New and Old Theoretical Tools for Evaluating Cross Sections for Ion-Atom Collisions

C. D. Lin[1], A. T. Le[1], Teck G. Lee[2] and C. N. Liu[3]

[1]Department of Physics, Kansas State University, Manhattan, KS 66506 USA
[2]Physics Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831 USA
[3]Department of Physics, FuJen Catholic University, Taipei, 24205, Taiwan
e-mail: cdlin@phys.ksu.edu

Abstract. The close-coupling method for ion-atom collisions using atomic orbital and molecular orbitals as basis functions are reviewed. Recent development using hyperspherical close-coupling method is discussed. Examples for a few collision systems are examined to resolve differences among theoretical calculations and experiments**.**

Key words: ion-atom collisions, close-coupling theory, hyperspherical method.

INTRODUCTION

Cross sections for ion-atom collisions for many species over a broad range of energies are part of the Atomic and Molecular data that are needed in many applications that are the focus of the present Joint ITC14 and ICAMDATA2004. While some of these data can be measured experimentally in the laboratories, clearly cross sections evaluated by reliable theoretical calculations are in need as well. Except for much higher collision energies where perturbation theories may be employed, practically all the other theoretical tools for the calculation of cross sections in the intermediate and low energies are all based on the close-coupling (or coupled-channel) methods. In this report, I will try to evaluate the region of validity of the different models that are in use by the theorists today and report some recent developments.

CLOSE-COUPLING METHOD – SEMICLASSICAL MODEL

For collisions where the de Broglie wavelength of the projectile is much less than the typical interaction range, the motion of the heavy particles can be described by a classical straightline trajectory. In this semiclassical approximation, the motion of the electron is governed by the time-dependent Schrödinger equation. In the spirit of the close-coupling method, the idea is to expand the time-dependent wavefunction $\Psi(\vec{r},t)$ approximately by a truncated expansion

$$\Psi\left(\mathrm{r},\mathrm{t}\right)=\sum_{\mathrm{k}=1}^{\mathrm{N}}\ \mathrm{a}_{\mathrm{k}}\left(\mathrm{t}\right)\phi_{\mathrm{k}}\left(\mathrm{r},\mathrm{t}\right) \tag{1}$$

with time-dependent amplitudes $a_k(t)$ for the occupation of the state $\phi_k(\vec{r},t)$. Ideally the basis states $\phi_k(\vec{r},t)$ should be the eigenstates of the separated atoms so that $a_k(t)$ as $t\to\infty$ gives immediately the transition amplitudes from which the transition probabilities can be extracted directly.

There are two types of basis functions that are commonly used by the theorists. One is the Atomic-orbital close-coupling (AOCC) method [1,2] where the basis sets are given by

$$\begin{aligned}\hat{\phi}_{\mathrm{k}}^{\mathrm{A}}\left(\mathrm{r},\mathrm{t}\right)&=\phi_{\mathrm{k}}^{\mathrm{A}}\left(\mathrm{r}_{\mathrm{A}}\right)\exp\left(\mathrm{i}\upsilon_{\mathrm{A}}\cdot\mathrm{r}-\frac{1}{2}\mathrm{i}\int^{\mathrm{t}}\ \mathrm{dt}'\ \upsilon_{\mathrm{A}}^{2}-\mathrm{i}\varepsilon_{\mathrm{k}}^{\mathrm{A}}\mathrm{t}\right)\\ \hat{\phi}_{\mathrm{k}}^{\mathrm{B}}\left(\mathrm{r},\mathrm{t}\right)&=\phi_{\mathrm{k}}^{\mathrm{B}}\left(\mathrm{r}_{\mathrm{B}}\right)\exp\left(\mathrm{i}\upsilon_{\mathrm{B}}\cdot\mathrm{r}-\frac{1}{2}\mathrm{i}\int^{\mathrm{t}}\ \mathrm{dt}'\ \upsilon_{\mathrm{B}}^{2}-\mathrm{i}\varepsilon_{\mathrm{k}}^{\mathrm{B}}\mathrm{t}\right)\end{aligned} \tag{2}$$

where $\phi_k^C(\vec{r}_C)$ (C=A,B) denotes the eigenstates of the atom C. The phase-dependent factors in Eq. (2) implies that the atomic orbitals are moving with either A or B centers. Their presence are essential if the resulting transition probabilities obtained from $|a_k(t\to\infty)|^2$ are to be Galilean invariant. Thus in the AOCC calculations the main task is to include all the important basis orbitals into the close-coupling expansion.

The other common approach is the Molecular-orbital close-coupling (MOCC) method [1,3]. In its earliest form, the method is called perturbed stationary state approximation (PSS) [4] where $\phi_k(\vec{r},t)$ are the molecular orbitals $\Phi_k(\vec{r};R(t))$. According to the PSS model, for slow collisions the electron sees the joint field from the two centers and thus the molecular orbitals are more appropriate for describing the electronic evolution. Thus PSS model has been commonly used to interpret or estimate the transition probabilities for slow collisions. The main task in the collision between two atoms or atom and molecules is the calculation of the BO potential curves and their couplings. However, the PSS model does not account for the translational motion of the electron with respect to either center, and thus the calculated transition probabilities are not Galilean invariant [5]. Therefore there are many attempts to correct this deficiency, with the introduction of electron translational factors (ETF). To satisfy the asymptotic boundary conditions, the ETF should be reduced to the plane-wave phase factors as in Eq. (2), but there is no well-defined procedure to derive the ETF's at finite range of R.

Despite of this intrinsic limitation, practical ad hoc ETF's have been widely used in the literature. Thus in the MOCC calculation, the molecular orbitals and the ETF's used should be described [3].

Both the AOCC and MOCC calculations have been applied to many ion-atom collisions in the past two to three decades and details can be found in several review articles [2,3] and monograph [1]. In the past decade, however, we have witnessed a substantial diminishing activities in this area, particularly in collisions using highly charged ions from ECR and EBIT sources. Nonetheless, new interest in collisions of multiply charged ions with atoms and molecules continue to emerge, with the new finding that X-rays observed in comets [6-8] are likely coming from the radiation emitted following electron capture by multiply charged ions from the solar winds.

CLOSE-COUPLING METHOD – QUANTUM MECHANICAL APPROACH

Cross sections for ion-atom collisions at low energies are difficult to obtain experimentally. The only technique that would allow experimentalists to probe collisions at eV/amu or less is the merged-beam experiments such as those at Oak Ridge National Laboratory [9,10]. Thus reliable theoretical methods are expected to provide the cross sections data needed for many applications.

The practical approach for treating ion-atom collisions is based on the molecular orbital close-coupling expansion where the motion of the heavy particles is treated quantum mechanically. The standard PSS approach, as in the semiclassical version, although intuitively attractive in providing a description of the collision dynamics, encounters practical difficulty in its numerical implementation, again due to the incorrect asymptotic boundary conditions. To correct this seemingly "minor" error, however, it has taken the efforts of many theorists for many years. Corrections to the coupling matrix elements similar to those in the semiclassical formulation were used in the quantal solution of the motion of the heavy particles, but the validity of such approximations has never been well tested due to the lack of detailed experimental results in the low energy region. An alternative approach, based on the full quantum mechanical formulation of the rearrangement collisions, introduces the so-called reaction coordinates ξ by replacing the internuclear separation R [11,12]. This method has been used by a few theoretical groups [13-17] to obtain scattering cross sections for a number of collision systems. Since ad hoc parameters were introduced in their formulation, the validity of the theoretical results based on the reaction coordinate method has not been well tested either. This situation has changed within the last year. The results from the so-called common reaction-coordinate (CRC) method have now been tested against the calculations of the recently developed hyperspherical close coupling (HSCC) method [18]. The HSCC method has been rigorously formulated for the one-electron ion-atom collision systems without any ad hoc parameters. By comparing the HSCC and CRC results [19], it has been found that they agree quite well even at the partial-wave cross sections. This is good news. The CRC method, which has been well-developed and can be applied to many-electron ion-atom and ion-molecule collisions, can now be used with confidence if the calculations are carried out carefully. In other words, we believe that the theoretical tools for calculating reliable ion-atom collisions at low energies are available despite that ad hoc parameters are used in the theory.

HYPERSPHERICAL CLOSE-COUPLING METHOD

In this section we outline our hyperspherical close-coupling method for ion-atom collisions. The full description can be found in Liu et al. [18]. Recent modifications to diabatic basis expansion can be found in Lee et al. [20] and in Hesse et al. [21]. Let $\vec{\rho}_1$ be the vector between the two nuclei and $\vec{\rho}_2$ be the vector from the center-of-mass of the two nuclei to the electron. Introduce the hyperradius R and the hyperangle ϕ

$$R = \sqrt{\frac{\mu_1}{\mu}\rho_1^2 + \frac{\mu_2}{\mu}\rho_2^2}, \qquad \tan\phi = \sqrt{\frac{\mu_2}{\mu_1}}\frac{\rho_2}{\rho_1}, \tag{3}$$

where μ is an arbitrary normalization mass. By expressing the total wavefunction in the body-frame, one can write [18]

$$\Psi\left(R,\Omega,\hat{\omega}\right) = \sum_{\nu}\sum_{I} F_{\nu I}\left(R\right)\Phi_{\nu I}\left(R,\Omega\right)\bar{D}^{J}_{IM_J}\left(\hat{\omega}\right), \tag{4}$$

This expression is analogous to the Born-Oppenheimer (BO) expansion except that the hyperradius R is the adiabatic parameter. Here $\hat{\omega}$ is the set of three Euler angles and $\overline{D}$ is the Wigner rotational function, $\Omega=(\alpha,\theta)$, where θ is the angle between the two radius vectors $\vec{\rho}_i$ (i=1,2), I (M_J) is the projection of the angular momentum J along the body-frame (laboratory) axis. The adiabatic "channel functions" $\Phi_{\nu I}(R,\Omega)$ and the potential curves are first obtained by solving the two-dimensional eigenvalue problems at each R, just as in the BO expansion and the scattering information is obtained by solving the resulting coupled hyperradial equations for $F_{\nu I}(R)$. Such standard approach is not computationally efficient when the number of channels that have to be included is large, as would be the case when one treats problems involving highly excited states. We chose to diabatize the channel functions approximately [20,21]. Let Φ^A and Φ^B be adiabatic and diabetic basis functions, respectively. A rigorous diabatization is achieved through $\Phi^B = C\Phi^A$ where C satisfies $CP + dC/dR = 0$ with the matrix P given by $\mathrm{P}_{\mathrm{ij}} = -\left\langle \Phi_{\mathrm{l}}^{\mathrm{A}} \middle| \mathrm{d}/\mathrm{dR} \middle| \Phi_{\mathrm{j}}^{\mathrm{A}} \right\rangle$. This is the method used by Heil et al. [22]. It has a number of problems-- including that one needs to calculate P_{ij} which is rather difficult near the avoided crossing region. We chose to perform only partial diabatization by approximating

$$\mathrm{P}_{\mathrm{ij}} \approx \frac{\left[\left\langle \Phi_{\mathrm{l}}^{\mathrm{A}}(\mathrm{R}) \,|\, \Phi_{\mathrm{j}}^{\mathrm{A}}(\mathrm{R}) \right\rangle - \left\langle \Phi_{\mathrm{l}}^{\mathrm{A}}(\mathrm{R}) \,|\, \Phi_{\mathrm{j}}^{\mathrm{A}}(\mathrm{R}+\Delta\mathrm{R}) \right\rangle\right]}{\Delta\mathrm{R}}. \tag{5}$$

This approximate diabatization has the advantage that there is no need to calculate accurate P_{ij} and only the overlap integrals of the channel functions are to be calculated. Since the diabatization is not exact, there will be some remaining small nonadiabatic couplings as well as the new potential couplings. In practice, our goal is to diabatize only avoided crossing which is sharp and narrow, thus the diabatization is performed only if the overlap between neighboring points is larger than some parameter α. Note that the partial diabatization does not introduce errors so long as all the remaining coupling terms are kept in the calculation. However, this procedure introduce two major advantages: (1) There is no need to calculate the nonadiabatic coupling terms using dense grid points since any sharp avoided crossings will be diabatized. (2) Weakly coupled channels can be eliminated so that the number of channels used in the calculation can be reduced substantially.

With the new HSCC theory available, we decided to go back to some collision systems where "outstanding" discrepancy has been known for years. One of such systems is the collisions of O^{8+} with H [20]. This collision system has been studied since the early 1980's. In Fig. 1 we compare the total electron capture cross sections for energies from about 0.1-2.0 keV/amu. The experimental data are from Meyer et al. [23], taken in 1985. Among the theoretical calculations, it appears that the MOCC calculations of Kimura and Lane [24] and the AOCC calculations of Fritsch and Lin [25] are in best agreement with the experiment, with the cross section rapidly decreasing at lower energies. On the other hand, the most sophisticated 46-state MOCC calculations of Shipsey et al. [26] show substantial discrepancy with the experiment. In this calculation, they included all the MO's that converge to the n=4,5,6 and some n=7 states of O^{7+} and the initial state. In a recent paper, we used the HSCC method to study this collision system. Our HSCC results, as shown in Fig. 1, are in much better agreement with the results of Shipsey et al. In the HSCC calculations, we included all the n=5 and n=6 states of O^{7+} and the initial state. The I=0 and I=1 potential curves of these states are shown in Fig. 2a. We have also used a much smaller basis set, including only seven channels as shown in Fig. 2b. The results from the two calculations are shown to agree quite well. From the potential curves, it is clear that charge transfer occurs mainly through the two avoided crossings near R=17 for the n=6 states of O^{7+} and near R=9.5 for the n=5 states of O^{7+}. At higher energies the R=17 crossing is expected to be diabatic and the n=5 states will be populated. At decreasing collision energies the R=17 crossing will become effective in populating the n=6 states. This is indeed the case. We compare the partial n=5 and n=6 electron capture cross sections in Fig. 3a and 3b. In Fig. 3a, except for the results from the AOCC calculation of Fritsch and Lin [25], the partial cross sections are in good agreement among the calculations. In Fig. 3b we show that capture to n=6 indeed dominantes at low energies.

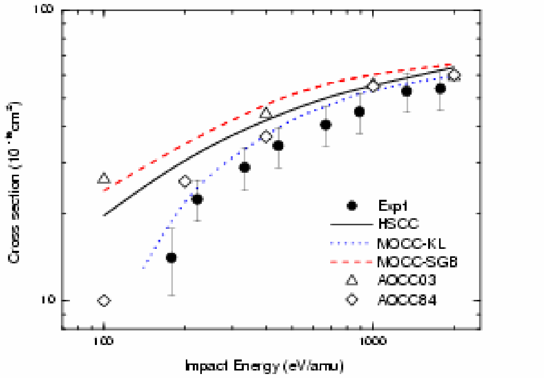

FIGURE 1. Total electron capture cross sections for O^{8+}+H collisions. The experimental data are from Meyers et al. [23]. The HSCC and AOCC03 results are from Lee et al. [20]. For the others, MOCC-KL, see [24]; MOCC-SGB, see [26] and AOCC84, see [25].

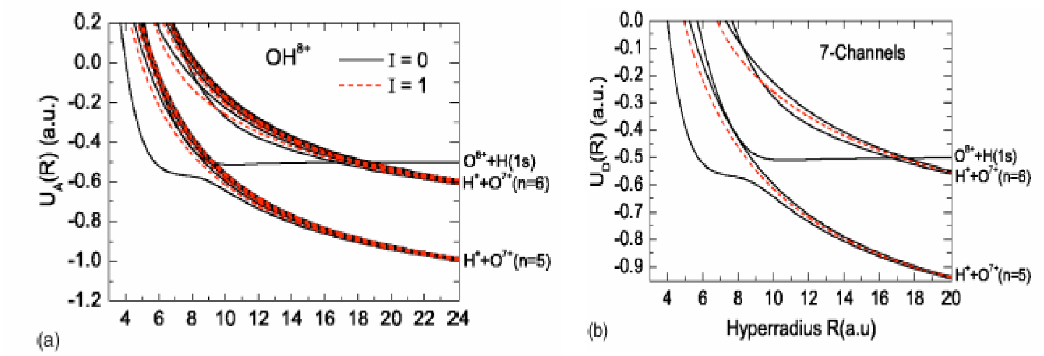

FIGURE 2. (a) Adiabatic vs (b) truncated diabatic potential curves for $(OH)^{8+}$. Only the I=0 and I=1 curves are shown.

The new HSCC calculation, together with the elaborate MOCC calculation appears to indicate that the experimental total electron capture cross section in Meyers et al. is questionable. That would mean that the results of Kimura and Lane and of Fritsch and Lin are also questionable. In Kimura and Lane, it appears that the n=6 states of O^{7+} were neglected in the basis set, thus their low energy results are incorrect. In Fritsch and Lin, they used atomic orbitals nearly identical to the MO's used by Shipsey et al., but used a semiclassical theory with curved trajectories. In Lee et al [20], AOCC calculations using the same basis set as in Fritsch and Lin [25] but with straightline trajectories were carried out. From Fig.1 and Fig.3a,b it is clear that the new AOCC results are also in agreement with other calculations based on molecular orbitals We speculated that there are numerical errors in the AOCC code when the curved trajectories were used.

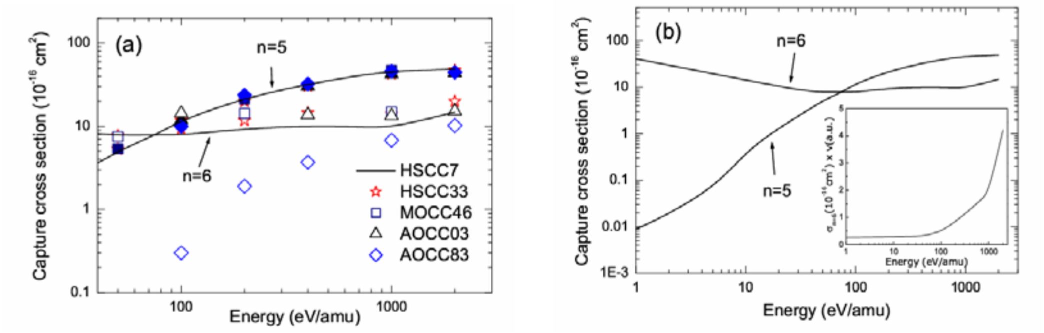

FIGURE 3. Partial cross sections for electron capture to n=5 and n=6 states in O^{8+}+H collisions. Adopted from Lee et al. [20].

The take-home message from this example is that the theoretical methods for doing ion-atom collisions are available. In implementing the calculations, however, care should be taken. In the semiclassical MOCC calculations, the effect of different electron translational factors appear to affect the final results insignificantly. On the other hand, the inclusion of the dominant MO's should never be compromised. At lower collision energies, calculations including large number of MO's are not desirable. Using the diabatic basis set as in the HSCC calculation, it appears that the basis set can be truncated significantly, thus reducing the chance of numerical errors as well.

ION-ATOM COLLISIONS AT LOW ENERGIES

The concept of electron translational factors is not applicable when performing MOCC calculations where the motion of the heavy particles is treated quantum mechanically. Since the 1960's the so-called common reaction coordinates (CRC) have been introduced to low-energy ion-atom collisions and the method has been implemented since the 1980's and 1990's for a number of collision systems. Criteria for choosing the reaction coordinates have been proposed and used in the calculations [13-17]. Since experimental data for low-energy ion-atom collisions are rare, and often only total charge transfer cross sections are available, thus the reliability of the CRC calculations have not been critically tested. With the recently developed HSCC method which is valid for low-energy ion-atom collisions for the one-electron systems, a detailed comparative study of the CRC and HSCC calculations has been carried out recently, see Le et al. [19].

In the CRC calculation, a reaction coordinate $\vec{\xi}$ is used to replace the internuclear separation $\vec{\rho}_1$. The total wavefunction is expanded as

$$\Psi^J\left(\vec{\rho}_2,\vec{\xi}\right)=\sum_k \chi_k\left(\vec{\xi}\right)\Phi_k\left(\vec{\rho}_2;\vec{\xi}\right) \qquad (6)$$

where $\vec{\rho}_2$ is the electronic coordinates. In the implementation used by Errera et al. [15], the reaction coordinate is defined in terms of some switching functions and the resulting coupled equations in $\vec{\xi}$ contain additional terms resembling those from the effect of electron translational factors.

Compare the expansion (6) with (4), we can see that to some extent the reaction coordinate ξ resembles the hyperspherical radius. In Le et al., the HSCC and the CRC calculations were compared for the He^{++}+H collisions. The cross sections at low energies are very small for this system. In Fig. 4a the coupling matrix elements from HSCC and from CRC are compared. The partial wave cross sections at center-of-mass energy of 100 eV are compared in Fig. 4b. It is clear that the coupling matrix elements from the CRC in the reaction coordinates are very close to those from the HSCC except at the small internuclear separations. Despite of these differences, the partial wave cross sections agree very well, see Fig. 4.

The good agreement between CRC and the HSCC for this system at the partial wave cross section level is quite gratifying since it supports the validity of the CRC approach despite of the somewhat *ad hoc* choice of reaction coordinates. The CRC method is a rather mature theory, and has been applied to many-electron ion-atom collisions as well as to ion-molecule collisions. Thus in principle reliable cross sections can be obtained from theoeretical calculations. Since the calculations are rather time consuming, such careful studies probably can only be done for a limited number of collision systems where the data are of great importance. In the future the diabatization procedure used in the HSCC method should be implemented in the CRC calculations or any MOCC calculations to avoid the time-consuming evaluation of coupling matrix elements

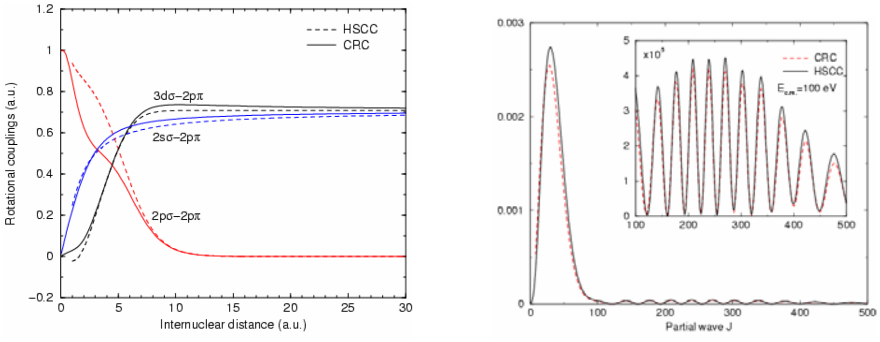

FIGURE 4. Comparison of (a) rotational couplings and (b) partial wave charge transfer cross sections from the CRC and the HSCC calculations. From [19].

OTHER RECENT DEVELOPMENTS

In addition to the close-coupling methods discussed in this report, the so-called hidden crossing (HC) theory [27-29] and the direct solution of the time-dependent Schrodinger equation (TDSE) [30-32] have also found some recent developments. Both methods have not been extensively applied to many systems, although we have witnessed that the recent HC calculations for He^{++}+H [33] at low energies are in good agreement with HSCC and the CRC results. The TDSE method in general can be expected to be useful in the higher energy region where ionization is also important.

SUMMARY

In this report we summarize and discuss the various theoretical approaches for ion-atom collisions from the low-energy end to the intermediate energy region where ionization becomes important. We have shown that basic theory and computational tools are available for carrying out reliable calculations if the each system is studied carefully. In many instances erroneous results were reported in the literature due to some errors in the numerical calculations or in the insufficient basis functions used in the MOCC or the AOCC calculations. As fewer people are doing ion-atom and ion-molecule collision calculations but the demand of such data continues to exist, in the future, funding probably should be made available from the user's community for such data.

ACKNOWLEDGMENT

This work is supported in part by the Chemical Sciences, Geosciences and Biosciences Division, Office of Science, U.S. Department of Energy.

REFERENCES

1. B. H. Bransden and M. R. C. McDowell, *Charge Exchange and Theory of Ion-Atom Collisions* (Clarendon, Oxford, 1992).
2. W. Fritsch and C. D. Lin, *Phys. Rept*. **202**, 1 (1991).
3. M. Kimura and N. F. Lane, *Adv. At. Mol. Opt. Phys*. **26**, 79 (1990).
4. H. S. Massey and R. A. Smith, *Proc. R. Soc. London, Ser. A* **142**, 142 (1933).
5. J. B. Delos, *Rev. Mod. Phys*. **53**, 287 (1981).
6. P. Beiersdorfer, et al., *Science* **300**, 1558 (2003).
7. C. M. Lisse et al., *Science* **292**, 1343 (2001).
8. V. Kharchenko et al., *Ap. J*. **585**, L73 (2003).
9. R. Rejoub, et al., *Phys. Rev. A* **69**, 052704 (2004).
10. T. Mroczkowski, D. W. Savin, R. Rejoub, P. S. Krstić, and C. C. Havener, *Phys. Rev. A* **68**, 032721 (2003).
11. M. H. Mittleman, *Phys. Rev*. **188**, 221 (1969).
12. W. R. Thorson and J. B. Delos, *Phys. Rev. A* **18**, 135 (1978).
13. M. Gargaud, R. McCarroll, and P. Valiron, *J. Phys. B* **20**, 1555 (1987).
14. H. Croft and A. S. Dickinson, *J. Phys. B* **29**, 57 (1996).
15. L. F. Errea, C. Harel, H. Jouin, L. Méndez, B. Pons, and A. Riera, *J. Phys. B* **31**, 3527 (1998).
16. R. McCarroll and D. S. F. Crothers, *Adv. At., Mol., Opt. Phys*. **32**, 253 (1994).
17. A. Riera, *Mol. Phys.* **88**, 199 (1996).
18. C. N. Liu, A. T. Le, T. Morishita, B. D. Esry, and C. D. Lin, *Phys. Rev. A* **67**, 051801 (2003).
19. A. T. Le, C. D. Lin, L. F. Errea, L. Mendez, A. Riera and B. Pons, *Phys. Rev. A* **69**, 062703 (2004).
20. Teck G. Lee, Anh-Thu Le and C. D. Lin, *Phys. Rev. A* **70**, 012702 (2004).
21. M. Hesse, A. T. Le and C. D. Lin, Phys. *Rev. A* **69**, 052712 (2004).
22. T. G. Heil, S. E. Butler, and A. Dalgarno, *Phys. Rev. A* **23**, 1100 (1981).
23. F. W. Meyer et al , *Phys. Rev. A* **32**, 3310 (1985).
24. M. Kimura and N. F. Lane, *Phys. Rev. A* **35**, 70 (1987).
25. W. Fritsch and C. D. Lin, *Phys. Rev. A* **29**, 3039 (1984).
26. E. J. Shipsey, T. A. Green, and J. C. Brown, *Phys. Rev. A* **27**, 821 (1983).
27. E. A. Solov'ev, Sov. *Phys. Usp*. **32**, 228 (1989).
28. S. Yu Ovchinnikov *Phys. Rev. A* **42** 3865 (1990).
29. P. S. Krstic, D. R. Schultz and R. K. Janev, *J. Phys. B* **29,** 1941 (1996).
30. A. Kolakowska, M. S. Pindzola, and D. R. Schultz, *Phys. Rev. A* **59**, 3588 (1999)
31. M. S. Pindzola, *Phys. Rev. A* **60**, 3764 (1999)
32. M. E. Riley and B. Ritchie, *Phys. Rev. A* **59**, 3544 (1999)
33. P. S. Krstic, *J. Phys. B* **37**, L217 (2004).