

LETTER TO THE EDITOR

Quasi-molecular binding corrections to the two-state atomic expansion method for electron capture at low energies†

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Abstract. The two-centre, two-state atomic expansion method previously developed for calculating electron capture cross sections for ion-atom collisions at intermediate energies is generalised to the lower energy region. By replacing the asymptotic energy defect term between initial and final states of the atomic expansion theory by the difference of the corresponding quasi-molecular energies, the effect of transient molecule formation during the collision is partially accounted for. The increased quasi-molecular binding at small internuclear separation has the effect of reducing electron capture cross sections at *lower incident energies*; the cross sections thus calculated show improved agreement with experimental data.

In a previous letter (Lin 1978), we showed that electron-capture cross sections for ion-atom collisions are well predicted by the simple two-centre, two-state atomic expansion (TSAE) method if the projectile velocity v is comparable to the orbital velocity v_k of the target electron to be captured. By examining the region of validity of the two-state atomic expansion method, it was concluded that the method gradually becomes inadequate as v deviates from v_k . Crucial test of the deviation of the theory on the high energy side ($v > v_k$) is hampered by the scarcity of reliable experimental data. However, in the lower energy region (typically $v/v_k \lesssim 0.5$), systematic studies of electron-capture cross sections for various combinations of projectiles and targets are becoming available (Tawara *et al* 1978), thus permitting a more careful examination of the deviation of the theory.

As the projectile velocity v deviates from v_k toward the adiabatic limit $v = 0$, it is well known from the early work of Massey and Smith (1933) that slow ion-atom or atom-atom collisions are better described in terms of transient molecules. In this model, the electrons follow their molecular orbitals adiabatically throughout the collision. Electronic transitions (including charge transfer) occur only at values of R , the internuclear separation, where the non-adiabatic coupling term is significant. On the other hand the mechanism for inelastic transitions at higher energies ($v \gg v_k$) is treated differently: the electrons are not fast enough to follow the motion of the projectile and their motion is assumed to follow primarily their atomic states in the separated-atom limit throughout the collision. Electronic transitions are due to the perturbing Coulomb interaction between the projectile nucleus and target electrons.

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At the lower end of the intermediate energy region (typically $0.5 \geq v/v_k \geq 0.1$), both the molecular and atomic descriptions in the previous paragraph are not valid. Extension of the molecular orbital theory to this energy region is complicated by the large number of molecular potential curves and coupling terms that has to be included (Winter and Lane 1978). On the other hand, the high-energy plane-wave Born approximation (PWBA) and the semiclassical approximation (SCA) for direct Coulomb ionisation processes have been modified to account for the increase of quasi-molecular binding energy (Basbas *et al* 1973) for slow ion-atom collisions in this energy region. In this article, we elucidate the structure similarity between the two-state atomic and two-state molecular expansion; the effect of quasi-molecule formation is then introduced into the TSAE theory. This modified TSAE theory is used to compute electron-capture cross sections at lower energies and the results are compared with experimental data.

Following our earlier work on the TSAE approximation (Lin *et al* 1978, Lin 1978), we adopt an independent electron approximation for the multi-electron ion-atom collisions by considering only the active electron involved in the capture process. The motion of this electron is governed by the time-dependent Schrödinger equation

$$H\psi(r, t) = i \frac{\partial}{\partial t} \psi(r, t) \quad (1)$$

where the electronic Hamiltonian is

$$H = -\frac{1}{2}\nabla^2 - \frac{Z_A}{r_A} - \frac{Z_B}{r_B}, \quad (2)$$

with $Z_A(Z_B)$ the effective charge of the target (projectile) and $r_A(r_B)$ the distance of the electron from the target (projectile). By expanding $\psi(r, t)$ in terms of travelling atomic basis functions and including only the initial state centred at A and the final state centred at B , a set of coupled equations in the TSAE approximation is obtained (Lin *et al* 1978)

$$\begin{aligned} id_A &= \frac{(h_{AB} - S_{AB}h_{BB})}{1 - S^2} e^{i(\omega t + \delta)} d_B \\ id_B &= \frac{(h_{BA} - S_{BA}h_{AA})}{1 - S^2} e^{-i(\omega t + \delta)} d_A \end{aligned} \quad (3)$$

where d_A and d_B are the elastic and charge transfer amplitude respectively. The matrix elements S_{ij} , and h_{ij} ($i, j = A, B$) are defined explicitly in Lin *et al* (1978) and $S^2 = S_{AB}S_{BA}$; the energy defect ω is defined as $\omega = E_A - E_B$ with E_A and E_B the binding energy of the electron before and after the capture, respectively. The distortion δ is given by

$$\delta = \int_{-\infty}^t \left(\frac{h_{AA} - S_{AB}h_{BA}}{1 - S^2} - \frac{h_{BB} - S_{BA}h_{AB}}{1 - S^2} \right) dt. \quad (4)$$

It is to be recognised that each term in the integrand of (4) represents the amount of distortion of the potential experienced by the active electron due to the projectile or the target nuclear field. To see this, we note that in the limit $v = 0$, the approximate molecular potential curves $U(R)$ of H of equation (2) can be obtained by the method

of linear combination of atomic orbitals (LCAO). By expanding the static electronic wavefunction as

$$\psi(\mathbf{r}, R) = a(R)\psi_A + b(R)\psi_B \quad (5)$$

where ψ_A and ψ_B are the atomic wavefunctions centred around the two nuclei, it is straightforward to show that $U(R)$ satisfies

$$\begin{bmatrix} E_A + (h_{AA} - S_{AB}h_{BA})/(1 - S^2) & (h_{AB} - S_{AB}h_{BB})/(1 - S^2) \\ (h_{BA} - S_{BA}h_{AA})/(1 - S^2) & E_B + (h_{BB} - S_{BA}h_{AB})/(1 - S^2) \end{bmatrix} \begin{bmatrix} a \\ b \end{bmatrix} = U(R) \begin{bmatrix} a \\ b \end{bmatrix}. \quad (6)$$

By comparing the diagonal matrix elements in (6) with the integrand of (4), we see the exponential term in (3) represents the time integral of the difference of two potentials calculated in the *diabatic* atomic basis. The off-diagonal terms in (6) occur in the coupling terms of (3) which determine the transition from one state to the other.

The success of TSAE implies that the collision is well represented by the *diabatic* approximation in the atomic basis when the collision velocity is $v \sim v_k$. As the projectile velocity v decreases, the orbital electron has time to adjust its motion with respect to the changing Coulomb field due to the projectile nucleus, thus a non-*diabatic* (adiabatic) modification of (3) is necessary. Since the coupling term in (3) is dominated by the oscillatory exponential term, an initial approximation to the adiabatic correction is to replace the exponents of (3) by the time integral of the *adiabatic molecular potential curves* calculated from the Hamiltonian (2). We thus propose to extend the TSAE theory to the lower energy region by replacing the exponent $(\omega t + \delta)$ of (3) by the time integral of the difference of the corresponding two adiabatic molecular potential curves which dissociate to E_A and E_B respectively in the asymptotic limit. This modification is expected to be more important for collisions at small impact parameters, corresponding to small R , where the diabatic potential curves in the atomic basis (the diagonal terms of (6)) differ more significantly from the adiabatic molecular potential curves. On the other hand, the molecular curves in the large R region are well represented by the LCAO approximation and the adiabatic correction introduced will not change the transition probabilities for large impact parameters significantly.

The importance of quasi-molecular binding correction for electron capture at low values of v/v_k can be seen from figure 1. In figure 1, we show the K-shell electron-capture cross sections of Si atoms to the K-shell of F^{9+} ions in the energy region from 400 KeV/amu to 2.4 MeV/amu, corresponding to v/v_k from 0.34 to 0.84. The experimental data are taken from Tawara *et al* (1978). Notice the TSAE predictions (the full curve) agree well with experimental data at the high energy side, but deviate substantially (up to a factor of 10) from experimental values in the low energy region. By including the quasi-molecular binding correction (the broken curves), the cross sections in the low energy region are significantly reduced, in much better agreement with experimental data.

To see the origin of the large reduction of capture cross sections at small incident energies, we show in figure 2 the impact parameter dependence of $\rho P(\rho)$, the product of impact parameter ρ and the capture probability $P(\rho)$ per target K-shell electron, as a function of ρ for three energies. Notice that $\rho P(\rho)$ is reduced significantly for small impact parameters in calculations which adopt binding energy correction (the broken curves), as compared with the normal TSAE calculations (the full curves). The

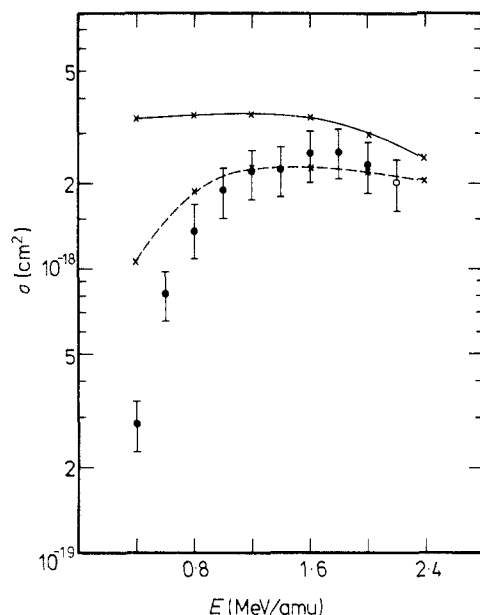


Figure 1. The electron-transfer cross sections from the Si K-shell to the F^{9+} projectile K-shell as a function of the projectile energy. The experimental cross sections are from Tawara *et al* (1978). The theoretical predictions based upon the two-state atomic expansion (TSAE) are given by full curves, the results with quasi-molecular binding energy correction are given by broken curves.

change in $P(\rho)$ at large impact parameters is small, especially for the higher collision energies. In all the calculations we use the experimental K-shell binding energy for Si. The effective charges used are $Z_A = 13.6875$, $Z_B = 9$ in the TSAE calculations; on the other hand, in the adiabatic potential curves, Z_A is chosen to be $(2E_k)^{1/2}$, where $E_k = 67.58$ au is the Si K-shell binding energy. This latter choice ensures the molecular curves computed from the Hamiltonian (2) converge to the correct

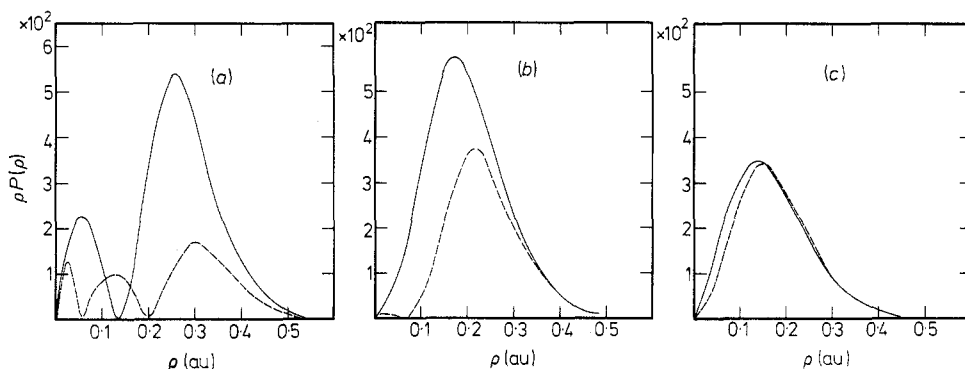


Figure 2. $\rho P(\rho)$ per target Si K-shell electron as a function of ρ for three different impact energies of F^{9+} , (a) 400 KeV/amu; (b) 1200 KeV/amu; (c) 2400 KeV/amu. The full curves are from the usual TSAE calculations and the broken curves are results with binding energy corrections.

experimental dissociation energy E_A and E_B at large R . The adiabatic potential curves are obtained from the computer program developed by Power (1973)†.

The difference in $P(\rho)$ in the two calculations is determined primarily by the difference in the oscillatory exponential terms in (3). The argument of the exponent can be rewritten as an integral over R ,

$$\frac{1}{v} \int_{\rho}^{R_{\infty}} dR (U_A - U_B) R / \sqrt{R^2 - \rho^2} \quad (7)$$

where U_A and U_B are either the diagonal terms of (6) in the TSAE calculations or the adiabatic potential curves when a binding energy correction is included. At large values of R , the two sets of potential curves do not differ appreciably, thus the transition probabilities at large ρ are nearly identical. On the other hand, the difference in the two sets of potentials at small R results in the difference in $P(\rho)$ for small ρ 's. Since the argument of the exponential term of (3), as given in (7), is inversely proportional to v , the oscillation of the exponential term is more rapid for small v , thus the modification of $P(\rho)$ at small v is more drastic, resulting in large changes in capture cross sections.

In summary, from the result of figure 1, we conclude that it is important to include the binding energy increase due to quasi-molecule formation in slow ion-atom collisions in the theory of electron capture in this energy region. The *ansatz* introduced in this article extends the validity region of the TSAE theory to lower collision energies for ion-atom collisions.

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† The one electron diatomic molecule (ONDM) program developed by Power is available from the Quantum Chemistry Program Exchange, Chemistry Department, Indiana University, Bloomington, Ind. 47401, USA.