

Extension of model potential methods to treat charge transfer in open shell systems. Application to the Si^{3+}/He , He^{2+}/He (2^1S) and He^{2+}/He (2^3S) systems

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Abstract

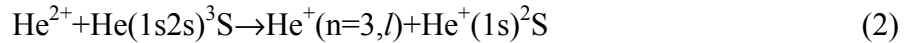
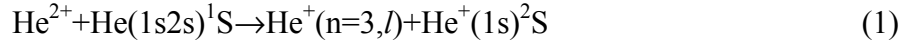
Charge transfer reactions in ion-atom collisions are investigated theoretically for systems involving open-shell configurations. Both model potential and *ab-initio* methods are used to treat the adiabatic states of the collision complex. A quantum mechanical treatment of the collision dynamics is used. Electron capture cross sections for two representative systems (He^{2+} in collision with either 2^1S or 2^3S metastable He and for Si^{3+} with ground state He) are calculated in the eV-keV energy range.

1. Introduction

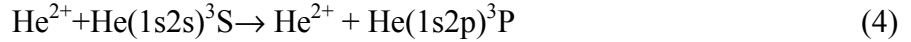
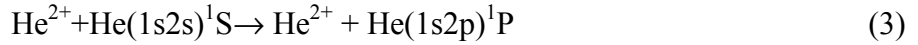
Model potential methods have proved very successful in the theoretical treatment of the dynamics of charge transfer by multiply charged ions A^{q+} from atomic H targets. Experiments show that these methods are excellent not only for closed shell ions such as C^{4+} , N^{5+} , O^{6+} , Al^{3+} , Si^{4+} and Ar^{8+} [1-6] but also for closed sub-shells such as N^{3+} , Si^{2+} and Ar^{6+} [7,8]. Basically, the reason is that charge transfer occurs at relatively large internuclear distances, primarily by electron capture into excited Rydberg states of $\text{A}^{(q-1)+}$. As a consequence, the ionic core A^{q+} plays a passive role and its effect can often be adequately described by an effective (or model) potential. This greatly simplifies the computation of the network of adiabatic molecular potentials (and non-adiabatic matrix elements) of the collision complex. For ions with charge $q \geq 2$ charge units, such networks reveal a finite number of effective avoided crossings, which control the charge transfer process. And since the non-adiabatic coupling is dominant only in the vicinity of avoided energy crossings, a fairly small (usually less than 10) basis set of adiabatic states is sufficient to describe the charge transfer process (at least for $q \leq 6$). With a simple modification [8], the model potential methods can also be adapted to deal with a restricted class of two active electron systems involving single electron capture from ground state He targets. Systems such as Si^{4+}/He and Ar^{6+}/He have been successfully treated in this way [8, 9]. In this presentation, we consider an extension of the model potential approach to treat systems in which either the ion or the neutral target has an open-shell configuration. We shall consider two such systems, which are representative of two different types of processes. The first involves capture by a structureless ion from a neutral target in an excited open-shell configuration, the second capture by an open-shell ion from a ground state neutral target.

1.1 He²⁺/metastable He

One of the simplest (and most instructive) examples of single electron capture from an excited neutral target is that of He²⁺ ions in collision with neutral He in an excited metastable state. The conversion of He²⁺ to He⁺ by charge exchange in collisions with ground state He is inefficient for energies below 10 keV/amu, the most favourable reaction at lower energies being double electron capture (which of course leads to no net change in the ionic abundance). On the other hand, it is expected that He²⁺ can easily capture an electron from metastable He, leading to the production of two singly charged He⁺ ions. From elementary considerations based on the over-barrier model [10], electron capture takes place mainly to the n=3 quantum level of He⁺ according to reactions [12]



Because of the proximity of the excitation channels corresponding to the (1s2p) configuration of He, it is also necessary to take account of the excitation processes



These reactions occur in the vicinity of avoided crossings of the adiabatic energies of the collision complex He₂²⁺ at internuclear distances beyond 10 a₀. An accurate description of the adiabatic potentials of the excited states of the He₂²⁺ system is therefore required. Some simplification can of course be expected since for internuclear distances greater than about 5a₀, the overlap of the 1s orbital centred on different nuclei is negligible.

Calculations by Fritsch [11] would suggest that the cross section for the single electron capture for electron capture from the metastable He (2¹S) state attains cross sections of the order of 10⁻¹⁴ cm² at an energy of 4 keV/amu.

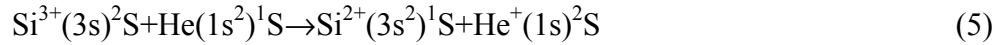
Since the He₂²⁺ system only involves two electrons, it is fairly straightforward to carry out an accurate configuration interaction calculation of the adiabatic potentials. It therefore provides an ideal testing ground for a model potential approach, which is considerably easier to implement than a full *ab-initio* calculation. In order to obtain the correct asymptotic energy limits of both the singlet and triplet channels, it is necessary to introduce spin dependent potentials. Of course, the introduction of such spin dependent potentials has been used before, but the procedure has never really been tested in a rigorous way.

1.2. Si³⁺/He

The Si³⁺/He system is a typical example of capture by an open shell ion from a ground state atom. This system has been the subject of several extensive theoretical investigations [13,14] based on *ab-initio* calculations of the adiabatic potentials and non-adiabatic coupling matrix element of the Si³⁺/He system. The results of [14] are consistent with the measured

rate constant [15] of $6 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ at an effective temperature of 4000K. On the other hand, the results of [13] are a factor of 3 smaller at these low energies. We should remark, that in comparing theory with experiment, Si^{3+} is of particular interest for ion-trap experiments since it has no long-lived metastable states which might interfere with the interpretation of the ionic decay and its charge to mass (3/28) ratio avoids possible confusion with other contaminants.

The aim of the present work is to re-examine the theoretical calculations on the Si^{3+}/He system to analyse the difference between the different theoretical calculations. From the network of reaction channels in the Si^{3+}/He system [13,14] it is clearly established that at low energies, electron capture takes place primarily according to the reaction



via a $^2\Sigma$ avoided crossing with the entry channel at $6a_0$. All the calculations exhibit a well defined peak in the non-adiabatic radial coupling in the vicinity of the crossing. From the earlier calculations, it is seen that there is a maximum in the cross section for a centre of mass energy of around 17 eV (ion energy in the laboratory system of 120 eV). For higher energies, the calculated cross sections are not too sensitive to the height of the radial coupling peak value $A(R_x)$. But on the lower energy side of the Landau-Zener maximum, the cross section depends quite critically on $A(R_x)$. It may be remarked that as a general rule, $A(R_x)$ is related to the minimum energy separation Δ_x in the case of an isolated avoided crossing according to the formula

$$A(R_x) = (q-1)/2R_x^2 \Delta_x \quad (6)$$

The calculations [13] yield a minimum energy separation, which is not compatible with (6). So while the results of [13] are reliable for energies greater than a centre of mass energy of 10eV, they are susceptible to error at lower energies. On the other hand, in the calculations [14] the radial coupling peak and minimum energy separations are compatible with (6). Rather than attempt to refine the *ab-initio* calculations, we have opted in this work for a model potential method.

2. Methods

Both model potential and *ab-initio* methods have been used to calculate the adiabatic potential energies of the collision complex. In the model potential approach, an effective two-centre Hamiltonian is constructed from a superposition of the model potentials of the ionic core and the neutral atom. When one or both of the colliding partners have an open-shell configuration, the atomic (and/or ionic) model potentials are spin dependent and it may be necessary as in the case of electron capture by He^{2+} from metastable He, to make two separate calculations, one for the singlet series, the other for the triplet series. However, in the Si^{3+}/He system, the dominant reaction channel involves only capture to the ground singlet state of Si^{2+} and capture to the triplet states is negligible. For that reason it is only necessary to treat the

case of a model potential for the singlet series of Si^{2+} . The parameters used to describe the different potentials may be found in [16].

In the *ab-initio* calculations, the adiabatic energies are determined by standard variational techniques using a basis of Slater-type orbitals expressed in prolate spheroidal coordinates, (of the same type as in the model potential calculations). A complete configuration-interaction calculation using all the basis set orbitals is adopted. The main originality of our calculations arises from the method used to compute the bielectronic matrix elements [17].

Non-adiabatic matrix elements are calculated in a standard way and the transformation from an adiabatic to a diabatic basis set is carried out as described in [2], with Galilean invariance being insured by the introduction of appropriate reaction coordinates [18]. The coupled dynamical equations are solved in a fully quantum mechanical calculation.

Results and discussion

3.1. He^{2+}/He metastable

By and large, the *ab-initio* and model potential calculations are in excellent agreement both for the position and energy separations of the avoided crossings. The largest apparent difference concerns the position of the long distance singlet avoided crossing. It is seen from Table 1 that the error of the *ab-initio* calculation for the dissociation limit is about 0.25% in the singlet case and 0.05% in the triplet case. This is sufficient to explain the differences between the *ab-initio* and model potential determinations of the crossing radii. Since the model potential parameters are chosen to give the correct dissociation limit it is probable that the model potential results are more precise than the *ab-initio* results for both the position and energy separation of the avoided crossings. In any case, even without any adjustment of the dissociation limit, both the *ab-initio* and model potential calculations will yield very similar results for the collision process.

Table 1 Comparison of <i>ab initio</i> and model potential avoided crossing parameters for the system $\text{He}^{2+}/\text{metastable He}$					
		Model Potential		Ab-initio	
Symmetry	Crossing	$R_x(a_0)$	$\Delta_x(\text{eV})$	$R_x(a_0)$	$\Delta_x(\text{eV})$
Singlet	$\Sigma_1-\Sigma_4$	18.38	0.85	18.17	0.89
	$\Sigma_4-\Sigma_5$	11.45	0.58	11.55	0.57
Triplet	$\Sigma_1-\Sigma_4$	19.93	0.26	19.77	0.27
	$\Sigma_2-\Sigma_4$	10.83	0.18	10.84	0.16

In view of the excellent agreement of the model-potential adiabatic energies with the *ab-initio* calculations, we have chosen to calculate the non-adiabatic matrix elements using model-potential wave functions. This choice was dictated not only by the desire to simplify

the calculations. The main reason is that reactions (1-3) are governed by very long range interactions (avoided crossing radii in the range 10-20 a_0). Past experience with such calculations [19] indicate that, under such conditions, model potential techniques have the advantage, in that they guarantee the numerical accuracy of the matrix elements (within the physical limitations of the method). Another reason was the need to modify the adiabatic basis to take account of the lack of Galilean invariance of the standard scattering equations. One way to do so is to introduce appropriate reaction coordinates such that all non-adiabatic coupling terms vanish in the asymptotic limit. This procedure has given satisfactory results and we have been able to use the programme developed by Gargaud et al.[2] without any major modification.

The results for the electron capture and excitation cross sections are presented graphically in figures 1 and 2.

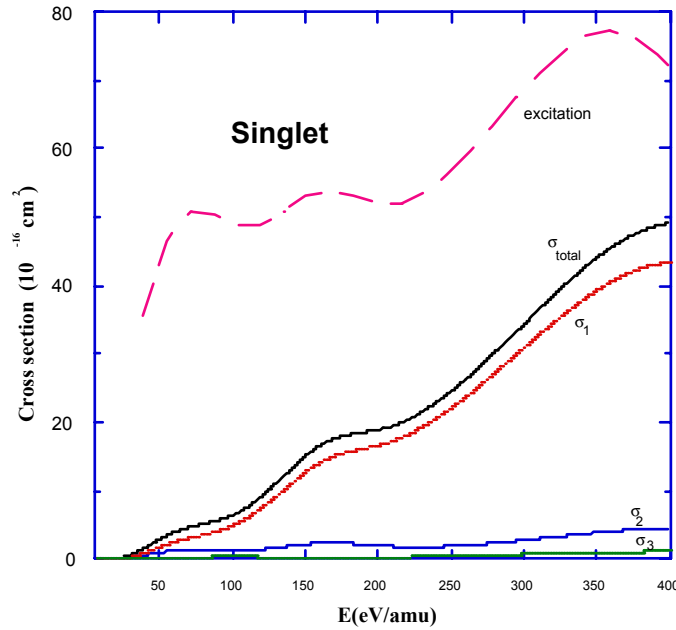


Figure 1. Cross sections in units of 10^{-16} cm^2 for electron capture and excitation in collisions of He^{2+} with $\text{He}(2^1S)$. The quantities σ_1 , σ_2 and σ_3 refer to electron capture into the individual Stark states of $\text{He}^+(n=3)$, σ_{total} designates the electron capture cross section summed over all Stark states and $\sigma_{\text{excitation}}$ designates the excitation cross section of $\text{He}(1s,2p)^1P$.

The most striking aspect of the results concerns the very different behaviour of the singlet and triplet systems. The onset of electron capture by He^{2+} from $\text{He}(2^1S)$ occurs at about 30 eV/amu and the cross section rises uniformly with increasing energy, attaining a value of about $5 \times 10^{-16} \text{ cm}^2$ at 400 eV/amu. Above 400 eV/amu, the cross-section levels off and it is reasonable to expect that our calculations are consistent with those of Fritsch [11] at energies above 4 keV/amu. The onset of electron capture by He^{2+} from $\text{He}(2^3S)$ occurs at much lower energies (about 1 eV /amu) and the cross section rises to a maximum of about $2 \times 10^{-14} \text{ cm}^2$ at a collision energy of 350 eV/amu.

One other notable feature concerns the excitation channels. The cross-section for excitation of $\text{He}(1s,2p)^1P$ in the singlet system is much larger than the electron capture cross-section, ranging from $5 \times 10^{-15} \text{ cm}^2$ at 60 eV/amu to a maximum of $8 \times 10^{-15} \text{ cm}^2$ at 350 eV/amu. The dominance of the excitation channel is also found in the calculations of Fritsch. On the other hand, excitation of the $\text{He}(1s,2p)^3P$ in the triplet system is negligible. The dominant electron capture channel for both the singlet and triplet systems is the Stark Σ state ($n_1=0, n_2=2$). The cross-section for electron captures to the Stark Σ state ($n_1=1, n_2=1$) is an order of magnitude smaller than the cross section for the dominant channel. Electron capture to the ($n_1=2, n_2=0$) Stark State is negligible.

It would be of great interest to have some experimental measurements on this relatively system involving collisions of He^{2+} with metastable He. The electron capture and excitation mechanisms are highly selective in the energy range below 1 keV/amu.

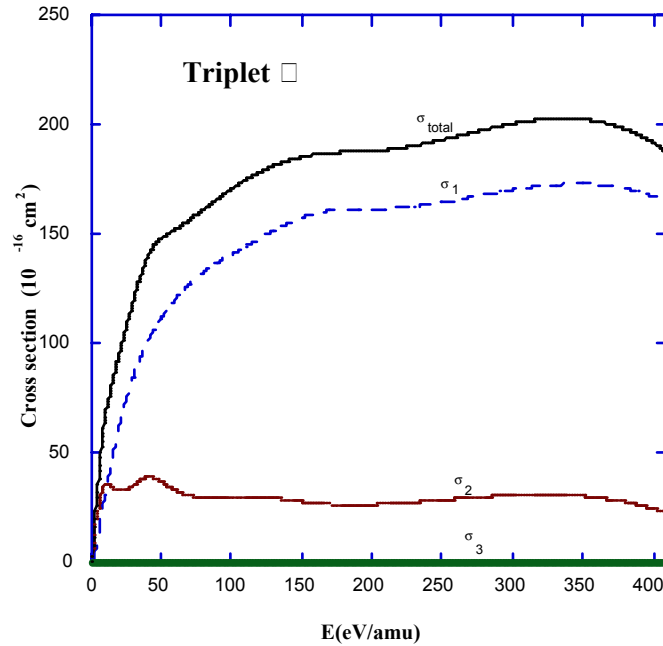


Figure 2. Cross sections in units of 10^{-16} cm^2 for electron capture and excitation in collisions of He^{2+} with $\text{He}(2^3S)$. The quantities σ_1 , σ_2 and σ_3 refer to electron capture into the individual Stark states of $\text{He}^+(n=3)$, σ_{total} designates the electron capture cross section summed over all Stark states. Excitation cross section of $\text{He}(1s,2p)^3P$ is negligible.

3.2. Si^{3+}/He

An indication of the accuracy of the model potential method can be ascertained by a comparison with [13, 14] for the location of the avoided crossing R_x , the minimum energy separation Δ_x in eV, and the peak of the radial coupling matrix $A(R_x)$ in a.u. Our calculations [14] are in satisfactory agreement with [14]. In [13], the peak intensity of the radial coupling appears to be a little too small.

Our calculated electron capture cross sections [16] are listed in table 3. A comparison of the results [13,14] is presented in graphical form in figure 3.

The rate constant k_{ct} for charge transfer has been calculated from the cross sections by averaging over a Maxwellian distribution of the collision partners. The results are presented in tabular form in Table (4) and in graphical form in figure (6), where a comparison is made with our theoretical and experimental values.

Table 2. Comparison of curve crossing parameters and maximum peak intensity of radial coupling			
	$R_x(\text{a.u.})$	$\Delta_x(\text{eV})$	$A_x(R_x) (\text{a.u.})$
Present work [16]	6.28	0.33	2.25
Honvault et al. [13]	6.00	0.25	1.80
Stancil et al. [14]	6.3	0.27	2.5

Table 3. Si^{3+}/He electron capture cross sections in units of 10^{-16}cm^2	
E(eV/amu)	Total cross section
0.039	4.28
0.078	5.73
0.155	7.92
0.233	9.96
0.582	13.5
1.25	16.0
2.50	16.8
4.36	16.8
10.0	15.3
22.5	12.9
40.0	11.1
125.0	7.83
187.9	6.98
250.0	6.49

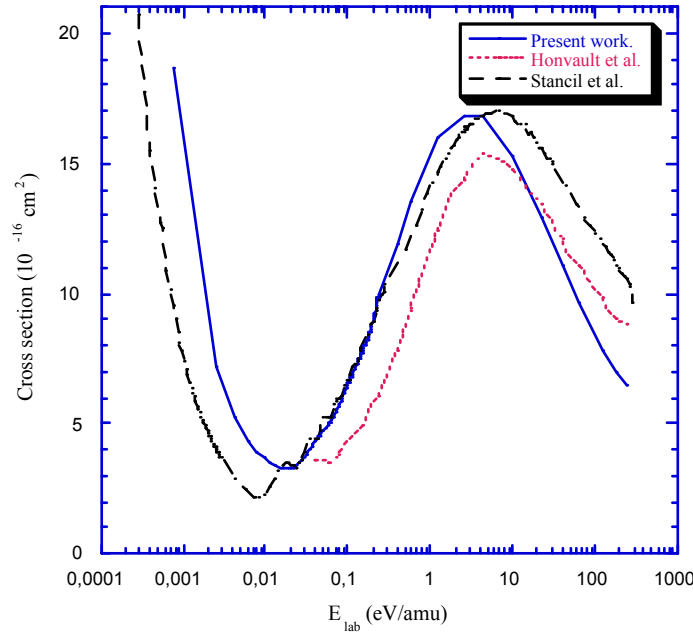


Figure 3. Si^{3+}/He total electron capture cross section (units of 10^{-16}cm^2) as a function of the ion energy in the laboratory system.

Table 4. Si ³⁺ /He electron capture rate coefficient (units of 10 ⁻⁹ cm ³ s ⁻¹)				
T(K)	Present work [16]	Stancil et al. [14]	Honvault et al. [13]	Fang et al. [15]
10	9.38×10 ⁻²	2.92×10 ⁻²		6 ×10 ⁻¹
50	6.44×10 ⁻²			
100	5.63×10 ⁻²			
200	5.51×10 ⁻²			
500	7.34×10 ⁻²	6.34×10 ⁻²	0.2×10 ⁻¹	
1000	1.17×10 ⁻¹	1.15×10 ⁻¹		
4000	4.09×10 ⁻¹	4.07×10 ⁻¹		
10000	9.10×10 ⁻¹	8.81×10 ⁻¹	4.8×10 ⁻¹	
30000	2.03	1.96	1.46	
50000	2.76	2.71	2.19	
100000	3.95	4.06	3.59	

In making a comparison between the different theoretical models, it should be borne in mind that our present calculations take no account of the influence of non adiabatic coupling with the excited $^2\Sigma^+$ state, whose asymptotic separated atoms corresponds to the $\text{Si}^{3+}(3p)^2P + \text{He}(1s^2)^1S$. This channel is closed for centre of mass energies less than 8 eV and in the thermal energy range of astrophysical interest (100-10⁵K), its influence is negligibly

small. Indeed the calculations [13] indicate that the two-state model should be valid up to energies of the order of eV/amu (well beyond the excitation threshold). For energies less than the excitation threshold of the $\text{Si}^{3+}(3p)^2P + \text{He}(1s^2)^1S$ a two-state model was used in [14]. In this energy range, where the cross section undergoes a strong variation with energy, their results are in excellent agreement with [15]. The discrepancy at very low energies (less than 0.01 eV) is of little physical significance. The upturn of the cross section at 0.02 eV/amu is an indication of a Langevin-type trajectory effect [5], which depends sensitively on very long-range interactions, which have not been optimised in our calculations. It would seem that the results of [13] are not reliable below 10 eV/amu).

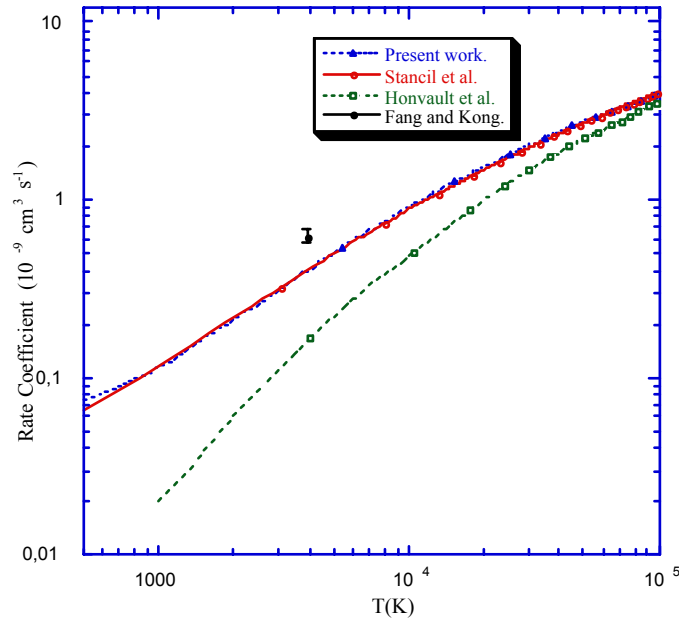


Figure 4. Si^{3+}/He charge transfer rate (units of $10^{-9} \text{ cm}^3 \text{ s}^{-1}$) as a function of temperature.

For energies above the excitation threshold a 5-state model was used in [14] and calculated cross sections tend to be larger than ours for energies greater than about 10 eV/amu. It is surprising that the difference with [14] should be so large, given that the two-state model is expected to be valid up to the highest energies presented in the Table 3.

Our calculated charge transfer rate constants [16] (for the whole range of temperatures studied) are in excellent agreement with [14] and they are also consistent with the experimental result [15] (bearing in mind the difficulty of defining the effective ion-trap temperature).

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