LA-UR- 00 - 4321

Approved for public release;
distribution is unlimited.

Title: LOW ENERGY (e,2e) IONIZATION OF ARGON IN THE
EQUAL ENERGY SHARING GEOMETRY

Author(s): S. Mazevet
G. Nguyen Vien
C. Tannous
K. Fakhreddine
J. Langlois
R.J. Tweed
O. Robaux

Submitted to: Publication of The Many Particle Spectroscopy Proceedings,
Conference Held in Halle, Germany, August, 2000

Los Alamos

NATIONAL LABORATORY

Los Alamos National Laboratory, an affirmative action/equal opportunity employer, is operated by the University of California for the U.S. Department of Energy under contract W-7405-ENG-36. By acceptance of this article, the publisher recognizes that the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or to allow others to do so, for U.S. Government purposes. Los Alamos National Laboratory requests that the publisher identify this article as work performed under the auspices of the U.S. Department of Energy. Los Alamos National Laboratory strongly supports academic freedom and a researcher's right to publish; as an institution, however, the Laboratory does not endorse the viewpoint of a publication or guarantee its technical correctness.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, make any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

RECEIVED

SEP 28 2000

OSTI

LOW ENERGY (e,2e) IONIZATION OF ARGON IN THE EQUAL ENERGY SHARING GEOMETRY.

S. Mazevet¹, G. Nguyen Vien⁴, C. Tannous², K. Fakhreddine³, J. Langlois⁴, R. J. Tweed⁴, and O. Robaux⁴

¹Theoretical Division, Los Alamos National Laboratory, Los Alamos, NM87545, USA

²Laboratoire de Magnétisme de Bretagne, Université de Bretagne Occidentale, CNRS UPRES A 6135, BP: 809 - 29285 Brest Cedex, France

³Lebanese University and CNRS, BP: 11-8281, Beirut, Lebanon

⁴Laboratoire des Collisions Electroniques et Atomiques, Université de Bretagne Occidentale, BP: 809 - 29285 Brest Cedex, France

INTRODUCTION

Quantum Defect (QD) information is widely exploited in modern spectroscopy, to characterize Rydberg states and in the calculation of the photoionization cross sections of various atomic and molecular species ^{1,2}. In the present work, we show that QD information, used within the Distorted Wave Born Approximation (DWBA) framework, might also prove useful for the description of ionization processes by presenting an alternative way to account for the short range interactions (static and exchange) in the calculation of the final state continuum distorted waves. The range of validity of this approach reaches beyond that ³ of the commonly used Furness-McCarthy local exchange approximation⁴. Compared to the determination of the Hartree-Fock non-local operator ⁵, which becomes rapidly a tedious task as the size of the target increases, our method allows for a target-independent procedure which can be readily applied to much larger atomic or molecular systems.

The parameters of the Green-Sellin-Zachor ⁶ parametric form of the electron-ion potential are optimized in order to reproduce the QD using the canonical function method⁷. The canonical function method (CFM) is a powerful means for solving accurately the Radial Schrödinger Equation (RSE). The quantum eigenvalues of the RSE are obtained to any desired accuracy without having to evaluate the eigenfunctions. Several parametric potentials are discussed extensively in the literature and we already used several functional forms ² adapted to different atomic systems. We studied recently ⁸ the QD of some rare gases with the Klapisch parametric potential ⁹ and found that in some cases it was very difficult to optimize parameters that provide an accurate representation of the experimental QD. We believe, the Green-Sellin-Zachor ⁶ is better

suited to our present study as the parameter space is small (two-dimensional) which allows for an efficient search of the optimized parameters.

The electron-ion potentials obtained for each Rydberg series are further modified to account classically for the electron-electron interaction in the final state. Calculations performed within the DWBA framework for the ionization of argon in the equal energy sharing geometry ($\mathbf{k}_a = -\mathbf{k}_b$), which is reasonably well documented both theoretically and experimentally, clearly validate our approach and shows significant improvements over previous treatments.

This paper is organized as follows: Section 2 is devoted to the presentation of the CFM, section 3 describes the optimization method we use based on the CFM. In section 4 we describe the results whereas section 5 contains our conclusion and discussion of the results.

THE CANONICAL FUNCTION METHOD

The canonical function method (CFM) ⁷ is a powerful means for solving the Radial Schrödinger Equation (RSE). The CFM turns the Radial Schrödinger equation into a regular initial value problem and allows the full determination of the spectrum of the Schrödinger operator bypassing the evaluation of the eigenfunctions. The Canonical Function Method (CFM), developed by Kobeissi et al. to integrate the RSE, consists in writing the general solution as a function of the radial distance r in terms of two basis functions $\alpha(E; r)$ and $\beta(E; r)$ for some energy E .

Generally, one avoids using the wavefunction but if needed, the functions $\alpha(E; r)$ and $\beta(E; r)$ can be used to determine it at any energy with the expression:

$$\Psi(E; r) = \Psi(E; r_0)\alpha(E; r) + \Psi'(E; r_0)\beta(E; r) \quad (1)$$

where $\Psi(E; r_0)$ and $\Psi'(E; r_0)$ are the wavefunction and its derivative at some initial distance r_0 . At the selected distance r_0 a well defined set of initial conditions are satisfied by the canonical functions and their derivatives, specifically $\alpha(E; r_0) = 1$ with $\alpha'(E; r_0) = 0$ and $\beta(E; r_0) = 0$ with $\beta'(E; r_0) = 1$. The prescription to solve the RSE is to proceed from r_0 simultaneously towards the origin ($r = 0$) and towards ∞ . During the integration, the ratio of the canonical functions is monitored until saturation signaling the stability of the eigenvalue spectrum.

The saturation of the $\frac{\alpha(E; r)}{\beta(E; r)}$ ratio with r yields a position independent eigenvalue function $F(E)$. The latter is defined with the help of two associated energy functions:

$$l_+(E) = \lim_{r \rightarrow +\infty} - \frac{\alpha(E; r)}{\beta(E; r)} \quad (2)$$

and:

$$l_-(E) = \lim_{r \rightarrow 0} - \frac{\alpha(E; r)}{\beta(E; r)} \quad (3)$$

The eigenvalue function is defined in terms of:

$$F(E) = l_+(E) - l_-(E) \quad (4)$$

Its zeroes yield the spectrum of the RSE. An example of behavior of $F(E)$ is displayed in Figure 1. The eigenfunctions may be obtained for any $E = E_k$ where E_k is a zero of $F(E)$.

Figure 1. Typical behavior of the eigenvalue function with energy. The vertical lines indicate the eigenvalue position.

The speed and accuracy of the method have been tested and compared to standard integration algorithms in a variety of cases and for a wide of range of potentials. We also point out that the method has been generalized to the phase shift estimation¹⁰ as well to the continuum coupled channel problem¹¹. In potential optimization problems, the method can only be of great value because of its speed, accuracy and ease of programming. Accordingly, one has to pick an appropriate optimization method and use the CFM as a subroutine for a given parametric potential.

OPTIMIZATION PROCEDURE

An extensive review of the applications of model potentials has been given by Hibbert¹² and Aymar et al.². The functional form suggested by Green et al.⁶ is given by:

$$V(r) = -(1/r)[(Z-1)\omega(r) + 1],$$

with $\omega(r) = 1/[\epsilon_1(\exp(r/\epsilon_2) - 1) + 1]$ (5)

where ϵ_1 and ϵ_2 are parameters that are determined by the optimization procedure.

The optimization problem, at hand, is over-determined since the experimental set of energy levels might consist of tens of values whereas the potential depends only on two values, namely ϵ_1 and ϵ_2 . This over-determination allows us to use several criteria for the optimization procedure and later on to select the best one that achieves results closest to experiment. The optimization procedure consists of defining an objective function and finding its minimum in the two-dimensional parameter space ϵ_1, ϵ_2 . The

Series	ϵ_1	ϵ_2
l=0	3.625	1.036
l=1	3.62	1.06
l=2	3.6344	1.036

Table 1. Czylik-Green parameters for the first three Rydberg series of Argon.

objective function is a quadratic consisting of the difference between some picked levels and those produced by the parametric potential through the solution of the RSE with the CFM.

We adopted several strategies based on the following observations: The quantum defect value is not stable for the low levels but tends to a given value as the energy increases. Despite the stability of the quantum defect for the higher levels, the experimental and therefore numerical accuracy decreases when the energy increases. Therefore a compromise should be achieved by selecting the levels in order to define the objective function to minimize.

We found that a reasonable compromise should be based on the following operations that differ with rare gases:

1. Pick some level and take the average of a number of higher ones.
2. Pick two high levels for which the Quantum defect has stabilized within a given accuracy.
3. Pick a low level and a high one for which the Quantum defect has already stabilized.

All the above operations should yield roughly the same values for the parameters before running the final check in order to test the accuracy of the obtained eigenvalues. The optimization program itself is based on a globally convergent method for solving non-linear system of equations: the multidimensional secant method developed by Broyden ¹³. It is based on a fast and accurate method for the iterative evaluation of the Jacobian of the objective function needed during the minimization procedure. It is a Quasi-Newton method that consists of approximating the Jacobian and updating it with an iterative procedure. It converges superlinearly to the solution like all secant methods.

There are several ways to perform the integration of the RSE on the basis of the CFM. One may use a fixed step scheme such as the explicit Runge-Kutta fourth order method (RK4) or a Variable Step with Control of Accuracy (VSCA). Optimization wise, the RK4 method is faster than VSCA but less accurate. To compromise, we first perform an initial search of the parameters with RK4 and then finalize the results using the VSCA method. Table [1] shows the parameters obtained for the first three Rydberg series of argon, optimized using the experimental energy levels tabulated by Moore ¹⁴.

To judge the accuracy of our optimization we compare in table [2,3] our results for the energy levels and corresponding quantum defect obtained using the RK4 and VSCA integration scheme with those of Czydlik et al. ¹⁵. The results displayed in

Experimental levels ¹⁴	Calculated levels (RK4)	Calculated levels (VSCA)
-0.309522	-0.214082	-0.310563
-0.124309	-9.87422E-02	-0.124506
-6.76780E-02	-5.69743E-02	-6.76904E-02
-4.25540E-02	-3.70845E-02	-4.25546E-02
-2.92210E-02	-2.60593E-02	-2.92238E-02
-2.13080E-02	-1.93126E-02	-2.13062E-02
-1.62200E-02	-1.48846E-02	-1.62210E-02
-1.27620E-02	-1.18223E-02	-1.27614E-02
-1.03020E-02	-9.61654E-03	-1.03015E-02
-8.49000E-03	-7.97521E-03	-8.49011E-03
-7.11800E-03	-6.72092E-03	-7.11771E-03

Table 2. Comparison between the experimental¹⁴ and calculated energy levels of the Rydberg series of Argon. The levels calculated with the CFM are obtained either with fixed step (RK4) or variable step (VSCA) integration. All values are given in Rydberg.

Experimental QD	Calculated QD (RK4)	Calculated QD (VSCA)
0.202561	0.838726	0.205576
0.163723	0.817645	0.165967
0.156063	0.810516	0.156415
0.152366	0.807174	0.152400
0.150046	0.805324	0.150326
0.149399	0.804191	0.149110
0.148104	0.803444	0.148345
0.148016	0.802940	0.147808
0.147664	0.802574	0.147425
0.147091	0.802298	0.147161
0.147199	0.802084	0.146957

Table 3. Comparison between the experimental and calculated QD of the Rydberg series of Argon. The levels calculated with the CFM are obtained either with fixed step (RK4) or variable step (VSCA) integration.

table [2,3] clearly favor, as expected, the VSCA integration scheme. In contrast to the VSCA, the RK4 integration scheme is limited to fourth order accuracy.

Scattering method and results

We now turn to the implementation of the optimized pseudo-potentials to the case of (e,2e) ionization in the equal energy sharing case ($\mathbf{k}_a = -\mathbf{k}_b$). Within a standard DWBA model and when a symmetric kinematic is considered (i.e. equal energy sharing between the two outgoing electrons) the exact unsymmetrized T -matrix element is approximated as ^{16, 17}

$$\langle \mathbf{k}_a \mathbf{k}_b \Phi_{J_i L_i M_i}^{ion} | T | \Phi_{J L M}^{atom} \mathbf{k}_0 \rangle \equiv \langle \chi^{(-)}(\mathbf{k}_a) \chi^{(-)}(\mathbf{k}_b) | V | \phi_{LM} \chi^{(+)}(\mathbf{k}_0) \rangle, \quad (6)$$

and both final state distorted waves, $\chi^{(-)}(\mathbf{k}_a)$ and $\chi^{(-)}(\mathbf{k}_b)$ are chosen as eigenfunctions of the electron-ion system. In this situation, the exact collision state with final-state boundary condition, $\Psi^{(-)}(\mathbf{k}_a, \mathbf{k}_b)$, is approximated as the product of two outgoing distorted waves. As for the calculation of the incoming distorted wave, the Furness-McCarthy local exchange approximation which, valid for scattering energies greater than 25eV³, is commonly used is the calculation of the outgoing distorted waves. Furthermore, the distorting potential is purely Coulombic asymptotically, and thereby neglects any e-e correlation in the final state.

It is well known ^{18, 19} that the exact final state wave function can be reasonably approximated as the product of two Coulomb waves provide the use of effective charges that satisfy the condition

$$\frac{Z_a^{eff}}{k_a} + \frac{Z_b^{eff}}{k_b} = \frac{1}{k_a} + \frac{1}{k_b} - \frac{1}{|\mathbf{k}_a - \mathbf{k}_b|}. \quad (7)$$

In the present case, we focus on the equal energy sharing geometry $\mathbf{k}_a = -\mathbf{k}_b$ and impose on the effective charge the condition

$$Z_a^{eff} = Z_b^{eff}. \quad (8)$$

Accordingly, we modify the form of our pseudo-potentials and replace in (5), and for all r values, the unit charge by an effective charge Z^{eff} which satisfy (7) and (8):

$$Z^{eff} = \frac{3}{4}. \quad (9)$$

This choice of screening charge insures that each outgoing electron experiences the exact classical force asymptotically. It was further suggested that the use of such effective charges suffices to take into account the electron correlation for the ionization of rare gas atoms in equal energy sharing geometry ¹⁸.

In the spirit of a DWBA method based on pseudo potentials and to describe the ionization process of argon at energy beyond the validity of the Furness-McCarthy local exchange potential (below 25eV), we use the parametric form suggested by Jungen et al ²⁰ to describe the incoming distorted wave. This pseudo-potential is adjusted to reproduce the ab initio elastic phase shift of McEachran et al ²¹ up to an energy of 30eV and includes static, exchange and polarization effects. At energy above 30eV, the Furness-McCarthy local exchange potential is used in the entrance channel. To

Figure 2. Comparison of the *ab-initio* elastic scattering phaseshift of McEachran et al (solid line) with the phaseshift obtained using the parametric potential of Jungen et al. (opaque symbols) and the Furness-McCarthy local exchange potential (filled symbols).

gauge the improvement introduced using such a parametric potential to describe the incoming projectile, we show in Fig 2 a comparison of the elastic scattering phaseshift obtained using the pseudo-potential of Jungen et al, using the Furness-McCarthy local exchange approximation and the *ab-initio* results of McEachran et al which leads to scattering parameters in good agreement with the experimental values. The significant improvement introduced in the calculation of the elastic scattering phaseshift, and consequently in the determination of the radial part of the incoming distorted wave, strongly suggests that a superior description of the ionization process is to be expected.

Fig 3 shows the variation of triply differential cross section (TDCS) as a function of the scattering angle for various values of excess energy, equally shared between the two outgoing electrons. The results obtained using the pseudo-potentials defined in the previous sections for the incoming and outgoing distorted waves are compared to calculations where the Furness McCarthy local-exchange potential⁴ is used in both the entrance and the exit channels and to the experimental measurements available²². Since the experimental measurements are not absolute, they have been systematically normalized to the DWBA calculations at a scattering angle $\theta = 270$ degrees except for an incident energy of $E_i = 17.8\text{eV}$ (i.e. $E_{exc} = 2\text{eV}$) and $E_i = 19.8\text{eV}$ (i.e. $E_{exc} = 4\text{eV}$) where the experiment is normalized to obtain the best visual fit to the theory.

For the highest incident energy considered here, $E_0 = 35.8\text{ eV}$ (i.e. $E_{exc} = 20\text{eV}$), little differences in the magnitude of the TDCS is noticeable between the two theoretical models. In contrast, the use of the pseudo-potentials calculated in the previous section clearly improves the prediction of the shape of the TDCS. This is particularly the case of the angular region between 230 and 320 degrees. Although improved, the TDCS is however still slightly underestimated outside this particular angular range. We stress that at this particular energy, the Furness-McCarthy local exchange approximation is used in the calculation of the incoming distorted wave. Further, this result

Figure 3. Behavior of the TDCS as a function of scattering angle in equal energy sharing geometry for various values of the excess energy as indicated on each graphs. DWBA calculations (thin line), DWBA calculations + pseudo-potentials (thick line), experiment (triangle)

also validates our procedure for calculating the outgoing distorted wave for an energy interval (i.e 35.8eV for the incoming electron) where the Furness-McCarthy local exchange potential is still in its lower energy limit of validity. Similar remarks pertain for the magnitude of the TDCS at the next lower incident energy ($E_{exc} = 8\text{eV}$). At this particular regime where the incoming distorted wave is now also described using pseudo-potentials, our optimized potentials largely improves the description of the experimental TDCS, especially in the angular region between 240 and 300 degrees.

At the two lowest energies considered here, marked differences are now noticeable between the TDCS obtained using the two different theoretical models (i.e DWBA and DWBA+pseudo-potentials). First, the overall magnitude of the TDCS is largely reduced when parametric potentials are used. Additional calculations (not shown here) indicate that the use of effective charges is largely at the origin of this reduction. Unfortunately, the improvement introduced can not be gauged against the experimental data as the measurements are not absolute. The reduction in amplitude of the variation of the TDCS where experimental measurements are available can be traced back to the influence of the pseudo-potential combined with the use of the effective charges in the exit channel 23. Finally, when the pseudo-potentials of Jungen et al. are introduced to describe the entrance channel distorted wave little improvements are observed in the calculations of the TDCS where experimental measurements are available. Its effects on the calculated cross sections are mainly felt at the lowest and highest angular region where experimental measurements are not available.

Conclusions

In this work, we showed that QD information provides means to select and tune a class of pseudo-potentials. These can subsequently be used in ionization studies by electron impact with proper modifications to account for the electron correlation in the final state. Ionization of argon in the equal energy sharing geometry, shows that this procedure provides an efficient treatment of the final state interactions, extending beyond the energy region where the commonly used Furness-McCarthy local exchange potential is valid, and yet providing a much simpler alternative to the complete Hartree-Fock treatment. This might turn out to be particularly valuable when considering the ionization of molecular systems.

ACKNOWLEDGMENTS

Helpful correspondence, regarding mathematical aspects of the RSE, with Dr. Jeff Cash are gratefully acknowledged.

REFERENCES

1. C. Jungen, *Molecular Applications of Quantum Defect Theory*, Institute of Physics Publishing (1996).
2. M. Aymar, C. H. Green, and E. Luc-Koenig, *Rev. Mod. Phys.* 68, 1015 (1996).
3. M.E. Riley and D.G. Trular, *J. Chem. Phys.* 63, 2182 (1975).
4. J. B. Furness and I. E. McCarthy *J. Phys. B* 6 2280 (1973).
5. K. D. Winkler, D. H. Madison and H. P. Saha *J. Phys. B* 32, 1987 (1999).
6. A. E. S. Green, D. L. Sellin and A. S. Zachor, *Phys. Rev.* 184, 1 (1969).
7. H. Kobeissi, *J. Phys. B* 15, 693 (1982).
8. C. Tannous, K. Fakhreddine and J. Langlois, *J. Phys. IV France* 9 Pr6-71 (1999).
9. M. Klapisch, *Comp. Phys. Comm.* 2, 239 (1971).
10. H. Kobeissi, K. Fakhreddine and M. Kobeissi, *Int. J. Quantum Chemistry*, Vol XL, 11 (1990).
11. H. Kobeissi, K. Fakhreddine *J. Physique II (France)* 1, 38 (1991).
12. H. Hibbert, *Adv. At. Mol. Phys.* 18 309 (1982).
13. Broyden, *CG: Mathematics of Computation*, 19, 557 (1965).
14. C. E. Moore, *Atomic energy levels*, NBS Publications (1971).
15. P. P. Szydluk and A. E. S. Green, *Phys. Rev. A* 9, 1885 (1974).
16. I. E. McCarthy, *Aust. J. Phys.* 48, 1 (1995).
17. I. E. McCarthy and E. Weigold, *Electron-atom collisions*, Cambridge University Press (1995).
18. C. Pan and A. F. Starace, *Phys Rev A* 45, 4588 (1992).
19. R. K. Peterkop, *Theory of Ionization of Atoms By Electron Impact* (Colorado Associated University Press, Boulder) (1977).
20. C. Jungen, A.L. Roche, M Arif, *Phil. Trans. A*, 355, 2520 (1997).
21. R. P. McEachran, A. D. Stauffer, *J. Phys. B* 16, 4023 (1983).
22. B. Rouvellou, S. Rioual, J. Roeder, A. Pochat, J. Rasch, C. T. Whelan, H. R. J. Walters and R. J. Allan, *Phys. Rev. A* 57, 3621 (1998).
23. S. Mazevet, K. Fakhreddine, G. Nguyen Vien, R. J. Tweed, and J. Langlois, in preparation.