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Single Photoionization of Sodium (Na)

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Abstract: *We have calculated the single photoionization cross section [SPICS] of Sodium [Na] ($1s^2$ $2s^2$ $2p^6$ 3s)] using configuration interaction (CI) wave function for the initial state in both length and velocity forms and Coulomb wave function for the final state of the dipole matrix element. In the single photoionization absorption of a single-photon by an atom by the ejection of one electron. Comparison is made with available experimental observations and other theoretical predictions. Our present calculated result is encouraging.*

Keywords: *Absorption, Atom, Photoionization, Photon, Wave functions.*

I. Introduction

Alkali metal atom is a popular subject of theoretical and experimental investigations, because of abundant elements in the universe and their simple electronic structure, with only one valence electron outside energetically separated inner cores. Photon alkali metal atom scattering is of both fundamental and practical interest to physicists. Theoretical models have been successful in explaining aspects of scattering problem for particular experiments but a full solution to the scattering problem has been slow to emerge as evidenced by several area in which theory still disagree with experiments. Knowledge of accurate optical oscillator strengths is needed in laser physics, plasma physics, astrophysics, atmospheric physics, and fusion research. It is also required in testing the accuracy of wave functions involved in the transition matrix elements. The agreement between the length (f_L) and velocity (f_V) forms of the oscillator strengths reflects an accuracy of the wave functions. Exact wave functions are exact solutions of the exact Schrödinger wave equation. In practice, it is not possible to solve Schrödinger wave equation except for the hydrogen atom. Alternative to solving the Schrödinger equation, the configuration interaction method is widely used in atoms, molecules, ions clusters and solids. A number of different theoretical approaches [1-4] to photon atom or photon molecule scattering problems have been introduced which have the interesting feature of including a large number of channels. In contrast to a method like the close-coupling approximation, and R-matrix method which treats a small number of channels exactly, methods such as the Glauber approximation, the eikonal-Born series method, and the second-order potential method include all channels, but in an approximate way. The close-coupling method is successfully applied to the scattering of photon by atoms, molecules, and ions. The total wave function for an (N+1)-electron system consists of an n-electron target's eigen functions and a set of unknown functions representing the integro-differential (ID) equations which are derived from the variational principle. If it were possible to retain an infinite number of terms in the expansion (including the open channel) the close-coupling method would yield the exact solutions to the physical problems. In practice, a finite number of terms are retained. In many cases the convergence is very slow and many equations have to be solved which makes the close-coupling (CC) method complicated from the computational point of view. In the light of the convergence as well as the cumbersome computational problem, we have proposed a new linear-algebraic approach to photon atom scattering which allows the incorporation of any number of target states in order to achieve regular and systematic improvement of results.

Tiwary and his coworkers [5-16] have extensively investigated both the length and velocity forms of both the relativistic and non-relativistic optical oscillator strengths in several atoms and ions using Hartree-Fock (HF) and configuration interaction (CI) wave functions. Recently, Tiwary [13-16] has shown that the choice of configurations and orbital's employed in configurations play an extremely important role in order to have a very compact CI calculation which yields an excellent agreement between f_L and f_V. Recently, Berrington et al [17] have calculated the length and velocity forms of the oscillator strengths for alkali metal atoms. Considerable disagreement between the length and velocity values exists. Weise et al [18] have reported the experimental value of the oscillator strength for alkali metal atom. Since the discovery of the photoeffect the variation of the photoionization cross section in the vicinity of the threshold has attracted continuing interest of both experimentalists as well as theorists. This is not surprising because the nature of the interaction between photons and atoms or molecules or ions or clusters or solids is most sensitively exhibited in the low energy region, where the excited electrons are still around or slowly leave the system. However, before the advent of the synchrotron radiation as a tunable light source in the VUV and soft x-ray region, most threshold and resonance studies were restricted to the theoretical calculations and crude comparisons far from threshold with the few data points available from discharge lamps or x-ray tubes. Consequently, the first decade of synchrotron radiation work on atoms, molecules, ions, clusters and solids was concentrated on cross section measurements to assess the different theoretical predictions particularly near threshold. For example the review articles by Samson and Starace [19-20] give an excellent overview of the progress made experimentally as well as theoretically up to 1982. In recent years, extensive experimental and theoretical investigations [21-33] have been made in order to understand the theoretical effects in atomic and molecular photionization. Cooper minima, shape resonance and the effect of inter-channel coupling on the cross sectional behaviour of main lines were among prominent issues studied both experimentally and theoretically. Advances in theoretical methods revealed the importance of electron correlation on the cross section and angular distributions of the emitted photoelectrons. The threshold behavoiur has proved very helpful in helping to verify the predictive power of the different theoretical approaches beyond the one-particle picture. The synchrotron radiation has accelerated the development in the measurement of the photoionization cross section. However, today we see that the improvement in theory has led to sophisticated computational methods to meet the challenge of new experimental results.

There has been much interest in the study of systems that are dominated by electron correlation. The search for electron correlation in its simplest form has taken place in the world of one-electron processes. A very broad definition of electron correlation would be any effect arising from interaction between photon and electron. Electron correlation seems, however, to play an important role in atomic physics. The concept of the correlation in atomic physics is extended to many areas of research, e.g., molecular physics, condensed matter physics, superconductivity, collision physics. In strongly correlated systems, the independent particle model fails to provide adequate information about the system. One photon single ionization of the alkali metal atom is one of the best model system on which to investigate the effect of electron correlation. Single photoionization consists in the absorption of a single-photon by an atom or molecule followed by the ejection of one electron. The final state consists of an ion and one continuum electron, i.e.,

$h\nu + A \rightarrow A^+ + e^-$

In the case of complex atoms and molecules, the single photoionization process can be divided into two classes (a) the normal Auger process via core ionization and (b) the resonant single Auger process via resonant core excitation [21-22]. From theoretical point of view, multi-electron atoms and molecules are extremely difficult because of the core electrons. The subject of single photoionization of alkali metal atom has been of intense growing interest to both experimentalists and theorists because single photoionization in alkali metal atom gives basic informations on the electron correlations. A number of experiments [21-23, 25, 33-36] and calculations [37-40,44-51] have been carried out for the single photoionization of alkali metal atom.From theoretical point of view, the challenging problems is how to describe the one electron in the continuum i.e., single-continuum wave function. The subject of various forms of the single-continuum wave functions (SCWF) is of growing interest because it is needed to solve a very broad range of problems, for examples, single photoionization. Several asymptotic forms of single-continuum wave functions, which are solution of the Schrödinger equation at large distances for one electron system in different coordinate systems are available in the literature. In brief, we will describe these wave functions. However, the asymptotic wave functions are not adequate at small distances. One needs wave functions which are valid in the entire configuration space i.e. single-continuum wave function which can be obtained solving the Schrödinger equation for one electron system without imposing any constraint but unfortunately this is not feasible. For this reason, we will describe several models which are valid in different situations.

At very high incident energies, one ejected electron is very far away from the residual ion, one can argue that these one escaping electron does not experience Coulomb force. Under this situation, one can describe one electron by one plane wave. One plane wave gives the threshold law which differs completely from the experimental threshold law. No matter, how far or how fast electrons are, they always experience Coulomb force. Hence this model is the crudest model and is used in the first Born approximation. Since, electrons always experience Coulomb force, so widely used model is one Coulomb wave function. This model has been employed in the calculation of the single photoionization of alkali metal atom. Since, this model does not contain correlation, hence it gives linear threshold law which disagrees with the experiment. This model gives the threshold law which disagrees with the experiment. For reliable calculations of single photoionization cross sections, one needs correlated single continuum wave functions especially in the vicinity of the threshold where electron correlation plays an extremely important role.

II. Theory : Basic Equations

Under the electric-dipole approximation, the differential cross section for the ejection of an electron with angular momentum l and energy ε in the energy range dε is

$$\frac{d\sigma}{d\varepsilon}=\frac{4\pi^2\alpha a_0^2}{3}\sum\frac{df}{d\varepsilon} \tag{1}$$

where $\frac{df}{d\varepsilon}$ is the differential oscillator strengths for the transition from the ground state ψ_i to the final state ψ_f.

The quantity $\frac{df}{d\varepsilon}$ is conveniently expressed in the length and velocity forms as

$$\frac{df_L}{d\varepsilon}=E\left|\langle\psi_f(\mathbf{r})|\,\mathbf{r}\,|\,\psi_i(\mathbf{r})\rangle\right|^2 \tag{2}$$

$$\frac{df_V}{d\varepsilon}=\frac{1}{E}\left|\langle\psi_f(\mathbf{r})|\,\nabla\,|\,\psi_i(\mathbf{r})\rangle\right|^2 \tag{3}$$

It is well known that equations (2-3) would provide the same results if ψ_i and ψ_f were exact.
Finally, the total cross section for the production of one continuum electron by single photon impact is

$$\sigma=\sum_l\int_0^E\frac{d\sigma}{d\varepsilon}\,d\varepsilon \tag{4}$$

In equation (4), summation over l corresponds to the contributions of all allowed final continuum configurations of the angular type $\varepsilon l\varepsilon'(l+1)$. Tiwary and his co-workers [7, 8, 10, 11, 13, 50] have extensively investigated the correlation in atoms and ions using the configuration-interaction (CI) wave functions. We have generated full CI wave functions for several atoms and ions and tested the accuracy of wave functions calculating the length and velocity forms of the optical oscillator strengths. The wave function of the ground state of all alkali metal atom is represented by the full CI wave function which includes full correlations and generated exactly in the same way as in our earlier works and hence not reported in details here. Our CI wave function can be written as

$$\psi(LS)\;=\;\sum_i a_i\;\phi_i\;(\alpha_i LS) \tag{5}$$

The coefficients a_i are the eigenvectors components of the Hamiltonian matrix with the typical element

$$H_{ij}\;=\;\langle\phi_j|\,H\,|\,\phi_i\rangle \tag{6}$$

ϕ_i are single-configuration functions from one-electron functions, whose orbital and spin momenta are coupled to form the common total angular-momentum quantum numbers L and S according to a prescription denoted in (5) by α_i.

We express the radial parts of the one-electron functions in analytical form as a sum of Slater-type orbitals, following Clementi and Roetti [29] :

$$P_{nl}(r)=\sum_{j=1}^{k}C_{jnl}\;r^{I_{jnl}}\;e^{-\xi_{jnl}r} \tag{7}$$

The parameters in (7) can be varied to optimize the energy of any state, subject to the orthonormality conditions.

$$\int_0^\infty P_{nl}(r)\,P_{n'l}(r)\,dr=\delta_{nn'} \tag{8}$$

The final state wave function is represented by a symmetrized one electron Coulomb wave function as follows :

$$\psi_f(\mathbf{r})=\frac{1}{\sqrt{2}}\sum(l,m,|\,l,M).\phi(\varepsilon,l,m|\,r) \tag{9}$$

where ε is kinetic energy of the escaping electron. In equation (9), $(l,m,\,|\,l,M)$ denotes the Clebsch-Gordan coefficients providing threshold final state and the one-electron spatial orbitals are given by

$$\phi(\varepsilon,l,m/r)=\left(\frac{2}{R\pi}\right)^{1/2}\frac{F_l(\eta,kr)}{r}\;Y_l^m(\hat{r}) \tag{10}$$

where F_l is the regular spherical Coulomb wave function of order l with

$$R = \sqrt{2\varepsilon} \quad \text{and} \quad \eta = -{}^{Z}\!/_{k} \tag{11}$$

The ϕ orbitals are normalized in the energy scale

$$\langle \phi(\varepsilon, l, m) | \phi(\varepsilon', l', m') \rangle = \delta(\varepsilon - \varepsilon')\delta_{l,l'}\,\delta_{m,m'} \tag{12}$$

III. Figures and Tables

Table-1: Basis functions for orbitals of the Na.

Orbitals *nl*	I_{jnl}	ξ_{jnl}	Clementi-Type Coefficient
4s	1	12.35049	0.07031
	2	4.72863	-0.29771
	3	3.01726	1.24571
	4	1.56431	-1.64543
5s	1	12.27499	0.04727
	2	4.63843	-0.20447
	3	1.59816	-1.98874
	4	1.53788	-3.27601
	5	1.14786	1.96828
	1	12.06740	0.03569
6s	2	4.82669	-0.14602
	3	1.09545	5.24752
	4	1.22348	-11.29634
	5	1.22311	7.83287
	6	0.89777	-2.28958
	2	5.68651	0.33009
3p	3	1.99603	-1.02870
	2	5.69899	0.20859
4p	3	1.48047	-2.17379
	4	1.47678	2.68347
	2	5.69899	0.20859
5p	3	1.28091	-2.61622
	4	1.28388	5.04953
	5	1.12353	-3.06735
	2	5.70153	0.10539
6p	3	0.83339	-9.01933
	4	1.12839	11.48466
	5	1.07836	-3.89756
	3	1.81198	1.00000
3d	3	1.86737	0.77342
	4	1.16917	-1.24426
4d	3	1.79072	0.70927
5d	4	0.97471	-3.78767
	5	0.97449	3.86445
	3	1.70014	0.65236
6d	4	0.89867	-5.80316
	5	0.89444	9.18885
	6	0.80285	-4.34921

Table-2: Configurations

$^2S^e$	$^2P^o$
$1s^2\,2s^2\,2p^6\,3s$ $1s^2\,2s^2\,2p^6\,ns$, n = 4, 5, 6 $1s^2\,2s^2\,2p^5$ (3s3p + 3s4p + 4s4p + 4s5p + 5s5p + 3p3d + 3p4s + 3p4d + 4p4d + 5p4d) $1s^2\,2s\,2p^6\,(3p^2 + 3p4p + 4p^2 + 4p5p)$	$1s^2\,2s^2\,2p^5\,3s^2$ $1s^2\,2s^2\,2p^5\,ns^2$, n = 4, 5, 6 $1s^2\,2s^2\,2p^5\,np^2$, n = 4, 5, 6 $1s^2\,2s^2\,2p^5\,nd^2$, n = 3, 4, 5, 6 $1s^2\,2s^2\,2p^5$ (3s4s + 3s5s + 4s5s) $1s^2\,2s^2\,2p^5$ (3p4p + 3p5p + 4p5p) $1s^2\,2s^2\,2p^5$ (3s3d + 3s4d +3d4s + 4s4d) $1s^2\,2s^2\,2p^4\,np^3$, n = 3, 4, 5, 6 $1s^2\,2s\,2p^6$ (4snp), n = 3, 4, 5, 6 $1s^2\,2s^2\,2p^6$ np, n = 3, 4, 5, 6

Table-3: Excitation energies and oscillator strengths of resonance, nonresonance, and inner-shell excitation transitions in Na.

Transition	Type of wave function	ΔE (au)	f_L	f_V
$1s^2\,2s^2\,2p^6\,3s\ ^2S^e \rightarrow 1s^2\,2s^2\,2p^6\,3p\ ^2P^o$	HF CI	0.409 0.405	0.74782 0.73692	0.73156 0.72217
$1s^2\,2s^2\,2p^6\,3s\ ^2S^e \rightarrow 1s^2\,2s^2\,2p^6\,4p\ ^2P^o$	HF CI	1.381 1.375	0.04851 0.05265	0.03779 0.05603
$1s^2\,2s^2\,2p^6\,3s\ ^2S^e \rightarrow 1s^2\,2s^2\,2p^5\,3s^2\ ^2P^o$	HF CI	4.936 4.879	0.07637 0.09110	0.06789 0.07893

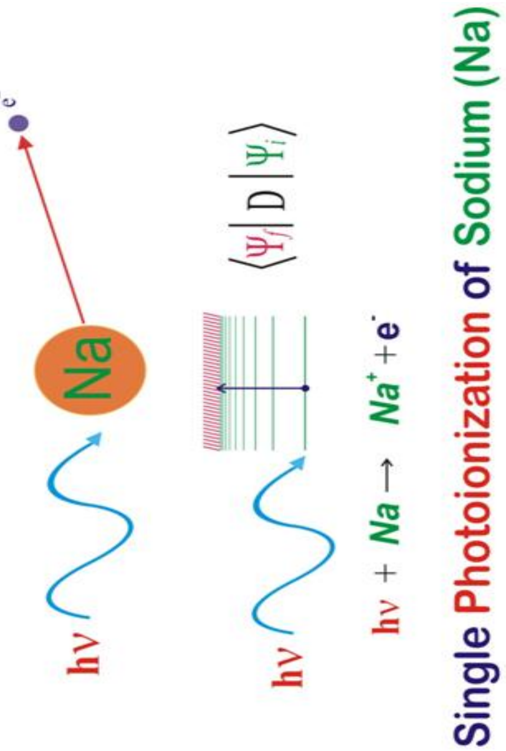

Fig.-1

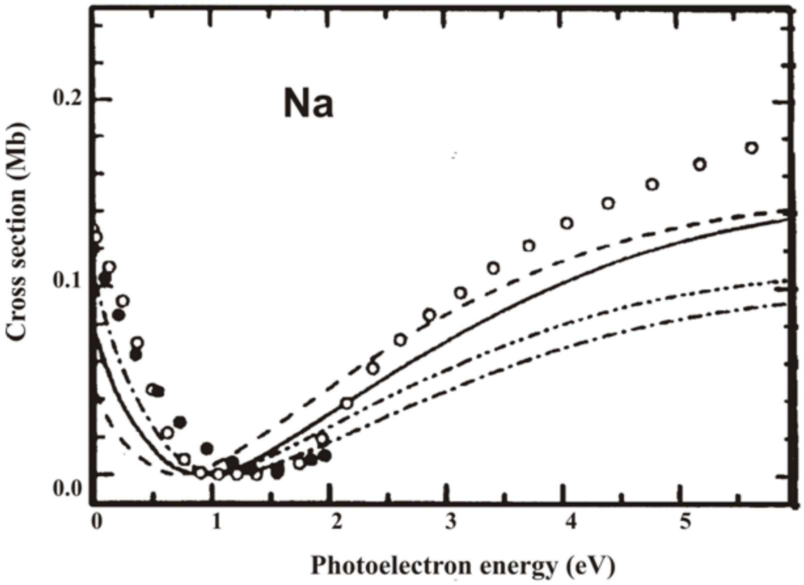

Fig.-2

Figure Caption

Fig-2: Photoionization cross section (Mb) for Na.

○ Hudson and Carter (Ref.54)

● Marr and Creek (Ref. 55)

— · — · — · — Kau et al (Length) (Ref. 52)

—··—··—··—·· Kaue et al (Velocity) (Ref. 53)

———————— Present Result (Length)

— — — — - Present Result (Velocity)

IV. Results and Discussion

Accuracy of the calculated collisional cross sections and oscillator strengths particularly for the neutral system, is in general very sensitive to the target wave functions. Hence the choice of the target wave functions plays a very important for the reliable results. It is well known that the configuration interaction wave function is correlated functions. We have generated fully controlled wave functions for alkali metal atoms using Tiwary approach [16-18].The orbital parameters are given in Table-1 and the configurations, eigenvalues and eigenvectors are shown in Table-2.Table-3 shows the HF and CI excitation energies and oscillator strengths, both f_L and f_V, of the resonance $1s^2\ 2s^2\ 2p^6\ 3s\ ^2S^e \rightarrow 1s^2\ 2s^2\ 2p^6\ 3p\ ^2P^0$, the nonresonance $1s^2\ 2s^2\ 2p^6\ 3s\ ^2S^e \rightarrow 1s^2\ 2s^2\ 2p^6\ 4p\ ^2P^o$, and the inner-shell excitation $1s^2\ 2s^2\ 2p^6\ 3s\ ^2S^e \rightarrow 1s^2\ 2s^2\ 2p^5\ 3s^2\ ^2P^o$ transitions.Several features of importance emerge from Table-3. First, the value of f_L and f_V for the resonance transitions are considerably larger and in good agreement with each other, whereas for the nonresonance and inner-shell excitation transitions the situation is reversed, i.e., the oscillator strength is small and the discrepancy is relatively large. Since the resonance transition involves no change in the principal quantum number, one may expect quite large oscillator strengths. The disagreement between f_L and f_V for the inner-shell transition indicates that the Auger transition is much more complex than the outer-shell transitions. Second, the HF f_L and f_V forms of the oscillator strengths for the resonance and nonresonance transitions are in satisfactory agreement, reflecting the fact that the electron correlation contributes only a few percent to the oscillator strengths.

In the case of inner-shell excitation, the HF values of oscillator strengths are very small and correlation can be a substantial part of the total. The configuration mixing has increased the values of optical oscillator strengths for the Auger and nonresonance transitions and decreased the oscillator strengths of the resonance transition. Third, the disagreement between the CI f_L and f_V values of the inner-shell transition is larger than the disagreement between the HF f_L and f_V values. This probably occurs because we neglect the relativistic effect in our calculation. Finally, the excitation energy (ΔE in atomic units) is decreased owing to the CI for all transitions under consideration.Single photoionization cross section is very sensitive to the wave functions used in the matrix elements and hence provides an opportunity to test the accuracy of wave functions. In order to test the accuracy of our configuration-interaction (CI) wave functions which have already produced reliable oscillator strengths, we have performed calculations for the single photoionization (SPI) cross sections of alkali metal atom using our CI wave function for the ground state and one Coulomb wave function for the final state.

We have calculated the single photoionization cross sections (SPICS) of sodium [Na ($1s^2\ 2s^2\ 2p^6\ 3s$)] employing Coulomb wave function for the final state and configuration interaction (CI) wave function for the initial state in both length and velocity forms of the dipole matrix element. Fig.-2 shows the SPICS of sodium (Na). It is seen from figure that our present result in length form is in better agreement with the experimental data [54, 55] in the high energy range. The present theoretical result in velocity form is better agreement with experimental result compare to present theoretical result in length form as well as other available theoretical results.

V. Conclusion

In this paper we have calculated the single photoionization cross section (SPICS) of Na using Coulomb wave function for the final state and configuration interaction (CI) wave function for the initial state in both length and velocity forms of the dipole matrix element. In the case of Na, Fig.-2 shows that our present result is more accurate than other theoretical results but there is still discrepancy between experiment and present theoretical result in high energy region which suggests to do more accurate calculation.

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