Resonant Charge Exchange in Atomic Collisions. II. Further Applications and Extension to the Quasi-Resonant Case*

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(Received 18 January 1965; revised manuscript received 26 February 1965)

Further applications are made of the author's previous discussion of charge exchange in wide-angle (small-impact-parameter) collisions between simple atoms. Oscillatory charge exchange is predicted for H-H⁻ and resonant double exchange for He-He⁺⁺ collisions. The case of near-resonant collisions is treated as a quasi-resonant process with damping, which arises from the lack of exact resonance. As in the resonant case, the frequency of oscillation can be predicted from the molecular model, and a qualitative estimate of damping is possible. A quality factor Q is introduced as a convenient parameter for classifying quasi-resonances in charge-exchange collisions. A discussion is given to account for the presence of oscillatory charge exchange in proton-helium collisions and the lack of oscillations in He⁺-H encounters. Pronounced oscillatory behavior is predicted for the He-Li⁺⁺ system, but not for H-He⁺ or H-He⁺⁺. A discussion is given of ionization by collisions between neutral atoms, such as H-H or H-He. The role of level crossing in resonant charge exchange also is discussed. The failure of the Landau-Zener theory to predict resonant charge exchange is shown to result from omission of quantum-mechanical phase factors. When a properly modified Landau-Zener model is used, oscillatory energy dependence is predicted in certain cases, in agreement with experiment and the present discussion. In general, oscillatory charge exchange is expected in high-Q collisions.

INTRODUCTION

IN a recent paper,[1] the author discussed the remarkable observations of resonant charge exchange in atomic collisions. The present paper predicts some new cases of resonant charge exchange. Also the theory is extended to describe several sets of phenomena that were inadequately treated previously.[1]

I. SYMMETRIC AND NONRESONANT CHARGE EXCHANGE

A. The Quasi-Resonant Case

A striking case of charge exchange is found in the experimental results of Everhart *et al.* on He-H⁺ collisions[1] (Fig. 1). The presence of a well-defined, damped oscillatory charge exchange in an asymmetric, nonresonant[2] collision is remarkable; also the high percentage $(P_0 > 50\%)$ of charge transfer is quite unexpected.

Previously, it was shown[1] that resonant charge exchange only occurred if $\omega/\Gamma \gg 1$, where ω is the charge-exchange frequency and Γ the damping width of the states involved. For the nonresonant case, an additional condition for quasi-resonant charge exchange is that $\omega/\Delta E \gg 1$, where ΔE is the difference in energy between initial and final states. The first condition is that many "beats" occur before the oscillation dies away;

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*Parts of this discussion were presented previously by W. Lichten, Bull. Am. Phys. Soc. **8**, 393, 529 (1963).

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[1] W. Lichten, Phys. Rev. **131**, 229 (1963). See this paper for references to earlier work.

[2] A collision involving $A^+ + B \to A + B^+$ is called *symmetric* if A and B are identical atoms, *asymmetric* if A and B differ, *resonant* if initial and final states are degenerate and *nonresonant* if initial and final states are nondegenerate. All four combinations of these conditions can occur.

the second is that the coupling be large enough to overcome any slight difference in energy between states. To further the analogy, one can expect to find a pair of states with a quasi u and g parity, respectively. This will occur at small internuclear distances, where the coupling is largest.

B. The Two-State Approximation

Consider in detail the two-state approximation for quasi-resonant charge exchange. Let λ be a measure of the range of interatomic forces. For $R \gg \lambda$, the system has two eigenstates S_1 and S_2, best described as the separated atoms in the atomic-orbital (AO) representation as AB^+ and A^+B. For $R \lesssim \lambda$, S_1 and S_2 are perturbed by an interaction H_{12}. At $R=0$, in the united atom, the states have definite and opposite parity. For
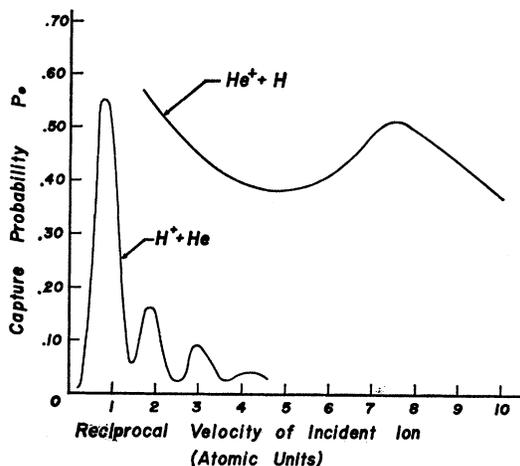
FIG. 1. Experimental results of charge exchange between H and He ions and atoms. See Ref. 6.

$0 < R \lesssim \lambda$, if $H_{12} \gg |E(A^+B) - E(AB^+)|$,[3] S_1 and S_2 are well described by approximately symmetric and antisymmetric eigenfunctions:

$$\psi_1 = [\psi(A^+B) + \psi(AB^+)]/\sqrt{2}$$
$$\psi_2 = [\psi(A^+B) - \psi(AB^+)]/\sqrt{2}. \qquad (1)$$

Consider first the *adiabatic* case of slow collisions when (in atomic units[1]) $\Delta E\tau \gg 1$, where $\Delta E = |E(A^+B) - E(AB^+)|$[3] and the collision time is $\tau \approx 2\lambda/v$. In this case, the system remains in one state throughout the collision and no charge exchange occurs.

Next, consider the case of *sudden* collisions, such that $(\Delta E)\tau \ll 1$. Here the transition from separated atoms to molecular ion occurs so fast that the initial AO eigenfunction must be expanded into a linear combination of molecular-orbital (MO) eigenfunctions.[1] The initial eigenfunctions become

$$\psi \begin{Bmatrix} A^+B \\ AB^+ \end{Bmatrix}_{R \approx \lambda} \rightarrow (\psi_2 \pm \psi_1)/\sqrt{2}.$$

It is to be noted that, for a sufficiently fast collision, the initial state of the molecular ion is the same as in the case of symmetric-resonant charge exchange.

Furthermore if S_2 and S_1 are widely separated in energy, $2\lambda |E_2(0) - E_1(0)|/v \gg 1$, there will be many exchanges of charge during the collision and a well-defined quasiresonance will be observed.

In order for a quasiresonant charge exchange to exist, both conditions must be satisfied[3]:

$$|E_2(0) - E_1(0)| \gg v/2\lambda \gg |E_2(\infty) - E_1(\infty)|$$
$$= |E(A^+B) - E(AB^+)|. \qquad (2)$$

C. Intermediate Case: Damping.
The Quality Factor Q

Zener and others[1,4] have considered the intermediate range between adiabatic and sudden transitions (Fig. 2). A transition probability of the form $P = e^{-v_0/v}$ was obtained, where v_0 is a constant velocity. It appears reasonable to assume such a relation as a rough approximation in the general case of quasi-resonant charge exchange. Then the probability of charge exchange in the two-state approximation is given by a modification of the empirical formula,[1]

$$P_0 = e^{-v_0/v}[\sin^2((\langle Ea\rangle/2v) - \beta)], \qquad (3)$$

[3] Instead of the energy separation of initial and final states, some authors claim one should use the energy separation at $R \approx \lambda$, where the transition from AO to MO states occurs. An important example is *asymmetric resonance*. For a detailed discussion of this case, see D. R. Bates and N. Lynn, Proc. Roy. Soc. **A253**, 141 (1959); D. Rapp and W. E. Francis, J. Chem. Phys. **37**, 2631 (1962); E. F. Gurnee and J. L. Magee, *ibid.* **26**, 1237 (1955); W. L. Fite, A. C. H. Smith and R. F. Stebbings, Proc. Roy. Soc. **A268**, 527 (1962). Except for the case where ionic repulsions destroy the accidental degeneracy, such as $He^{++} + H \rightarrow H^+ + He^+$ $(n=2)$, Fite *et al.* find no experimental evidence in favor of the distinction of Bates and Lynn between asymmetric and symmetric resonant charge exchange. Thus this paper treats the two types of resonance on an equal footing.

[4] N. Rosen and C. Zener, Phys. Rev. **40**, 502 (1932).
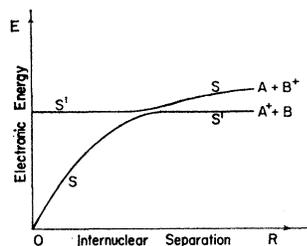
FIG. 2. Pseudo-crossing of two energy levels, the physical system governed by the Landau-Zener formula.

where v_0, $\langle Ea\rangle$, and β are constants. From the uncertainty principle,[1]

$$\Delta E\Delta\tau \approx 2\lambda |E_2(\infty) - E_1(\infty)|/v_0 \approx 1, \qquad (4)$$

which gives an estimate for v_0.[3] Since

$$|E_2(\infty) - E_1(\infty)| \neq 0,$$

the usual definition for

$$\langle Ea\rangle = \int_{-\infty}^{+\infty} (E_2 - E_1)dR$$

diverges. A more realistic estimate for $\langle Ea\rangle$ is obtained from the expression[5]

$$\langle Ea\rangle \approx \int_{-\lambda}^{+\lambda} (E_2 - E_1)dR \approx 2\lambda |E_2(0) - E_1(0)|, \qquad (5)$$

since charge exchange only occurs within the region of molecular binding. The phase shift β has been found to have the empirical value of $\pi/4$.[1,6]

If the expression $T = 2\lambda/v$, $T_0 = 2\lambda/v_0$ is substituted in (3), one obtains

$$P_0 = e^{-T/T_0} \sin^2[(\langle Ea\rangle/4\lambda)T - \beta], \qquad (6)$$

which is formally identical with the classical expression for a damped oscillator. Thus, charge exchange in the case of asymmetric resonance appears to be damped within the two-state approximation. The damping of *symmetric* resonance was found[1] to come from multistate processes. These processes are still present in asymmetric resonance and will, in general, have quite distinguishable behavior.

The usual formulation of asymmetric charge exchange by Landau, Zener, and others does not lead to an expression containing an oscillatory term, as in (3). It can be shown (see Appendix) that oscillatory terms do appear in the well-known Landau-Zener formula.[7]

[5] This expression was previously used in paragraph III-C.3 of Ref. 1.

[6] For further discussions of the phase shift β, see H. F. Helbig and E. Everhart, Phys. Rev. **136**, A674 (1964). This paper also contains a detailed discussion of the HeH^+ system.

[7] For a convenient summary of this theory, see L. D. Landau and E. M. Lifshitz, *Quantum Mechanics*, translated by J. B. Sykes and J. S. Bell (Addison-Wesley Publishing Company, Reading, Massachusetts, 1958).

It is convenient to define a quality factor

$$Q = \frac{\langle Ea \rangle}{v_0} \approx \left| \frac{E_2(0) - E_1(0)}{E_2(\infty) - E_1(\infty)} \right| . \tag{7}$$

Q is a measure of the sharpness of the quasi-resonance between the states E_2 and E_1. Q is the same as the well-known classical parameter for a damped oscillator, $Q = \omega T_0$, where ω is the classical oscillator frequency and T_0 is the decay time for the energy present in the oscillator.

Figure 3 shows charge-exchange probability as a function of reciprocal velocity for several values of the quality factor $\langle Ea \rangle / v_0 = Q$. It can be seen that for $Q < 1$ there is practically no trace of resonant behavior, for $Q \approx 3$ the resonance is heavily damped, and for $Q \gtrsim 6$ a well-defined resonance is present. In general Q will not achieve a value much larger than 10, since other causes of damping will be present. Thus for $Q \gtrsim 10$, the collision can be taken as resonant, for all practical purposes.

Figure 4 shows experimental results of Everhart et al.[1,6] for wide-angle scattering for H^+ collisions with He. The solid curve represents the empirical formula (3) with

$$\langle Ea \rangle = 5.71$$
$$v_0 = 0.85$$
$$Q = \langle Ea \rangle / v_0 = 6.7 .$$

It can be seen that the fit with the experimental data is good, which indicates that the two-state approximation represents well the H+He collisions. Further discussion of this case is given in paragraph II-C.

D. General Case of More Than Two States

The generalization of the sudden approximation is straightforward. The initial wave function is given in the AO approximation, expanded in the MO approximation at $R \approx \lambda$, and the phase factors calculated as a function of collision time. For the final state, the squares of the coefficients of the AO wave functions give the probability of a transition. An example of this was given for He^{++}-He collisions, where three states were required.[1]
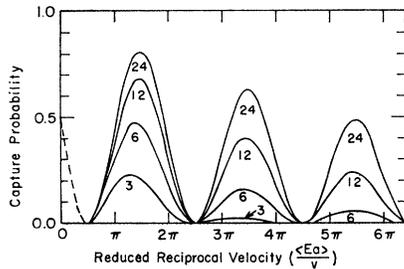
FIG. 3. Theoretical curves for quasi-resonant charge exchange for $Q = 3, 6, 12, 24$. A phase shift of $\pi/4$ is assumed in each case.
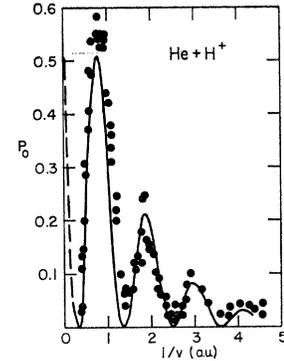
FIG. 4. Fit of experimental He+H^+ data to the empirical formula (3).

E. Other Processes: Electron Ejection by Knock-Out and Boil-Off Collisions

Brief mention should be made of other processes which produce change in charge state. The first, *knock-out* of electrons, usually is significant only for the lightest nuclei colliding at relatively high energies, and is not treated in this article.[8,9] The second, boil-off, is considered to be the most significant cause of multiple ionization in wide-angle, small-impact-parameter collisions in heavy atoms.[10]

II. APPLICATIONS

A. H-H⁻, H-H

An energy-level diagram for the H_2 system is shown in Fig. 5. It is of interest to consider the case of collisions between H^- and H. The H-H^- system is isoelectronic to He+He^+. Therefore both collisions are analogous. In the quasi-adiabatic approximation, the symmetric and antisymmetric states which interfere to cause charge exchange are $(\sigma_g)(\sigma_u)^2$ and $(\sigma_g)^2(\sigma_u)$, respectively. It is particularly worth noting that *both* states of H_2^- are virtual (autoionizable), since they lie above the ground state of H_2 over a wide range of internuclear distances.[11] Nevertheless, for small impact-

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[8] An important exception to this statement is the case of a negative ion, such as H^-, with an easily detached electron of low ionization potential. Here, at energies within the experimental range, stripping processes may interfere with resonant charge exchange.

[9] For a summary of stripping processes in atomic collisions, see the article by D. R. Bates in *Atomic and Molecular Processes*, edited by D. R. Bates (Academic Press, Inc., New York, 1962), Chap. 14.

[10] For further discussion, see the paper by A. Russek, Phys. Rev. **132**, 246 (1963). See also U. Fano and W. Lichten, Phys. Rev. Letters **14**, 627 (1965).

[11] See H. S. Taylor and F. E. Harris, J. Chem. Phys. **39**, 1012 (1963) for a summary of the controversy over the existence of a stable ground state of H_2^-. The resolution of this dispute does not affect the present discussion, since states need not be stable towards autoionization to play a role in fast collisions. (See Ref. 1, Sec. III-A). Indirect evidence in support of the prediction of resonant charge exchange in wide-angle collisions is found in the experimental work of Hummer, Stebbings, Fite, and Branscomb, Phys. Rev. **119**, 668 (1960) which is in relatively good agreement with the calculations of A. Dalgarno and M. R. C. McDowell, Proc. Phys. Soc. **A69**, 615 (1956). The latter authors used a set of curves for the H_2^- molecule which are similar to those in Fig. 8, and are therefore autoionizable. However, the experimental results obtained depended most heavily on small-angle, large-impact-parameter collisions, which is not the case under present discussion.
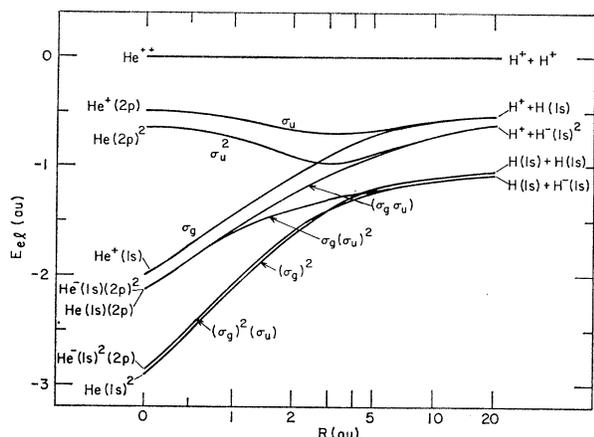
FIG. 5. Diabatic curves suitable for discussion of fast, zero-impact-parameter collisions of H atoms. Electronic energies of the H_2 system are shown for a few singlet states of interest. To the right, at large internuclear distances, the energies are those of the separated atoms and/or ions. At smaller internuclear distances, the energies are those of a single-configuration molecular-orbital wave function. At $R=0$, the energies are those of the He atom or ion. The similarity between this figure and Fig. 4 of Ref. 1 should be noted. For the united atom, Be^{n+} is isoelectronic to $He^{(n-2)+}$. For the separated atoms, He^{n+} is isoelectronic with $H^{(n-1)+}$.

The curves were constructed from calculated wave functions whenever possible, as is shown in the references. The remainder of the curves were constructed by plausible interpolation, or by the author's estimates.

References: H_2^{++} is the zero of energy, H_2^+, σ_g, σ_u (see Fig. 3, Ref. 1). H_2, σ_u^2 ($3.5 \leq R \leq 10$), E. R. Davidson, J. Chem. Phys. 35, 1189 (1961); $\sigma_g\sigma_u$, I. Tobias and J. T. Vanderslice, J. Chem. Phys. 35, 1852 (1961), also P. Phillipson and R. S. Mulliken, J. Chem. Phys. 28, 1248 (1958); σ_g^2, ($0.6 \leq R \leq 5$) Tobias and Vanderslice, op. cit. and W. Kolos and C. C. J. Roothaan, Rev. Mod. Phys. 32, 219 (1960). H_2^-, $(\sigma_g)^2\sigma_u(1 \leq R \leq 8)$ I. Fischer-Hjalmers, Arkiv Fysik 16, 33 (1959); 20, 461 (1961). $(\sigma_g)(\sigma_u)^2(1.1 \leq R \leq 3.5)$ estimates were based on the repulsive $^3\Sigma_u^+$ state calculated by Kolos and Roothaan, op. cit. The location of these curves is probably correct to ≤ 0.05 a.u. It can be seen that this error causes a very large uncertainty in the range of R for which H_2^- is unstable, but little error in predictions of events in fast collisions.

parameter collisions, resonant charge exchange is predicted. The relatively small ionization potential of $H^-(0.75$ V) leads one to suspect some incoherent destruction of the resonance by knock-out processes. However, it is likely that oscillatory charge exchange will be strong.[11] $\langle Ea \rangle$ for this collision can be estimated (See Fig. 5):

$$\langle Ea \rangle \approx 2\lambda[E(He^-,1s,2p^2)-E(He^-,1s^2,2p)].$$

Since

$$\lambda(H_2^-) \approx \lambda(H_2^+) = 1.5$$

$$\langle Ea \rangle = 3 \times 0.74 = 2.2 \text{ atomic units (a.u.)}.$$

In the case of collisions of neutral H on H, the situation is theoretically much less favorable for oscillatory charge transfer. As in the case of the analogous system $(He)_2^{++}$, four states can arise in a symmetric, two-electron system.[1] In the AO representation there are

three singlet states with wave functions:

$$\psi(H^- - H^+) = \psi_{AA},$$
$$\psi(H^+ - H^-) = \psi_{BB},$$
$$\psi(H - H) = \psi_{AB}, \tag{8}$$

and a triplet state. In the (MO) representation there are three singlet states:

$$\psi_N = \sigma_g^2,$$
$$\psi_V = (\sigma_g\sigma_u + \sigma_u\sigma_g)/\sqrt{2}, \tag{9}$$
$$\psi_Z = \sigma_u^2,$$

and the triplet state.

The transformation matrix between AO and MO wave functions is[12]

$$\begin{array}{c} \\ \psi_{AA} \\ \psi_{AB} \\ \psi_{BB} \end{array} \begin{array}{ccc} \psi_N & \psi_V & \psi_Z \\ \left[\begin{array}{ccc} 1/2 & \sqrt{2}/2 & 1/2 \\ \sqrt{2}/2 & 0 & -\sqrt{2}/2 \\ 1/2 & -\sqrt{2}/2 & 1/2 \end{array} \right]. \end{array} \tag{10}$$

Three-fourths of collisions between hydrogen atoms will be in the triplet state T. No other triplet states can be formed from $1s$ atomic orbitals (or $1\sigma_g$ or $1\sigma_u$ molecular orbitals).[13] Thus, in the absence of two, well-separated bands of states,[1] there is no reason to expect resonant charge exchange in three-fourths of H-H collisions. In the united-atom approximation, ψ_T goes to $He(1s,2p)^3P$, which lies close in energy (≈ 0.1 a.u.) to many other $^3P(1s,np)$ states. Damping caused by these states would be expected to produce a random mixture of H^+H^-, H-H and H^--H^+ separated atom states. Thus charge exchange would be incoherent.

It should be noted that stable H^- cannot be formed in any triplet collision between H atoms. Spin is conserved in fast collisions between light atoms. Thus any H^- formed in a triplet collision must be in a triplet state. Since no stable triplet state of H^- is known, any H^- atoms so formed must autoionize to H after the collision.[14]

The remaining quarter of all collisions are in the singlet ground state of H_2. At low energies ($v \ll 1$ a.u.), these collisions might be expected to be adiabatic and not to produce charge exchange. At high energies ($v \gg 1$ a.u.), one can apply the sudden approximation. Expanding the initial state in terms of MO wave functions, one obtains

$$\psi_{in} = \psi_{AB} = (\psi_N - \psi_Z)/\sqrt{2}. \tag{11}$$

Ignoring a common phase factor, one obtains for the

[12] Equation 17' in Ref. 1 has a misprint. It should read $\psi_{AB} = \psi_N - \psi_Z/\sqrt{2}$.

[13] It can be shown that in both the sudden and quasiadiabatic approximations the antisymmetrized orbital wave function is $\psi_T = (\psi_{AB} - \psi_{BA})/\sqrt{2} = (1\sigma_u 1\sigma_g - 1\sigma_g 1\sigma_u)/\sqrt{2}$.

[14] E. Holøien, Physica Norvegica 1, 53 (1961) has speculated over the existence of a bound $(1s,2p)$ ^3P state of H^-. However, at the time of the writing of this article, no one has succeeded in establishing the existence of such a state. Even if such a state did exist, it would be so weakly bound that its formation in fast collisions would be unlikely.

final state

$$\psi_f = [\psi_N - \psi_Z e^{i\phi}]/\sqrt{2}, \qquad (12)$$

where

$$\phi = (\langle Ea \rangle_{NZ}/v) \approx (2\lambda \Delta E(0)/v). \qquad (13)$$

Since $\lambda = 1.5$ for H_2, and $\Delta E(0) = E_Z(0) - E_N(0) = E(He2p^2) - E(He1s^2) = 2.2$ (See Fig. 5), $\phi \approx 6.6/v$. Expanding the final state into AO wave functions, one obtains for the probabilities:

$$P_1 = P_{AA} = \tfrac{1}{2} \sin^2(\tfrac{1}{2}\phi);$$

$$P_0 = P_{AB} = \cos^2(\tfrac{1}{2}\phi); \qquad (14)$$

$$P_{-1} = P_{BB} = \tfrac{1}{2} \sin^2(\tfrac{1}{2}\phi).$$

The maximum value for H^- formation is $P_{-1} = 0.5$. Since only the singlet collisions produce H^-, the maximum fraction of collisions is $\tfrac{1}{4} \times \tfrac{1}{2} = \tfrac{1}{8}$ in the case of exact resonance. However, one can see (Fig. 5) that the quality factor Q is given by the expression

$$Q = (E_Z(0) - E_N(0)/E(H^+H^-) - E(H\text{-}H))$$
$$= 2.2/0.45 = 5,$$

which corresponds to slightly heavier damping than in the case of $He + H^+$, where the maximum charge exchange was a bit above half the theoretical value. Thus, one would expect less than half the theoretical value of $\tfrac{1}{8}$, or somewhat less than 6%.

The experimental results of Lockwood, Helbig, and Everhart[15] show a weak resonant formation of H^-, with a maximum value of 4% for P_{-1}. Here, without detailed calculations, it is possible to predict experimental results approximately from a fairly general set of assumptions.[16]

B. He^{++}-He

The He^{++}-He system is isoelectronic with H-H. However, the initial state, $He^{++} + He$ is a singlet in all collisions, in contrast to H-H collisions. Thus the behavior is quite different. The problem of $He^{++} - He$ collisions has been solved in the sudden approximation[1]. This solution predicts a resonant oscillation of He^{++}, He^+ and He probabilities. A three-state approximation was used. The result holds only for large energies ($v \gtrsim 1$ a.u.). For lower energies, a different analysis is needed.

Table I shows correlations for adiabatic collisions ($v \lesssim 0.1$). Here the two symmetric and antisymmetric states derived from ($He^{++} + He$) go to the united atom states with configurations ($1s,2p$) and ($1s,2s$). Since

[15] G. J. Lockwood, H. F. Helbig, and E. Everhart, Bull. Am. Phys. Soc. **8**, 362 (1963).
[16] One might ask whether capture of an electron from an atom in a *singlet* state is more likely to produce H^-. By considering the spin eigenfunctions for the problem, one can show that the maximum capture probability is 25%. Thus, in fast collisions of H atoms with atoms or molecules in singlet states, such as H_2, N_2, and the rare gases of lower ionization potentials, one might expect twice as high a probability of H^- formation than in H-H collisions. All collisions which lead to capture in H^- triplet or singlet states would ionize the target atom. Thus, it would be of interest also to examine ions of the target atom for collisions involving an incident neutral atom.

TABLE I. Correlation of principal states of $(He)_2^{++}$.

Separated atoms	Parity	Molecular states Adiabatic	Quasiadiabatic
$\psi_{AB}(He^+ + He^+)$	g	$\psi_N(1s\sigma)^2$	$\psi_N(1s\sigma)^2$
$\psi_{BB}(He^{++} + He)$	u	$\psi_V(1s\sigma,2p\sigma)$	$\psi_V(1s\sigma,2p\sigma)$
$\mp\psi_{AA}(He + He^{++})$	g	$\psi(1s\sigma,2s\sigma)$	$\psi_Z(2p\sigma)^2$

these states are close in energy, the conditions for resonant charge exchange are not satisfied. Thus, at very low energies, one would not expect oscillatory charge exchange in small impact-parameter collisions.

The question remains whether oscillatory charge exchange can exist in the quasiadiabatic energy range $0.1 \lesssim v \lesssim 1$ a.u. Since there are an even number of electrons, it is not possible to make a diabatic, single configuration, molecular-orbital correlation between separated atom and molecular states. It seems reasonable, however, to make a quasiadiabatic correlation of the molecular states N, V, and Z (see Table I) with the separated atom states with wave functions ψ_{AB} and the degenerate pair ($\psi_{BB} \mp \psi_{AA}$), respectively. Then, as long as the quasiadiabatic approximation holds, only the V and Z states need be considered in He^{++}-He collisions (Fig. 6). In this case there is an oscillatory double charge exchange with frequency $\langle Ea \rangle_{VZ} \approx 8.5$.[1,17] This hypothesis can be tested by looking for resonant double charge exchange in the energy range 1–100 kev.

The arbitrary separation into three types of collisions is only an approximation. Thus, although He^+ production is predicted only in very fast velocity ranges, doubtlessly there will be some He^+ at all energies in He^{++}-He collisions.

C. Collisions Between He-H$^+$, H-He$^+$, H-He^{++}, H-He.

Figure 1 shows results of Everhart et al.[6] for wide-angle scattering of $He + H^+$ and $H + He^+$. Two re-
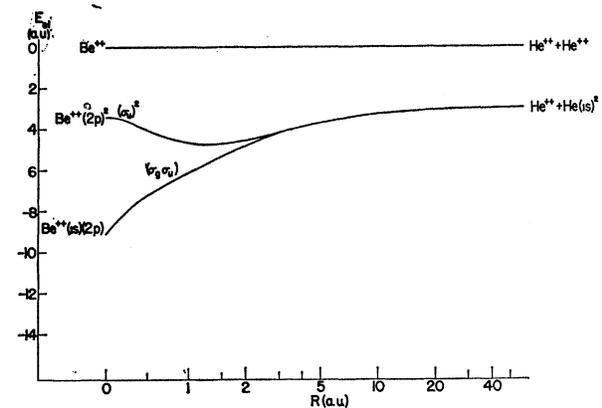
FIG. 6. Quasiadiabatic curves for collisions between He^{++} and He.

[17] The predictions of double charge exchange are in agreement with the calculations of D. Basu, S. C. Mukherjee, and N. C. Sil, *Proceedings of the Third International Conference on the Physics of Electronic and Atomic Collisions, London*, edited by M. R. C. McDowell (North-Holland Publishing Company, Amsterdam, 1964), p. 769.

markable features can be seen. First, a damped, but pronounced, resonant charge exchange exists for $He+H^+$. Second, $H+He^+$ has a quite different, structureless charge exchange. This section discusses these two cases.

In paragraph I-C it was shown that the results for $He+H^+$ agree with a two-state approximation, and the empirical values $Q = 6.7 = \langle Ea \rangle / v_0 = 5.7/0.85$ were found. To compare these results with theory, see Table II and Fig. 7. Clearly the initial state for $He+H^+$ collisions is the ground state N of HeH^+, with the MO configuration $(1\sigma)^2$. It is plausible to hypothesize that the first excited singlet state $V(1\sigma)(2\sigma)$ is the second state which takes part in the quasi-resonant charge exchange. The energy separations $E_V(0) - E_N(0) = 2.28$ a.u. and $E_V(\infty) - E_N(\infty) = 0.40$ a.u., obtained from Table II, can be compared with the experimental values for $\langle Ea \rangle$ and $\langle v_0 \rangle$, respectively, by multiplication by 2λ [see Eqs. (4) and (5)]. As a rough estimate for λ, one can take a mean between $\lambda(H_2^+) = 1.48$ and $\lambda(He_2^+) = 0.74$, $\lambda(HeH^+) \approx 1.1$. The derived values

$$E_Z(0) - E_N(0) = 5.7/2.2 = 2.6$$

and

$$E_V(\infty) - E_N(\infty) = 0.85/2.2 = 0.4,$$

agree well enough with experiment to make it reasonable to assume N and V are the two states involved.[18]

It should be noted that the third singlet state Z is so far away from N at $R = \infty$, $E_Z(\infty) - E_N(\infty) = 2.4$ a.u., that no appreciable excitation of Z would be expected below proton velocities of

$$v_0 = 2\lambda[E_Z(\infty) - E_N(\infty)] = 2.2 \times 2.4 = 5.3 \text{ a.u.}$$

This is a proton energy more than 600 keV, which is outside the experimental range. Also it may be noted that, in contrast to the isoelectronic system $He-He^{++}$, the quality factor Q for excitation of Z, and thereby double charge exchange, is highly unfavorable.

In He^+-H collisions the role of spin statistics is the same as in the H-H system (paragraph II-A). Both

atoms are in doublet states, so that $\frac{3}{4}$ of the collisions are in the triplet state T and $\frac{1}{4}$ are in the singlet state V.[19] Since no other principal state of HeH^+ is a triplet, there is no chance for triplet resonant charge exchange. The resonant charge exchange arising from singlet collisions would amount to only a few percent at experimental energies, and thus is negligible.

It can be shown that Q is unfavorably small for resonant charge exchange in the HeH^{++} system. Finally, in the case of collisions between atomic H and He, one might expect a good resonant charge exchange producing $He^+ + H^-$ with values of v_0, $\langle Ea \rangle$, and probabilities comparable to the case of $He+H^+$. However, since $\frac{3}{4}$ of the H^- ions would be lost, it would be desirable to look at the recoil He ions to observe a favorable charge exchange. All these requirements would make this experiment an extremely difficult one.

Thus it may be concluded that only $He+H^+$, and no other combination of He and H atoms or ions is expected to present a favorable experimental case for observation of quasiresonant charge exchange.

D. Other Quasi-Resonant Systems: Li-He

The increasing complexity of many electron systems makes clear theoretical predictions difficult. One source of additional complexity is that small impact-parameter collisions no longer happen for atoms for high values of atomic number Z. This admits transitions among molecular orbitals with different values of Λ, the component of orbital angular momentum along the internuclear axis. Another source of complexity is that many electrons are taking part in the collision. These matters will not be treated further in this paper.[10]

However, a few remarks will be made about the simplest such system Li-He. The correlation of the lowest molecular orbitals is shown in Table III and Fig. 8.

In order to obtain a wave function made up of a mixture of two widely separated bands of states, it is necesssry to remove an electron from the tightly bound K shell of Li. Such a process is likely to happen only at

TABLE II. Principal states[a] of HeH^+.

United atom ($R=0$, Li^+)		Molecular orbital configuration ($R \approx \lambda$)	Separated atoms ($R = \infty$, He+H)	
State	Electronic energy (a.u.) $-E$		State	Electronic energy (a.u.) $-E$
$(2p)^2\ Z^b$	1.78	$(2p\sigma)^2$	$\psi_{BB}(H^- + He^{++})$	0.53
$(1s,2p)\ ^1P\ V$	5.00	$(1s\sigma,2p\sigma)$	ψ_{AB} $\{H+He^+$	2.50
$(1s,2p)\ ^3P\ T$	5.03	$(1s\sigma,2p\sigma)$	ψ_{BA} $\}$	
$(1s)^2\ ^1S\ N$	7.28	$(1s\sigma)^2$	$\psi_{AA}(He+H^+)$	2.90

[a] It is assumed that the correct MO correlation for fast collisions is $1s\sigma(Li^+) - 1s(He)$ and $2p\sigma(Li^+) - 1s(H)$. See D. R. Bates and T. R. Carson, Proc. Roy. Soc. (London) A234, 207 (1956). A different set, given by C. A. Coulson, *Valence* (Oxford University Press, New York, 1961), 2nd ed., p. 105, assumes an adiabatic correlation of molecular orbitals.
[b] This state is a mixture of the atomic states ^1S and ^1D. The correct energy is $E(2p\sigma)^2 = 1/3E(^1S) + \frac{2}{3}E(^1D)$. This relation is misprinted in the legend to Fig. 4, Ref. 1.

[18] A similar discussion was given by E. Everhart (Ref. 6).

FIG. 7. Correlation diagram for principal states of the HeH system. See Ref. 6 for an energy-level diagram for the HeH$^+$ system. Energy is shown in atomic units (1 a.u. = 27.2 eV).

[19] A correct discussion of the statistics of He$^+$-H collisions was first given by Rapp and Francis (see Ref. 3). See also the discussion by Everhart (Ref. 6).

TABLE III. Correlation diagram for the Li-He molecule.

United atom (B)	MO	Separated atoms (Li+He)
$1s$	$1s\sigma$	Li $(1s)$
$2s$	$2s\sigma$	He $(1s)$
$2p$	$2p\sigma$	Li $(2s)$.

very fast collisions. Thus resonant charge exchange is unlikely in Li^+-He or He^+-Li collisions. Rather, Li^+-He collisions are likely to produce nonresonant capture to Li or Li^-.

In order to produce resonant capture, Li^{++} on He or He^{++} on Li collisions should occur. Here the accidental degeneracy between $Li^{++}+He$ and $He^{++}+Li$, plus the wide separation of the corresponding molecular states may produce a quasiresonant charge exchange, even at relatively low ion energies. It should be pointed out that this exchange would be in contradiction to the conclusions of Bates and Lynn.[3,20]

Single electron capture could occur through the coupling of two states which go to $Li^{++}(1s)+He(1s)^2$ and $Li^+(1s)^2+He^+(1s)$. As in the case of He^{++}-He, this resonant single exchange would occur at relatively high energies and would be fairly heavily damped.

Note added in proof. Perel, Vernon, and Daley [Phys. Rev. **138**, A937 (1965)] have just observed remarkable structure in Cs-Cs^+, Rb-Rb^+, Cs-Rb^+, and Rb-Cs^+ charge-exchange collisions. The present author interprets their data as a resonant, or high-Q, quasi-resonant charge exchange with

$$\langle Ea \rangle \approx 4.4 \text{ a.u.,}$$

in fortuitous agreement with the value found in H-H^+ collisions. If this hypothesis is correct, oscillatory charge exchange should be pronounced in wide-angle collisions
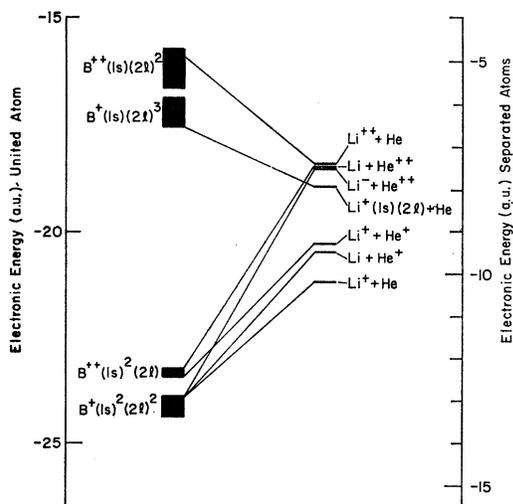
FIG. 8. Correlation diagram for the LiHe system and some states of the various ions.

[20] Also, in contrast to the He^{++}-He case, double resonant charge exchange does *not* occur in the fast approximation in Li-He^{++} or He-Li^{++} collisions. Thus, there is a genuine question as to how strongly the quasi-resonant double charge exchange would occur at lower energies.

between alkali and alkali ions, with $\langle Ea \rangle$ close to the hydrogenic value. It would be extremely interesting to make an experimental test of this somewhat speculative surmise.

APPENDIX

Quasi-Resonant Charge Exchange and the Landau-Zener Formula

The famous Landau-Zener model[1] will be compared with the discussion of this paper. A comparison was made with the author's treatment of damping of resonant charge exchange.[1] A somewhat similar discussion will be given here.

In the Landau-Zener theory, charge exchange happens when two potential curves S and S' cross (Fig. 2). S goes asymptotically to the separated atoms $A+B^+$; S' to A^++B. A transition from S to S' at the crossing point causes a charge exchange $A+B^+ \rightarrow A^++B$. The prediction of the Landau-Zener model is shown in Fig. 9. This disagrees with experimental results of Everhart *et al.*[6] (Fig. 1) on two counts:

(1) The maximum predicted charge exchange is 0.5, which is less than the observed value for H^++He.

(2) The observed capture probability is oscillatory; the predicted behavior is smooth.

This failure is not explained by the details of the interaction assumed in the model. Bates[1] has shown that these details show up largely in the behavior at the high-speed limit. Instead, the model fails because of a more fundamental defect, namely, its semiclassical nature. A collision involves two successive crossings of the curves S and S'. It is assumed in the model that the transition probabilities are independent; charge exchange occurs only for *one* transition. Two transitions
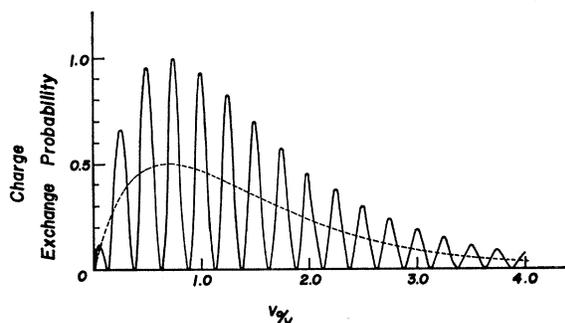
FIG. 9. Charge-exchange probability in the case of a pseudo-crossing. The broken line represents the results of the Landau-Zener formula. The solid line indicates the nature of the results when the phase is taken into account.

or no transition do not cause charge transfer. Elementary probabilty theory gives $P=2p(1-p)$, where p is the transition probability at a single crossing and P is the charge exchange probability for the entire collision. This expression has a maximum value of $P=\frac{1}{2}$ when $p=\frac{1}{2}$. When the model is changed so that phase factors are kept in the wave functions, the interference between successive crossings lets P become oscillatory and reach a maximum of unity.

To avoid mathematical complexity, this behavior will be illustrated by a simplification. Assume that the two eigenfunctions ψ_S and $\psi_{S'}$ exist and correspond to the eigenstates S and S', respectively. Assume that transitions only occur between these states in the immediate vicinity of the crossing point (see Fig. 2) and that an interaction term V exists for a finite time as the atoms traverse the crossing point. Assume that the interaction has the same magnitude and duration during both approach and separation of the atoms.

It is simplest to use the sudden approximation at each transition region and to expand the wave function into a Heisenberg representation in each region. Initially, let the atoms be $A+B^+$, which corresponds to the state S. At the crossing point, where S and S' are degenerate, the interaction term V removes the degeneracy and makes two new eigenstates, which are mixtures of S and S':

$$\psi_A=(\psi_S+\psi_{S'})/\sqrt{2}\,e^{iVt}, \qquad (A1)$$
$$\psi_B=(\psi_S-\psi_{S'})/\sqrt{2}\,e^{-iVt}.$$

Expand S as a linear combination of ψ_A and ψ_B, let the phase factors precess for a time t, and re-expand the wave function into the old representation. Then, one obtains

$$\psi=(\psi_A e^{iVt}+\psi_B e^{-iVt})/\sqrt{2}. \qquad (A2)$$

The new wave function can be rewritten in the S, S' basis set:

$$\psi=\psi_S \cos(Vt)+i\psi_{S'} \sin(Vt). \qquad (A3)$$

The probability of a transition is given by the square of the coefficient of $\psi_{S'}$, $p_1=\sin^2(Vt)$. The probability of no transition is just $1-p_1=\cos^2(Vt)$. Since V and t are small, these probabilities vary slowly with ionic velocity.

Now let the colliding atoms enter the region past the crossing point and emerge to cross once more. From the Heisenberg representation, one gets the phase factors of the wave function just before the second crossing:

$$\psi=\psi_S \cos(Vt)e^{i\phi}+i\psi_{S'} \sin(Vt)e^{-i\phi}, \qquad (A4)$$

where the phase factor ϕ has been presented in a conveniently symmetric form. In this case

$$\phi=\langle Ea\rangle/2v\approx\lambda(E_{S'}-E_S)_{\max}/v.$$

Now re-expand the wave function in the set ψ_A, ψ_B for the second crossing, which lasts for a time t':

$$\psi=(\psi_A e^{iVt'}+\psi_B e^{-iVt'}/\sqrt{2})\cos(Vt)e^{i\phi}$$
$$+\psi i(_A e^{iVt'}-\psi_B e^{-iVt'}/\sqrt{2})\sin(Vt)e^{-i\phi}. \qquad (A5)$$

The final wave function is

$$\psi=\psi_S[\cos(Vt')\cos(Vt)e^{i\phi}-\sin(Vt')\sin(Vt)e^{-i\phi}]$$
$$+\psi_{S'}[i\sin(Vt')\cos(Vt)e^{i\phi}+i\cos(Vt')\sin(Vt)e^{-i\phi}]. \qquad (A6)$$

The final transition probability is obtained by squaring the amplitude of the coefficient of $\psi_{S'}$ in (A6) and by setting $t=t'$, because of symmetry:

$$P=4\sin^2(Vt)\cos^2(Vt)[\cos^2(\phi)]. \qquad (A7)$$

The charge transfer probability P is a slowly varying function of ionic velocity $\sin^2(2Vt)$ multiplied by a rapidly varying function $\cos^2(\phi)$, which ranges from zero to unity.

Thus, resonant charge exchange occurs, with a maximum probability P of unity, rather than one-half. Finally, the charge exchange probability

$$P=4p_1(1-p_1)[\cos^2(\phi)] \qquad (A8)$$

has an *average* value

$$P_{\mathrm{av}}=2p_1(1-p_1) \qquad (A9)$$

which is just the semiclassical value.[7]

Such interference phenomena are well known in wave mechanics. An analogous case is "Ramsey flop," where two separated radio-frequency oscillating fields induce transitions in a molecular beam. The resulting interference has been calculated theoretically and verified experimentally.[21]

One might wish to find the generality beneath this simplified set of assumptions. The symmetry between approach and separation clearly occurs in any fast collision, since energy losses during the glancing blow are negligible. Secondly, the proof really rests on the assumption that the quality factor is large, $Q\gg1$. This can be seen by making the substitutions $\phi\approx\lambda(E_{S'}-E_S)_{\max}$, $Vt\approx\lambda$; these conditions must hold if one is to say that a "crossing" of two curves exists. Thus the Landau-Zener model with inclusion of phase is equivalent to a high quality factor $Q\gg1$, and both lead to the prediction of oscillatory charge exchange.

Figure 9 illustrates a hypothetical case of quasi-resonant charge exchange arising from level crossing with $Q\gg1$. The Landau-Zener formula was used to find the average probability in expression (A9); (A8) was used to construct the over-all curve.

It thus appears to be a general result that resonant charge exchange should occur in high-Q collisions.[22] This conclusion appears to be model-independent.[23]

[21] See N. F. Ramsey, *Molecular Beams* (Oxford University Press, New York, 1956), p. 124.

[22] In charge exchange collisions involving *two* charged products, such as $A+B\to A^++B^-$, the presence of a long-range Coulomb potential invalidates the use of the expression (7) for Q. In this case a special investigation must be made to determine Q. (See Ref. 3).

[23] Oscillatory transition probability has been obtained by a modification of the Landau-Zener model by W. D. Ellison and S. Borowitz, Ref. 17, p. 790. See also Iu. N. Demkov Ref. 17, p. 831.