INTERNATIONAL REVIEW OF ATOMIC AND MOLECULAR PHYSICS (IRAMP)
Volume 1, No. 2, July-December 2010, pp. 137-141, © *International Science Press, ISSN: 2229-3159*

REVIEW ARTICLE

PHOTOIONIZATION OF ATOMS AND MOLECULES USING CONFIGURATION-AVERAGE DISTORTED-WAVE METHODS

M.S. PINDZOLA, C.P. BALLANCE, S.D. LOCH AND J.A. LUDLOW
Department of Physics, Auburn University, Auburn, AL 36849, USA

J. COLGAN
Theoretical Division, Los Alamos National Laboratory, Los Alamos, NM 87545, USA

M.C. WITTHOEFT AND T.R. KALLMAN
NASA Goddard Space Flight Center, Greenbelt, MD 20771, USA

Abstract: We review the application of configuration-average distorted-wave methods to the photoionization of atoms and molecules. The configuration-average distorted-wave methods are then applied to calculate photoionization cross sections for outer and inner subshells of the C atom and the outer subshell of the C_2 molecule. Comparisons are made with previous R-matrix and distorted-wave calculations.

1. INTRODUCTION

Photoionization cross sections for atoms and molecules are needed to better understand the physics and chemistry of the interstellar medium using X-ray absorption spectroscopy [1, 2]. In particular, photoionization cross sections are needed for various charge states of the astrophysically abundant elements from C to Fe, as well as heavier elements like Kr, Xe, and Pb [3]. Photoionization cross sections are also needed for diatomic molecules like C_2, O_2, and CO.

The configuration-average approximation [4] has been found to be quite useful for calculating the many photoexcitation and photoionization cross sections needed for the modeling of complex laboratory plasmas [5]. A semi-relativistic configuration-average distorted-wave method, developed for electron collisions with atoms and their ions [6, 7], may be applied to calculate photoionization cross sections for atoms and low-charged atomic ions [8]. A fully-relativistic configuration-average distorted-wave method, developed for electron collisions with atomic ions [9, 10], may be applied to calculate photoionization cross sections for high-charged atomic ions[11]. A non-relativistic configuration-average distorted-wave method, developed for electron collisions with diatomic molecules and their ions [12, 13], may be applied to calculate photoionization cross sections for molecules and low-charged molecular ions.

In this article, we make a full presentation of all three configuration-average distorted-wave (CADW) methods so that they may be easily compared and used for the photoionization of all atoms, diatomic molecules, and their ions. As test cases, we carry out semi-relativistic CADW calculations for the photoionization of the outer and inner subshells of the C atom, fully-relativistic CADW calculations for the photoionization of the inner subshell of the C atom, and non-relativistic CADW calculations for the photoionization of the outer subshell of the C_2 molecule. We compare the CADW results with previous R-matrix and distorted-wave calculations.

The rest of the article is organized as follows: in Section 2 we review the configuration-average distorted-wave methods as applied to the photoionization of atoms and molecules, in Section 3 we present photoionization cross sections for the C atom and the C_2 diatomic molecule, while in Section 3 we give a brief summary of future plans. Unless otherwise stated, all quantities are given in atomic units.

2. THEORY

2.1 Semi-Relativistic CADW Method for Atoms

The photoionization of an atomic configuration has the general form:

$$(n_i l_i)^{w_i} \rightarrow (n_i l_i)^{w_i - 1} \varepsilon_f l_f, \qquad \ldots (1)$$

where n is the principal quantum number, l is the angular quantum number, w is the occupation number of the subshell, and ε is the electron energy. In the dipole length gauge for the external electromagnetic field, the configuration-average photoionization cross section is given by:

$$\sigma_{ion} = \frac{8\pi\omega}{ck_f} \sum_{l_f} \frac{2w_i \max\left(l_i, l_f\right)}{3\left(4l_i + 2\right)}$$

$$\left[D\left(n_i l_i \rightarrow \varepsilon_f l_f\right)\right]^2, \qquad \ldots (2)$$

where $k_f = \sqrt{2\varepsilon_f}$, ω is the radiation field frequency, and c is the speed of light. For $l_i = 0$, $l_f = 1$, while for $l_i \neq 0$, $l_f = l_i \pm 1$. The radial dipole integral is given by:

$$D\left(n_i l_i \rightarrow \varepsilon_f l_f\right) = \int_0^\infty dr\, P_{\varepsilon_f l_f}\left(r\right) r\, P_{n_i l_i}\left(r\right) \qquad \ldots (3)$$

The energies and bound radial orbitals, $P_{nl}(r)$, are calculated in the Hartree-Fock relativistic (HFR) approximation [4], which includes the mass velocity and Darwin corrections within modified Hartree-Fock differential equations. The continuum radial orbitals, $P_{\varepsilon l}(r)$, are calculated by solving a single channel radial Schrodinger equation, where the Hartree local exchange distorting potential is constructed with HFR bound orbitals and the continuum normalization is chosen as one times a sine function.

2.2 Fully-Relativistic CADW Method for Atoms

The photoionization of an atomic configuration has the general form:

$$\left(n_i \kappa_i\right)^{w_i} \rightarrow \left(n_i \kappa_i\right)^{w_i - 1} \varepsilon_f \kappa_f, \qquad \ldots (4)$$

where n is the principal quantum number, κ is the total angular quantum number ($\kappa = -(l + 1)$ for $j = l + \frac{1}{2}$ and $\kappa = +l$ for $j = l - \frac{1}{2}$), w is the occupation number, and ε is the electron energy. In the dipole approximation for the external electromagnetic field, the configuration-average photoionization cross section is given by:

$$\sigma_{ion} = \frac{8\pi\omega}{cp_f}\left(1 + \frac{\varepsilon_f}{2c^2}\right) \sum_{l_f, j_f} w_i \frac{\left(2j_f + 1\right)}{3} \begin{pmatrix} j_i & 1 & j_f \\ \frac{1}{2} & 0 & -\frac{1}{2} \end{pmatrix}^2$$

$$\times \left[D\left(n_i \kappa_i \rightarrow \varepsilon_f \kappa_f\right)\right]^2 \qquad \ldots (5)$$

where $p_f = \sqrt{\left(2\varepsilon_f + \frac{\varepsilon_f^2}{c^2}\right)}$, ω is the radiation field frequency, and c is the speed of light. The sum over l_f includes only terms for which $l_i + l_f + 1$ is an even number. The radial dipole integral is given by:

$$D\left(n_i \kappa_i \rightarrow \varepsilon_f \kappa_f\right)$$

$$= \int_0^\infty dr \left[P_{\varepsilon_r \kappa_r}\left(r\right) r\, P_{n_i \kappa_i}\left(r\right) + Q_{\varepsilon_r \kappa_r}\left(r\right) r\, Q_{n_i \kappa_i}\left(r\right)\right]. \qquad \ldots (6)$$

The energies and bound radial orbitals, $P_{n\kappa}(r)$ and $Q_{n\kappa}(r)$, are calculated in the Dirac-Fock (DF) relativistic approximation [14]. The continuum radial orbitals, $P_{\varepsilon\kappa}(r)$ and $Q_{\varepsilon\kappa}(r)$, are calculated by solving a single channel radial Dirac equation, where the Dirac local exchange distorting potential is constructed from DF bound radial orbitals and the continuum normalization is chosen as one times a sine function.

2.3 Non-Relativistic CADW Method for Diatomic Molecules

The photoionization of a molecular configuration has the general form:

$$\left(n_i l_i \lambda_i\right)^{w_i} \rightarrow \left(n_i l_i \lambda_i\right)^{w_i - 1} \varepsilon_f l_f \lambda_f, \qquad \ldots (7)$$

where n is the principal quantum number, l is the angular quantum number, $\lambda = |m|$ is the magnetic quantum number, w is the occupation number of the subshell, and ε is the electron energy. In the dipole length gauge for the external electromagnetic field, the configuration-average photoionization cross section is given by:

$$\sigma_{ion} = \frac{8\pi\omega}{3ck_f} \sum_{l_f} w_i \left(\left[DC\left(n_i l_i \lambda_i \rightarrow \varepsilon_f l_f \lambda_i\right)\right]^2 + \left[DS\left(n_i l_i \lambda_i \rightarrow \varepsilon_f l_f \lambda_i\right)\right]^2 \right) \qquad \ldots (8)$$

for $\lambda_i = 0$ and

$$\sigma_{ion} = \frac{8\pi\omega}{3ck_f}\sum_{l_f} w_i \left(\begin{array}{l} \left[DC\left(n_il_i\lambda_i \to \varepsilon_f l_f \lambda_i\right)\right]^2 + \\ \frac{1}{2}\left[DS\left(n_il_i\lambda_i \to \varepsilon_f l_f \left(\lambda_i - 1\right)\right)\right]^2 + \\ \frac{1}{2}\left[DS\left(n_il_i\lambda_i \to \varepsilon_f l_f \left(\lambda_i + 1\right)\right)\right]^2 \end{array} \right) \quad \ldots (9)$$

for $\lambda_i \neq 0$, where $k_f = \sqrt{2\varepsilon_f}$, ω is the radiation field frequency, and c is the speed of light. The radial and angular dipole integrals are given by:

$$DC\left(n_il_i\lambda_i \to \varepsilon_f l_f \lambda_f\right) = \int_0^\infty dr \int_0^\pi d\theta P_{\varepsilon_f l_f \lambda_f}(r,\theta)\, r\cos\theta\, P_{n_il_i\lambda_i}(r,\theta) \quad \ldots (10)$$

$$DS\left(n_il_i\lambda_i \to \varepsilon_f l_f \lambda_f\right) = \int_0^\infty dr \int_0^\pi d\theta P_{\varepsilon_f l_f \lambda_f}(r,\theta)\, r\sin\theta\, P_{n_il_i\lambda_i}(r,\theta) \quad \ldots (11)$$

The energies and bound orbitals, $P_{nl\lambda}$ (r, θ), are calculated in a self-consistent field (SCF) approximation based on a linear combination of Slater type orbitals [15]. The bound orbitals are then transformed [16] onto a two dimensional (r, θ) numerical lattice. The continuum orbitals, $P_{\varepsilon l\lambda}(r,\theta)$ are calculated by solving a single channel (r, θ) Schrodinger equation, where the Hartree local exchange distorting potential is constructed from SCF bound orbitals and the continuum normalization is chosen as one times a sine function.

3. RESULTS

The semi-relativistic CADW method of Section (2.1) was used to calculate photoionization cross sections for the *C* atom. The outer subshell transition:

$$1s^22s^22p^2 \to 1s^22s^22p\varepsilon l, \quad \ldots (12)$$

has an ionization potential of 10.0 eV. A radial doubling mesh with 1800 points was used to represent the bound and continuum radial orbitals. The bound radial orbitals in the initial configuration were used to calculate the Hartree local exchange distorting potential for the $l = 0, 2$ continuum radial orbitals, the so-called unrelaxed core approximation. The semi-relativistic CADW cross section results are presented in Fig. 1. The CADW results are found to be in reasonable agreement with Hartree-Slater distorted-wave photoionization calculations[17] and with the non-resonant background in *R*-matrix photoionization calculations [18]. The inner subshell transition:

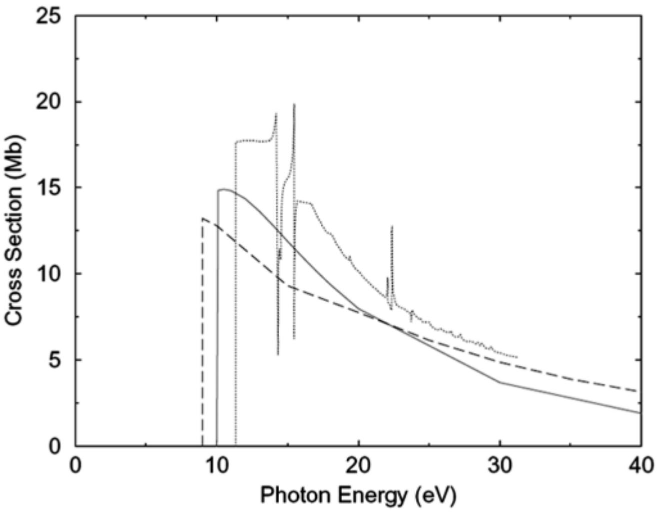

Fig. 1: Photoionization of the outer $2p$ subshell of the Carbon atom. Solid curve: Semi-relativistic CADW calculations, dashed curve: Hartree-Slater distorted-wave calculations [17], and dotted curve: R-matrix calculations [18] (1.0 Mb = 1.0 × 10^{-18} cm^2).

$$1s^22s^22p^2 \to 1s2s^22p^2\varepsilon l, \quad \ldots (13)$$

has an ionization potential of 298 eV. A radial doubling mesh with 1800 points was again used to represent the bound and continuum radial orbitals. The unrelaxed core approximation was used to calculate the $l = 1$ continuum radial orbital. The semi-relativistic CADW cross section results are presented in Fig. 2. The CADW results are found to be in reasonable agreement above the K-shell threshold with Hartree-Slater distorted-wave total photoionization calculations [17] and with the non-resonant background in *R*-matrix total photoionization calculations [19].

The fully-relativistic CADW method of Section (2.2) was used to calculate photoionization cross sections for the *C* atom. The inner subshell transition:

$$1s^22s^22\bar{p}^2 \to 1s2s^22\bar{p}^2\varepsilon\kappa, \quad \ldots (14)$$

has an ionization potential of 298 eV. A radial doubling mesh with 1200 points was used to represent the bound and continuum radial orbitals. The unrelaxed core approximation was used to calculate the $\kappa = 1, -2$ continuum radial orbitals. The fully relativistic CADW cross section

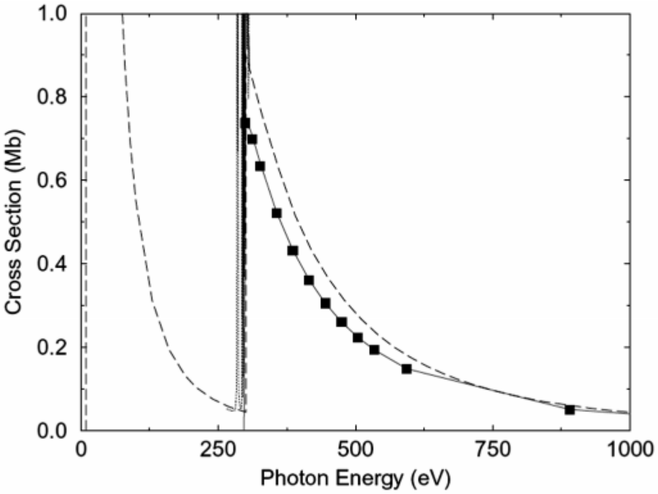

Fig. 2: Photoionization of the inner 1*s* subshell of the carbon atom. Solid curve: semi-relativistic CADW calculations, dashed curve: Hartree-Slater distorted-wave calculations [17], dotted curve: *R*-matrix calculations [19], and solid squares: fully-relativistic CADW calculations (1.0 Mb = 1.0 × 10^{-18} cm^2).

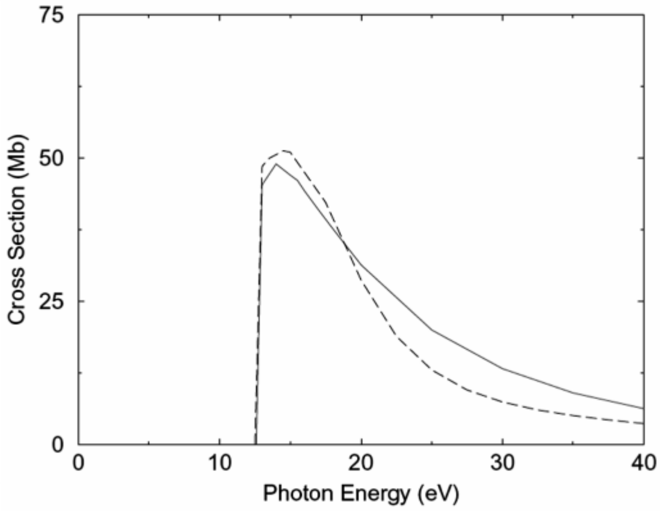

Fig. 3: Photoionization of the outer 2*p*π subshell of the Carbon diatomic molecule. Solid curve: non-relativistic CADW calculations, and dashed curve: Hartree-Fock distorted-wave calculations [20] (1.0 Mb = 1.0 × 10^{-18} cm^2).

results presented in Fig. 2, are found to be in excellent agreement with the semi-relativistic CADW calculations.

The non-relativistic CADW method of Section (2.3) was used to calculate photoionization cross sections for the C_2 molecule at an internuclear separation of $R = 2.35$. The outer subshell transition:

$$1s\sigma^2 2p\sigma^2 2s\sigma^2 3p\sigma^2 2p\pi^4 \rightarrow 1s\sigma^2 2p\sigma^2 2s\sigma^2 3p\sigma^2 2p\pi^3 \varepsilon l\lambda, \quad \ldots (15)$$

has an ionization potential of 12.6 eV. A uniform radial mesh starting at $\Delta r = 0.10$ with 25,000 points and a uniform angular mesh starting at $\Delta\theta = 0.015625\pi$ with 64 points was used to represent the bound and continuum orbitals. The unrelaxed core approximation was used to calculate the $l\,\lambda$ = 00, 10, 11, 20, 21, 22, 30, 31, 32 continuum orbitals. The non-relativistic cross section results presented in Fig. 3, are found to be in reasonable agreement with Hartree-Fock distorted-wave photoionization calculations [20].

4. SUMMARY

In conclusion, we have presented three different configuration-average distorted-wave methods for the photoionization of atoms and diatomic molecules. All are very efficient and reasonably accurate for the production of non-resonant photoionization cross sections, as seen in the examples for C and C_2. The semi-relativistic CADW method for atoms may be easily applied for any subshell of any atom or its ion. The fully-relativistic CADW method for atoms provides a benchmark for the inner subshells of heavy atoms and their ions. The non-relativistic CADW method for diatomic molecules may also be easily applied for any subshell of any molecule and its ion.

In the future, a semi-relativistic CADW method used to include resonant contributions in the electron-impact excitation of atoms and their ions [6, 7] will be applied to calculate resonant photoionization contributions. We also plan to extend the fully-relativistic CADW method for atoms and the non-relativistic CADW method for diatomic molecules to include resonant photoionization contributions. Our ultimate goal is to develop an efficient method for the calculation of total photoionization cross sections for those atoms, molecules, and their ions that are needed to better understand laboratory and astrophysical plasmas.

ACKNOWLEDGMENTS

This work was supported in part by grants from the US Department of Energy, the US National Science Foundation, and the US National Aeronautics and Space Administration. Computational work was carried out at the National Energy Research Scientific Computing Center in Oakland, California and the National Institute for Computational Sciences in Knoxville, Tennessee.

REFERENCES

[1] F. Paerels, A.C. Brinkman, R.L.J. Van der Meer, J.S. Kaastra, E. Kuulkers, A.J.F. Den Boggende, R. Predehl, J.J. Drake, S.M. Kahn, D.W. Savin, and B.M. McLaughlin, *Astrophys. J.*, **546**, 338, (2001).

[2] T. Kallman and M. Bautista, *Astrophys. J. Suppl. Series*, **133**, 221, (2001).

[3] B. Sharpee, Y. Zhang, R. Williams, E. Pellegrini, K. Cavagnolo, J.A. Baldwin, M. Phillips, and X.W. Liu, *Astrophys. J.*, **659**, 1265, (2007).

[4] R.D. Cowan, *The Theory of Atomic Structure and Spectra*, University of California Press, Berkeley, 1981.

[5] D.P. Kilcrease, J. Abdallah, J.J. Keady, and R.E.H. Clark, *J. Phys. B* **26**, L717, (1993).

[6] M.S. Pindzola, D.C. Griffin, and C. Bottcher, (NATO ASI), *B* **145**, 75, (1986).

[7] M.S. Pindzola, C.P. Ballance, J.A. Ludlow, S.D. Loch, and D.C. Griffin, *J. Phys. B* **43**, 025201, (2010).

[8] O. Peyrusse, *J. Phys. B* **32**, 683, (1999).

[9] M.S. Pindzola and M.J. Buie, *Phys. Rev. A* **37**, 3232, (1988).

[10] M.S. Pindzola, J.A. Ludlow, F. Robicheaux, J. Colgan, and C.J. Fontes, *Phys. Rev. A* **80**, 052706, (2009).

[11] M.S. Pindzola, J.A. Ludlow, and J. Colgan, *Phys. Rev. A* **81**, 063431, (2010).

[12] M.S. Pindzola, F. Robicheaux, J.A. Ludlow, J. Colgan, and D.C. Griffin, *Phys. Rev. A* **72**, 012716, (2005).

[13] M.S. Pindzola, C.P. Ballance, J.A. Ludlow, S.D. Loch, and J.P. Colgan, *J. Phys. B* **43**, 065201, (2010).

[14] I.P. Grant, *Relativistic Quantum Theory of Atoms and Molecules*, Springer Press, New York, (2007).

[15] Theoretical Chemistry Group 1970 Computer Code Named ALCHEMY, San Jose, CA: IBM Research Laboratory.

[16] M.A. Morrison, *Comput. Phys. Commun.*, **21**, 63, (1980).

[17] R.F. Reilman and S.T. Manson, *Astrophys. J. Suppl. Series*, **40**, 815, (1979).

[18] K.T. Taylor and P.G. Burke, *J. Phys. B* **9**, L353, (1976).

[19] M.F. Hasoglu, S.A. Abdel-Naby, T.W. Gorczyca, J.J. Drake, and B.M. McLaughlin, *Astrophys. J.*, **724**, 1296, (2010).

[20] N.T. Padial, L.A. Collins, and B.I. Schneider, *Astrophys. J.*, **298**, 369, (1985).