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Validity of the Langevin capture model for charge exchange processes at thermal energies

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Abstract

A detailed coupled state quantum mechanical calculation using an adiabatic basis is analysed to investigate the validity of the Langevin model for very low energy charge transfer processes in ion–atom collisions. Taking as an example the N^{3+}/H system, it is shown that the success of the Langevin model in describing the energy variation of the cross section is due to the accuracy of the phase averaging procedure in the double passage through the avoided crossing. On the other hand, the model does not yield the correct isotopic dependence of the cross sections. These can only be accurately determined by a coupled state calculation. At low thermal and sub-thermal energies less than 1 meV, the phase averaging procedure breaks down and quantum tunnelling effects become important. In these conditions, the energy variation of the cross section exhibits an appreciable departure from the Langevin model.

1. Introduction

The merged beam measurements of Pieksma *et al* [1] involving collisions of Si^{4+} ions with neutral D atoms show that for energies less than about 100 meV amu^{-1} the electron capture cross section exhibits an inverse velocity dependence, in accordance both with the coupled state calculations and with the Langevin capture model. However, the coupled state calculations predict that the electron capture cross sections for Si^{4+}+H should be a factor of 1.9 larger than for Si^{4+} + D, whereas the Langevin model predicts a factor of only 1.4. This disagreement is a strong indication that one or more of the assumptions of the Langevin model is of doubtful validity. If such is indeed the case, then it is of interest to understand why the Langevin model, which yields the correct inverse velocity dependence of the cross section in the 10–100 meV amu^{-1} energy range, does not predict the correct isotope dependence.

Other shortcomings of the Langevin model have been revealed by the recent calculations of Glassgold *et al* [2] concerning the determination of momentum transfer cross sections in H^++H collisions. While the Langevin model is satisfactory for energies above 10 meV, it is

less satisfactory for energies less than 10 meV, being at best a crude approximation down to energies of 0.1 meV. It fails for even smaller energies.

The Langevin model assumes that in an exothermic reactive collision between atomic systems with a given energy, the reaction takes place only for those collisions, for which the classical centrifugal barrier is less than the collision energy [3]. In the low collision energy range (typically of a few eV or less), this assumption is satisfactory for ion–neutral systems by virtue of the strongly attractive long-range interaction potential between the reactants, which varies as R^{-4} (where R is the ion–neutral distance). Most applications of the Langevin model also make the additional simplifying assumption that the reaction probability is constant for all effective collisions. For example, in the case of reactive ion–molecule collisions, this probability is often taken as unity, because of the large number of reactive channels. In the case, with which we are concerned in this work, namely charge transfer in ion–atom systems, there are only two coupled channels. Then, the charge transfer probability, while still assumed constant, is much smaller than unity. If the main concern is to determine how the cross section varies with energy, the absolute value of the probability is critical. But if absolute cross sections are required, it is necessary to estimate the probabilities with precision.

It is therefore clear that there are several sources of error in the Langevin model at very low energies. The most obvious is the incapacity of a classical (or semi-classical) description of the dynamics to correctly allow for quantum mechanical tunnelling effects. The coupled state calculations of McCarroll and Valiron [4, 5] and Rittby *et al* [6] on the N^{3+}–H system showed that resonant structures in the cross section do indeed occur at very low energies. These are related to the presence of quasi-bound states in the entry channel, which can tunnel through the centrifugal barrier. So, for any given collision energy, classically forbidden reactions can occur for angular momentum beyond the Langevin limit. But, while it is indeed found that for collision energies greater than a few meV, the contribution of classically forbidden reactions is appreciable, it is rarely of dominant importance. So, it is unlikely that any resonant structure can explain the isotope effect observed in the 10–100 meV range. A more probable source of error arises from the way the charge transfer probabilities are determined. These are often estimated by a Landau–Zener-type model together with some phase averaging procedure to take account of interference between different reaction paths [7, 8]. For energies greater than a few meV, the phase averaging procedure is satisfactory, but at energies less than a few meV, it may lead to a significant underestimation of the reaction rate [2].

In the coupled state calculations there is no need to make any of the simplifying assumptions commonly used in the Langevin model. But in view of its ease of application, especially to study systems for which the non-adiabatic interactions leading to charge exchange are not available, it is of some to understand more fully the conditions under which the Langevin model can be reliably used.

Recent calculations by Barragán *et al* [9] of the electron capture cross sections in collisions of O^{2+} and N^{2+} ions with atomic hydrogen had shown an even larger divergence of the Langevin capture model from the coupled states calculation. They find that in these systems, as in N^{3+}+H, the presence of resonance structures in the cross sections becomes increasingly important as the energy decreases below 10 meV amu^{-1} while, for energies exceeding 10 meV amu^{-1}, the contribution of the resonances to the total cross sections remains small. But even allowing for the presence of resonance structures, it would seem that the overall energy dependence of both the O^{2+}+H and N^{2+}+H cross sections does differ significantly from the Langevin model even in the 10–100 meV range.

In the calculations of Barragan *et al* [9], no simple pattern emerges for energies less than 10 meV. The resonance widths appear to be comparable with the energy scale and it becomes meaningless to attempt a separation of the resonance contribution from the background. Some

earlier calculations by the same authors [10] did suggest that at very low energy the charge transfer cross section attains a maximum. But more recent work [9] indicated that this may have been due to numerical errors and, when corrected, no maximum was observed.

Unfortunately, both the O^{2+}+H and N^{2+}+H systems are quite complex. The electron capture process takes place via avoided crossings which involve strong configuration mixing and the accuracy of even the best calculations cannot be guaranteed with absolute certainty. But aside from the problem of determining the non-adiabatic coupling in the vicinity of the avoided crossing regions, it is equally important to ensure an accurate representation of the long-range interaction between the ion and the neutral atom. At low meV energies, the R^{-4} dependence of this interaction in the asymptotic region governs the inverse velocity dependence of the cross section and the characteristics of the tunnelling resonances. For this reason, we propose to reinvestigate the electron capture cross section in the energy range 0.1–100 meV for the simpler N^{3+}H system. Apart from the fact that this system is fairly representative of a wide class of multiply charge ions in collision with a neutral atom, it has the advantage that the interaction potentials and the non-adiabatic matrix elements are known with precision over the entire range of internuclear distances, which control the charge transfer process.

Atomic units will be used throughout except where otherwise stated.

2. Method

The adiabatic states intervening in the electron capture process can be accurately generated by a one-electron model [11], in which the $N^{3+}(1s^2 2s^2)\,^1S$ ion core is represented by an effective potential of the form

$$V_{N^{3+}}(r) = -\frac{1}{r}[3 + (4 + 0.4608r)\exp(-2.422r)]. \tag{1}$$

This potential has been optimized to reproduce the spectroscopic energies of the ensemble of ground and excited states of $N^{2+}(1s^2 2s^2 nl)$ to within a few meV. Taking the N nucleus as A and the H nucleus as B, the electron Hamiltonian is then given by

$$H_e = T + V_{N^{3+}}(r_a) - \frac{1}{r_b} + U_{core} \tag{2}$$

where T is the electronic kinetic energy, r_a, r_b are the radial distances of the electron from nuclei A and B, respectively. The core–core interaction is designated by U_{core}. Since the electron capture process is governed by the non-adiabatic interactions for large internuclear distances, it is sufficient for all practical purposes to approximate U_{core} by the nuclear repulsion term, namely

$$U_{core} = \frac{3}{R}. \tag{3}$$

The eigenenergies E_i and eigenvectors $|\chi_i\rangle$ of the Hamiltonian (2) are determined for a range of R by a standard variational method using a set of monoelectronic Slater orbitals $|\upsilon\rangle$, expressed in prolate spheroidal coordinates $\lambda = (r_a + r_b)/R$, $\mu = (r_a - r_b)/R$. In the low energy regime with which we are concerned, only two $^2\Sigma$ states, designated as Σ_1, Σ_2, are involved in the charge exchange process [4]. There is a well-defined avoided crossing around $9a_0$ with a minimum energy separation of 0.3 eV. For the charge transfer to occur at very low energies, special conditions are required. The energy gap at avoided crossing must be neither too large nor too small for the electron capture probability to be significant. For systems such as N^{3+}/H, involving a single molecular orbital (Type I), favourable avoided crossing are located at distances between about 7 and $12a_0$, while for systems such as O^{2+}/H, involving two molecular

orbitals (Type II), favourable crossings are located at somewhat shorter distances (between 4 and $10a_0$). In the case of the N^{3+}/H system, both the entrance channel N^{3+}+H(1s) and the electron capture channels $N^{3+}(1s^22s^23s)^2S+H^+$ are correlated to a $^2\Sigma$ state. These are labelled, respectively, as $2^2\Sigma$ and $1^2\Sigma$ states. The non-adiabatic coupling between these two states is of radial type. Detailed results of the adiabatic potential curves and of the non-adiabatic coupling matrix elements have been given in [4].

The non-adiabatic radial matrix elements are generated from the eigenvectors $|\chi_i\rangle$ expressed in terms of the Slater-type orbitals as follows:

$$|\chi_i\rangle = \sum_j C_{ij}(R)|\upsilon_j\rangle \tag{4}$$

where the column vectors of the matrix $\mathbf{C}$ are the eigenvectors of H_e. The radial coupling matrix elements may then be written as

$$\left\langle \chi_i \left| \frac{\partial}{\partial R} \chi_j \right\rangle = \sum_{kl} C_{il}(R) \left\{ \left[\frac{dC_{jk}}{dR} \right] \langle \upsilon_l | \upsilon_k \rangle + C_{jk} \left\langle \upsilon_l \left| \frac{\partial}{\partial R} \upsilon_k \right\rangle \right\} . \right. \right. \tag{5}$$

In the energy range investigated in this work, it is quite satisfactory to use the standard definition of the non-adiabatic coupling, in which the radial derivative $\partial/\partial R$ in (5) is taken with respect to the centre of mass of the nuclei. However, we have also carried out some calculations with the reaction coordinate formalism [12] in which the radial derivative $\partial/\partial R$ is replaced by

$$\frac{\partial}{\partial R} + \frac{z}{R}\frac{\partial}{\partial z} \tag{6}$$

where the origin of coordinates is located at any arbitrary point on the internuclear axis and z is the projection of the electron on this axis. However, for the energy range of interest in this work, there is no real need to introduce reaction coordinates. Indeed, for energies less than a few eV, all coordinate systems give the same result (see section 3).

The different integrals appearing in (5) or with the operator (6) can be evaluated analytically, while the derivative of the C_{ij} matrix elements are calculated numerically using the finite difference formula

$$\frac{dC_{ij}(R)}{dR} = \frac{C_{ij}(R+\delta R) - C_{ij}(R-\delta R)}{2\delta R}. \tag{7}$$

In the calculations, a value of $\delta R = 10^{-3}a_0$ was found to be satisfactory.

The wavefunction of the collision system is then written in the form

$$\psi(\mathbf{r}, \mathbf{R}) = \sum_{j=1}^{2} F_j(\mathbf{R})\chi_j(\mathbf{r}, R). \tag{8}$$

Substituting (8) into the Schrödinger equation we obtain a system of coupled partial differential equations, which, in matrix form, can be written as

$$\left[\nabla^2_{\mathbf{R}} + 2m_{a,b}\{E_T\mathbf{I} - \mathbf{E}(R)\}\right]\mathbf{F}(\mathbf{R}) = [\mathbf{Q}(\mathbf{R}) + \mathbf{P}(\mathbf{R}) \cdot \nabla_{\mathbf{R}})]\mathbf{F}(\mathbf{R}) \tag{9}$$

where E_T is the relative kinetic energy and $\mathbf{E}$ is a diagonal matrix, whose elements are the adiabatic energies

$$E_{ij}(R) = E_j(R)\delta_{ij}. \tag{10}$$

The matrix elements of $\mathbf{Q}$ and $\mathbf{P}$ involve the non-adiabatic coupling terms

$$Q_{ij}(R) = -\int \chi_i^*(\mathbf{r}, R)\nabla^2_{\mathbf{R}}\chi_j(\mathbf{r}, R)\, d\mathbf{r} \tag{11}$$

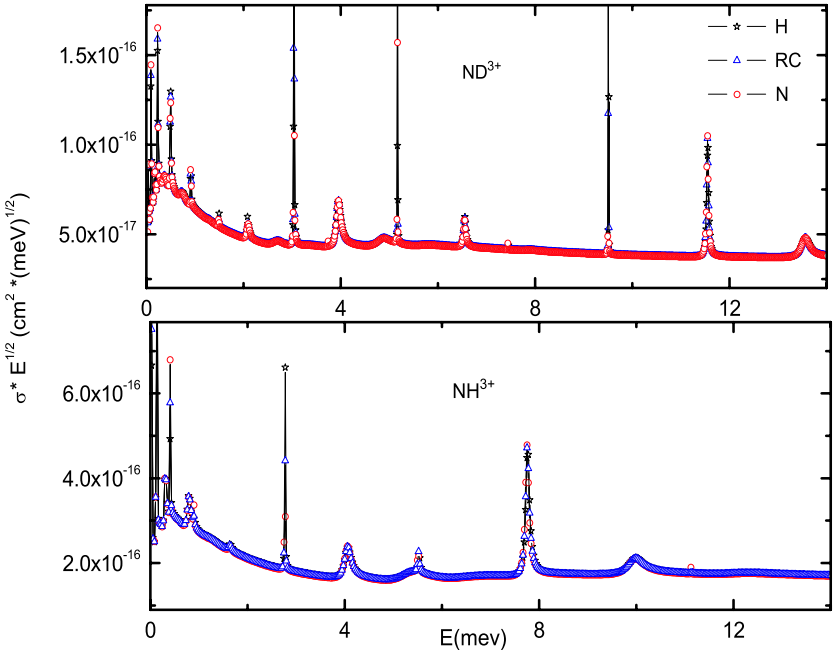

Figure 1. Variation of the charge exchange cross-section σ as a function of the centre of mass energy E for the N^{3+}/H, D systems. In order to facilitate comparison with the Langevin model, the quantity plotted is $\sigma\sqrt{E}$ in units of $cm^2(meV)^{1/2}$. Calculations have been performed using both reaction coordinates (triangle), coordinate origin on H (or D) atom (star) or coordinate origin on N (circle).

(This figure is in colour only in the electronic version)

$$P_{ij}(R) = -2\int \chi_i^*(\mathbf{r}, R)\nabla_{\mathbf{R}}\chi_j(\mathbf{r}, R)\,\mathrm{d}\mathbf{r}. \tag{12}$$

Standard procedures are used to obtain the dynamical equations for a fully quantum mechanical description of the nuclear motion. As in most other calculations of this kind, there is a considerable practical advantage in making an adiabatic–diabatic transformation [13] which removes the first derivative terms from the equations reducing them to a set of coupled second-order differential equations with no first-order derivative. Standard numerical techniques based on log derivative methods [14, 15] are used to solve these equations and extract the elements of the S-matrix.

It should be remarked that at these very low energies, it is very important to ensure an accurate description of the very long-range interaction in the entry channel. This does not raise any serious problem in our work since our calculated potential converges smoothly to the polarization potential $-q^2\alpha/R^4 = -20.25/R^4$.

3. Results

In figures 1 and 2, we present the total cross sections for the N^{3+}+H and N^{3+}+D systems. Results for the coupled two-state adiabatic expansion are given both for the standard adiabatic variables, which do not describe the exact asymptotic conditions, and for a system of reaction coordinates [12], which do allow for a correct description of the asymptotic conditions.

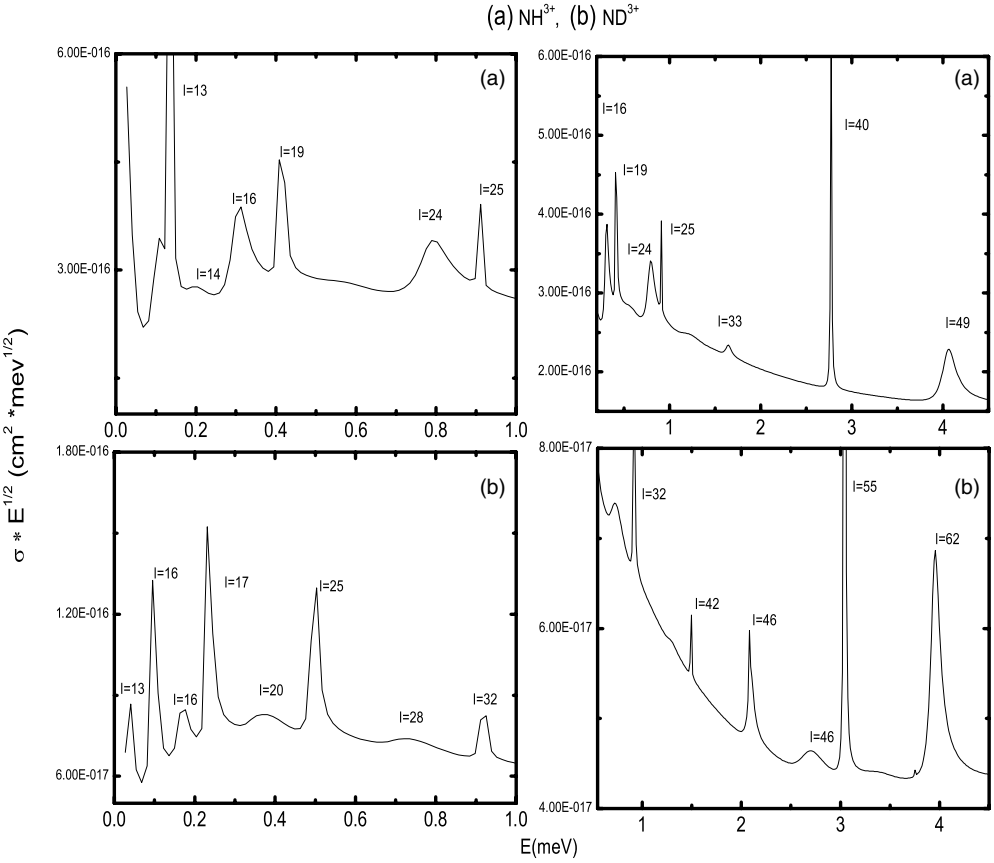

Figure 2. Variation of the quantity $\sigma\sqrt{E}$ (see caption of figure 1) with E in the range 0.003–4 meV. The labels used to identify the resonance peaks designate their angular momentum. It may be observed that these resonance peaks correspond to quantum tunnelling through the centrifugal barrier.

In order to facilitate the comparison of the coupled state calculations with the Langevin model, the cross sections have been multiplied by $E^{1/2}$. Their most striking feature is the presence of a number of well-identified (and stable) resonance peaks. For energies in excess of a few meV, these resonances are well localized and few in number. But their overall contribution to the cross section is quite small for energies above a few meV and can be considered separately. So, except for these specific resonance energies, it is found that the cross section does indeed vary as $E^{1/2}$ for both isotopic systems, just as predicted by the Langevin model.

Another general result is that the use of standard adiabatic variables is quite satisfactory throughout the energy range investigated. The only observable influence of reaction coordinates concerns the height of the some of the resonance peaks, but their position is unchanged.

But, the main apparent weakness of the Langevin model stems from its failure to describe correctly the isotopic dependence of the N^{3+}+H and N^{3+}+D cross sections. Two effects contribute to the isotope effect. Firstly, the range of angular momentum leading to charge exchange is governed by the long-range potential, which results in a cross section inversely

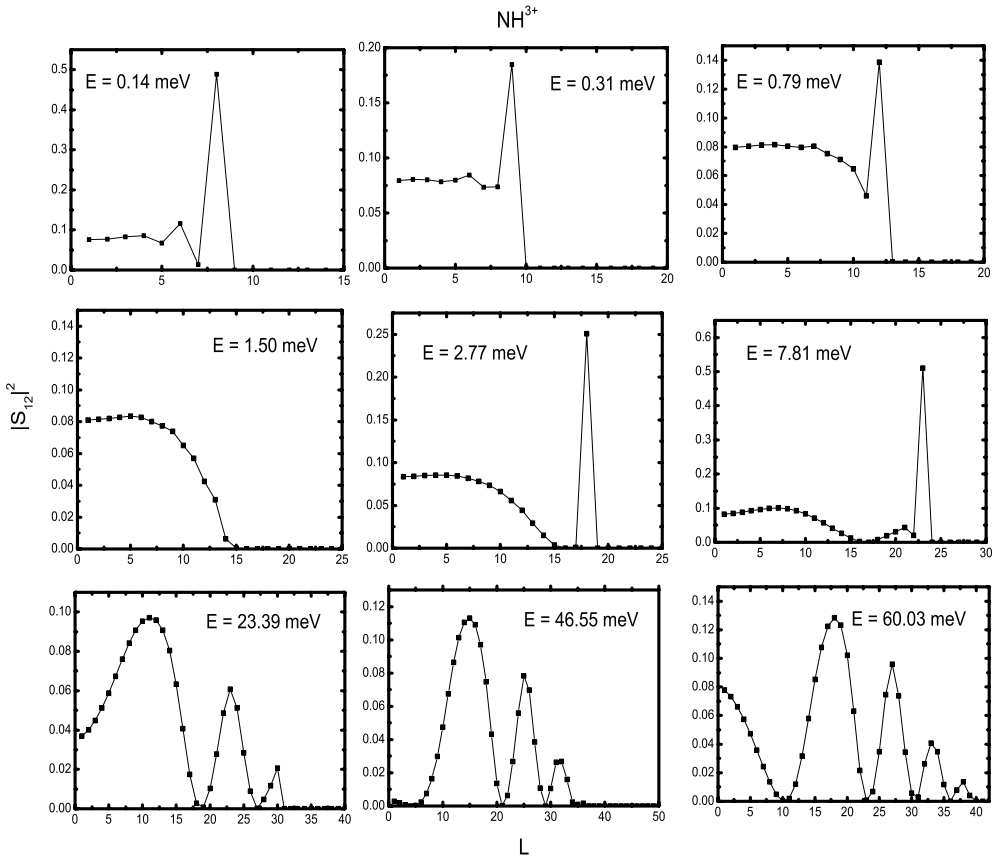

Figure 3. Variation of the N^{3+} + H charge exchange probability $|S_{12}^{L}|^2$ plotted as a function of the angular momentum quantum number L for several centre of mass energies in the 1–100 meV range.

proportional to the square root of the reduced mass. This effect is correctly taken account of in the Langevin model. Secondly, the charge transfer probability depends on the mass-dependent non-adiabatic coupling in the vicinity of the avoided crossing. This second effect is calculated correctly in the coupled state method but, in the Langevin model, it is estimated in an approximate way. So it is not surprising that the isotopic dependence of the cross section is not well described. On the other hand, since the charge transfer probability (when averaged over angular momentum) is independent of energy, the Langevin model does indeed yield the correct energy variation of the cross section for a given isotope. However, implicit assumptions made in the averaging procedure need to be examined. In the coupled state calculations, the charge transfer probability oscillates as a sinusoidal function of the angular momentum. For energies above 10 meV, the usual averaging procedure is surprisingly accurate but as the energy decreases below 10 meV the frequency of the oscillations decreases and at very low energies the probability exhibits a monotonic variation with the angular momentum quantum number L. Under these conditions, the averaging procedure is unsatisfactory. But since no very simple pattern emerges from the total cross section results, it is of interest to present a partial wave analysis of the coupled state results, which makes it possible to separate the various factors which govern the total cross section.

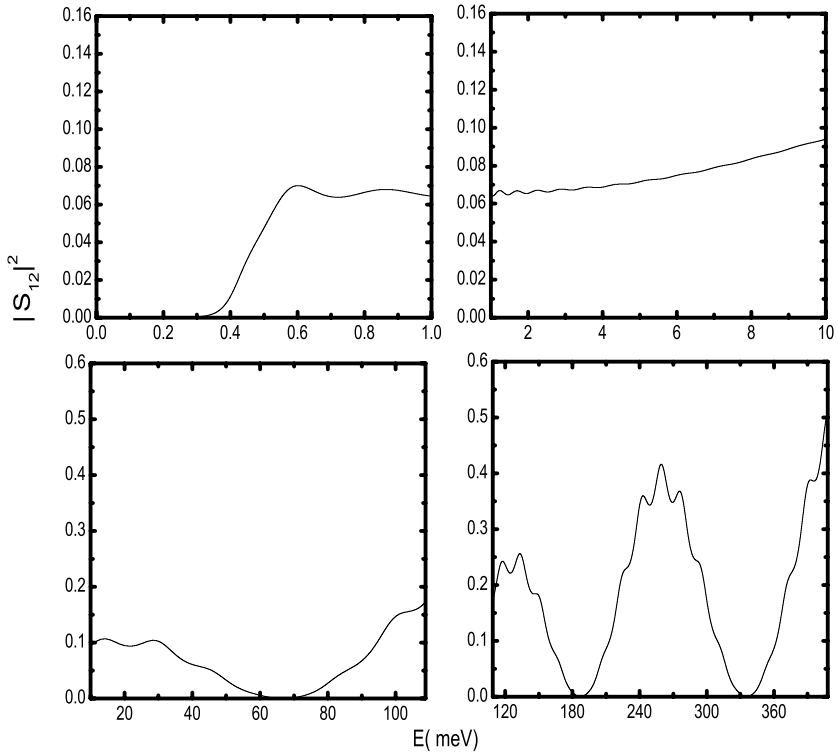

Figure 4. Variation of the N^{3+} + H charge exchange probability $|S_{12}^L|^2$ plotted as a function of the centre of mass energy E in the 1–400 meV range for the angular momentum quantum number $L = 10$.

In figure 3, we present a representative sample of $\left|S_{12}^L\right|^2$ where $S_{i,j}^L$ is an element of the S-matrix for the angular momentum quantum number L. The total cross section is then given by

$$Q_{12} = \sum_{L=0}^{\infty} (2L+1)\left|S_{1,2}^L\right|^2. \tag{13}$$

If we identify $(L + 1/2)$ with the semi-classical quantum angular momentum, S_{12}^L can be considered as corresponding to the semi-classical charge transfer probability of the Langevin formula. The maximum value $L = L_c$, determined from the classical centrifugal barrier is given by

$$L_c + \frac{1}{2} = \sqrt{2mE}\left(\frac{81}{E}\right)^{1/4} = 3\sqrt{2m}E^{1/4}. \tag{14}$$

From these results, it is observed that since quantum tunnelling is only efficient near the maximum of the centrifugal barrier, there is, in general, only one value of the angular momentum where there is a strong resonance. It occurs for the first value of L exceeding L_c. The height and width of the resonance depend of course on the barrier height, which will vary with the collision energy. But, in general, it is possible to isolate the (non-classical) resonance contribution from the classically accessible contribution for $L < L_c$. And, if the resonance contribution is excluded, the close coupled and Langevin models are in excellent agreement for energies greater than about 4 meV.

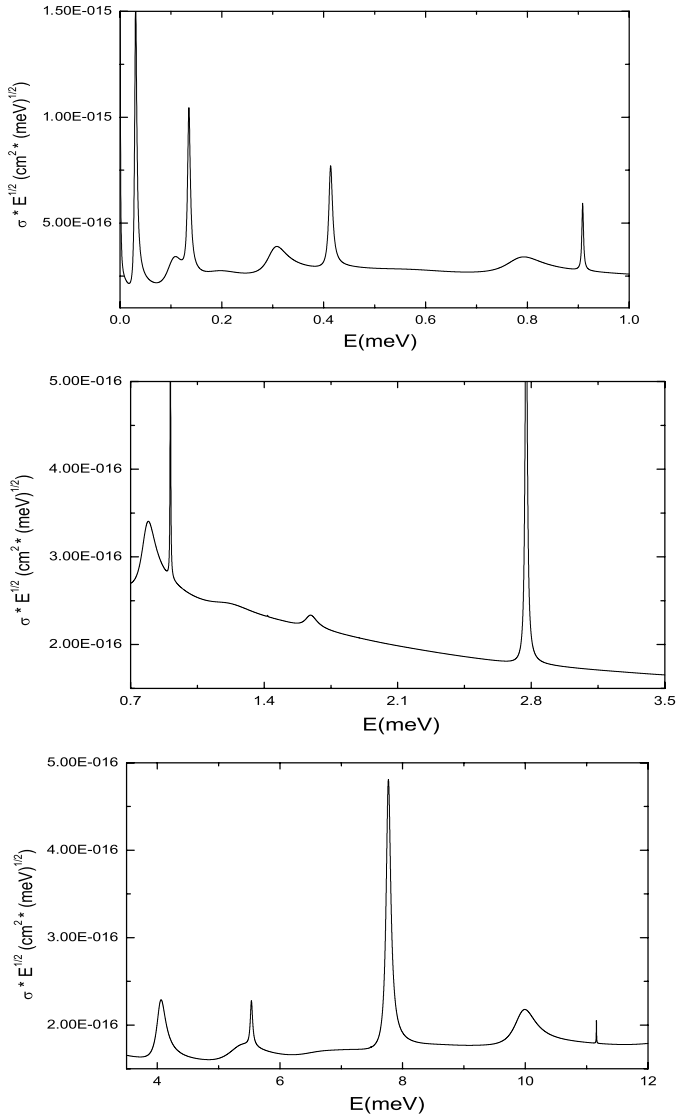

Figure 5. Detailed behaviour of the N^{3+} + H charge exchange cross sections in the centre of mass energy range from 0 to 12 meV. The existence of an intermediate regime between 1 and 4 meV indicates the breakdown of the phase averaging procedure used in the Langevin model to sum over angular momentum (see the text for discussion).

It is seen from figure 3 that for collision energies exceeding a few meV, the probability $\left|S_{12}^{L}\right|^2$ oscillates as a function of L. For example, at an energy of 23 meV, there are three peaks fairly evenly spaced between 0 and L_c. This oscillatory behaviour is quite regular and is characteristic of a Landau–Zener-type avoided crossing, arising from the phase difference of the two reaction paths leading to charge transfer. When summed over L, these oscillations average out to give a total probability fairly independent of energy. So, the notion of a constant probability in the Langevin model remains valid.

However, we see that the notion of a constant mean probability for $L < L_c$ is manifestly not the case for exceedingly low energies less than about 1 meV. Then, the probability

oscillations disappear. The probability is fairly constant for small values of L and then decreases monotonically to L_c. For example, at an energies around 0.1 meV, the charge transfer probability for the N^{3+}/H system is about 0.08 for $0 < L < 10$, then decreasing uniformly to zero for $L = L_c = 14$. The corresponding probability for the N^{3+}/D system is much lower, about 0.015. It is therefore clear that at these very low energies, the averaging procedure used implicitly in the Langevin LZ model will underestimate the cross section. This is borne out by the results of the coupled states calculation.

In figure 4, we present an alternative illustration of $\left|S_{12}^{L}\right|^2$ to show its variation with the collision energy for a given value of L. For example, for $L = 10$, we observe the existence of a threshold energy around 0.4 meV, caused by the centrifugal barrier. Of course, this threshold will vary with L. For energies above threshold, the charge transfer probability becomes an oscillatory function of the energy.

In figure 5, a detailed presentation of the total cross sections is shown for an extended range of energies from 0.1 to 12 meV. It covers three distinct regimes. For collision energies down to about 4 meV, the quantity $\sigma\sqrt{E}$ is practically constant around 1.7 cm^2 (meV)$^{1/2}$, indicating that the phase averaging procedure of the Langevin model is valid. But, between 4 and 1 meV, $\sigma\sqrt{E}$ increases, attaining a higher plateau of about 3.5 cm^2 (meV)$^{1/2}$ at around 1 meV, which remains constant as E decreases. This behaviour is due to the breakdown of the phase averaging procedure around a few meV. So between 1 and 4 meV, no simple procedure is satisfactory for approximating the sum of the probabilities over the angular momentum. However, for very low energies below 1 meV, the charge exchange probability no longer oscillates and, aside from the resonance contribution, $\sigma\sqrt{E}$ is practically independent of the angular momentum up to the critical Lanevin value. This explains the existence of a second plateau of $\sigma\sqrt{E}$ at very low energies below 1 meV.

Of course, the resonance contribution to these very low energy (<1 meV) cross section is much larger than at higher energies in the meV range. But in this case, the resonance contribution is quite distinct. The reason is that resonances are controlled by the long-range interaction and tunnelling through the centrifugal barrier, while the phase averaging effects are governed by the non-adiabatic interaction in the region of the avoided crossing.

4. Conclusion

In conclusion, our calculations show that while the Langevin model does indeed give an excellent prediction of the energy variation of the charge transfer cross section down to energies of a few meV for any given isotope, it does not provide accurate value of the cross sections. For this reason, it does not give the correct isotopic dependence of the cross section. The main reason stems, not from any major defect of the Langevin capture model as such, but from the way the charge transfer probability in the avoided crossing region has been determined. For example, the use of the Landau–Zener approximation introduces errors in the determination of the isotope effect. And the phase averaging often used in summing over partial wave amplitudes introduces errors in the sub-thermal regime.

The effect of quantum mechanical tunnelling through the centrifugal barrier close to maximum is also absent from the Langevin model but the resonances are governed by the long-range interaction and their influence can be accurately calculated. Besides, the overall resonant contribution is not appreciable at energies exceeding 10 meV.

So, aside from the very low thermal energy range where the effect of quantum tunnelling needs to be explicitly included, the remarkable success of the phase averaging procedure

explains why the Langevin model is predicting the correct energy variation of the cross section (even though the absolute value may be in error).

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