Vol 18 No 12, December 2009
1674-1056/2009/18(12)/5296-05

Chinese Physics B

© 2009 Chin. Phys. Soc.
and IOP Publishing Ltd

An alternative view of condensed-phase photoionization*

Ma Xiao-Guang(马晓光)†, Yang Chuan-Lu(杨传路),
Gong Yu-Bing(龚玉兵), and Wang Mei-Shan(王美山)

Department of Physics, Ludong University, Yantai 264025, *China*

(Received 20 November 2008; revised manuscript received 7 May 2009)

This paper proposes an accurate valuable interpretation scheme to study the evolvement of the photoionization processes from the isolated to the condensed atoms by a unique *ab initio* method. The variations of the photoionization cross sections of the atomic sodium with the photoelectron energy and the boundary radius of the atomic configuration space are studied in this new scheme by the *R*-matrix method. The discrepancy in the photoionization spectra of the isolated and the condensed sodium has been explained quantitatively and understood successfully by this alternative view in detail for the first time.

Keywords: condensed-phase photoionization, sodium, configuration space
PACC: 3280F, 3280, 3380E

1. Introduction

The solid-state effects and the transition mechanism from the isolated atomic property to the macroscopic condensed property have always been interesting subjects for physicists.[1−5] A fully quantitative understanding of the implications and relations between the photoionization processes and cross sections of the isolated and the condensed atoms has remained a challenge as yet. Many theories have been developed to purely deal with either the solid photoemission[6,7] and the local field effects[8−10] or the photoionization cross section of the isolated atoms. However, the method which can interpret quantitatively the difference of the photoionization processes between the isolated and the condensed atoms by a unique *ab initio* procedure is still scarce.

2. An alternative view of condensed-phase photoionization

In this work, a valuable scheme has been presented in order to interpret the differences of the photoionization processes in the isolated and the condensed atoms. The story begins with the Dalton's postulate that atoms retain their identity even in chemical combination with other atoms.[10] Most of the configuration state space of the bound atoms will be enveloped by some boundary radius. If a reasonable radius around the atomic nuclear has been specified, the configuration state space of the atom can be divided into two regions: the outer region and the inner region. The influence of the environment on the atomic states in the inner region is usually weak, so the property of the isolated and condensed atom in this region is not different largely and almost identical. However, the atomic states in the outer region will be influenced largely by the environment. The property of the isolated and condensed atom in this region will be very different due to the different environment. As a simple approximation, only the difference of the electronic distribution of the isolated and condensed atoms in the outer region has been taken into account to explain the difference of the property and the dynamic process for the isolated and condensed atom.

Most differences of the photoionization process for the isolated and condensed atoms can be explained by the different construction schemes of the initial and final states of the photoionization system in the outer region. All of the configuration state space of the photoionization system can be made from the wavefunctions of the target electrons and the photoelectron. The configuration state space of the initial state is made with only the bound electrons. It is open for the isolated atom and has been squeezed into a limited region for the condensed atom respectively. After the photoionization process occurs, the photoelectron escaping from the isolated atoms only receives a long

*Project supported by the Natural Science Foundations of Ludong University (Grant Nos 22270301 and L20072804). The computations were carried out partly on the Dawn-4000A supercomputer at Provincial Key Laboratory of Atomic and Molecular Physics in Ludong University.
†Corresponding author. E-mail: hsiaoguangma@163.com

range Coulomb interaction. So the photoelectron will leave the target atom rapidly and the higher the photoelectron energy is, the faster the photoelectron will escape. Then the influence of the photoelectron on the final state of the isolated atom will be small and the final state of the isolated atom should be most like the states of the target atom. When constructing the initial and final states of the isolated atom, the inner region of the configuration state space of the target atom should be enlarged as possible in order to not only make the initial state have a convergent configuration state space but also make the influence of the photoelectron on the final state very small. For the condensed atoms on the other hand, the escaping photoelectron will not only interact with the target electrons in the outer region but also interact with the condensed environment. These interactions will make the proportion of the photoelectron in the construction of the final states larger. When constructing the wavefunction of the condensed atom, the radius of the configuration state space of the target atom should be decreased reasonably according to the actual conditions of the condensed atom. The initial states of the condensed atom have been squeezed into a limited inner region while the final states will be most influenced by the target electrons in the outer region and the photoelectron.

3. Application and discussion

In order to implement the above scheme, the *ab initio* close-coupling and R-matrix method[12−14] have been used to study the variation of the photoionization cross sections of the atomic sodium with the boundary radius R_A of the configuration space. Starting from the ground state (corresponding to the lowest state of $J = 1/2$, even parity) of the atomic sodium, we show the main ionization and excitation processes (corresponding to the final state of $J = 3/2$, odd parity) in the relativistic calculations using the computer code DARC[12] in Table 1. The initial and final states of the system are all made from the target electrons $1s, 2s, 2p, 3s, 3p,\ 3d$ and the s, p, d, f-photoelectrons respectively. The maximum densities of these bound electrons are marked respectively and only the probability density of the d-photoelectron is shown as an example in Fig.1. The difference of the photoionization process between the condensed atoms and the isolated atoms could be represented by the different separation mechanisms of the target configuration space.

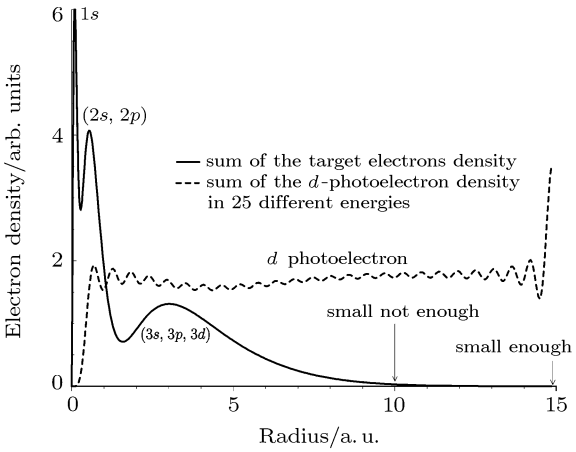


Fig.1. The electron density in the different separated configuration state space.

Table 1. The dominant photoionization processes of atomic sodium.

single photoionization and photoionization with excitations			single and double excitations		
No.	process	channels	No.	process	resonances
1	$3s \to kp$	1	1	$2p \to 3s$	1
2	$2p \to kl(ks, kd, k\overline{d})$	6	2	$2p \to 3d$	7
3	$2\overline{p} \to kl(ks, kd, k\overline{d})$	4	3	$3s \to 3p$	1
4	$2p3s \to 3d(\overline{d})kl(ks, kd, k\overline{d})$	18	4	$2s \to 3p$	3
5	$2\overline{p}3s \to 3d(\overline{d})kl(ks, kd, k\overline{d})$	11	5	$1s \to 3p$	3
6	$2s \to kl(kp, k\overline{p}, k\overline{f})$	4	6	$2p3s \to 3d3d$	11
7	$2s3s \to 3p(\overline{p})kl(ks, kd, k\overline{d})$	10	7	$2s3s \to 3p3d$	4
total channels of the photoionization processes		54	total correlation functions		30

Several experiments have been performed to obtain the photoionization cross sections of the atomic sodium.[15−24] Only a few studies[17] have compared the cross sections in the solid and the vapor conditions and raised a question that parts of the three broad maxima in solids might be due to the 2s excitations. However, they did not give the quantitative theoretical calculations and also did not interpret the third and fifth broad maxima shown in Fig.2(a) while no maxima exist in the same positions for the spectrum of the vapor. On the theoretical side, many works have been done to study purely the photoionization cross section of the free sodium atoms.[25−36] Only one work[37] has tried to interpret these maxima with the help of the so-called "plasmaron theory" which demands simultaneous excitation of the collective modes and the core electron. This theory correctly describes the positions of these peaks for Al. It fails, however, to give the positions of these peaks for Na and Mg.[5,37] At present a convincing explanation for these broad maxima has been given.

The theoretical photoionization cross sections of the isolated and condensed sodium have been compared with the results of the vapor[17] and the solid phase experiments[24] respectively in Fig.2. Only the length form has been shown because both the length and the velocity gauges show almost the same behavior which can eliminate the numerical problem with continuum funcitons.[14] The experimentally determined absolute values of the photoionization cross sections of the vapor sodium shown in Fig.2(b) cannot be made with an uncertainty better than 25%–30% and only the relative shape of the absorption spectrum was possible to be measured exactly.[17] The photoionization cross sections of the isolated sodium have been calculated with the boundary radius R_A=14.89 a.u. where the photoionization cross section will be convergent and does not vary with the radius any more for the present configuration state space. The most sharp peaks shown in Fig.2 have already been discussed and marked,[15,17] however, no definitive conclusion about the difference of the broad structures between the isolated and the condensed sodium has been reached previously. For the gas sodium, our theoretical calculations agree well with the vapor experiments in Fig.2(b) since the relativistic effects and the interchannel coupling arising from final state configuration mixing have been considered. To our knowledge, there are only a few studies which carefully investigated the photoionization cross section in this photoelectron energy region for the isolated sodium.[15]

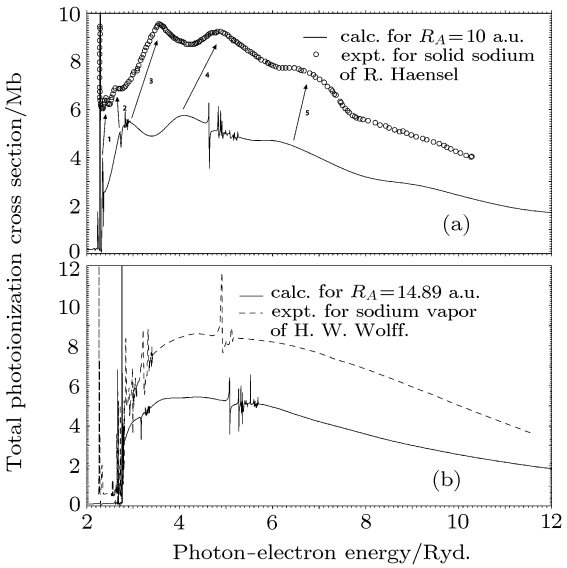


Fig.2. The theoretical solid-state calculations with 54 channels and 30 correlation functions in Table 1 compared with the experimental solid data[24] are shown in Fig.2(a). The probable relations of the maximum broad structures between the experimental and theoretical results are marked by arrows. The isolated atomic calculations with the same 54 channels and 30 correlation functions compared with the experimental vapor data[17] are plotted in Fig.2(b).

There are still some sharp structures in the theoretical results in Fig.2(a) which can be smoothed within the framework of band theory.[5] The solid theoretical results show unambiguously similar structures with the experimentally observed structures in solid sodium.[24] In some studies,[5,17] some broad structures of the solid sodium in Fig.2(a) were simply assigned to general solid-state effects without deeper investigation on their origins. Most of the broad structures of the photoionization cross section in solid, especially the third and fifth broad structures, have been calculated out by using the present scheme. The first broad structure shown in Fig2(a) is due to some double excitation processes. The position of the second is the threshold of the $2p3s \rightarrow 3dkl$ process and the subsequent series are $2s \rightarrow 3p$, $1s \rightarrow 3p$ and the simultaneous excitation of the 2p and 3s electrons which give the third broad structure. These structures might be broadened when going from the isolated atoms to the solid. The fourth broad maximum can be explained in terms of a one-electron model for free atoms due to the delayed onset of transitions from the 2p-states to d-symmetric final states.[15] However, no maximum exists in the spectrum of sodium vapor at the position where we find the third and the fifth maxima in the

solid. These deviations at the absorption maximum between the solid and gas cross sections are most due to the coherent interference of the outgoing photoelectron in the final states. The most striking feature is the broad fifth maximum at the 6.5 Ryd., which is probably due to the strong coupling of the outer electrons with the photoelectron in solid. The theoretically predicted behavior is qualitatively reproduced by the experiment.

The evolution of the energy-dependent photoionization cross sections of the atomic sodium with the boundary radius of the atomic configuration space varying from 1.85 a.u. to 14.89 a.u. is shown in Fig.3. The core radius of the atomic sodium calculated with Thomas–Fermi approximation is 1.85 a.u.[38] The boundary radius of the configuration space should not be less than this radius because most of the important orbitals will be outside of the target atoms shown in Fig.1. From 1.85 a.u. to 2.60 a.u., the photoionization cross sections calculated will be negative at some photoelectron energies. The photoionization cross sections will always be positive in the whole energy region when the radius is greater than 2.61 a.u. But we think that the first reasonable radius should be 4.21 a.u., which is the atomic radius in metal sodium. The evolvement of the photoionization cross sections with the photoelectron energy and the boundary radius can be evidently characterized by the propagation of the wave in water around the center (20 Ryd., 15 a.u.). The appearance or enhancement of some broad maxima should be due to the contributions of the interference between the electrons of residual ion and the outgoing electrons. As the radius becomes bigger, the cross sections will be convergent to the radius 14.89 a.u. and the cross sections vary so slightly that they can be completely ignored.

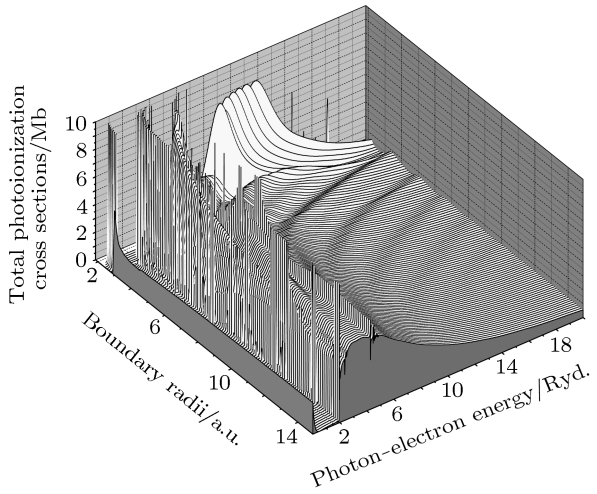


Fig.3. The variation of photoionization cross sections of atomic sodium with photoelectron energy for different configuration space.

4. Conclusion

In conclusion the present method appears capable of yielding accurate cross sections both for solid and free atoms. It also shows that our atomic approach can be successfully used to explain quantitatively the different behavior of the solid and isolated atoms. As a result all broad maxima can be explained quite adequately by the solid-state calculations. The evolvement of the photoionization cross sections from the isolated atoms to the condensed atoms can be represented by the evolution of the atomic configuration space. The results for both the isolated and condensed atoms are so beautiful that more and deeper analyses should be needed. A more detailed description of our scheme will be presented in our future work.

References

[1] Lagendijk A, Nienhuis B, Tiggelen B A V and Vries de P 1997 *Phys. Rev. Lett.* **79** 657

[2] Jansen T, Swart M, Jensen L, Duijnen P and Snijdens J 2002 *J. Chem. Phys.* **116** 3277

[3] Ma X G 2006 *Phys. Lett.* A **348** 310

[4] Sun W G, Ma X G and Cheng Y S 2004 *Phys. Lett.* A **326** 243

[5] Manson S T 1978 *The Calculation of Photoionization Cross Sections: An Atomic View* ed. Cardona M and Ley L *Photoemission in Solids I — General Principles* (Berlin, Heidelberg, New York: Springer-Verlag) p135

[6] Abbati I, Braicovich L, Rossi G, Lindau I, Pennino U del and Nannarone S 1983 *Phys. Rev. Lett.* **50** 1799

[7] Molodtsov S L, Halilov S V, Servedio V D P, Schneider W, Danzenbacher S, Hinarejos J J, Manuel R and Laubschat C 2000 *Phys. Rev. Lett.* **85** 4184

[8] Nesvizhskii A I 2001 *Thesis: Theory and Interpretation of L-shell x-ray Absorption* University of Washington

[9] Ma X G 2009 *Chin. Phys.* B **18** 161

[10] Ma X G, Gong Y B and Qu Z J 2009 *Chin. Phys.* B **18** 1451

[11] Bader R F W 1990 *Atoms in Molecules — A Quantum Theory* (Oxford: Clarendon Press)

[12] Berrington K A, Burke P G, Dourneuf M Le, Robb W D, Taylor K T and Ian Vo Ky 1978 *Comput. Phys. Commun.* **14** 367
[13] Berrington K A, Burke P G, Butler K, Seaton K J, Storey P J, Taylor K T and Yan Y 1987 *J. Phys.* B **20** 6379
[14] Bailey S M W 1997 *Thesis: Relativistic Atomic Photoionization* The Queen's Univeristy of Belfast
[15] Cubaynes D, Voky L, Wuilleumier F J, Rouvellou B, Hibbert A, Faucher P, Bizau J M, Journel L, Saraph H E and Bely-Dubau F 1998 *Phys. Rev.* A **57** 4432
[16] Codling K, Hamley J R and West J B 1977 *J. Phys.* B: *At. Mol. Phys.* **10** 2797
[17] Wolff H W, Radler K, Sonntag B and Haensel R 1972 *Z. Phys.* **257** 353
[18] Martin R L, Davidson E R, Banna M S, Wallbank B, Frost D C and McDowell C A 1978 *J. Chem. Phys.* **68** 5006
[19] Krummacher S, Schmidt V, Bizau J M, Ederer D, Dhez P and Wuilleumier F 1982 *J. Phys.* B: *At. Mol. Phys.* **15** 4363
[20] Suzer S, Breuckmann B, Menzel W, Theodosiou C E and Mehlhorn W 1980 *J. Phys.* B: *At. Mol. Phys.* **13** 2061
[21] Cubaynes D, Bizau J M, Wuilleumier F J, Carre B and Gounand F 1989 *Phys. Rev. Lett.* **63** 2460
[22] Cubaynes D, Bizau J M, Richter M and Wuilleumier F J 1991 *Europhys. Lett.* **14** 747
[23] Richter M, Bizau J M, Cubaynes D, Menzel T, Wuilleumier F J and Carre B 1990 *Europhys. Lett.* **12** 35
[24] Haensel R, Keitel G, Sonntag B, Kunz C and Schreiber P 1970 *Phys. Stat. Sol.* A **2** 85
[25] Craig B I and Larkins F P 1985 *J. Phys.* B: *At. Mol. Phys.* **18** 3569
[26] McGuire E J 1970 *Research Report SC-RR-721* Sandia Laboratories
[27] Amusia M Ya, Cherepkov N A, Pavlin I, Radojevic V and Zivanovic D J 1977 *J. Phys.* B: *At. Mol. Phys.* **10** 1413
[28] Theodosiou C E and Fielder W 1982 *J. Phys.* B: *At. Mol. Phys.* **15** 4113
[29] Chang T N and Kim Y S 1982 *J. Phys.* B: *At. Mol. Phys.* **15** L835
[30] Isenberg E M, Carter S L, Kelly H P and Salomonson S 1985 *Phys. Rev.* A **32** 1472
[31] Msezane A Z, Armstrong-Mensah W and Niles J 1990 *Phys. Rev.* A **42** 1286
[32] Tayal S S, Msezane A Z and Manson S T 1994 *Phys. Rev.* A **49** 956
[33] Liu J C and Liu Z W 1994 *J. Phys.* B: *At. Mol. Phys.* **27** 4531
[34] Saha H 1994 *Phys. Rev.* A **50** 3157
[35] Msezane A Z, Francis N and Julian N 1990 *J. Phys.* B: *At. Mol. Phys.* **23** L691
[36] Craig B I and Larkins F P 1985 *J. Phys.* B: *At. Mol. Phys.* **18** 3713
[37] Hedin L and Lundqvist S 1969 *Solid State Physics* 23 ed. Seitz F, Turnbull D and Ehrenreich H, (New York and London: Academic Press) p1
[38] Brudner H J and Borowitz S 1960 *Phys. Rev.* **120** 2053