

THE THEORETICAL DESCRIPTION OF AN ASYMMETRIC, NONRESONANT CHARGE TRANSFER PROCESS; $Li + Na^+ \rightleftharpoons Li^+ + Na$ THE TWO-STATE APPROXIMATION †

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The charge transfer process for the collision $Li + Na^+ \rightleftharpoons Li^+ + Na$ has been studied theoretically by a two-state, impact parameter approach using molecular wavefunctions. Including the coupling term $\langle \psi_1 | \partial / \partial R | \psi_2 \rangle$ due to the breakdown of the Born–Oppenheimer approximation, we obtain total charge transfer cross sections in good agreement with experimental results.

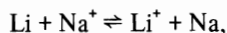
1. Introduction

Many experimental measurements of the total charge transfer between various alkali atoms and alkali ions have been reported in the literature [1–4]. The results for the symmetric resonant charge transfer (e.g., $Li + Li^+ \rightarrow Li^+ + Li$) show the presence of oscillatory structure super-imposed on a cross section that increases with decreasing velocity [1]. The cross section for the asymmetric non-resonant charge transfer (e.g., $Li + Na^+ \rightarrow Li^+ + Na$) shows a similar behavior at high velocities but has a maximum amplitude and then decreases with decreasing velocity. Similar oscillatory structure is present in the asymmetric case [2].

The case of symmetric, resonant charge transfer has been interpreted as a phase interference between the $^2\Sigma_g^+$ and the $^2\Sigma_u^+$ states due to the energy difference of their potential energy curves [1]. This interpretation assumes that the electron starts out initially with equal probability to be in either the $^1\Sigma_g^+$ or $^2\Sigma_u^+$ state but that no transitions can occur

between these two states. For the asymmetric non-resonant case, however, the two states are not degenerate at infinity, and this approach cannot be used.

We report herein a study of the asymmetric, non-resonant charge transfer ‡



in which the first two adiabatic molecular states are used and in which we include the Born–Oppenheimer breakdown term $\langle \psi_1 | \partial / \partial R | \psi_2 \rangle$ as the coupling term between states. We find that the results are in good agreement with experiment.

2. Details of the method

The total wavefunction for the scattering system can be expressed in a multistate expansion

$$\Psi = \sum_i F_i(R) \psi_i(r, R), \tag{1}$$

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‡ In the two-state approximation, $Li + Na^+ \rightarrow Li^+ + Na$ and $Na + Li^+ \rightarrow Na^+ + Li$ are equivalent processes. See discussion (section 4).

where R is the internuclear distance and \mathbf{r} represents all the electronic coordinates. F_i describes the nuclear wavefunction while ψ_i describes the electronic wavefunction. For sufficiently high energies (e.g., $E > 100$ eV), one can assume that the nuclei move in straight trajectories. Incorporating this approximation (which is called the impact parameter method) into the molecular wavefunction approach [5] and taking the nuclear wavefunction to be

$$F_i(\mathbf{R}) = a_i(z) \exp\left[i \int_{-\infty}^z k_i(z') dz'\right] \quad (2)$$

[where $z^2 + b^2 = R^2$, b is the impact parameter, $k_i = [2M(E - V_i)]^{1/2}$, E is the translational energy for the separated system ($E = \frac{1}{2}Mv^2$) and V_i is the energy of the i th molecular state], we obtain the set of coupled equations

$$da_i(z)/dz = - \sum_j \Gamma_{ij}(z) \exp[-i\omega_{ij}(z)] a_j(z), \quad (3)$$

where $\omega_{ij}(z) = (1/v) \int_{-\infty}^z (V_j - V_i) dz'$ and

$$\Gamma_{ij} = (z/R)M_{ij} + (b/R)N_{ij}, \quad (4)$$

$$M_{ij} = \langle \psi_i | \partial/\partial R | \psi_j \rangle, \quad (5)$$

$$N_{ij} = \langle \psi_i | 1/R \partial/\partial \theta | \psi_j \rangle. \quad (6)$$

One of the difficulties in using this approach has been the evaluation of the coupling terms M_{ij} and N_{ij} , which are not translationally invariant [5,6]. We have, therefore, formulated a simple and straightforward method for obtaining matrix elements which possess translational invariance. We define an average value \bar{M}_{ij} for the matrix element (5) as

$$\bar{M}_{ij} = \int d^3r \rho_{ij}(\mathbf{r}) M_{ij}(\mathbf{r}) / \int d^3r \rho_{ij}(\mathbf{r}), \quad (7)$$

where $M_{ij}(\mathbf{r})$ is the matrix element in (5) evaluated with the origin taken at point \mathbf{r} and $\rho_{ij}(\mathbf{r})$ is the weighting function $[\rho_{ij}(\mathbf{r}) = |\phi_i^*(\mathbf{r})\phi_j(\mathbf{r})|]$ for that point \mathbf{r} . For a diatomic molecule, $M_{ij}(\mathbf{r})$ is a linear function of the distance z along the internuclear axis (not to be confused with the z of the impact parameter method). Therefore, we can find a point \bar{z} such that

$$\int d^3r \rho_{ij}(\mathbf{r})(z - \bar{z}) = 0. \quad (8)$$

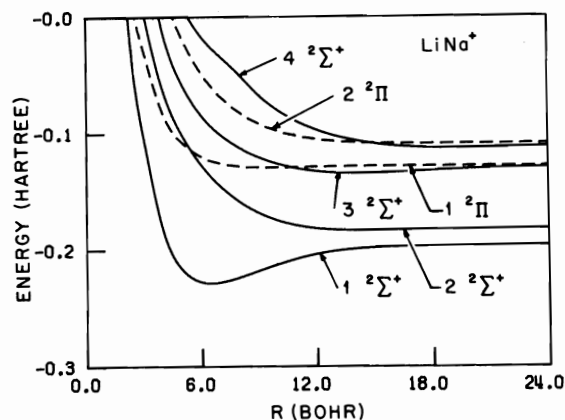


Fig. 1. The theoretical energy curves for LiNa^+ . The first four $2\Sigma^+$ states and the first two 2Π states are included (1 hartree = 27.211 eV, 1 bohr = 0.52917 Å).

Eq. (7) can, therefore, be replaced by

$$M_{ij} = M_{ij}(\bar{z}), \quad (9)$$

where \bar{z} specifies the origin for the coordinate system in which M_{ij} is evaluated. This method does not ignore the overlap between basis functions (which becomes significant at smaller distances). Since $M_{ij} = -M_{ji}$, the coupling terms remain hermitian. The method is independent of any restrictions imposed in obtaining eq. (3).

The electronic wavefunctions ψ_i were evaluated using ab initio effective potentials \ddagger resulting in the potential curves in fig. 1. The bonding energy of the

\ddagger The effective potentials are derived from Hartree-Fock atomic orbitals. See refs. [7-9]. The basis set for fig. 1 consisted of s, p, and d contracted gaussian basis functions appropriate for the $n = 2$ and $n = 3$ states of Li and for the $n = 3$ and $n = 4$ states of Na. The coupling constants were evaluated with the most diffuse basis functions eliminated. The effective potential method [7-9] assumes that the core orbitals do not change with R and hence breaks down for small R ($< 3.5 a_0$). We have found that modifying the potential curves and coupling terms for such small R does not lead to significant changes in the charge transfer cross sections reported herein. The energy defect, $\Delta E(\infty)$, obtained from ab initio Hartree-Fock calculations is 0.0141 hartree while the experimental value is 0.0093 hartree. In the scattering calculations [eq. (3)], we have shifted the calculated potential curves (fig. 1) to match the experimental energy defect.

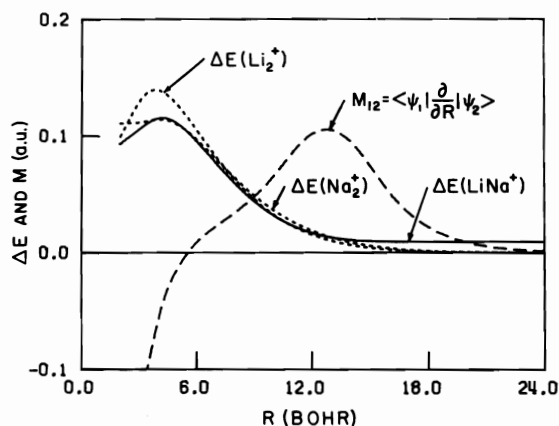
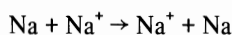
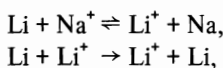


Fig. 2. The potential energy difference curves [$\Delta E = V_2(R) - V_1(R)$] for (a) Li Na^+ (solid line), (b) Li_2^+ (dotted line), and (c) Na_2^+ (dotted line). Also plotted is the coupling term $M_{12}(R)$ for Li Na^+ (dashed line).

$1^2\Sigma^+$ state is calculated to be $0.0326 h = 0.89 \text{ eV}$ with an $R_e = 6.47 a_0$ which compares well with the results of Hartree-Fock calculations by Bertocini et al. [10] ($D_e = 0.92 \text{ eV}$ and $R_e = 6.5 a_0$).

3. Results

Eq. (3) was used to solve for the total charge transfer cross section for the process $\text{Li} + \text{Na}^+ \rightleftharpoons \text{Li}^+ + \text{Na}$, using a two-state approximation. The low-lying potential energy curves for the Li Na^+ molecule are shown in fig. 1. [Hartree atomic units ($\hbar = 1, e = 1, m_e = 1$) are used unless otherwise stated.] In fig. 2 we compare the potential energy differences [$\Delta E(R) = V_2(R) - V_1(R)$] for the two lowest states of Li Na^+ , Li_2^+ , and Na_2^+ . They are very similar except for the presence of an energy defect for Li Na^+ [$\Delta E(\infty) = 0.0093h$]. Also plotted in fig. 2 is the coupling term $M_{12} = \langle \psi_1 | \partial/\partial R | \psi_2 \rangle$ between the $1^2\Sigma^+$ and $2^2\Sigma^+$ states of Li Na^+ . The coupling term is zero at infinity, starts rising around $\approx 24 a_0$, reaches a maximum near $13 a_0$, and drops toward zero at smaller R [until interactions with the cores cause M_{12} to change sign (at $R \approx 5.5 a_0$) and become negative]. The total charge transfer cross sections for



are shown in fig. 3 as a function of inverse velocity. A common oscillatory structure appears in all three cross sections, but for the asymmetric case, a maximum occurs in the cross section at a velocity around 0.14 au . A comparison between the theoretical results and the experimental results of Daley and Perel [2] is shown in fig. 4. The overall agreement is good^{††}.

4. Discussion

We find that in the two-state approximation the asymmetric, non-resonant charge transfer process for $\text{Li} + \text{Na}^+ \rightleftharpoons \text{Li}^+ + \text{Na}$ can be explained by a simple mechanism that is consistent with the process involved in the symmetric, resonant charge transfer. The transformation of the orbitals from being left and right atomic orbitals ($R > 20 a_0$) to being bonding and antibonding molecular orbitals ($R < 6 a_0$) takes place in the region where the orbitals begin to overlap. This transformation is represented by the coupling term

^{††} After completion of our work, a paper by Bottcher and Oppenheimer [11] appeared reporting a theoretical treatment of the $\text{Li} + \text{Na}^+ \rightleftharpoons \text{Li} + \text{Na}$ charge transfer process. They also found oscillations in the total cross section but obtained total cross sections about 30% above the experimental values. Some points to note are: (1) They calculate transfer probabilities neglecting back coupling (i.e., assuming $a_1 \approx 1, a_2 \ll 1$). This approximation is not valid for the velocity region of interest ($v > 10^7 \text{ cm/sec} = 0.05 \text{ au}$). (2) Their $\Delta E(R)$ is in good agreement with ours for smaller $R (< 10 a_0)$. However, their $2^2\Sigma^+$ curve shows kinks ($10 < R < 12$) and appears to converge toward the $1^2\Sigma^+$ curve. This behavior does not appear in our results or in other calculations of diatomic alkali molecules (see refs. [8,10,12,13]), indicating some difficulty with either the model potential or with the basis sets in their calculations. [We do find an avoided curve crossing involving the $4^2\Sigma^+$ and $5^2\Sigma^+$ states at $R \approx 7.5 a_0$ (see fig.1); this corresponds to the crossing of the $2^2\Sigma_u^+$ and $3^2\Sigma_g^+$ states of Li_2^+ and of Na_2^+ .] (3) The problem of translational invariance in evaluating $M_{12} = \langle \psi_1 | \partial/\partial R | \psi_2 \rangle$ has been ignored. We find that the crossing point, $M_{12} = 0$, occurs at $R = 10.0 a_0$ when the origin is at the Li, no crossing occurs when the origin is at the Na, and $M_{12} = 0$ at $R = 5.5$ using \bar{z} from (9). Since the location of the crossing point depends on the origin chosen, there appears to be no justification for the Bottcher-Oppenheimer interpretation of the mechanism for charge transfer.

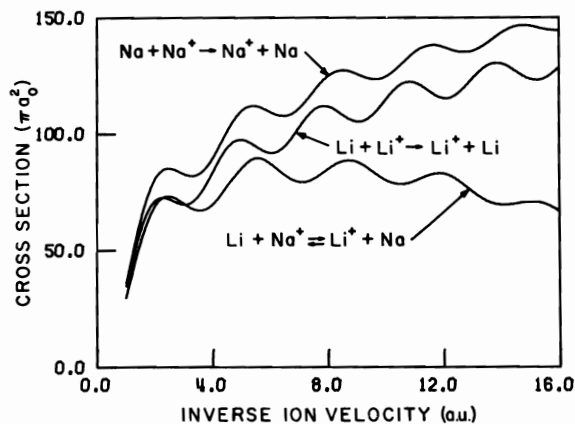


Fig. 3. The total charge transfer cross sections (two-state approximation) as a function of inverse ion velocity for Li Na^+ , Li_2^+ , and Na_2^+ (1 au velocity = 2.18×10^8 cm/sec, $\pi a_0^2 = 0.89 \times 10^{-16}$ cm 2).

$M_{12} = \langle \psi_1 | \partial / \partial R | \psi_2 \rangle$, which grows from zero at $24 a_0$ to a maximum at $13 a_0$ and then decreases with smaller R (see fig. 2). One might expect transitions between states in this entire region. However, the energy difference ΔE starts growing rapidly for $R < 15 a_0$ (see fig. 2), which soon prevents transfer between states [due to rapid oscillations of exponential terms in eq. (3)]. Thus, transitions between states occur only at long range where M_{12} is large, but where ΔE is still small (between $\approx 12 a_0$ and $22 a_0$ for Li Na^+). We denote this region as the *transition region*.

For smaller R , no transitions occur between states. However, in this intermediate region, the two states undergo a relative change in phase ($\Delta\phi$) as a result of the evolution of their phase factors [see eq. (2)] on different potential energy curves. The resultant phase change is

$$\Delta\phi \approx \int_{-R_0}^{R_0} (1/\nu) \Delta E(R) dz, \quad (10)$$

where R_0 is some average internuclear distance of the transition region.

As the nuclei separate, they again pass through the transition region. If there were no change in phase, then the coupling term would reverse the transition process (since Γ has changed sign) and no charge transfer would occur. However, $\Delta\phi$ in general is not zero, and we obtain a charge transfer probability which de-

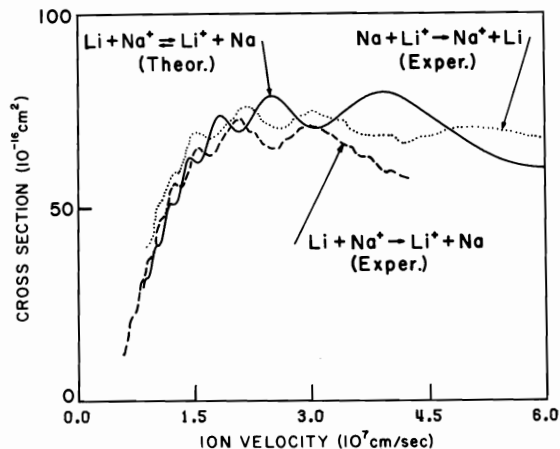


Fig. 4. Comparison of the total charge transfer cross sections for Li Na^+ for theoretical (two-state) and experimental results [2].

pends on the extent of phase interference.

We would therefore expect a charge transfer probability $P(\nu, b)$ similar to that for the symmetric resonant case but weighted by a product of the amplitude probability for being on either state in the intermediate region, i.e., $\ddagger\ddagger$

$$P(\nu, b) \approx 4 |\bar{a}_1 \bar{a}_2|^2 \sin^2 \left[\frac{1}{2} \int_{-R_0}^{R_0} (1/\nu) \Delta E(R) dz \right], \quad (11)$$

where $\bar{a}_1 \equiv a_1(R_I)$ and $\bar{a}_2 \equiv a_2(R_I)$ are the (constant) values of a_1 and a_2 in the intermediate region ($|a_1|^2 + |a_2|^2 = 1$). The \bar{a}_i are a function of Γ and $\Delta E(\infty)/\nu$. For the symmetric resonance case, $|a_1(R_I)|^2 = |a_2(R_I)|^2 = \frac{1}{2}$ and we obtain the familiar form for the resonant charge transfer probability [1].

For slowly varying $\Delta\phi(\nu, b)$, one would expect from (11) to find oscillatory structure in the *differential* cross section both (i) as a function of inverse velocity for fixed scattering angle and (ii) as a function of scattering angle for fixed velocity.

For high energies, the extent of the transition between states in the transition region is sufficiently large to allow the two states to be equally populated

$\ddagger\ddagger$ Eq. (11) is appropriate for $\Gamma = (z/R)M$. For coupling between Σ and Π states, $\Gamma = (b/R)N$. In this case, Γ has the same sign in both the coupling and uncoupling regions so that (11) should be replaced by $P(\nu, b) \approx 4 |\bar{a}_1 \bar{a}_2|^2 \times \cos^2(\frac{1}{2} \Delta\phi)$.

($\bar{a}_1 \approx \bar{a}_2$). Thus, at high energies, the charge transfer cross section becomes similar to that for the symmetric resonant case. However, as the velocity decreases the probability for a transition decreases due to the oscillatory behavior of the right hand side of eq. (3). Thus, the total cross section reaches a maximum and then falls off toward zero. We would expect this maximum to occur for the smallest velocity (v_{\max}) for which the cosine part of the exponential term in (3) remains large while the sine part remains small in the transition region, i.e., when

$$\Delta E(\infty) \Delta z / v_{\max} \approx \pi / 4, \quad (12)$$

where Δz is a measure of the width of the transition region. This result is in close accord with the "near-adiabatic" theory proposed by Massey [14]. For Li Na^+ , $\Delta E(\infty) = 0.0093$ h, and $v_{\max} \approx 0.14$ au corresponding to $\Delta z \approx 12 a_0$ in (12).

Since the energy difference curves $\Delta E(R)$, for Li Na^+ , Li_2^+ , and Na_2^+ are very similar (see fig. 2), we expect similar cross sections at high energies (cf., fig. 3). Also, since the maximum in the energy difference occurs at roughly the same internuclear distance for all three (the maximum for Li Na^+ occurs at $R = 4.2 a_0$), we expect similar oscillatory structure in all three cases [1].

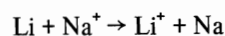
In the two-state approximation, the process $\text{Li} + \text{Na}^+ \rightarrow \text{Li}^+ + \text{Na}$ and the reverse process $\text{Na} + \text{Li}^+ \rightarrow \text{Na}^+ + \text{Li}$ are equivalent. To understand the experimentally observed difference (cf., fig. 4) between these two processes, one must consider coupling to other states in (3). When we carried out calculations using a four-state approximation including the $3 \ ^2\Sigma^+$ and $4 \ ^2\Sigma^+$ states, we found little change in the cross section for $v < 0.2$ au #. On the other hand, we found that including the $1 \ ^2\Pi$ state (in addition to the $1 \ ^2\Sigma^+$ and $2 \ ^2\Sigma^+$) leads to significant changes ##. Because of the crossing of the $2 \ ^2\Sigma^+$ and $1 \ ^2\Pi$ states at $R = 5.4 a_0$, an electron in the $2 \ ^3\Sigma^+$ state can transfer over to the $1 \ ^2\Pi$ state ($\text{Li } 2p$ at infinity) in the intermediate region of the $1 \ ^2\Sigma^+ \rightleftharpoons 2 \ ^2\Sigma^+$ transfer process.

This is consistent with the experimental results of ref. [3], which indicate that transitions occur only to the states with the smallest energy defect. For $\text{K} + \text{Li}^+ \rightarrow \text{K}^+ + \text{Li}$, three Σ states would be needed.

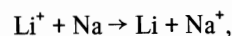
Results of the multistate calculations will be presented later.

This leads to a decrease in \bar{a}_2 of (11) and to a finite value for a_3 . As a result, the total charge transfer cross section for the $\text{Li} + \text{Na}^+ \rightarrow \text{Li}^+ + \text{Na}$ process is, on the average reduced. For the $\text{Na} + \text{Li}^+ \rightarrow \text{Na}^+ + \text{Li}$ process, however, the total charge transfer cross section is the sum of the $2 \ ^2\Sigma^+ \rightarrow 1 \ ^2\Sigma^+$ and the $2 \ ^2\Sigma^+ \rightarrow 1 \ ^2\Pi$ cross sections####.

Thus, one expects the net cross sections for



to be smaller than for



as observed experimentally [2]. In addition, we find that the inclusion of the $1 \ ^2\Pi$ state shifts the phase of the oscillatory structure so that the theoretical maxima and minima coincide with the experimental locations.

5. Conclusion

We see that the two-state charge transfer process can be described in terms of a three-step process.

First, at large R ($22 a_0$ to $12 a_0$ for Li Na^+), the nuclei pass through a transition region where electronic transitions occur between the states (the coupling between states results from the orbitals changing from atomic orbitals at large R to molecular orbitals at small R). The extent of the transition depends on the coupling term and the ratio of the energy defect to the velocity.

Second, at smaller R ($R < 15 a_0$ for Li Na^+), a relative phase change occurs between the two molecular states due to the difference in energy of the potential energy curves. The change in phase is inversely proportional to the velocity.

And *third*, the transition region is reentered and the states decouple, changing from molecular orbitals back to atomic orbitals. If there had been no relative phase change (modulus 2π), we would reobtain the

Transitions from the $1 \ ^2\Pi$ state to the $2 \ ^2\Pi$ state upon separation of the atoms leads to minor modifications in the cross sections.

original atomic state with which we started[†]. However, because of the phase changes, there are interference effects that can lead to a finite probability of ending up on the other atomic state.

As a result one expects the differential charge transfer cross sections to show oscillatory structure both as a function of velocity and as a function of scattering angle (this is found in the theoretical calculations). Oscillations in the total cross section will occur if there is a maximum in the energy difference curve [1].

These results should have general applicability for charge and excitation energy transfer in atomic and molecular scattering systems.

[†] This is true for $\Sigma-\Sigma$ transitions where $\Gamma = (z/R)M$ and has a different sign for the initial and final transition regions. For $\Sigma-\Pi$ transitions, $\Gamma = (b/R)N$ has the same sign for both transition regions. As a result, a *maximum* in the transfer probability occurs when the phase change is zero [and thus a maximum when $b = R_0$ (the location of the crossing point)].

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