

Low-Energy Charge Transfer in Multiply-Charged Ion-Atom Collisions Studied with the Combined SCVB-MOCC Approach

D. L. Cooper¹, P. C. Stancil², A. R. Turner¹, J. G. Wang², N. J. Clarke¹, and B. Zygelman³

¹Department of Chemistry, University of Liverpool, PO Box 147, Liverpool L69 7ZD, UK. E-mail: dlc@liv.ac.uk, art@liv.ac.uk

²Department of Physics and Astronomy and Center for Simulational Physics, The University of Georgia, Athens, GA, 30602-2451, USA. E-mail: stancil@physast.uga.edu, wangjg@physast.uga.edu

³Department of Physics, University of Nevada, Las Vegas, NV, 89154-4002, USA.
E-mail: bernard@physics.unlv.edu

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Abstract: A survey of theoretical studies of charge transfer involving collisions of multiply-charged ions with atomic neutrals (H and He) is presented. The calculations utilized the quantum-mechanical molecular-orbital close-coupling (MOCC) approach where the requisite potential curves and coupling matrix elements have been obtained with the spin-coupled valence bond (SCVB) method. Comparison is made among various collision partners, for equicharged systems, where it is illustrated that even for total charge transfer cross sections, scaling-laws do not exist for low-energy collisions (i.e. < 1 keV/amu). While various empirical scaling-laws are well known in the intermediate- and high-energy regimes, the multi-electron configurations of the projectile ions results in a rich and varied low-energy dependence, requiring an explicit calculation for each collision-partner pair. Future charge transfer problems to be addressed with the combined SCVB-MOCC approach are briefly discussed.

Keywords: charge transfer; spin-coupled theory; valence bond

1 Introduction

Charge transfer (also known as electron capture or charge exchange) is an important inelastic collision process in astrophysical and laboratory plasmas. It can have a significant effect on the ionization structure of a gas and, under certain conditions, can contribute to or produce a photon emission spectrum.

The process involves the binary collision of two heavy-particles, usually an atomic ion A (projectile) of initial charge q with a neutral atom or molecule B (target), in which m electrons are transferred from the neutral target to the projectile



The total number of electrons transferred in a single collision can be equal to the total number present on the target, but the cross section usually decreases rapidly with the number of electrons transferred. In most situations, and in particular for the low-energy regime (< 1 keV/amu), the transfer of one electron, often called single electron capture (SEC), is the dominant process. The focus here will be restricted to SEC, i.e. $m = 1$.

Charge transfer was first studied in the 1920s and has since been an active field of research in the atomic physics community. Over the nearly eight decades of study, numerous combinations of projectiles A , targets B , and charges q have been investigated, yielding an impressive body of knowledge. In particular, various empirical relations involving q , the target ionization potential, or other parameters, have been found which can be used to predict cross sections for collision systems for which data are lacking. These scaling relations have proved useful in many modeling applications. A majority of the effort has been applied to the intermediate- and high-energy regimes ($E > 10$ keV/amu) where the scaling-laws are applicable. Unfortunately, the relevant energies for most astrophysical and laboratory plasmas are well below 1 keV/amu, an energy range where most scaling-laws break-down. In this energy regime, the relative velocity of the heavy particles is much smaller than that of the bound electrons. During the collision, the electron can be shared by both heavy particles, forming a quasi-molecule AB^{q+} . After the collision, the probabilities associated with the electron residing on either A or B depend sensitively on the electronic structure of the quasi-molecule over the whole range of internuclear distances, including the interaction or “bonding” region, the asymptotic or separated-atom limit ($R \rightarrow \infty$), and often the united-atom limit ($R \rightarrow 0$). A theoretical description of the mechanism was first given in 1933 by Massey and Smith [1], which bears the modern name of the Molecular-Orbital Close-Coupling (MOCC) method. However, the approach can be computationally expensive and no simple scaling-type relations can be extracted from it. Furthermore, the method consists of two steps: (i) calculation of the electronic structure and associated couplings of the quasi-molecule system AB^{q+} and (ii) solution of the relevant scattering equations, ultimately yielding the charge

transfer cross section. The required computational resources for these two steps is no longer an impediment. The primary obstacle is human-power: if accurate knowledge of the cross section for reactions of the type (1) are required for low-energy modeling applications, then each $A^{q+} - B$ collision system has to be investigated explicitly.

We have assembled a unique group for studying the charge transfer process with the MOCC method and, in particular, we are the only group using the Spin-Coupled Valence Bound (SCVB) method, which has particular advantages for this type of application. Over the last decade a significant number of collision systems have been investigated by our group with the combined SCVB-MOCC approach. We summarize here some of those results, concentrating on the total (as opposed to state-selective) cross sections. We start with a brief outline of our implementation of the SCVB and MOCC methods, and we conclude with a discussion of issues we plan to address in the future.

2 Electronic structure calculations

Spin-coupled valence bond (SCVB) theory [2, 3] is a flexible *ab initio* approach that is well suited to the calculation of the potential energy curves and coupling matrix elements that are required for each collision-partner pair. The methodology may be used to describe several states of each spin and spatial symmetry to consistent accuracy, over the required range of internuclear distance R .

For each system, the effective starting point is the optimization of a spin-coupled wavefunction of the form:

$$\Psi = \hat{\mathcal{A}} \left(\varphi_1^2 \varphi_2^2 \dots \varphi_n^2 \Theta_{pp}^{2n} \phi_1 \phi_2 \dots \phi_N \Theta_{SM}^N \right) \quad (2)$$

The active-space spin function, Θ_{SM}^N , is fully optimized in the full spin space for N active electrons with total spin quantum number S and projection M . Each of the spin-coupled orbitals (ϕ) is fully optimized in a flexible atom-centred Gaussian basis set, without any localization or overlap constraints. The doubly-occupied inactive orbitals (φ) may be similarly optimized, simultaneously with the active orbitals but, in the present work, it proved more useful to import (fixed) natural orbitals from suitable CASSCF calculations. Θ_{pp}^{2n} is the perfect-pairing spin function for the inactive electrons.

At convergence, a set or 'stack' of virtual orbitals is generated for each active electron. Where appropriate, additional orbitals, to be used as virtuals, may be imported from atomic calculations for (say) the neutral target. Further configurations are generated by so-called "vertical" replacements of active orbitals with virtuals from their own stack. Usually it is necessary only to include selected low-lying virtuals. Additionally, certain cross excitations into other stacks may proved useful - especially those excitations leading to double occupancy of virtuals (so-called "ionic" con-

figurations). The final SCVB wavefunctions are obtained from a nonorthogonal CI calculation based on a compact set of configurations. Each state typically has a single dominant configuration; each of these may be used as an additional reference function when generating excitations into virtual orbitals.

The compactness of the final SCVB wavefunctions is a great asset when calculating the required radial ($\partial/\partial R$) and rotational (L_y) couplings, and the transition dipole moments. The radial couplings are obtained via an appropriate central difference approximation, involving separate SCVB calculations at nuclear separations $R + \delta$ and $R - \delta$. It is normally straightforward also to monitor any changes to the atomic parentage of each state over the entire range of R .

3 Scattering calculations

The quantum-mechanical molecular-orbital close-coupling (MOCC) theory, as mentioned earlier, was originally introduced by Massey and Smith and is also known as the perturbed stationary state (PSS) model. Modern implementations of the method have been described by many authors (see for example Kimura and Lane [4]). We provide here only a brief outline - most of the details can be found in Zygelman et al. [5]. As a practical matter, the MOCC method involves solving a coupled set of second order differential equations. The solutions are the expansion coefficients, or scattering amplitudes, of the total system wavefunction expanded over a truncated set of adiabatic molecular eigenfunctions. In the adiabatic representation, transitions between channels are driven by elements (radial \underline{A}_R and rotational \underline{A}_θ) of the vector potential $\underline{A}(\mathbf{R})$, in which \mathbf{R} is the internuclear distance vector. Since the adiabatic description contains first-order derivatives, it is numerically convenient to make a unitary transformation [5, 6], which is affected by the radial portion of $\underline{A}(\mathbf{R})$, to a diabatic representation

$$\underline{U}(R) = \underline{W}(R)[\underline{V}(R) - \underline{P}(R)]\underline{W}^{-1}(R) \quad (3)$$

where $\underline{U}(R)$ is the diabatic potential matrix, $\underline{V}(R)$ is the diagonal adiabatic potential, μ is the reduced mass, $\underline{W}(R)$ is an appropriate unitary transformation matrix, and

$$\underline{P} = \frac{1}{\mu R^2} \sqrt{J(J+1)} \underline{A}_\theta \quad (4)$$

where J is the total angular momentum. In this description, transitions are driven by the off-diagonal elements of $\underline{U}(R)$.

In all of our calculations to date, except for the newest work on $\text{B}^{2+} + \text{H}$ and $\text{O}^{3+} + \text{H}$, the rotational coupling term \underline{P} was deemed unimportant at low energies for the particular systems being studied. We do not include the so-called electron translation factor (ETF), which was originally introduced by Bates and McCarroll [7] to correct for non-zero long-range couplings

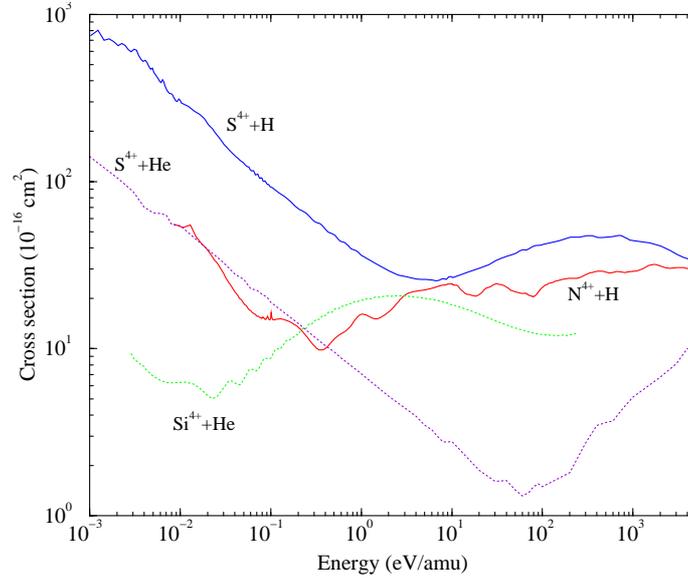


Figure 1: Comparison of SCVB-MOCC results of SEC for $q = 4$ systems. See the text for cross section references.

between dipole-connected states and also for other perceived defects of the PSS formulation. One such supposed defect arises from the well-known origin-dependence of the radial coupling matrix element \underline{A}_R (or $\partial/\partial R$), but Zygelman et al. [5] were able to show that the computed final cross sections should be invariant to such a change of origin. Effects due to ETFs and due to any neglected rotational couplings are expected only to be important for $E > 1$ keV/u, but must ultimately limit the range of validity of our calculations.

The charge transfer cross section is given by

$$\sigma_{i \rightarrow f}(E) = \frac{\pi}{k_i^2} \sum_J (2J + 1) |\underline{S}_J|_{i,f}^2 \quad (5)$$

where the S -matrix is

$$\underline{S}_J = [\underline{I} + i\underline{K}_J]^{-1} [\underline{I} - i\underline{K}_J]. \quad (6)$$

and \underline{I} is the identity matrix. The K -matrix is obtained from the scattering amplitude after a partial wave decomposition [5]. The coupled scattering equations are integrated using the log-derivative method of Johnson [8].

4 Survey of charge transfer calculations

Combining the SCVB approach with our implementation of the quantal MOCC method, a number of multi-charged, multi-electron heavy ion collisions with H and He have been investigated.

Figures 1 through 4 summarize the total cross sections for the systems studied. We find good agreement with other reliable theoretical and experimental data, where available, as discussed in the original publication for each collision system. While we present here only the total cross sections, state-selective cross sections are also generated by our method. Relatively little reliable experimental data are available at the state-selective level. One exception is the $N^{4+} + H$ system, for which recent experimental measurements are in excellent agreement with our calculations [9]. In our recent work on S^{4+} , we have gone to considerable pains to assess the accuracy of the state-selective cross sections by means of comparisons with other theoretical methods.

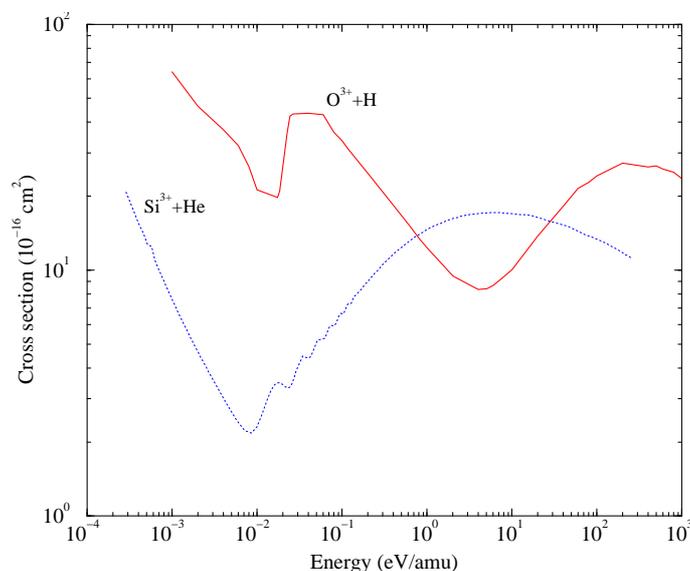


Figure 2: Same as Figure 1, but for $q = 3$.

Various equicharged systems are compared in Figures 1 through 3. A number of simple analytical models (for example the classical over-the-barrier (COB) and Born-Lindhard models; see [10]) suggest that the cross sections depend only on the projectile charge and on the neutral target ionization potential for intermediate- to high-collision energies. As a result, the total charge transfer cross section from an equicharged system is often adopted in the place of missing data. If this proved accurate at all energies, then there would be little need for elaborate calculations, as described here. However, such a procedure is questionable, at best, at intermediate energies and it fails at low-energies. This low-energy failure of scaling-laws tends not to be appreciated by modelers who adopt them for applications such as fusion devices or astrophysical environments. The error involved in adopting the same cross section for equicharged systems is illustrated in Figure 1 for $q = 4$, the largest charge considered to date by our group. Cross sections for the $N^{4+} + H$ [5, 11, 12] and $S^{4+} + H$ [13] systems agree to within a factor of two for $E > 10$ eV/amu,

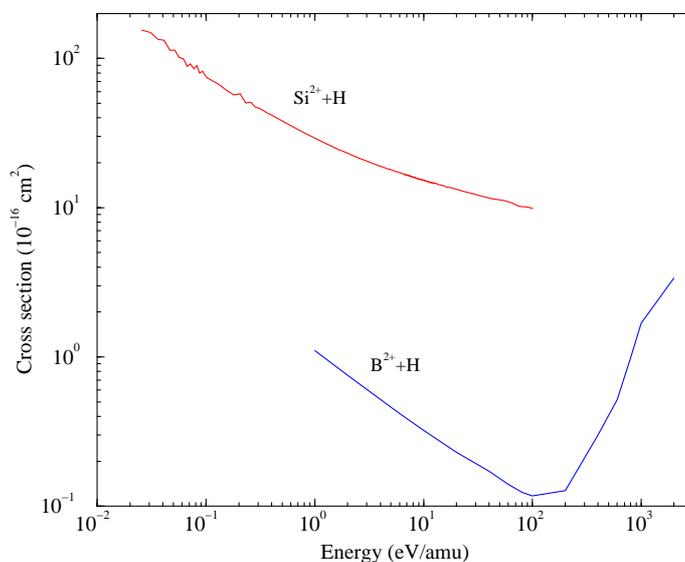


Figure 3: Same as Figure 1, but for $q = 2$.

but they rapidly diverge for smaller energies. The disagreement is even worse for the He target systems $\text{Si}^{4+} + \text{He}$ [14] and $\text{S}^{4+} + \text{He}$ [15]. The differences in low-energy equicharged cross sections is further illustrated in Figure 2 for $q = 3$ where we compare $\text{O}^{3+} + \text{H}$ [16] with $\text{Si}^{3+} + \text{He}$ [17] and in Figure 3 for $q = 2$. At 100 eV/amu, the $\text{Si}^{2+} + \text{H}$ [18] cross section is nearly two orders of magnitude larger than that of $\text{B}^{2+} + \text{H}$ [19].

The comparison in Figure 4 of the charge sequence $\text{Si}^{3+} + \text{He}$ and $\text{Si}^{4+} + \text{He}$ with SCVB-MOCC appears to confirm the COB prediction that the cross section should increase with q . This trend is further confirmed by a semiclassical MOCC calculation for $\text{Si}^{2+} + \text{He}$ by Suzuki et al. [20], which finds the cross section to be considerably smaller, at least over the energy range shown in Figure 4, since the reaction is endoergic by 8.24 eV and by the multichannel Landau-Zener calculation of Tawara et al. [21] for Si^{5+} . The measurements of Tawara et al. [21] for Si^{3+} , Si^{4+} , and Si^{5+} with He hint at a positive q -scaling, but the energy range of the experiments correspond to the region where all the cross sections have a similar magnitude.

5 Summary and future directions

Single electron capture (SEC) in collisions of multiply-charged multielectron ions with atomic neutrals is important in a range of astrophysical and laboratory plasma environments. Particularly in the low energy regime, simple scaling laws do not apply, and explicit calculations are required for each collision-partner pair. Our own implementation of an *ab initio*, fully-quantal combined

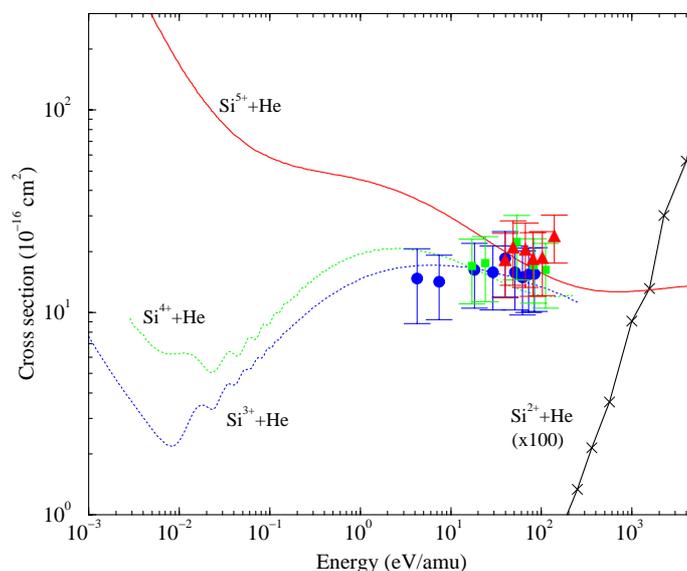


Figure 4: Comparison of SEC results for collisions of Si^{2+} , Si^{3+} , Si^{4+} , and Si^{5+} with He. SCVB-MOCC: Si^{3+} , Stancil et al. [17] and Si^{4+} , Stancil et al. [14]; semiclassical MOCC: Si^{2+} , Suzuki et al. [20]; and multichannel Landau-Zener: Si^{5+} , Tawara et al. [21]. Experiments of Tawara et al. [21]: Si^{3+} , blue circles; Si^{4+} , green squares; and Si^{5+} , red triangles.

SCVB-MOCC approach has proved particularly successful for studies of this type of system. The calculations reveal a rich and varied low-energy dependence even for the total SEC cross sections, as exemplified here for collisions of selected boron, nitrogen, oxygen, silicon and sulfur ions with neutral H or He targets.

We are currently working on extending our method to study fine-structure effects, to incorporate radiative effects (i.e., radiative charge transfer) in a unified approach, and to deal with molecular targets such as H_2 . In the latter case, we consider the vibrational degree-of-freedom in the spirit of the infinite-order sudden approximation, resulting not only in electronic-state-selective results, but also in molecular target (H_2) and product (H_2^+) vibrationally-resolved cross sections. Additionally, it would be worthwhile to continue our studies of the target isotope effect [3], not addressed here, to the isotopomers of H_2 . Finally, we intend to extend the applicability of our approach to higher energies by including ETF effects and by accounting for the continuum channel, the neglect of the latter being a well-know failing of the MOCC approach at higher energies.

Acknowledgments

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