm{i}\frac{4\pi\Omega}{\omega}\Big) = n'^2 \,. \tag{3}$$

When the frequency $\omega \neq 0$ of the external electromagnetic field, the magnetic permeability μ $(= \mu' + \mathrm{i}\mu'')$, the dielectric constant ϵ $(= \epsilon' + \mathrm{i}\epsilon'')$, the optical conductivity Ω $(= \Omega' + \mathrm{i}\Omega'')$, and the refractive index n' $(= n + \mathrm{i}\kappa)$ in reality must be a complex function of frequency. Then the photoionization cross section σ can be expressed as following from Eq. (3) if the photoionization quantum efficiency equals unity[11]

$$\sigma(\omega) = \frac{\sqrt{2}\omega}{Nc}\sqrt{\sqrt{(\mu'^2 + \mu''^2)\Big[\Big(\epsilon' - \frac{4\pi\Omega''}{\omega}\Big)^2 + \Big(\epsilon'' + \frac{4\pi\Omega'}{\omega}\Big)^2\Big]} - \mu'\Big(\epsilon' - \frac{4\pi\Omega''}{\omega}\Big) + \mu''\Big(\epsilon'' + \frac{4\pi\Omega'}{\omega}\Big)}\,, \tag{4}$$

where N is the number density of the system, c is the speed of light. The photoionization cross section in Eq. (4) is a strict expression without using any mathematical approximation and physical models. It is a strict and complete expression of photoionization cross section based on Beer–Lambert's law. The expressions in Ref. [12] are only the special forms of the present Eq. (4), where the conductivity and the magnetics have not been considered. In most ordinary cases where the real part of the magnetic permeability $\mu' = 1$, the imaginary part of the magnetic permeability $\mu'' = 0$ and the optical conductivity $\Omega = 0$, this is true and the expressions in Ref. [12] can give the accurate description of the photoionization cross sections in these conditions, and one can predict that the theoretical results will be in agreement with the experimental ones using those simple forms. However, for some cases, especially in some important scientific project, such as in the laser-driven fusion processes, the expressions in Ref. [12] may be invalid and incomplete, one should use Eq. (4) to describe the photoionization cross sections of atoms under these ultra-conditions.

Neglecting the magnetic and conductivity effects, equation (4) then can be expressed simply in a series expansion on the microscopic dipole polarizability of a particle.[5] Taking only the first order approximation, one can obtain the fundamental expression Eq. (1) for photoionization cross sections used for ideal gas from Eq. (4) in most theoretical studies. Equation (1) gives only the property of an isolated atom or molecule and is usually invalid to describe the photoionization cross sections of atoms in a condensed system. However, one can use these photoionization cross sections of isolated atoms as the necessary input data for modelling the photoionization processes of atoms embedded in plasmas and neutral fluids, condensed matter, etc. For this purpose, equation (4) can also be rewritten as[11]

$$\sigma(\omega) = \mathrm{DIF} \times \sigma_i(\omega)\,, \tag{5}$$

where

$$\mathrm{DIF} = \frac{1}{2\sqrt{2}\pi N\zeta}\sqrt{\sqrt{(\mu'^2 + \mu''^2)\Big[\Big(\epsilon' - \frac{4\pi\Omega''}{\omega}\Big)^2 + \Big(\epsilon'' + \frac{4\pi\Omega'}{\omega}\Big)^2\Big]} - \mu'\Big(\epsilon' - \frac{4\pi\Omega''}{\omega}\Big) + \mu''\Big(\epsilon'' + \frac{4\pi\Omega'}{\omega}\Big)}\,. \tag{6}$$

Equation (5) indicates that the photoionization cross sections for the atoms or molecules in the condensed system can be obtained by transforming the photoionization cross section σ_i of the same species particle in ideal gas using a transforming function DIF. Since DIF is the function of the number density, the dielectric constant, the magnetic preambility, and the optical conductivity of the macroscopic system, it may be referred to as *Dielectric Influence Function* (DIF). For dilute and ideal gas, the number density N is so small that there are almost no interactions among particles, and DIF → 1. Equation (1) becomes the accurate expression for photoionization cross sections in these conditions. However, as the number density of the system increases, the influence of the dielectric properties and some other collective effects on cross section become more and more important, and these influence are not negligible for high-density system or condensed matter. In this situation the DIF is not near unity in some energy range, and it can include not only higher power dielectric terms but also the interactions among atoms.

The present expressions for photoionization cross sections of atoms show that the photoionization process in condensed systems can be studied by coupling two kinds of interactions or effects, which can be studied respectively. One is the quantum quantity, which represents the photoionization cross sections of an isolated particle in Eq. (1). The other is the classical quantity part, which may represent most of the important influence of the macroscopic effects, such as the interactions of atoms and the electron overlap effects on the photoionization cross section, and can be described by the function DIF in Eq. (6). The dielectric influence function DIF represents the influence of both particle interactions and all higher-power terms in the expansion of $\epsilon^{1/2}$, which has been neglected in Eq. (1). It is the function coupling the microscopic and the macroscopic properties and represents the variations of photoionization cross section in condensed system with these macroscopic parameters. It can be seen that the Lax's expression in Eq. (2) is similar to the present Eqs. (4) and (5). The factor $(8\pi^3\omega/3c)I_{ba}(\omega)$ is an alternative expression for photoionization cross section σ_i of isolated atom in Eq. (1), and the factors in the brackets that take account of the modification of the electromagnetic field in the crystal play a similar role as the DIF factors in the present work. The present expressions in Eqs. (4) and (5) are only dependent on the properties of the system explicitly while Eq. (2) is dependent not only on the properties (n, ϵ) of the system but also on the external electric field E which is not the property of the system.

Equation (5) is a solid expression and gives a convenient way to understand the influence of the macroscopic electromagnetic responses such as the observable dielectric constant on the microscopic property-photoionization cross sections. In the non-magnetic and non-conductivity matter, the DIF has the following relations according to Eq. (6):

$$\text{if } \epsilon' \leq \frac{\epsilon''^2 - 64(\pi N\zeta)^4}{16(\pi N\zeta)^2}\,, \quad \text{then DIF} \geq 1\,; \tag{7}$$

$$\text{if } \epsilon' > \frac{\epsilon''^2 - 64(\pi N\zeta)^4}{16(\pi N\zeta)^2}\,, \quad \text{then DIF} < 1\,. \tag{8}$$

Equations (7) and (8) indicate that the DIF may have positive influence on photoionization cross section if the real and imaginary parts of the dielectric constant have the relation of Eq. (7), otherwise, the negative influence in Eq. (8). One can define the number density N as the *Density Turning Point* (DTP), where the DIF equals unity. DTP function then can be expressed as following,

$$\text{DTP} = N(\omega) = \frac{\sqrt{\sqrt{\epsilon''^2 + \epsilon'^2} - \epsilon'}}{2\sqrt{2}\pi\zeta}\,. \tag{9}$$

The DTP is always a function of the photon energy of the external electromagnetic field. It represents that there is different influence of macroscopic and microscopic properties of material at different photon energies on photoionization cross sections. Equation (9) indicates that the macroscopic property of the material at different photon energy may have a critical point, where the photoionization cross section may have notable change. The DTP can be used to explain the variations of photoionization cross sections with the number density.

3 Applications and Discussions

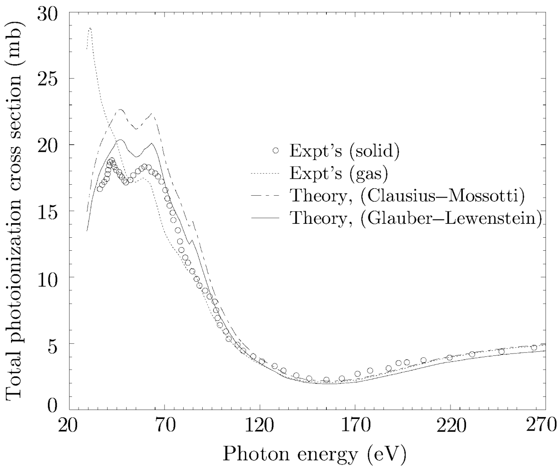

Fig. 1 Total photoionization cross-sections of gold atom. The circles stand for the solid gold experimental data; the dotted line is for the ideal gas experimental results; the dashed-dotted line is for the theoretical studies of Ref. [15]; and the solid line is for the present theoretical studies of solid gold.

Figure 1 shows the comparison of the gold photoionization cross section among the solid phase experiment[13] determined by use of synchrotron radiation on thin films, the ideal gas experimental results[14] obtained from the photoabsorption experiments, the theoretical results calculated by using the Clausius–Mossotti (virtual cavity) model,[15] and the present theoretical results calculated by using the Glauber–Lewenstein model (real cavity) with the radius among atoms at the solid phase number density $N = 8.72 \times 10^{-3} a_0^{-3}$. The magnetic permeability and the optical conductivity have not been considered in this work. Both the theoretical photoionization cross sections have good agreement in structure and in magnitude with the experimental results of gold crystal. This shows that the present method is reliable to obtain the photoionization cross sections of solid system from ideal gas photoionization cross sections. Figure 1 also shows that the theoretical results calculated using Clauber–Lewenstein model is better than those from Clausius–Mossotti model. This is because that in the virtual cavity model, the electromagnetic field inside the cavity, i.e., the local field, is modified by the presence of the cavity, but the modification of the field outside the cavity is disregarded. Hence the local filed introduced in this way is not exactly the field that couples to the atom in reality. On the contrary, however, in the real cavity model the mutual modification of the fields outside and inside the cavity are taken into account in a consistent way. It may be therefore expected that the real cavity model is more suited for describing the photoionization cross sections in condensed matter than the virtual cavity model. Furthermore, the more correct the model of electric susceptibility for the condensed matter, the more accurate the photoionization cross sections obtained from the present expressions will be. A complete discussion for the reason of the difference between the theoretical results and the experimental photoionization cross sections can be found in other works.[12,15]

In summary, the new expressions correctly show the dependence of the photoionization cross sections σ on the number density. The microscopic properties of atoms and the macroscopic properties of the matter composed of these atoms have been coupled by the DIF factor in order to obtain the photoionization cross sections of atoms in condensed system from ones of ideal gas reasonably. These DIF functions represent the classical influence of the macrosystem consisting of all surrounding particles in condensed system on the photoionized atoms. A DTP function has been proposed as a judgment for the direction of the variations of the photoionization cross section with the number density. The results show that the suggested method is reliable and would open a new way to calculate the photoionization cross sections of condensed system.

Appendix: Local Field Models

It is well known that the polarizability of the system of atoms or molecules may differ very much from the sum of polarizabilities of constituent particles, even when the wave functions of electrons on different atoms do not overlap. In order to relate the relative permittivity (dielectric constant) of a medium to its number density and mean dynamic polarizability, some models have been introduced.

For the special case, such as ideal gases, the dielectric constant without local field effects may be expressed as

$$\epsilon = 1 + 4\pi N\alpha \,. \tag{A1}$$

For polarized atoms/molecules arranged in cubic crystals, the relation between polarizability and the dielectric function can be obtained using the well-known Clausius–Mossotti model which represents the interactions of the polarized particles in the crystals,

$$\epsilon = 1 + \frac{4\pi N\alpha}{1 - 4\pi N\alpha/3} \,. \tag{A2}$$

This formula is found to work well for a wide class of dielectric liquids and gases. But it is the virtual cavity model, i.e., the local field, is modified by the presence of the cavity, but the modification of the field outside the cavity is disregarded. Hence the local field introduced in this way is not exactly the field that couples to the atom in reality.

On the contrary, the Glauber–Lewenstein model defines a more accurate relationship for dielectric constant and polarizability as

$$\frac{(\epsilon - 1)(2\epsilon + 1)}{3\epsilon} = \frac{4\pi}{3} N\alpha \,, \tag{A3}$$

which is a real cavity model in which the modification of the fields outside and inside the cavity are taken into account in a consistent way. Recent experiments have reported that the real cavity model may be favored.

Since the atomic/molecular dipole polarizability is complex valued, the real part ϵ' and the imaginary part ϵ'' of the dielectric function $\epsilon(\omega)$ may be expressed in general as

$$\epsilon' = \sum_{j=0}^{\infty} e_j (4\pi N \sqrt{\eta^2 + \zeta^2})^j \cos(j\theta) \,,$$

$$\epsilon'' = \sum_{j=0}^{\infty} e_j (4\pi N \sqrt{\eta^2 + \zeta^2})^j \sin(j\theta) \,, \tag{A4}$$

where $\theta = \arctan(\zeta/\eta)$, e_j is the coefficient which maybe represent the collective influence effects of macroscopic matter. For Glauber–Lewenstein model and under the condition $|\epsilon| \geq 1$, the values of e_j are $e_0 = e_1 = 1$, $e_2 = 1/3$, $e_3 = -1/9$, $e_4 = -1/27$, $e_5 = 5/81$, and $e_6 = -1/81$, etc.

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