

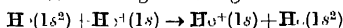
Use of diabatic and adiabatic representations in three-state close-coupled calculations of He⁺-He resonant charge exchange collisions

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The symmetric resonant charge exchange collision



has been considered within the laboratory ion energy range 100-3000 eV in a semiclassical three-state close-coupled approximation in the diabatic and adiabatic molecular representations, the latter being obtained by a unitary transformation of the former. The nuclear motion is treated classically using the impact parameter method, while the electronic motion is treated quantum-mechanically. Within the inherent limitations of the diabatic representation chosen, the two sets of calculations yield identical results. The diabatic equations are very nearly decoupled but still show a significant effect of the coupling between the two lowest ²Σ_g states of He₂⁺ at low energies. The agreement with experiment is found to be very good. Relative merits and demerits of the use of diabatic and adiabatic representations in atomic collision problems as evidenced by this work are discussed.

1. INTRODUCTION

In a previous paper (Bhattacharyya & Raj Dastidar 1975), to be referred to as I, we reported our calculations of He⁺-He charge transfer probability in diabatic and adiabatic representations in the decoupled approximation. The term *Diabatic* was used in the sense as defined by Smith (1969), i.e. the radial component of the nuclear momentum coupling between two electronic states was taken to have vanished identically. From the correlation diagram of He₂⁺ (Fig 1 in I) where only the three lowest states are shown, it is seen that the ²Σ_g state degenerate with the ground ²Σ_u state crosses another ²Σ_g state going over to the excited He*(1s2s) + He⁺(1s) separated-atom limit, and hence the inelastic transition He(1s²) → He(1s2s) competes with the elastic (direct or charge exchange) channels at all energies above the threshold. (Actually the lowest state (state 2) is crossed by an infinite number of states (Lichten 1963, Barat *et al* 1972), as a consequence of which a number of inelastic channels are opened up.) In I we neglected the coupling between those two ²Σ_g states and sought to assess the

relative utility of the decoupled diabatic and adiabatic representations in the He^+-He charge exchange collision problem.

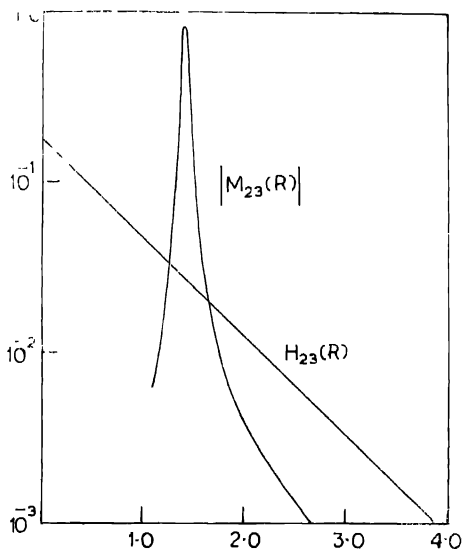


Fig 1 Diabatic coupling term $H_{23}(R)$ and adiabatic coupling term $M_{23}(R)$, the latter at $E_{lab} = 1000$ eV, $b = 1.0 a_0$.

In the present work we have extended the earlier calculations to take into account the coupling between the two ${}^2\Sigma_g$ states. In the diabatic representation the two potential curves cross, and the coupling is provided by the off-diagonal potential matrix element, whereas in the adiabatic representation the crossing is avoided and the coupling occurs via the relative nuclear motion. We have in general restricted ourselves to impact parameters $\geq 1a_0$ and as such ignored the effects of the ${}^2\Sigma_u-{}^2\Pi_u$ and ${}^3\Sigma_g-{}^2\Pi_g-{}^2\Delta_g$ rotational couplings (cf Barat *et al* 1972, Fig 1) which have been shown to excite the $1s \rightarrow 2p$ and higher inelastic transitions and to influence the resonant charge transfer probability in high-energy close collisions (McCarroll & Piacentini 1971, Barat *et al* 1972). Our treatment has been semiclassical, in the sense that we have treated the electronic motion quantum-mechanically and the nuclear motion classically (Nikitin 1968).

Atomic units are used throughout except where otherwise stated.

2. THEORY

The Schrödinger equation for a system of nuclei and electrons is given by

$$i \frac{\partial}{\partial t} \Psi(\mathbf{r}, \mathbf{R}) = H \Psi(\mathbf{r}, \mathbf{R}) \quad \dots (1)$$

where \mathbf{r} is the combined electronic coordinate and \mathbf{R} the nuclear coordinate; $H = H_{el} + (\mathbf{p}_{nu} \mathbf{p}_{nu})/2\mu$, where H_{el} is the electronic Hamiltonian with fixed nuclei including the internuclear Coulomb repulsion, \mathbf{p}_{nu} the relative nuclear momentum and μ the reduced nuclear mass. Spin-orbit interactions and relativistic effects are ignored.

For the nuclear motion we define a classical trajectory of the form $\mathbf{R} = \mathbf{R}(t)$ pertinent to the collision problem. The time-dependent Schrödinger equation for the electronic motion is then

$$i \frac{\partial}{\partial t} \psi(\mathbf{r}, \mathbf{R}(t)) = H_{el} \psi(\mathbf{r}, \mathbf{R}(t)) \quad \dots (2)$$

(Nikitin 1968, Wilets & Wallace 1968)

We now introduce a real, 3-state orthonormal series expansion

$$\Psi(\mathbf{r}, \mathbf{R}(t)) = \sum_{l=1}^3 c_l(t) \psi_l(\mathbf{r} \cdot R) \quad \dots (3)$$

where the set of electronic wavefunctions ψ_l constituting the molecular representation contains the internuclear distance R parametrically, and all phase factors are included within the c_l 's. Substitution of eq (3) in eq (2) leads to the set of coupled equations

$$i \dot{c}_k = \sum_l c_l \left\langle k \left| H_{el} - i \frac{\partial}{\partial t} \right| l \right\rangle \quad \dots (4)$$

In the impact parameter approximation the classical nuclear trajectory is given by

$$\mathbf{R} = \mathbf{b} + \mathbf{v}t \quad \dots (5)$$

where \mathbf{b} is the impact parameter; assuming azimuthal symmetry, and putting $z = vt$,

$$\frac{\partial}{\partial t} = \frac{vz}{R} \frac{\partial}{\partial R} + \frac{vb}{R^2} \frac{\partial}{\partial \theta} \quad \dots (6)$$

The states 1, 2 and 3 are the $^2\Sigma_u$ and the two $^2\Sigma_g$ states respectively as marked in figures 1 of I. In a coordinate frame rotating with the internuclear line,

the second term on the right side of eq. (6) corresponds to rotational coupling between states of electronic angular momenta differing by ± 1 , and thus does not contribute to the Σ - Σ coupling. Consequently the coupled equations become, in matrix notation,

$$i\dot{c} = (H+M)c \quad \dots (7)$$

where c is a column matrix and H and M are square matrices

$$H_{kj} = \langle k | H_{el} | j \rangle$$

$$M_{kj} = \frac{vz}{R} \left\langle k \left| -i \frac{\partial}{\partial R} \right| j \right\rangle = \frac{vz}{R} (P_R)_{kj} \quad \dots (8)$$

Properties of the matrix $P = \langle | p_{nu} \rangle$ have been discussed in detail by Smith (1969). We make use of the following three properties

$$(i) \quad P_{ll} = 0, \quad \text{all } l \quad \dots (9)$$

$$(ii) \quad P_{kl} = -P_{lk}, \quad l \neq k \quad \dots (10)$$

(iii) Under a unitary transformation C , P transforms as

$$P' = C^{-1}PC + C^{-1}(p_{nn}C) \quad \dots (11)$$

Since state 1 has u -symmetry and states 2 & 3 have g symmetry, it is obvious that $P_{12} = P_{13} = 0$. A further simplification is now introduced by putting $H_{12} = H_{13} = 0$, which is obviously justified except at very small distances where the impact parameter approximation does not hold anyway. Thus in the diabatic representation the coupled equations reduce to

$$i\dot{c}_1 = c_1 H_{11}$$

$$i\dot{c}_2 = c_2 H_{22} + c_3 H_{23}$$

$$i\dot{c}_3 = c_2 H_{23} + c_3 H_{33}. \quad \dots (12)$$

Denoting the adiabatic energies by E_1, E_2, E_3 and making use of eqs (9) and (10), the corresponding adiabatic equations are seen to be

$$i\dot{c}_1 = c_1 E_1$$

$$i\dot{c}_2 = c_2 E_2 + c_3 M_{23}$$

$$i\dot{c}_3 = -c_2 M_{23} + c_3 E_3 \quad \dots (13)$$

The states 1 and 2 are degenerate at large R corresponding to the initial channel $\text{He}_A(1s^2) + \text{He}_B^+(1s)$, and for our present problem also to the final channel $\text{He}_A^+(1s) + \text{He}_B(1s^2)$. Thus in either set of equations

$$|c_1(-\infty)| = \frac{1}{\sqrt{2}}, \quad |c_2(-\infty)| = \frac{1}{\sqrt{2}}, \quad c_3(-\infty) = 0 \quad \dots (14)$$

An elementary LCAO expansion of the molecular wavefunction at large R shows that the probability of electron transfer from atom A to atom B is given by

$$P = \frac{1}{2} |c_2(\infty) - c_1(\infty)|^2 \quad \dots \quad (15)$$

3. DETAILS OF CALCULATIONS

Henceforward we denote the coefficients in eq (3) by c_i in the diabatic representation and by a_i in the adiabatic representation. The first of equations (12) is uncoupled, its solution being

$$c_1(t) = c_1(-\infty) \exp(-i \int_{-\infty}^t H_{11} dt) \quad \dots \quad (16)$$

To find the charge transfer probability P we need solve the second and third of eqs. (12) for c_2 subject to the initial boundary condition (14) and the unitarity condition

$$|c_1|^2 + |c_2|^2 + |c_3|^2 = 1, \text{ i.e. } |c_2|^2 + |c_3|^2 = \frac{1}{2}, \text{ all } t. \quad \dots \quad (17)$$

We choose $c_2(t)$ and $c_3(t)$ to have solutions of the form

$$c_j(t) = C_j(t) \exp(-i \int_{-\infty}^t H_{jj} dt), \quad j = 2, 3 \quad \dots \quad (18)$$

This changes eqs. (12) into the form

$$i\dot{C}_2 = C_3 H_{23} \exp[i \int_{-\infty}^t (H_{22} - H_{33}) dt] \quad \dots \quad (19)$$

$$i\dot{C}_3 = C_2 H_{23} \exp[-i \int_{-\infty}^t (H_{22} - H_{33}) dt]$$

Similarly for the adiabatic case the coupled eqs. (13) give

$$a_1(t) = a_1(-\infty) \exp(-i \int_{-\infty}^t E_1 dt) \quad \dots \quad (20)$$

and the coupled equations

$$i\dot{A}_2 = A_3 M_{23} \exp[i \int_{-\infty}^t (E_2 - E_3) dt] \quad \dots \quad (21)$$

$$i\dot{A}_3 = -A_2 M_{23} \exp[-i \int_{-\infty}^t (E_2 - E_3) dt]$$

Eqs. (19) and (21) were converted into a more suitable form for numerical solution by changing the time-dependence to z -dependence, and were solved by the fourth-order Runge-Kutta method. Following Nikitin (1968) the lower limit of the phase integrals were changed from $-\infty$ to a definite instant of time, $-\tau_0$ which was sufficiently removed from the point/s of stationary phase and where the oscillations were sufficiently rapid to decouple the equations.

The diabatic potential matrix elements of He_2^+ as given by Olson (1972) had been used in I as an approximation to the "standard" diabatic potentials. Since the phases of oscillations of the charge transfer probability in I agreed quite well with the experimental results of Nagy *et al* (1971) and Erikson *et al* (1972), we used the same representation in this work. Certain limitations of this representation became evident in the course of the work, and will be discussed presently. For $H_{11}(R)$ we used the potential given by Gupta & Matson (1967).

The adiabatic energies and the radial coupling term M_{23} were obtained via a unitary transformation of the diabatic representation by a matrix of the form

$$C = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos \alpha & \sin \alpha \\ 0 & -\sin \alpha & \cos \alpha \end{pmatrix} \quad \dots \quad (22)$$

Since C diagonalizes H ,

$$E_1 = H_{11}, \quad \text{and} \quad \alpha = \frac{1}{2} \text{arc tan} \left(\frac{2H_{23}}{H_{33} - H_{22}} \right). \quad \dots \quad (23)$$

Further, since $(P_R)_{adta} = 0$, relation (11) yields

$$(P_R)_{adta} = C^{-1} \left(-i \frac{\partial}{\partial R} C \right) \quad \dots \quad (24)$$

and hence

$$(M)_{adta} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & -i \\ 0 & i & 0 \end{pmatrix} (vz/R) \frac{\partial \alpha}{\partial R} \quad \dots \quad (25)$$

Also, from (23),

$$\frac{\partial \alpha}{\partial R} = \frac{1}{2u^2} \left(H_{23} \frac{\partial H_d}{\partial R} - H_d \frac{\partial H_{23}}{\partial R} \right),$$

where

$$u^2 = H_d^2(R) + H_{23}^2(R), \\ H_d(R) = \frac{1}{2}[H_{22}(R) - H_{33}(R)].$$

Calculations were done using double precision arithmetic on an IBM 370/155 computer. The Runge-Kutta step width (along z) was adjusted by trial so that (i) an accuracy upto six significant figures, in many cases even more, was achieved in the values of $|A_2|^2$, $|A_3|^2$, $|C_2|^2$ and $|C_3|^2$, and (ii) the unitarity condition was satisfied to within an error bound $\leq 2-3$ parts in 10^6 (For energies < 200 eV

this error sometimes grow as high as 1 part in 10⁴; however, for $b > R_0$, it never exceeded 1 part in 10⁶.) Test calculations by using a value of t_0 twice as large reproduced the P -values upto an accuracy of 4-5 decimal figures, proving convincingly the decoupling of the equations beyond $|t| = t_0$

The charge transfer probability in the decoupled approximation were also calculated from the formulas

$$P_{dt\alpha} = \sin^2 \frac{1}{2}\theta_{21}, \quad P_{adt\alpha} = \sin^2 \frac{1}{2}\phi_{21} \quad \dots \quad (26)$$

where

$$\theta_{21} = \int_{-\infty}^{\infty} (H_{22} - H_{11}) dt, \quad \phi_{21} = \int_{-\infty}^{\infty} (E_2 - E_1) dt.$$

The difference potential was fitted to the form $H_{22}(R) - H_{11}(R) = A \exp(-BR)$, where $A = 4.2682$, $B = 1.195$. Thus $\theta_{21} = (2/v)AbK_1(Bb)$, where K_1 is the first order modified Bessel function of the second kind (Boyd & Dalgarno 1958).

Calculations were done over a wide range of incident ion energies from 100 eV to 3000 eV. Figures 2-5 display some of the results.

In I we compared the phases of oscillation of the charge transfer probability curve with the results of Nagy *et al* (1971) and Erikson *et al* (1972) by correlating the impact parameter b with the scattering angle after the method of Everhart (1963). Here, however, we use the formula

$$\theta_{CM} = \pi - 2b \int_{R_0}^{\infty} \frac{dR/R^2}{\sqrt{(1-V(R))/E - b^2/R^2}} \quad \dots \quad (27)$$

where $V(R) = \frac{1}{2}[V_u + V_g(R)]$ and R_0 is the distance of closest approach

Using $V_u(R) = H_{11}(R) - H_{11}(\infty)$ and $V_g(R) = H_{22}(R) - H_{22}(\infty)$, the integration in eq. (27) was carried out by Gauss-Mehler quadrature. The product $E\theta$ (lab. system) is given in table 1 over a range of b -values, which also includes

Table 1 Values of $E\theta$ (lab) as a function of impact parameter b

$b(a_0)$	$E\theta$ (KeV deg)	
	This work	Everhart (1963)
0.8	4.10	4.40
1.0	2.79	3.11
1.2	1.91	2.17
1.4	1.34	1.54
1.6	0.93	1.08
1.8	0.64	0.74
2.0	0.44	0.48
2.2	0.30	0.31
2.4	0.21	0.21

Everhart's results for comparison. The fairly large discrepancy between the two sets of results is presumably due to the error in the values of $V_u(R)$ and $V_g(R)$ used by Everhart, who obtained them chiefly from Phillipson's tables (1962) using Koopmans' theorem. Figure 6 shows the locations of the extrema points of the close-coupled charge transfer probability in the adiabatic representation joined by smooth lines, together with the experimental points of Nagy *et al* and Eriksen *et al*.

4. DISCUSSION OF RESULTS

The purpose of this work has been to explore the effect of the coupling in He^+-He resonant charge exchange collision and to assess therefrom the relative merits and demerits of the diabatic and adiabatic molecular representations in low-energy atomic collision problems. Choice of molecular representation in an atomic collision process has always been a vexatious problem, and a number of authors such as Lichten (1963), O'Malley (1967), Levine *et al* (1969), Smith (1969), Johnson (1974) among others have suggested use of different representations to meet different ends and with varying degrees of rigour. A close approximation to Smith's "standard" radial diabatic representation has been used by Lane and co-workers (Evans, Cohen & Lane 1971, Cohen, Evens & Lane 1971 and Evans & Lane 1973) for certain inelastic atom-atom and ion-atom collision processes in Helium, and recently also by Andresen & Nielsen (1975) for collisions between ground-state and excited H-atoms. Smith's representation has been attacked on the ground that the molecular wavefunctions are R -independent and cannot reflect the "dynamical" nature of an atomic collision problem (Gabriel & Taulbjerg 1974; they also quote Smith as admitting to have received analogous comments from certain other sources). We, however, chose to make use of this representation mainly because of the particular advantage it promised to offer in calculating the radial coupling term required in the adiabatic close-coupled calculations, as is evident from eq (25).

As mentioned earlier, Olson's values for the diabatic potentials have been used as an approximation to the "standard" diabatic potentials. The lower and upper $^2\Sigma_g$ adiabatic potentials as given by Gupta & Matsen (1967) and by Michels (1967) respectively were indeed reproduced by the unitary transformation (22) to a high degree of accuracy (2-3 parts in 1000), but the off-diagonal term $H_{23}(R)$, which is smaller than the diagonal terms by about two orders of magnitude at small R , was found to be uncertain by about 100% at $R = 1a_0$. The expression (24) for $P_{(R)adia}$ which is obtained by putting $P_{11} = 0$ in Olson's representation is of order $\frac{\partial}{\partial R} \left(\frac{H_{23}}{H_d} \right)$ and in general much less uncertain than H_{23} .

The extreme singularity in the nature of $M_{23}(R)$ as shown in figure 1 demands the utmost accuracy in its evaluation, and this has indeed been so far the biggest

hurdle in the path of adiabatic close-coupled calculations which is also known as the perturbed stationary state approximation (Bates *et al* 1953). Except for the systems H₂⁺ (see Rosenthal (1971) for a complete bibliography), HeH⁺ (Green *et al* 1974) and LiNa⁺ (Melius & Goddard 1974) very few radial coupling matrix elements have been computed so far. Melius & Goddard (1972) showed a way of circumventing this problem by replacing $M_{23}(R)$ by its value at some mean \bar{R} , but this procedure is feasible only if the matrix element is well-behaved about \bar{R} . On the other hand, the regular behaviour and the small size of the diabatic coupling term H_{23} very nearly decouples (12) except at very low energies, and hence in the present case uncertainties in H_{23} would affect the diabatic close-coupled calculations only very slightly.

Figures 2-5 show that within the abovementioned limitations, the diabatic and adiabatic close-coupled calculations give identical results. A comparison

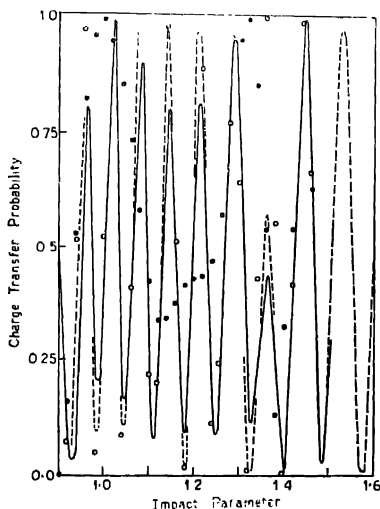


Fig. 2. Close-coupled diabatic and adiabatic charge transfer probability for laboratory-ion energy $E = 100$ eV. Full-line curves: adiabatic calculations; broken-line curves: diabatic calculations; closed circles: adiabatic decoupled calculations; open circles: diabatic decoupled calculations.

of the adiabatic close-coupled and decoupled calculations indicates the strength of the Σ - Σ radial coupling. As was clearly shown in I, the diabatic decoupled P -values simply oscillate between zero and one, and they are found to agree very well in phase with the close-coupled calculations except at very low energies.

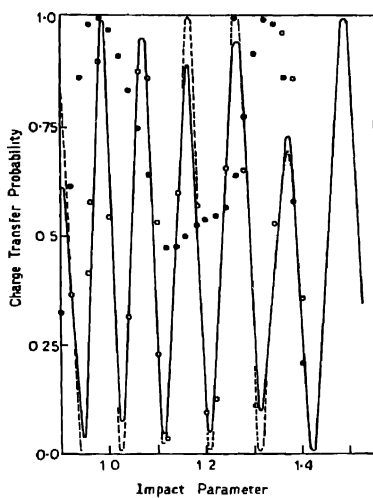


Fig. 3 Same as Fig. 2 for $E = 200$ eV.

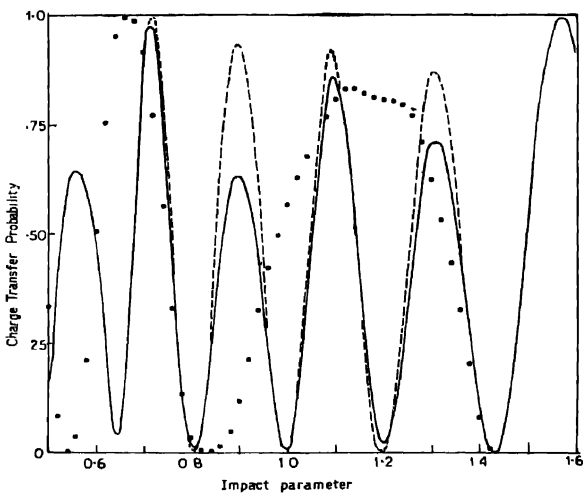


Fig. 4. Same as Fig. 2 for $E = 1000$ eV.

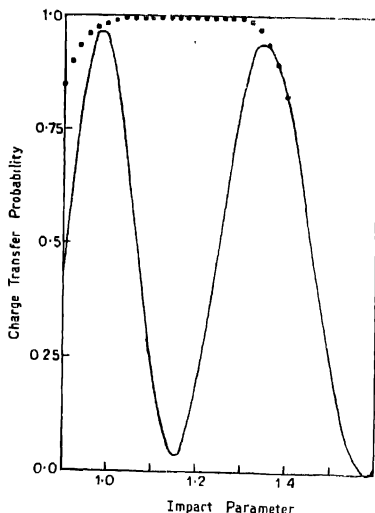


Fig. 5. Same as Fig. 2 for $E = 3000$ eV.

For this reason they are shown here only for the two lowest energies, 100 and 200 eV, where there appears a marked irregularity in the P - b curves near $b \sim R_x$. Loronts & Aberth (1965) in their experiments on He⁺-He elastic differential scattering observed in this energy region an anomaly in the oscillations at $E\theta \approx 1.7$ KeV deg, which corresponds to $b \approx 1.3$. Although there are no charge transfer experiments within our knowledge at these energies, our results are in accord with Marchi's (1969) explanation of this feature in the elastic scattering experiments, as mentioned in I.

Figure 6 compares the phases of oscillation of the charge transfer probability in the adiabatic close-coupled calculations with the experiments of Nagy *et al* (1971) and Erikson *et al* (1972). The excellent agreement for $b \geq 1.0$ clearly indicates that in this region, the Σ - Σ radial coupling provides the most significant influence on resonant charge transfer. The diabatic close-coupled results are virtually indistinguishable from the adiabatic ones, while the diabatic decoupled results (cf. Figure 3 in I) agree in general to within 2-3%. The slight disagreement for $b < 1.0$ as seen in figure 6 corresponding to $E\theta \geq 3$ KeV deg. (cf. table 1) is presumably due to the Σ_u - π_u and Σ_g - π_g - Δ_g rotational couplings which, as mentioned already, we have neglected. These couplings have been found to contribute to the damping as well as to the dephasing of the oscillations in the charge transfer probability in close collisions where $E\theta > 3$ KeV deg (McCarroll

& Piacentini 1971, Barat *et al* 1972). We chose not to extend the impact parameter method much below $b = 1a_0$ and thus ignored this coupling.

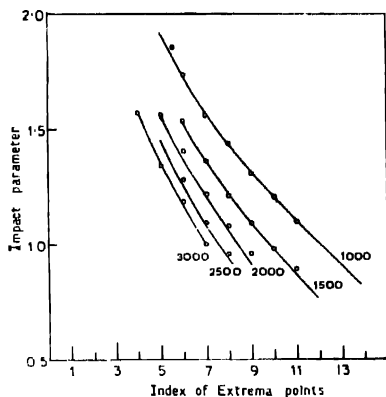


Fig. 6. Locations of the extrema in the charge transfer probability curves at different ion energies (eV) indexed from right to left plotted against impact parameter. Full-line curves smoothly join the results of adiabatic close-coupled calculations. Experimental points of Nagy *et al* (1971) and Eriksen *et al* (1972) are shown.

Thus the following conclusions may be drawn about the choice of molecular representations :

(i) For He^+-He charge transfer collision, the diabatic representation is more useful than the adiabatic one since it is very nearly decoupled

(ii) Any error in the (off-diagonal) potential coupling would affect the diabatic calculations, although in the present case the effect is small

(iii) When the adiabatic representation is obtained by a unitary transformation of the diabatic one, the error in the coupling elements of the latter does not propagate, or propagates only slightly, into the former

Thus it is seen that for low-energy atomic collisions the standard diabatic representation is more advantageous to work with; if the coupling terms are doubtful or subject to error, one can always transform into the adiabatic representation and use the p s approximation, and eq (25) makes the calculations of the required coupling terms trivially simple

Figure 7 shows the 'envelopes' of the charge transfer probabilities in the diabatic and adiabatic close-coupled calculations together with the experimental values of P_{maximum} . The observed damping can of course be predicted only

partly in our work, which considers only the outermost and the sharpest crossing of the lower $^2\Sigma_g$ state by the upper one leading to the inelastic $1s \rightarrow 2s$ channel. As mentioned earlier, the diabatic state 2 is actually crossed by an infinite number of states, all below $R = 1.4 a_0$, but they are less sharp than the 2-3 crossing considered in this paper and as such their influence on the resonant charge transfer channel can extend to larger impact parameters. This is presumably the reason why the experimental P -values are damped even beyond $b = 1.4 a_0$.

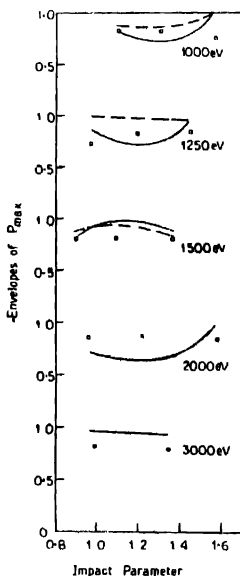


Fig. 7. Envelopes of the maxima of charge transfer probability as obtained from the close coupled calculations plotted against impact parameter. Full-line curves: adiabatic representation; broken-line curves: diabatic representation. Experimental values of P_{maximum} are shown.

as is seen from figure 7. However, considering the uncertainties involved in the numerical values of the coupling terms, the agreement between theory and experiment as displayed in the figure is strong enough to suggest that the $1s \rightarrow 2s$ transition is indeed the main inelastic channel competing with the elastic (direct or charge exchange) channels. Smith (1964) showed from quantum mechanical calculations that due to the interference between scattering from the g and u potentials, a damping is predicted in a two-state theory too. It would therefore

be of interest to compare the results of a three-state quantum mechanical calculation with the present results

We have not made any calculations of the total cross-section in this work; since the close-coupled P -values deviate from the decoupled values only upto $b \sim 1.4 a_0$, it is clear that the coupling does not affect the total cross-section significantly (Sample calculations show that the total cross-sections as given in I change by less than 1% due to the coupling.) Moiseiwitsch (1956), using a linear combination of atomic orbitals with variationally adjusted exponents, obtained a total cross-section curve that is virtually identical with ours in I. The reason for the discrepancy between our results and the data of Nagy *et al* (1969) for $E < 600$ eV is not clear, and since the collision energies are about two orders of magnitude larger than the excitation threshold, it cannot be due to any failure of the impact parameter approximation. We note, however, that the results of Hayden & Utterback (1964) agree with ours very well, and the results of Hasted & Stedeford (1956) show the same variation with energy as ours but differ by a constant factor ~ 1.3

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