

A graphic method for computing multi-atomic resonant photoemission cross section

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Abstract. A graphic method for studying multi-atom resonant photoemission process in molecules and solids is presented in this work. The Feynman diagrams have been applied to describe the interactions between atoms in MnO molecules. The theoretical results show that the resonant contribution exhibits a strong distance-independent and element specific effects for the neighboring atoms. Two mechanisms, the interactions between the atoms and the reabsorption process have been supposed in the present work to explain the multi-atomic resonant photoemission for the first time.

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Key words: multi-atomic resonant photoemission; electronic correlation effect; Feynman diagram.

1 Introduction

The cross section of the multi-atomic resonant photoemission receives contributions from two main channels, the direct photoionization and the resonant photoionization channels [1]. The characteristics of the two parts are obvious due to different interaction operators, different symmetry selection, polarization and angular distribution properties [1-3]. The intensity of the direct photoionization channel is related to a transition element which, in the dipole and one-particle approximation, is given by a dipole transition element between the ionized core orbital and a continuum orbital [2]. The resonant part depends instead on a resonance-continuum hamiltonian matrix element which, in the independent particle approximation, may be reduced to a two-electron integral involving the core orbital, the continuum orbital, the bound virtual orbital of the core excitation and the bound ionized orbital [1]. Recently, the multi-atomic resonant photoemission has

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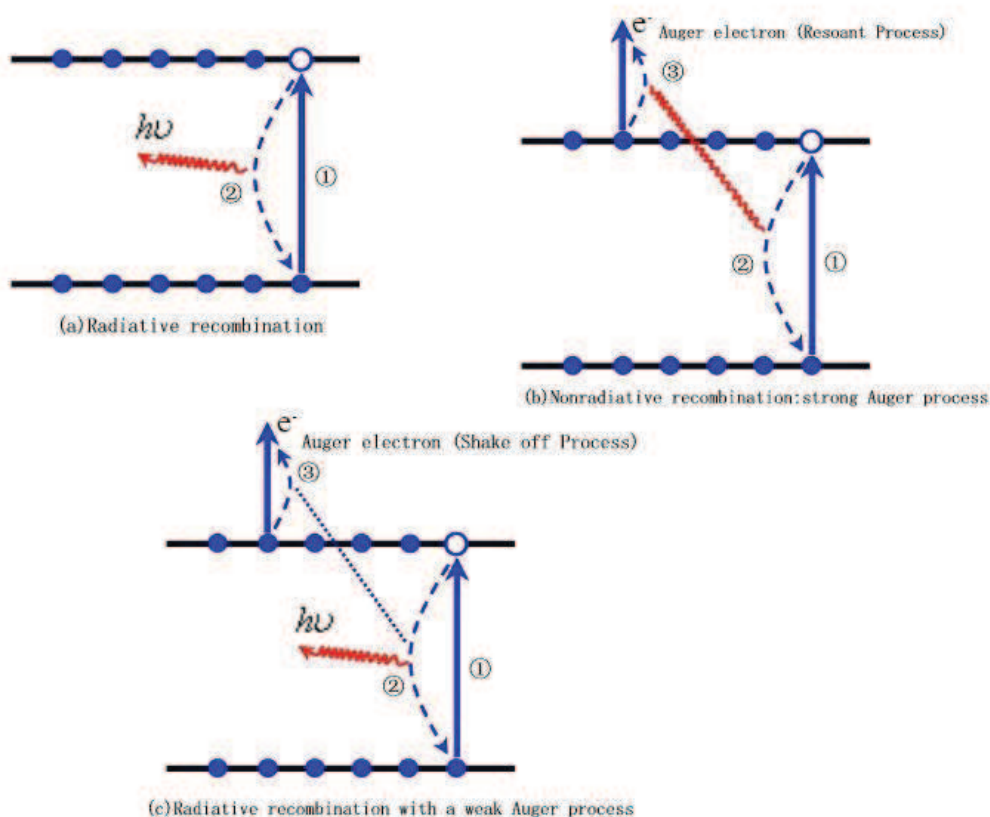


Figure 1: The photoemission processes of the multi-electron excitation for single atom resonance.

been found in MnO solid without the theoretical confirmation. It is the main object of the present study to estimate quantitatively the resonant intensity with the Feynman diagram of two electron matrix element which contains two core orbitals strongly localized at different atomic sites. The diagram rules describing the electron interaction in one atom have been extended into the interaction between the electrons of the nearby atoms.

The well-known intra-atomic single-atom resonant photoemission (SARPE) [2] has been generalized to apply to multi-atomic resonant photoemission (MARPE) [1] in the present work. In the photoabsorption of atoms, the existence of the multi-electron excitation process has been known for a long time. The mechanism of multi-electron excitation in photoabsorption can be considered due to shake-up and shake-off processes as shown in Fig. 1. When an inner-shell vacancy is created by photoabsorption, another atomic electron is excited to an unoccupied bound state in the shake-up process, while it is ejected into the continuum in the shake-off process. Such ionization and excitation processes in inner shell electrons far above threshold have been extensively studied [1-11].

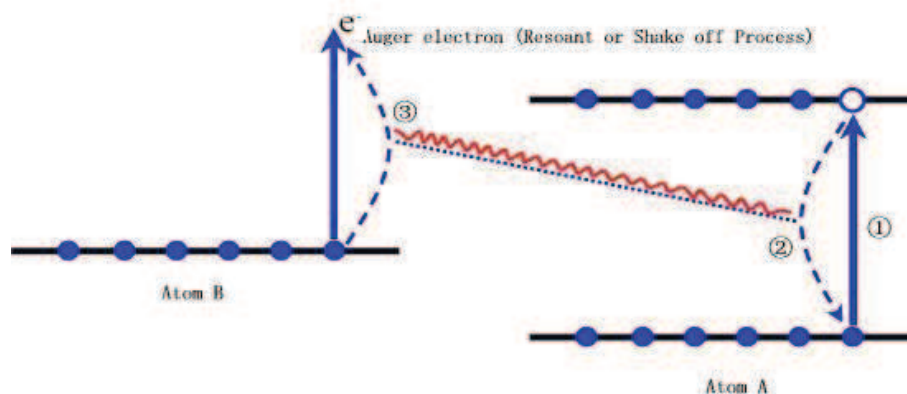


Figure 2: The multi-atomic resonant photoemission process.

In particular, the interaction between the out-going electron and the remaining system depends on the chemical environment of the atom, which can be studied by quantum chemical methods.

For multi-atomic resonant photoemission process, the core ionization, however, constitutes a strong perturbation of the molecule, and may contribute a significant electronic effect. Firstly, the valence electrons relax significantly to compensate for the presence of the positive core hole in the same atom as shown in Fig. 2. The departing photoelectron can interact strongly with the valence electrons of the neighbouring atoms. The interaction between the out-going electron and the remaining system depends on the chemical structures of molecules. Inter-shell and intra-shell correlations in an atom are expected to have a particularly large impact on satellite spectra, which originate in multi-electronic transitions in the same atom. In the present work, the diagrams and the corresponding rules for the multi-atomic resonant photoemission have been given.

2 Theory and applications

In order to study the multi-atomic resonant photoemission, the theory is extended from the excitation and ionization process of electrons in one atom. It is well known that the relation between the atomic and molecular polarizability $\alpha(\omega)$ and the induced dipole moment P can be expressed by

$$P = [\alpha(\omega) \frac{F}{2} e^{-i\omega t} + \alpha^*(\omega) \frac{F^*}{2} e^{i\omega t}] Z \quad (1)$$

if an atom is perturbed by the time-dependent external radiation field $\frac{F}{2} e^{-i\omega t} + \frac{F^*}{2} e^{i\omega t}$. This dipole operator represents the interactions between a photon and an electron in

atom. In the z-axis, the dipole moment is given by

$$P_z = \frac{\langle \Psi_N^L | -Z | \Psi_N^L \rangle}{\langle \Psi_N^L | \Psi_N^L \rangle} \quad (2)$$

where Ψ_N^L is the atomic and molecular unperturbed wavefunction. If the wavefunction is normalized and only the first order of the external radiation field is considered, P_z is reexpressed by

$$P_z = -\langle \Psi^0 | Z | \Psi^1 \rangle - \langle \Psi^1 | Z | \Psi^0 \rangle. \quad (3)$$

Where Ψ^0 and Ψ^1 are the unperturbed wavefunction and perturbed wavefunction by the first order of the external radiation.

Under the perturbation of the external field, the wavefunction of the system has been perturbed. The first-order perturbation wavefunction of the system also can be expressed by

$$\Psi_f^1 = -\sum_f |\Psi_f^0\rangle \langle \Psi_f^0 | \frac{FZ}{2} | \Psi_i^0 \rangle \left[\frac{e^{-i(E_i - \omega t)}}{E_i - E_f - \omega} + \frac{e^{-i(E_i + \omega t)}}{E_i - E_f + \omega} \right] \quad (4)$$

where Ψ_i^0 and Ψ_f^0 are the initial and final states wavefunction of the system respectively, i.e., before and after the interactions, and E_i and E_f is the energies of the initial and final states respectively. Using the time-dependent perturbation theory, substitute the wavefunction in Eq. (4) into Eq. (3), according to the definition of the polarizability, the polarizability can be expressed by

$$\alpha(\omega) = -\sum_f |\langle \Psi_f^0 | Z | \Psi_i^0 \rangle|^2 \left[\frac{1}{E_i - E_f - \omega} + \frac{1}{E_i - E_f + \omega} \right]. \quad (5)$$

The energy denominator in the second term vanishes when the photon energy ω satisfies $\omega = E_i - E_f$. Using the principal-value integration, Eq. (5) is re-expressed by

$$\alpha(\omega) = -\sum_f |\langle \Psi_f^0 | Z | \Psi_i^0 \rangle|^2 \left[\frac{1}{E_i - E_f - \omega} + P \frac{1}{E_i - E_f + \omega} - i\pi\delta(E_i - E_f + \omega) \right] \quad (6)$$

Since the first term in Eq. (6) does not contain a vanishing denominator, it has no contribution to the cross section. The photoabsorption cross section can usually be represented in terms of linear polarizability according to Eq. (6)

$$\sigma(\omega) = \frac{4\pi\omega}{c} \zeta(\omega) \quad (7)$$

where ζ is the imaginary part of the complex dynamic polarizability α of an isolated atom or molecule. Substitute Eq. (6) into Eq. (7), one can get the expression of the photoabsorption cross sections in the coordinate represent (length) and the momentum represent (velocity) space respectively. The relationship between these two forms is derived from

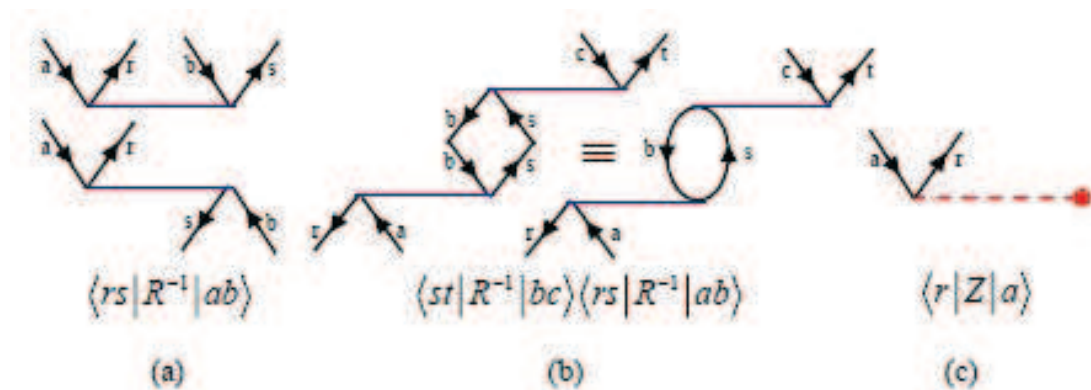


Figure 3: First, Second and Zero order diagrams for photoionization processes [8].

the commutation relation between the Hamiltonian and dipole operator. The cross section in the length form is

$$\sigma(\omega) = \frac{8\pi\omega}{ck} |\langle \Psi_f^0 | Z | \Psi_i^0 \rangle|^2 = \frac{8\pi\omega}{ck} |\langle r | Z | a \rangle|^2 \quad (8)$$

and in the velocity form

$$\sigma(\omega) = \frac{8\pi\omega}{ck} |\langle \Psi_f^0 | \sum_i \frac{\partial}{\partial Z_i} | \Psi_i^0 \rangle|^2. \quad (9)$$

k is the electron momentum in the final states. In the following of the present work, r and a represent the wavefunction Ψ^0 and $|Psi^1$ respectively. The length form and velocity form should be equivalent if the wavefunction is exact one of the system. In the present work, we use these two forms to test the accuracy of the wavefunction.

In Eq. (8), the photoabsorption cross sections are directly related with the dipole transition matrix element which can be represented by Fig. 3(c). While the Coulomb interaction between two electrons, i.e., the electronic correlation can influence the photoionization process which can be represented by the Coulomb matrix element as shown in Figs. 3(a) and (b). The corresponding algebraic expression of a given diagram then can be obtained with some rules [5-7]. The diagrams of Fig. 3(a) represents the first-order diagrams and will give a coupling of the photoionization process ($a \rightarrow r$) with some single excitation transition processes ($b \rightarrow s$). The corresponding algebraic expressions for Fig. 3(a) respectively are

$$\langle \bar{z} \rangle_{ar} = \sum_s \frac{\langle z \rangle_{bs} \langle v \rangle_{arbs}}{\epsilon_a - \epsilon_r + \epsilon_b - \epsilon_s} \quad (10)$$

and

$$\langle \bar{z} \rangle_{ar} = \sum_s \frac{\langle v \rangle_{arbs} \langle z \rangle_{bs}}{\epsilon_b - \epsilon_s + \omega}. \quad (11)$$

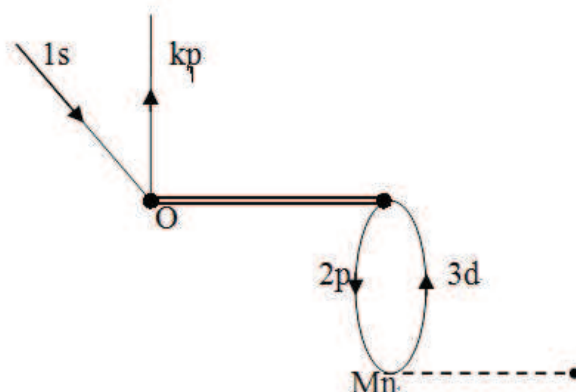


Figure 4: The diagram of the multi-atomic resonant photoemission of MnO.

The diagrams in Fig. 3(b) are the second-order diagrams because that there are two Coulomb interaction processes included. These are two of the auto-ionization processes.

$$\langle \bar{z} \rangle_{ar} = \sum_{s,t} \frac{\langle v \rangle_{arbs} \langle z \rangle_{ctv} \langle v \rangle_{bsct}}{(\epsilon_a - \epsilon_r + \epsilon_c - \epsilon_t)(\epsilon_a - \epsilon_r + \epsilon_b - \epsilon_s + \epsilon_c - \epsilon_t + \omega)} \quad (12)$$

Fig3.(b) will give a sharp resonance when the photon energy is equivalent to the absolute value of the energy difference between the states b and s under the final state correlation condition. As shown in the above algebraic expression Eq. (4), the resonance has been shifted by an energy $|\epsilon_a - \epsilon_r + \epsilon_b - \epsilon_s|$. In this diagrammatic representation, one can easily study and interpret the complex electronic correlations in photoionization processes.

Furthermore, if the electrons between atoms interact, the multi-atomic resonant emission process occurs, then, the photoabsorption cross section will be corrected by according to Eq. (11)

$$\langle \bar{z} \rangle_{ar} = \frac{\langle z \rangle_{b_2 s_2} \langle v \rangle_{a_1 r_1 b_2 s_2}}{\epsilon_{b_2} - \epsilon_{s_2} + \omega}. \quad (13)$$

The multi-atomic electron correlation can be represented in $\langle v \rangle_{a_1 r_1 b_2 s_2}$, where a_1, r_1 are the single-particle orbitals and b_2, s_2 are the orbitals of atoms. Then we can use the Feynman diagrams to study the multi-atomic resonant photoemission process.

3 Results and discussion

In the present work, we apply the Feynman diagrams to study the multi-atomic resonant photoemission cross sections of MnO. The measured intensity of O 1s photoelectrons coming from the single crystal of MnO exhibits significant enhancements when the photon energy is tuned to the $2p-3d$ absorption resonances of Mn [1-3]. The photoionization and photoexcitation processes represented by Goldstone diagram as shown in Fig.

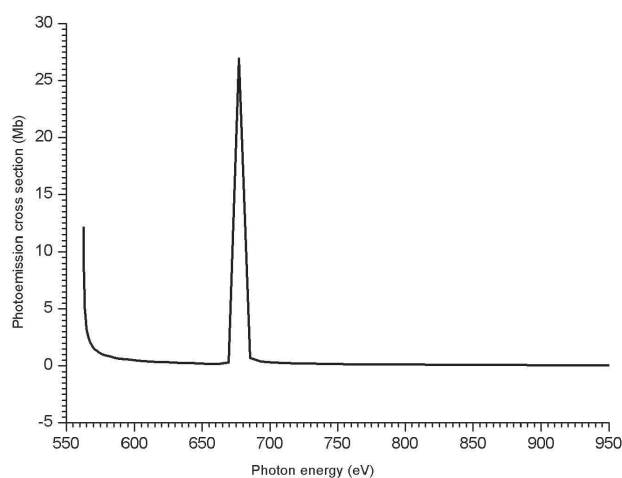


Figure 5: Comparison of the direct photoemission and the resonant photoemission processes.

4 can be converted into mathematical expressions as Eq. (13) which are constructed by the dipole momentum matrix of atomic Mn and Columbic interaction matrix between atomic Mn and O. In molecular MnO, the multi-centered wavefunction should be converted into one-centered wavefunction, hence the distance between the atomic O and Mn should be given firstly. The present study used the equilibrium distance $R=2.132$ a.u. in the calculation. The single-electron orbitals have been calculated by using MCHF package. The excited single-electron orbitals in the final excited states have been obtained from the package MYBNDV [12].

There are two channels of the photoionization and photoexcitation process, one is the direct ionization process and the other is the resonant ionization process. One $1s$ electron in Oxygen atom absorbs one photon and ionizes away from O atom in the direct photoionization process. This process can be represented by only one dipole momentum matrix which represents the interactions between the electron and photon. The resonant emission process occurs in MnO molecule as shown in Fig. 4. The $2p$ electrons in Mn absorb the photon energy and jump on the $3d$ orbital, then de-excites down to the $2p$ orbital again. As this process happens, the $1s$ electrons of Oxygen atom nearby are influenced by the changes of the Columbic field of Mn atom. The energy difference makes the $1s$ electron in O atom ionized into the continuum state kp . In the photoionization cross section, there will be a sharp peak due to this resonant ionization process.

In order to confirm the resonant process, in the present calculations, the external field induced $1s$ ionization dipole transition is given by $\langle kp|Z|O_{1s}\rangle$ without the Columbic interactions. The energy from Mn $2p$ to $3d$ transition can be expressed using the Columbic matrix $\langle Mn_{3d}|R|Mn_{2p}\rangle$. The effective ionization matrix then can be that the dipole

matrix times the Columbic interactions matrix: $\langle kp|Z|O_{1s} \rangle \langle Mn_{3d}|R|Mn_{2p} \rangle$. In experimental results, there also measured a obvious peak at about 680eV in molecule MnO. This peak can not be explained by the transitions of O or Mn atom along and is obviously different from isolated atomic absorption. The present multi-atomic resonant emission calculations show that this de-excitation process provides the energy to O 1s electrons. Which indicates the interactions between O and Mn make this peak appear. In Fig. 5, the enhancement of the cross section at about 680eV is also found to be caused by the resonant effect between the atomic Mn and O. In the future work, other systems will be studied to confirm this resonant emission process.

4 Conclusion

In summary, a diagram theory of multi-atomic resonant photoemission is presented to explain both the magnitude of the effect and the shape of the multi-atomic resonance enhancement. That the interatomic autoionization decay is dominated by the interaction between the dipole currents induced in each of the atoms is confirmed.

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