Resonant Charge Exchange in Atomic Collisions

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The remarkable results of Everhart *et al.* in observing resonant charge exchange in wide angle (small impact parameter) ion-atom collisions, are discussed in terms of the well-known impact parameter method. It is shown that previous theories based on adiabatic potential curves are inconsistent with the results of He⁺-He experiments. However, experimental results are correctly predicted from a Heisenberg representation consisting of the basis set of single configuration wave functions built up from molecular orbitals (independent-particle model). This set includes virtual (autoionized) states. In this representation, the collision can be assumed to be adiabatic except for very short or very long collision times. The case of double charge exchange is treated, and it is shown that a three-state approximation is required. The presence of phase shifts in empirical equations is a result of the breakdown of interference at zero-collision time. Damping is discussed. The results include the work of previous authors and are general enough to include new cases. In particular, charge exchange in He⁺⁺-He, Li⁺-Li, and Li⁺⁺-Li collisions is discussed and predictions of experimental results are made.

I. INTRODUCTION

RECENTLY, Everhart *et al.*[1-3] discovered a remarkable experimental result in large-angle symmetric, ion-atom scattering. For these collisions, it can be shown[3] from classical orbit theory that the distance of closest approach of the nuclei is small compared to atomic sizes. The electron capture probability plotted versus incident ion energy shows several pronounced peaks in the symmetric cases of $H^+ + H$ and $He^+ + He$ collisions (Fig. 1). The present paper is a theoretical discussion restricted to these wide-angle, zero impact parameter collisions.

A. History

The basic theory of charge exchange stems from the work of Heisenberg,[4] who introduced the concept of resonance in connection with the discussion of the excited states of the helium atom. This well-known term arises from the analogy between the quantum-mechanical system of two degenerate states and the classical system of two oscillators of the same frequency which are coupled together. Pauling[5] and Finkelstein and Horowitz[6] applied this concept to the stationary states of the H_2^+ molecule, the simplest example of resonance.[7] H_2^+ was viewed as a system of a hydrogen atom (H_a)

and a proton (H_b^+). ($H_a H_b^+$) is degenerate with ($H_a^+ H_b$). Two stationary states, split by an energy E, exist for the molecular ion at finite internuclear distance: One wave function is a symmetric sum of the two degenerate wave functions; the other is antisymmetric. $H_a H_b^+$ is not a stationary state of the total system, since it is a mixture of two stationary states. The total wave function oscillates sinusoidally between the extremes of $H_a^+ H_b$ and $H_a H_b^+$ with a charge exchange frequency of E/h. Bates, Massey and Stewart[8] applied these simple ideas to atomic charge exchange collisions. They applied the impact parameter method[9,10] (IPM), in which it is assumed that the nuclei move in classical orbits, such that the stationary electronic states are well defined at each instant of the collisions. Since these stationary states and their corresponding energy eigenvalues are known, one can solve for the probability of charge
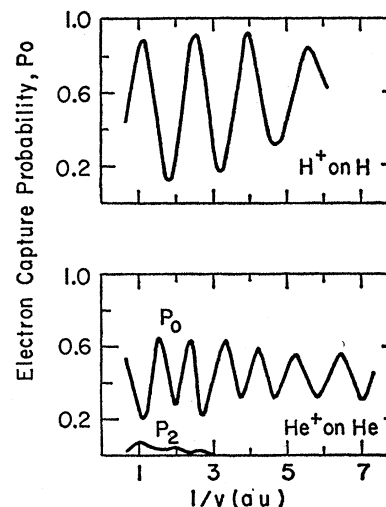

FIG. 1. Experimental results for charge exchange in wide angle scattering; P_0 is probability of the incident ion being scattered as a neutral particle; P_2 is probability of being scattered as a doubly ionized atom (references 1, 2, and 14).

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¹ For a discussion of H⁺ on H see G. J. Lockwood and E. Everhart, Phys. Rev. 125, 567 (1962).

² For a discussion of He⁺+He see F. P. Ziemba and E. Everhart, Phys. Rev. Letters 2, 299 (1959).

³ A summary of experimental results and some of the theory underlying these experiments is presented by F. P. Ziemba, G. J. Lockwood, G. H. Morgan, and E. Everhart, Phys. Rev. 118, 1552 (1960).

⁴ W. Heisenberg, Z. Physik 39, 499 (1926).

⁵ L. Pauling, Chem. Rev. 5, 173 (1928).

⁶ B. N. Finkelstein and G. E. Horowitz, Z. Physik 48, 118 (1928).

⁷ For an extremely simple discussion of these matters see L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1960), 3rd ed., pp. 14–19; see also L. Pauling and E. B. Wilson, *Introduction to Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1935), pp. 327–331.

⁸ D. R. Bates, H. S. W. Massey, and A. L. Stewart, Proc. Roy. Soc. (London) A216, 437 (1953) (see especially pp. 453–456); see also O. B. Firsov, Zh. Eksperim. i Teor. Fiz. 21, 1001 (1951); see also T. Holstein, J. Phys. Chem. 56, 832 (1952).

⁹ N. F. Mott, Proc. Cambridge Phil. Soc. 27, 553 (1931).
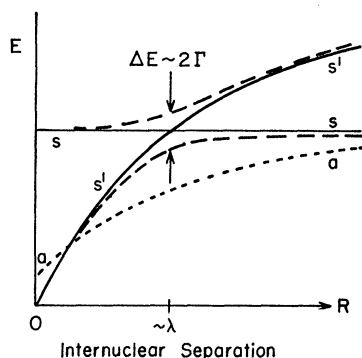
¹⁰ W. Kohn, Phys. Rev. 90, 383 (1953).

FIG. 2. Crossing of potential curves. Two potential curves for the states s' and s may cross in a certain approximation (such as in a single configuration molecular orbital theory). In a higher approximation, the curves repel each other. If the atoms approach each other slowly in state s, an adiabatic transition from s to s' will occur. If they approach each other rapidly, a diabatic transition from s to s will occur.

exchange in wide angle proton-hydrogen atom collisions, where the experimental results agree with theoretical calculations.[11] However, in the more general case of more than one electron, the problem is unsolved. Resonant charge transfer in wide angle scattering for many electron systems is the subject of this paper.

II. GENERAL THEORY

A. The Impact Parameter Method

The IPM[8–10] is based on the assumptions: (1) the nuclei move in classical orbits derivable from a potential; (2) the wave function of the total system is expanded in an adiabatic Heisenberg representation; that is, a set of stationary state wave functions and energies exist at all internuclear distances for each electronic state of the molecular system of atom plus ion. Assumption (1) holds best at the high-energy limit where the potential energy of the two nuclei is much larger than the total electronic energy. This corresponds to the case of impact parameters which are small compared to the dimensions of the atoms. For the case of bigger impact parameters electronic screening must be considered. Then assumption (1) loses force, since one cannot speak of an internuclear potential when the wave function consists of a mixture of stationary-state wave functions, each of which has a different energy eigenvalue. Some success has been achieved with a screened Coulomb potential.[1,12,13] However, due to the lack of theoretical justification it should be considered only useful in representing empirical data. In the present case of wide angle collisions between light atoms and ions (hydrogen or helium) at experimental energies (1–100 keV), electron screening plays a small role, and assumption number (1) of the IPM is well justified. The time-

dependent Schrödinger equation (in atomic units)[14] is

$$\mathcal{H}\Psi = i(\partial\Psi/\partial t), \tag{1}$$

where $\mathcal{H}$ is the Hamiltonian

$$\mathcal{H} = \frac{Z_A Z_B}{R} - Z_A \sum_{i=1}^{N} \frac{1}{|\varrho_i - \mathbf{R}_A|} - Z_B \sum_{i=1}^{N} \frac{1}{|\varrho_i - \mathbf{R}_B|}$$

$$+ \sum_{j>i} \frac{1}{|\varrho_i - \varrho_j|}, \tag{2}$$

and Ψ is the total wave function of the molecule (atom+ion)

$$\Psi = \sum_s c_s(t)\chi_s(\mathbf{R},\varrho_1,\varrho_2,\cdots\varrho_N), \tag{3}$$

where $R = |\mathbf{R}| = |\mathbf{R}_B - \mathbf{R}_A|$ is the internuclear distance, the $\varrho_1, \varrho_2, \varrho_3 \cdots \varrho_N$; $\mathbf{R}_A, \mathbf{R}_B$ are the coordinates of the N electrons and nuclei of the molecule, respectively, and the χ_s are solutions of the stationary-state Schrödinger equation

$$\mathcal{H}\chi_s = \epsilon_s\chi_s. \tag{4}$$

The solution to (1) for R not constant is given to zero order[8,15] by the adiabatic approximation:

$$c_s(t) = c_s(-\infty) \exp\left(-i\int_{-\infty}^{t} \epsilon_s(R[t'])dt'\right), \tag{5}$$

where the ϵ_s are the eigenvalues of (4).

To take account of departures from adiabaticity to first order, it is necessary to discuss the time dependence of the χ_s functions. Then one obtains a time dependence of the coefficients $c_s(T)$. This is given by the expression[8,15]

$$\frac{dc_p(t)}{dt} = -\sum_{s\neq p}\left\{c_s(t)\int d\tau\chi_p[\mathbf{R}(t),\varrho_i(t)]\frac{\partial\chi_s[\mathbf{R}(t),\varrho_i(t)]}{\partial t}\right.$$

$$\left.\times\exp\left(-i\int_{-\infty}^{t}\{\epsilon_s[R(t')]-\epsilon_p[R(t')]\}dt'\right)\right\}, \tag{6}$$

where $d\tau$ denotes integration over the electronic vari-

[11] See reference 1. However, there are some terms in the empirical equation for the data which are theoretically unexplained. These are discussed in a later section of this paper.

[12] E. Everhart, G. Stone, and R. J. Carbone, Phys. Rev. **99**, 1287 (1955).

[13] G. H. Lane and E. Everhart, Phys. Rev. **117**, 920 (1960).

[14] Atomic units will be used throughout this paper:

1 a.u. of energy $= \mu e^4/\hbar^2 = 2E_H = 27.2$ eV.

1 a.u. of length $= a_0 = \hbar^2/\mu e^2 = 0.53$ Å.

1 a.u. of velocity $= e^2/\hbar = 2.18\times10^8$ cm/sec.

1 a.u. of time $= \hbar^3/\mu e^4 = 2.42\times10^{-17}$ sec.

It is useful to note that the energy of an ion in atomic units is given by the relation

$$E = \tfrac{1}{2}mV^2 = \tfrac{1}{2}\times1836MV^2.$$

Since 1 a.u. $= 2.72\times10^{-2}$ keV, $E(\text{keV}) = 25MV^2$, where M is the atomic weight and V the velocity in a.u. Typical experimental ion velocities range from 0.1 to 1 atomic unit (see Fig. 1). In atomic units, the *angular* charge exchange frequency is $\omega = 2\pi\nu = E$, where E is the energy separation between the stationary states.

[15] L. I. Schiff, *Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1955), 2nd ed., pp. 213–216.

ables ϱ_1, $\varrho_2 \cdots \varrho_N$. Taking the time integration of (6),

$$\Delta c_p = -\int_{-\infty}^{+\infty} dt \sum_{s\neq p} c_s(t) \int d\tau X_p \frac{\partial X_s}{\partial t}$$

$$\times \exp\left[-i\int_{-\infty}^{t} (\epsilon_s - \epsilon_p)dt' \right]. \quad (7)$$

This can be seen to be similar in form to a Fourier integral. In analogy to Fourier theory, (7) is small if the collision is so slow that the time variation of the expression preceding the exponential factor contains few frequency components as high as the argument of the exponential function. This can be seen to be merely an expression of the uncertainty principle (in a.u.)

$$\Delta E \Delta t \approx 1, \quad (8)$$

where ΔE is the uncertainty in energy of a given state and $\Delta t = T$ is the duration of the collision. A convenient measure of the effective range of interatomic forces is the quantity λ

$$[\epsilon_s(R) - \epsilon_a(R)]_{max}\lambda = \int_0^\infty [\epsilon_s(R) - \epsilon_a(R)]dR = \frac{\langle Ea\rangle}{2}, \quad (9)$$

where ϵ_s and ϵ_a are the energies of the symmetric and antisymmetric states involved in charge exchange. In the special case that

$$\epsilon_s(R) - \epsilon_a(R) = \epsilon_0 e^{-\alpha R}, \quad \lambda = 1/\alpha. \quad (10)$$

It is reasonable to assume in the present case of zero impact parameter, that $2\lambda \approx vT$, where v is the relative velocity of the colliding nuclei. Then expression (7) becomes

$$2\lambda\Delta E \gtrsim v. \quad (11)$$

This defines the velocity for which diabatic behavior occurs.

An example of this relation occurs when two potential curves cross[16] (Fig. 2). The role of curve crossing becomes apparent in later paragraphs. It can be shown (see Appendix) that the crossing or noncrossing of potential curves is closely related to the damping of the resonance, and that (11) holds equally well for diabatic crossing of potential energy curves.

B. Diabatic Behavior

The major consequence of the deviation from adiabatic behavior is the breakdown of the two-state approximation. It often occurs that at least one of these states lies near in energy to a large number of other states of the same parity. By examining the examples given in succeeding sections (III C.1–III C.2) it can be seen that the total width 2Γ of the band of states involved usually amounts to only a few electron volts

(≈ 0.1 a.u.). By the uncertainty principle (7), in collisions lasting for times less than ≈ 10 a.u. the total electronic energy is uncertain by this amount. However, in these experiments[1–3] typical velocities are of the order of 0.1–1 a.u., typical interaction lengths ≈ 2 a.u. and, therefore, typical collision times ≈ 2–20 a.u. Thus, it must be assumed except for the lowest velocities, that the total wave function must include a mixture of electronic states lying in a band within a few electron volts of the state involved. Since the effect of mixing in additional states destroys interference, it does not appear unreasonable to take the width 2Γ as a measure of the damping of the resonance in charge exchange. (See Appendix.)

The frequency of charge exchange is given by the elementary relation $\omega = E = (\epsilon_s - \epsilon_a)$ in atomic units.[14] For a sharp, undamped resonance, there is the familiar relation

$$\frac{\omega}{\Gamma} = \frac{\epsilon_s - \epsilon_a}{\Gamma} \gg 1.$$

Thus, resonant charge exchange occurs most favorably when the ratio of energy splitting between symmetric and antisymmetric states to the width of the bands of competing states is large.

C. The Limit of Zero Collision Time

When the collision time is short compared to one period of resonant charge exchange, the width of any state is large compared to the separation of the interfering states, interference is destroyed totally, the final wave function becomes a 50-50 mixture of the two charge exchange states, and the electron capture probability is 0.5. Lockwood and Everhart[1] used an empirical equation to represent the experimental data for resonant charge exchange of the form (in a.u.)

$$P_0 = K_1 + K_2 \sin^2\left[\frac{\langle Ea\rangle}{2v} - \beta \right],$$

$$K_1 \approx 0, \quad (12)$$

$$K_2 \approx 1,$$

where K_1, K_2 are slowly varying functions of reciprocal velocity. Ideally, according to the IPM, $\beta = 0$. Everhart and Lockwood found an empirical value near $\beta = \pi/4$. Under these circumstances, the empirical expression (12) would predict $P_0(v = \infty) = \frac{1}{2}$. Thus, the phase constant β arises from the breakdown of coherent interference at high collision velocities.[17]

[16] L. Landau, Physik. Z. Sowjetunion 2, 46 (1932); E. C. G. Stückelberg, Helv. Phys. Acta 5, 369 (1932); C. Zener, Proc. Roy. Soc. (London) A137, 696 (1932); D. R. Bates, ibid. A257, 22 (1960).

[17] At even higher energies (≈ 1 MeV), the recoil velocity of the nuclei becomes large compared to electronic velocities. Under these circumstances, transfer of electronic momentum does not occur and the nuclei are stripped of all electrons and emerge from the collision totally ionized. However, these energies are well above the range covered by experiments so far.

D. R. Bates and R. McCarroll, Proc. Roy. Soc. (London) A245, 175 (1958) have modified the electronic eigenfunctions to take into account momentum transfer. Calculations for $H^+ - H$ by A. F. Ferguson and R. McCarroll, summarized in a review by D. R.

III. DETERMINATION OF THE STATES

Although interference between some combination of symmetric and antisymmetric states is necessary for resonant charge exchange, it is by no means clear how to obtain the required potential curves for these states. Bates, Massey, and Stewart[8] gave a basic expansion in terms of symmetrical and antisymmetrical molecular wave functions, but did not specify the wave functions or energies. Jackson[18] stated that the "two lowest molecular potential energy curves for the appropriate molecular ion should be used for calculation of resonance charge exchange." On the other hand, Ziemba and Russek[19] achieved agreement with experiment for $He-He^+$ collisions by assuming the symmetric and antisymmetric states to be separated by an energy of 107 eV (3.9 a.u.) at zero internuclear distance. Lockwood and Everhart[1] criticized this assumption as unjustified. They pointed out that the molecular wave function at $R=0$ is that of Be^+, whose ionization potential is only 18 eV ($\frac{2}{3}$ a.u.). Presumably, on the basis of the criterion of Jackson, they concluded that the difference in energy between any symmetric and any antisymmetric state cannot be larger than this value.

This contradiction lies even within the paper by Jackson,[18] who obtained the values of the energies of the states at zero internuclear distance by "symmetry arguments from the atomic energy levels of the beryllium atom," which are inconsistent with his own criterion. It is the purpose of this section to clarify these contradictions and set forth an unambiguous basis for determining the energies of the states required for a prediction of the frequency of resonant charge exchange.

A. Nature of the Intermediate States

First, it should be noted that a basis set consisting of stationary states in the molecule with fixed nuclei is not sufficient; nor is it necessary to use a set which corresponds *exactly* to the Heisenberg representation (states for which the Hamiltonian operator is strictly diagonal). In a representation which is built up of approximate wave functions, there are off-diagonal matrix elements of the Hamiltonian operator which cause transitions from one state to another. As long as the time associated with these transitions is long compared to the collision time, the approximations made have no harmful effect. For example, states above the ionization potential of the molecular system are good, since autoionization lifetimes ($\approx 40-400$ a.u.$\approx 10^{-14}-10^{-15}$ sec)[20] are large com-

pared to collision times ($\approx 1-10$ a.u.). Thus, the role of these virtual states cannot be neglected. An example of such a state is $(He)_2{}^+(1\sigma_g)(1\sigma_u)^2$ (see Sec. IIIC.2).

Furthermore, the adiabatic approximation (assumption number 2 of the IPM—see Sec. II) does not hold for states which are separated by energies which are small compared to the broadening caused by the uncertainty principle. [See expressions (6)–(8).] This nonadiabatic behavior is necessary to account for the damping phenomenon in resonant charge exchange. It will be shown how the adiabatic approximation gives completely wrong results for He^+-He charge exchange.

In succeeding paragraphs, an adiabatic Heisenberg representation with an approximate basis set of single configuration molecular orbital wave functions is set up and used.

B. Molecular Orbital Approximation

The molecular orbital, or Hund-Mulliken, approximation assumes an independent-particle model in which the stationary states of the molecule are built up of a product of one electron orbital wave functions. Thus, the total electronic wave function can be described by stating the electron configuration in terms of molecular orbitals. At small internuclear distances ($R\approx 0$) the molecular orbitals go over into the atomic orbitals of the united atom (atom formed by fusion of the nuclei of the two atoms which form the molecule). Since energy levels of the united atom are usually well known or easily estimated, one can obtain the energies of the molecular states at $R=0$. At medium internuclear distances ($R\approx\lambda$) the molecular orbitals (MO) can be described fairly accurately as a linear combination of atomic orbitals (LCAO). At very large internuclear distances ($R\gg\lambda$) where the MO approximation at times becomes inaccurate, one can specify the wave function of the entire system in terms of the wave functions of the separated atoms (Heitler-London or atomic orbital, AO approximation). Although these two approximations are quite different, it is possible to expand the basis set of the AO method in terms of the LCAO-MO wave functions. The MO approximation can be assumed to be reasonably accurate where charge exchange is effective ($R\lesssim\lambda$).

The MO wave functions are not strictly eigenfunctions of the true molecular Hamiltonian. The off-diagonal matrix elements which connect these approximate wave functions (electron correlation or configuration interaction) usually amount to a few electron volts (≈ 0.1 a.u.), and are small for collisions occurring in the energy range studied experimentally.[1-3] For more detailed treatments of the AO and MO theories, the reader is referred to standard works.[21]

Bates and R. McCarroll, Suppl. Phil. Mag. 11, 39 (1962), show some improvement over previous work. Nevertheless, the failure to account correctly for the phase shifts or for the diminished amplitude of the resonance indicate that these effects arise from a breakdown of the two-state approximation, as outlined in the present discussion.

[18] J. D. Jackson, Can. J. Phys. 32, 60 (1954).

[19] F. P. Ziemba and A. Russek, Phys. Rev. 115, 922 (1959).

[20] G. Wentzel, Z. Physik 43, 524 (1927); T-Y Wu, Phys. Rev. 66, 291 (1944).

[21] G. Herzberg, *Molecular Spectra and Molecular Structure* (D. Van Nostrand Company, Inc., Princeton, New Jersey, 1950), 2nd ed., Chap. 6; C. A. Coulson, *Valence* (Oxford University Press, Oxford, 1961), 2nd ed., Chaps. IV–VI.

C. Applications

1. H_2^+

The electronic energies $E_{el}=\Im C-Z_A Z_B/R$ [see expression (2)] of the H_2^+ molecule are shown in Fig. 3 and are summarized in Table I.

The electronic wave function of the initial state of the system is

$$\Psi_{init}=\Psi(t=-\infty, R=-\infty)=1s_B=\frac{1\sigma_g-1\sigma_u}{\sqrt{2}}.$$

By expression (5) the final wave function

$$\Psi_f=\Psi(t=+\infty, R=+\infty)$$

$$=\left[(1\sigma_g)\exp\left(-i\int_{-\infty}^{+\infty}\epsilon_g dt\right)\right.$$

$$\left.-(1\sigma_u)\exp\left(-i\int_{-\infty}^{+\infty}\epsilon_u dt\right)\right]\Big/\sqrt{2}$$

$$=\frac{1s_A}{2}\left[\exp\left(-i\int_{-\infty}^{+\infty}\epsilon_g dt\right)-\exp\left(-i\int_{-\infty}^{+\infty}\epsilon_u dt\right)\right]$$

$$+\frac{1s_B}{2}\left[\exp\left(-i\int_{-\infty}^{+\infty}\epsilon_g dt\right)+\exp\left(-i\int_{-\infty}^{+\infty}\epsilon_u dt\right)\right].$$

The squares of the coefficients of $1s_A$ and $1s_B$ give the probabilities P_0 and P_1 of charge exchange or nonexchange, respectively. Finally,

$$P_0=C_A{}^*C_A=\sin^2(\phi/2)$$
$$P_1=C_B{}^*C_B=\cos^2(\phi/2),\tag{13}$$

where

$$\phi=\int_{-\infty}^{+\infty}(\epsilon_u-\epsilon_g)dt.\tag{14}$$

Evaluation of ϕ is simplest for high velocities (zero impact parameter). Then $R\approx vt$, where v equals the velocity of the incident ion.[22] Then

$$\phi=\frac{\langle Ea\rangle}{v}=\frac{1}{v}\int_{-\infty}^{+\infty}[\epsilon_u(R)-\epsilon_g(R)]dR.\tag{15}$$

TABLE I. Lowest states of the H_2^+ molecule.

State	MO	United atom (He$^+$) approximation $(R=0)$	Electronic energy (a.u.) $(R=0)$	LCAO-MO approximation
Even	$1\sigma_g$	$1s$	-2	$\dfrac{1s_A+1s_B}{\sqrt{2}}$
Odd	$1\sigma_u$	$2p$	$-\frac{1}{2}$	$\dfrac{1s_A-1s_B}{\sqrt{2}}$

[22] More general formulas to handle lower velocities are given elsewhere. (See reference 8.)
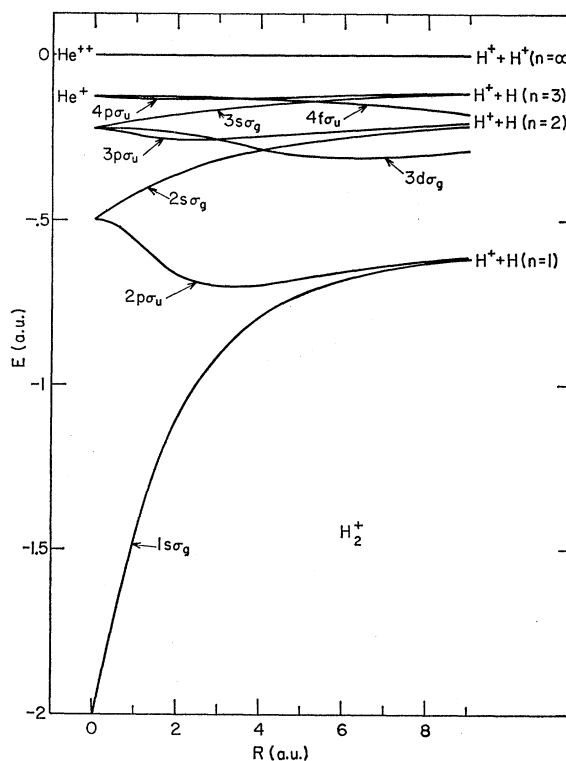

FIG. 3. Potential curves for $H^+ + H$. (See reference 23.) Only orbitals of σ type have been shown.

This result is in agreement with previous calculations,[1,8] since the adiabatic and molecular orbital wave functions are identical. $\langle Ea\rangle$ has been evaluated by Ziemba[1] from the exact H_2^+ energies[23] to be 4.88 a.u., which is in good agreement with the experimental value of (4.45±0.08), if one considers the simplified nature of the theory. The effective range can be evaluated by inserting the experimental value for $\langle Ea\rangle$, the value of $[\epsilon_u(0)-\epsilon_g(0)]=\frac{3}{2}$ a.u. (Table I) in expression (9). The result is $\lambda(H_2^+)$ $=1.48$ a.u. in agreement with the value of 1.5 for the mean radius of the charge distribution of the hydrogen atom,[24] which is a measure of the range of interatomic forces.

The weak damping of the $H-H^+$ resonance (Fig. 2) comes from the large ratio of $(\epsilon_a-\epsilon_s)/\Gamma=(\epsilon_u-\epsilon_g)/\Gamma$. Here, there is a single state which is far away from a group of closely spaced states (Fig. 3).

2. $He-He^+$

The electronic energies of the He^+-He system are summarized in Table II and Fig. 4.

The electronic wave function of the initial state of the system $(He_A{}^+He_B)$ is $\Psi_{init}=\Psi(T=-\infty, R=-\infty)$

[23] D. R. Bates, K. Ledsham, and A. L. Stewart, Phil. Trans. Roy. Soc. London **246**, 215 (1953).

[24] H. A. Bethe and E. E. Salpeter, Quantum Mechanics of One and Two-Electron Atoms (Academic Press Inc., New York, 1957), p. 17; or E. U. Condon and G. H. Shortley, Theory of Atomic Spectra (Cambridge University Press, New York, 1953), p. 117.
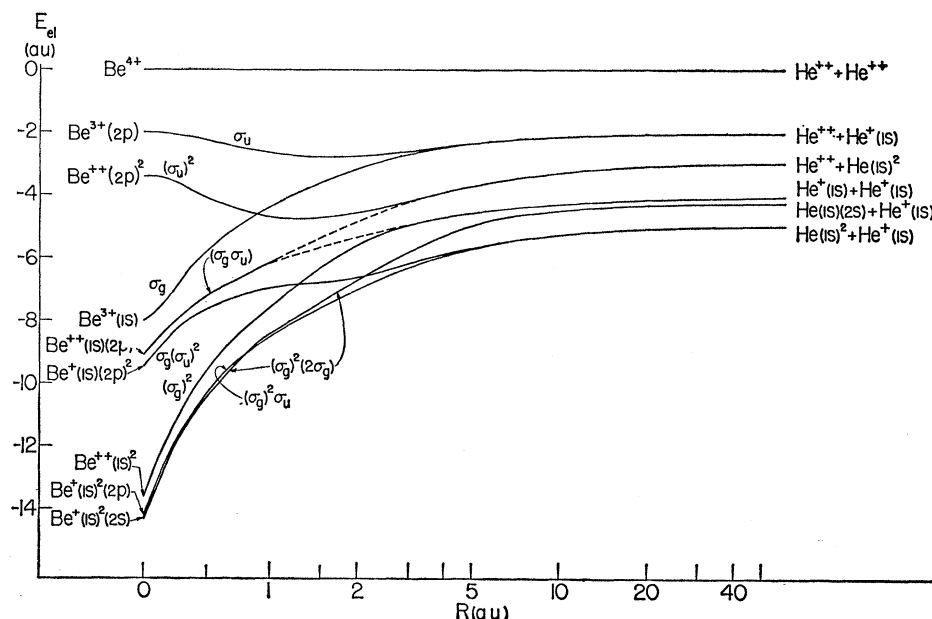
FIG. 4. Diabatic curves suitable for discussion of fast collisions involving He ions. These show the electronic energies of the He-He system for a few states of interest. To the right of the figure, at large internuclear distances, the energies are those of separated atoms and/or ions. At smaller internuclear distances, the energies are those of a single configuration molecular orbital wave function. At $R=0$, the energies are those of the Be^+ united ion. Since these are diabatic curves, crossing of states of like symmetry is permitted, in contrast with the non-crossing rule for adiabatic curves. (See Table II and Sec. III C.2 for further discussion.) Thus, there is not the usual adiabatic correlation between states of the united atom and separated atoms. 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 author's estimates. $(He)_2{}^{4+}$: Zero of energy. $(He)_2{}^{3+}$ σ_g, σ_u: Energies are obtained exactly by scaling E as Z^2 and R as $1/Z$ from the $H_2{}^+$ curves (Fig. 3). $(He)_2{}^{++}$: It is not possible to make a unique connection between molecular orbital and separated atom states. Here, the three molecular orbital $(\sigma_g)^2$, $(\sigma_g)(\sigma_u)$, and $(\sigma_u)^2$ states are visualized (dashed lines) as arising from the avoided crossing of the He^+-He^+ curve with the degenerate He^{++}-He and He-He^{++} states. $(He)_2{}^{++}$ $(\sigma_g)^2$ ($R=0.8$ to $R=1.8$ a.u.). [See W. Kolos and C. C. J. Roothaan, Rev. Mod. Phys. **32**, 219 (1960).] $(He)_2{}^+$ $(\sigma_g)^{-1}$, $(\sigma_u)^{-1}$. [See reference b, Table II. For term values of united or separated atoms, see reference a, Table II. In the case of virtual states, energies were estimated from term values of similar ions. Also configurations containing $(2p\sigma)^2$ were evaluated from the relation $E(2p\sigma)^2 = \frac{1}{3}E(^1S) = \frac{2}{3}E(^1D)$ (see reference b, Table II).]

$= 1s_A(1s_B)^2$. It is readily proven by writing this in an antisymmetrized product to be equivalent to a $(1s_A)^{-1}$ "hole" of the form $(1\sigma_g)^{-1} + (1\sigma_u)^{-1}/(2)^{1/2}$. This is formally identical to that derived for $(H_2)^+$ (13), (14), and (15), except that the labels u and g must be interchanged. Following this analogy, then one must find the value of $\langle Ea \rangle$, the area between the appropriate u and g curves.

Referring to Fig. 4 and Table II, one can see that these

TABLE II. States of $(He)_2{}^+$.

| State | MO designation | | United atom (Be$^+$) approximation ($R=0$) | Electronic energy ($R=0$) (a.u.) |
	For large R^c	For small R		
Odd	$(1\sigma_g)^2(1\sigma_u)$	$(1\sigma_g)^2(1\sigma_u)$	$(1s)^2(2p)$	-14.2[a]
Even (diabatic)	$(1\sigma_g)(1\sigma_u)^2$	$(1\sigma_g)(1\sigma_u)^2$	$(1s)(2p)^2$	-9.4[b]
Even (adiabatic)	$(1\sigma_g)(1\sigma_u)^2$	$(1\sigma_g)^2(2\sigma_g)$	$(1s)^2(2s)$	-14.3[a]

[a] Experimental value obtained from the reference by Charlotte E. Moore, *Atomic Energy Levels* (U. S. Government Printing Office, Washington, D.C., 1949), Vol. I, Natl. Bur. Std. (U. S.), Circ. 467.
[b] Calculated by the author from theoretical orbital energies given by P. E. Phillipson, Phys. Rev. **125**, 1981 (1962).
[c] At $R = \infty$, both $(1\sigma_g)^2(1\sigma_u)$ and $(1\sigma_g)(1\sigma_u)^2$ go to the separated atoms $He(1s)^2 + He^+(1s)$.

states start out as the degenerate ground state of the system $He(1s)^2 + He^+(1s)$. At smaller internuclear distances the u state becomes the lower of the two. It can be described unambiguously as $(1\sigma_g)^2(1\sigma_u)$ at all internuclear distances, and therefore becomes $Be(1s)^2(2p)$ at $R=0$. The g state can be described as $(1\sigma_g)(1\sigma_u)^2$ for large internuclear distances. However at $R \approx 2$ a.u., it is crossed by a $(1\sigma_g)^2(2\sigma_g)$ g state derived from $He^+(1s)$ and $He(1s)(2s)$. For values of R to the left of the crossing point, there is an ambiguity as to which g curve to assume for purposes of calculating $\langle Ea \rangle$. The adiabatic curve obeys the noncrossing rule of von Neumann and Wigner[25] and thus becomes $(1\sigma_g)^2(2\sigma_g)$, which is the lower choice and is almost indistinguishably close to the $(1\sigma_g)^2(1\sigma_u)$ u state. Finally, it goes to the united atom state $Be^+(1s)^2(2s)$ which is lower than the previously described odd state $Be^+(1s)^2(2p)$. On the basis of the adiabatic potential curve, one would expect a value near zero for $\langle Ea \rangle$ and, therefore, a lack of resonant charge exchange. This is clearly in disagreement with experiment.

[25] J. von Neumann and E. Wigner, Physik. Z. **30**, 467 (1929).

The upper alternative, which will be designated the *diabatic* curve, can be described as $(1\sigma_g)(1\sigma_u)^2$ at all internuclear distances and becomes $Be^+(1s)(2p)^2$ at $R=0$. If one uses this diabatic electronic energy curve of Fig. 4 (see also Table II), the value obtained for $\langle Ea \rangle$ is 7.8 a.u., in agreement with the experimental value of (7.1 ± 0.2) and the theoretical values of 7.0 and 6.6 previously obtained, respectively by Jackson[18] and Ziemba and Russek.[19] (The disagreement among theoretical calculations reflects small differences in theoretical potential energy curves for the He-He$^+$ system.) From expression (9), the observed value of $\langle Ea \rangle$ and $(\epsilon_a-\epsilon_s)_{\max}$ (see Table II), one obtains an effective range of 0.74 a.u.

To obtain agreement with experiment, it is therefore necessary to assume that the molecular system crosses the interfering $(1\sigma_g)^2(2\sigma_g)$ curve and remains on the *diabatic* curve given by molecular orbital theory. In fact, one can show that the $(1\sigma_g)(1\sigma_u)^2$ diabatic curve must cross an infinite number of curves of the form $(1\sigma_g)^2(n\sigma_g)$, for the experimental results to agree with theory. The occurrence of these crossings is consistent with the discussion based on the Landau-Zener theory.[16–26] For, if one uses a reasonable value for $\Delta E\approx0.1$ a.u., one finds $\Delta E(2\lambda)\approx0.15$ a.u., which is comparable only to the slowest collision velocity of 0.14 (Fig. 1).

Here again, as in H^+-H, the presence of an undamped resonance is caused by a favorable ratio of $(\epsilon_s-\epsilon_a)/\Gamma$ (Fig. 4). It is of further interest to note that the $(1\sigma_g)(1\sigma_u)^2$ state is above the ionization potential of (He)$_2^+$ for small values of R. (See Sec. IIIA.)

3. Other Systems: Li^+-Li, $Li^{++}-Li$, $He^{++}-He$

It is of interest to extend the theory of resonant charge exchange to cases that are not yet investigated.

The $Li-Li^+$ wave function before collision is $(1s_A)^2(1s_B)^2(2s_B)$, which can be written as $(1\sigma_g)^2(1\sigma_u)^2 \times (2\sigma_g-2\sigma_u)/(2)^{1/2}$. At $R=0$, the united atom wave function is C^+: $(1s)^2(2p)^2(2s-3p)/(2)^{1/2}$. The even and odd states are separated by the $(2s\rightarrow 3p)$ splitting, which is about $\frac{1}{2}$ a.u. However, this is somewhat smaller than the uncertainty in energy, which is the order of the total splitting of the states of the C$^+$ atom (ionization potential≈1 a.u.). Thus, conditions are unfavorable for a pronounced resonant phenomenon, since the oscillations would be of long period and would be heavily damped.

The situation is favorable, however, for Li-Li^{++}. Here the initial wave function is

$(1s_A)(1s_B)^2(2s_B)$

$$=[(1\sigma_g)^2(1\sigma_u)^2]\frac{[(1\sigma_u)^{-1}+(1\sigma_g)^{-1}]}{\sqrt{2}}\frac{[(2\sigma_g)-(2\sigma_u)]}{\sqrt{2}}.$$

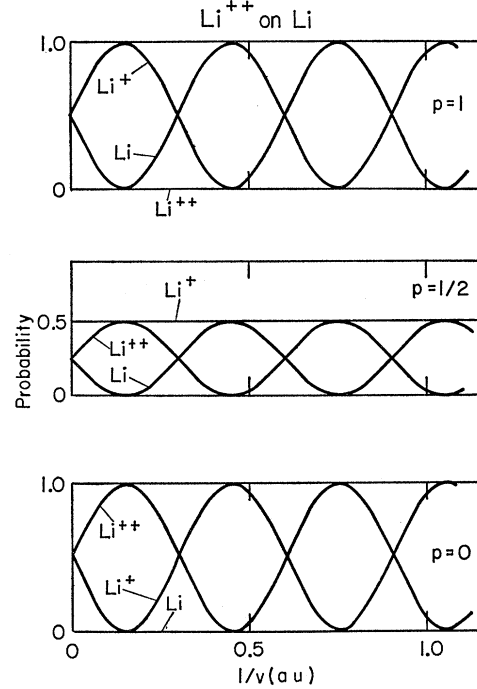Then, denoting the probability of capture of the $2s_B$

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26 See Appendix.

FIG. 5. Charge exchange for Li^{++}-Li collisions, shown for three values of p, the probability that the outer $2s$ electron is captured by the scattered ion. p is expected to be a slowly varying function of $1/v$. A phase shift has been applied to make the curves connect smoothly to the correct limit for $1/v=0$.

electron by p and probability of capture of a $1s_B$ electron by p', it is readily shown that

$$\begin{aligned} P_0&=pp' \\ P_1&=p+p'(1-2p) \\ P_2&=(1-p)-p'(1-p), \end{aligned} \tag{16}$$

where P_0, P_1, and P_2 are the probabilities of double-, single-, and nonelectron capture, respectively. As in Li-Li$^+$, the term p arising from the weakly bound outer electron is a slowly varying, heavily damped function of the electron energy. The period of oscillation of p' is determined by expressions (13), (14), and (15), where $\langle Ea \rangle$ is largely determined by the separation between the even and odd states of the (Li)$_2^{3+}$ core. Although detailed calculations for this molecule are not available, estimates can be made by a simple scaling procedure. It is remembered that $\langle Ea \rangle=2\lambda(\Delta E)_{\max}$, that $\lambda \alpha 1/Z$ and $(\Delta E)_{\max} \alpha Z^2$; therefore $\langle Ea \rangle \alpha Z$. Then, $\langle Ea \rangle$ for (Li)$_2^{3+}$ should be $\frac{3}{2}\langle Ea \rangle$ for isoelectronic (He)$_2^+$. Thus, the predicted value for (Li)$_2^{3+}$ is $\langle Ea \rangle\approx3.5Z=10.5$. Curves for P_0, P_1, and P_2 are shown in Fig. 5.

In the case of He^{++}-He collisions, the initial wave function is

$$\Psi(He^{++}-He)=\Psi_{BB}=(1s_B)^2=\frac{(\sigma_u-\sigma_g)(\sigma_u-\sigma_g)}{2}$$

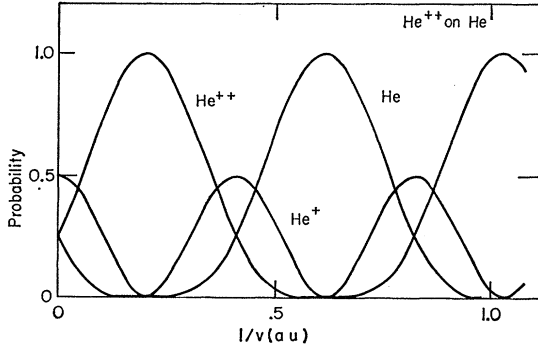$$=\frac{(\sigma_u{}^2+\sigma_g{}^2)}{2}-\frac{(\sigma_g\sigma_u+\sigma_u\sigma_g)}{2}.$$

FIG. 6. Charge exchange for He^{++} on He. A phase shift has been added to make the curves join smoothly to the correct values for $1/v=0$. Also, for simplicity of calculation, $\langle Ea\rangle_{NV}$ has been assumed to equal $\langle Ea\rangle_{VZ}$.

This wave function is seen to be a superposition of three MO states,

$$\Psi_{BB}=\frac{\Psi_N}{2}-\frac{\Psi_V}{\sqrt{2}}+\frac{\Psi_Z}{2}, \qquad (17)$$

where

$$\Psi_N=\sigma_g{}^2, \quad \Psi_V=\frac{1}{\sqrt{2}}(\sigma_g\sigma_u+\sigma_u\sigma_g), \quad \Psi_Z=\sigma_u{}^2 \quad (18)$$

are the wave functions of the three singlet states formed from two electrons in σ_g or σ_u orbitals.[27] The other two AO wave functions also can be expressed in terms of Ψ_N, Ψ_V and Ψ_Z:

$$\Psi(\text{He}-\text{He}^{++})=\Psi_{AA}=(\Psi_N+\sqrt{2}\Psi_V+\Psi_Z)/2$$
$$\Psi(\text{He}^+-\text{He}^+)=\Psi_{AB}=(\Psi_N-\Psi_Z)/2. \qquad (17')$$

These equations are readily solved for the MO functions in terms of the AO basis:

$$\Psi_N=(\Psi_{AA}+\Psi_{BB}+\sqrt{2}\Psi_{AB})/2$$
$$\Psi_V=(\Psi_{AA}-\Psi_{BB})/\sqrt{2} \qquad (19)$$
$$\Psi_Z=(\Psi_{AA}+\Psi_{BB}-\sqrt{2}\Psi_{AB})/2.$$

The transition from AO to MO states is shown in Fig. 4. For fast collisions, the final wave function can be obtained by expanding Ψ_{BB} in the MO basis set (17) and taking into account the phase relations. Then, ignoring a common phase factor, one obtains

$$\Psi_f=\tfrac{1}{2}[\Psi_N-\sqrt{2}\Psi_V e^{-i\phi_1}+\Psi_Z e^{-i\phi_2}], \qquad (20)$$

where

$$\phi_1=\frac{\langle Ea\rangle_{NV}}{v}=\int_{-\lambda}^{+\lambda}\frac{\epsilon_V-\epsilon_N}{v}dR,$$
$$\phi_2=\frac{\langle Ea\rangle_{NZ}}{v}=\int_{-\lambda}^{+\lambda}\frac{\epsilon_Z-\epsilon_N}{v}dR. \qquad (21)$$

[27] A fourth state Ψ_{AB}, with the orbital wave function $(\sigma_g\sigma_u-\sigma_u\sigma_g)/2$ is a $^3\Sigma_u{}^+$ state. Since the initial state in cases of experimental interest is almost always a singlet state and since singlet-triplet transitions can be neglected in fast collisions, triplet states have been neglected throughout this paper.

The value λ in the limits of integration indicates that the interaction takes place within the region of molecular binding. These integrals may be estimated from expression (9). Since $\lambda[(\text{He})_2{}^+]=0.74$ and $\lambda[(\text{He})_2{}^{3+}]=\tfrac{1}{2}\lambda[(\text{H})_2{}^+]=0.74$ also, it is reasonable to assume $\lambda[(\text{He})_2{}^{++}]=0.74$. Now

$$\epsilon_Z(0)=\epsilon[\text{Be}^{++}(2p)^2]=-3.4,$$
$$\epsilon_V(0)=\epsilon[\text{Be}^{++}(1s,2p)=-9.1,$$
$$\epsilon_N(0)=\epsilon[\text{Be}^{++}(1s)^2]=-13.65.$$

(See Fig. 4.) Then $\langle Ea\rangle_{NV}=6.7$, $\langle Ea\rangle_{NZ}=15.2$.

Expanding Ψ_{final} back into the original AO basis and taking the squares of coefficients, one obtains

$$P_2=P_{BB}=\tfrac{1}{8}\{3+2\cos(\phi_1)+\cos(\phi_2)$$
$$+2\cos(\phi_2-\phi_1)\},$$
$$P_1=P_{AB}\tfrac{1}{2}\sin^2(\tfrac{1}{2}\phi_2), \qquad (22)$$
$$P_0=P_{AA}=\tfrac{1}{8}\{3-2\cos(\phi_1)+\cos(\phi_2)$$
$$-2\cos(\phi_2-\phi_1)\}.$$

Very roughly, for $(\text{He})_2{}^{++}$, $\langle Ea\rangle_{NV}\approx\tfrac{1}{2}\langle Ea\rangle_{NZ}$; from (21) $\phi_2=2\phi_1$. Using this simplification, (22) reduces to

$$P_2=\cos^4(\tfrac{1}{2}\phi_1),$$
$$P_1=\sin^2(\tfrac{1}{2}\phi_1), \qquad (23)$$
$$P_0=\sin^4(\tfrac{1}{2}\phi_1).$$

(See Fig. 6).

The large separation of the energy curves for $(\text{He})_2{}^{++}$ (Fig. 4), indicates a more pronounced tendency to follow the adiabatic potential curves than in the case of $(\text{He})_2{}^+$. Thus, one would expect relatively heavy damping for $(\text{He})_2{}^{++}$. Nevertheless, enough oscillations should be present to test the theoretical predictions.

IV. CONCLUSIONS

It has been seen that the observed phenomena of wide angle resonant charge exchange scattering in multi-electron systems cannot be accounted for by an adiabatic theory. This has been circumvented in this paper by assuming a quasiadiabatic basis set of MO wave functions. This independent-particle formulation is adequate for discussion of resonant charge exchange and has been used to predict the results of experiments on new systems. On the other hand, for small angle scattering the impact parameters usually are large enough so that the adiabatic approximation still may be valid.

The necessity of a three state approximation (Sec. IIIC.3) appears to be quite general in the case of charge exchange involving two s electrons.

It should be pointed out that the present treatment has validity over a limited range of ion velocities ($v\approx0.1-1$). At higher velocities, diabatic transitions

between MO's take place. These account for breakdown of coherence (Sec. IIC), formation of multiply charged ions (Fig. 1), and charge exchange in nonresonant systems, such as He+H$^+$.[3] At lower velocities, the collisions become truly adiabatic. A discussion of these phenomena is outside the scope of the present treatment.

ACKNOWLEDGMENTS

APPENDIX

Damping Effects

This section compares the idea of damping effects (Sec. IIB) with the Landau-Zener treatment of curve crossing to show the close relation between the two points of view.

As a simplified model for damping, consider the interference between a single state of energy ϵ_s and a band of states of energy ϵ_a and width 2Γ. The probability of charge exchange due to coherent interference is given by an expression of the general form $P_A = |C_A|^2$, where

$$C_A = \frac{1}{2}\left[1 + \frac{1}{2\Gamma}\int_{\epsilon_s - \epsilon_a - \Gamma}^{\epsilon_s - \epsilon_a + \Gamma} e^{-i\epsilon\tau}d\epsilon\right]. \qquad (A1)$$

Then,

$$P_A = C_A{}^2 = \frac{1}{4}\left[1 + \frac{\sin^2(\Gamma t)}{(\Gamma t)^2} + \frac{2\sin(\Gamma t)\cos([\epsilon_s - \epsilon_a]t)}{\Gamma t}\right].$$

This function is shown in Fig. 7. It can be seen from (A1) that the oscillation in P_A is between the envelopes

$$P_A(\pm) = \frac{1}{4}\left[1 \pm \frac{\sin(\Gamma t)}{\Gamma t}\right]^2, \qquad (A2)$$

and the amplitude of oscillation is given by $P_A(+) - P_A(-) = \sin(\Gamma t)/(\Gamma t)$. As a measure of the mean decay time, one can take the value of the integral

$$\int_0^\infty \frac{\sin(x)}{x}dx = \frac{\pi}{2} \quad \text{or} \quad \Gamma\Delta t = \pi/2 = 1.57.$$

This is to be compared with the uncertainty principle $\Delta E\Delta T \approx 1$.

The process can be seen from a quite different point of view of the Landau-Zener formula.[16] The initial wave function contains a mixture of Ψ_s and Ψ_a. At the crossing point (Fig. 2) there is a probability $(1-P)$ of an
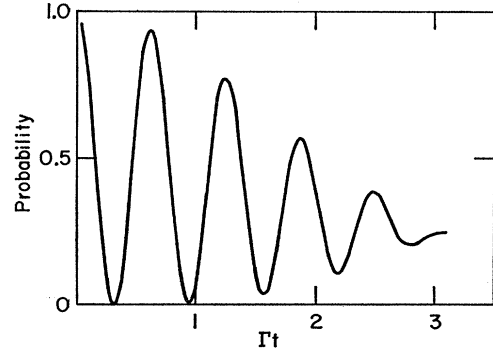

FIG. 7. Probability of coherent interference of a single state with a band of states of width 2Γ.

adiabatic transition to a mixture of the states s' and a. In such a mixture interference is absent. At the second traversal of the crossing point the same phenomena recur. Again a mixture of states a and s' fails to interfere, so that the over-all probability of constructive interference is equal to the probability of two successive diabatic transitions,[28] $P_0 = P^2$. P is given by the Landau-Zener formula[16]:

$$P = e^{-w},$$

where

$$w = \frac{2\pi(H_{ss'})^2}{\hbar v(d/dR)(\epsilon_s - \epsilon_{s'})}, \qquad (A3)$$

which becomes

$$2\pi(H_{ss'})^2/v(d/dR)(\epsilon_s - \epsilon_{s'}) \text{ in a.u.}, \qquad (A3')$$

$H_{ss'}$ is the off-diagonal matrix element connecting states s and s', and v the collision velocity. It is reasonable to assume that $H_{ss'}$ causes the splitting between the states at the crossing point. Then $\Delta E = 2H_{ss'}$. Furthermore, it is reasonable to assume

$$\Delta E \approx 2\Gamma$$

and

$$(\epsilon_s - \epsilon_{s'}) \approx (\epsilon_s - \epsilon_a)_{max}e^{-R/\lambda}.$$

Then

$$\frac{d(\epsilon_s - \epsilon_{s'})}{dR} = \frac{1}{\lambda}(\epsilon_s - \epsilon_a)_{max}e^{-R/\lambda}.$$

If $R \approx \lambda$, then

$$w = 2\pi e\Gamma^2\lambda/v(\epsilon_s - \epsilon_a)_{max}.$$

Taking the collision time $T/2 \approx \lambda/v$,

$$P_0 = e^{-2w}\exp[-2\pi e\Gamma^2 T\lambda/(\epsilon_s - \epsilon_a)_{max}].$$

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[28] This statement is not strictly correct. Inclusion of quantum-mechanical phase factors introduces oscillatory terms in the expression for the probability of two successive events. It can be shown that these terms have important bearing on the theory of asymmetric charge exchange. [See W. Lichten, Bull. Am. Phys. Soc. 8, 393 (1963).] Nevertheless, in the present application, these terms can be ignored.

Taking the approximate relation $2\Gamma/(\epsilon_s-\epsilon_a)_{max}\approx0.1$ (see Fig. 4).

$$P_0=e^{-0.1e\pi\Gamma T}=e^{-0.85\Gamma T}.$$

The mean life for decay is given by the relation $0.85\Gamma T=1$ or $\Gamma T=1.2$, which again agrees with the uncertainty principle $\Delta E\Delta T\approx1$.

Thus, two apparently quite different approaches agree. This tends to reinforce the conclusion that adiabatic potential curves are not important in the theory of fast atomic collisions. It would be interesting to find out if a more refined collision theory would bear out these arguments.

Calculation of the Scattering Constant from the Theory of Multiple Scattering*

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The expressions for the mean spatial and projected angles of multiple scattering are obtained using the distribution function for multiple scattering derived by Nigam, Sundaresan and Wu, and compared with those of Molière. It is shown that Molière's calculations involve the approximation of $\chi_c\sqrt{B}\rightarrow0$. The distribution function of Nigam et al. is found to give correction terms which are proportional to powers of $\chi_c\sqrt{B}$ and $\chi_c\sqrt{B}\ln(\pi/\chi_c\sqrt{B})$.

I. INTRODUCTION

THE theory of multiple scattering of a charged particle passing through matter has been worked out by Williams,[1] Goudsmit and Saunderson,[2] Molière,[3] Snyder and Scott,[4] and Lewis.[5] The formulation of the theory as done by Molière,[3] and Goudsmit and Saunderson[2] has the very interesting feature that the differential law of scattering enters into the theory of multiple scattering only through a single parameter, the screening parameter χ_a. Bethe[6] has established that the theory of Goudsmit and Saunderson[2] has a close quantitative relation to that of Molière.[3] The theory of Molière has been widely applied in the interpretation of experimental results. However, Nigam, Sundaresan, and Wu[7] have pointed out that the formula given by Molière for the scattering cross section of a charged particle by an atom in his theory of multiple scattering is inconsistent. This is because Molière's calculation of the scattering amplitude includes an inconsistent expansion of the phase shift in powers of $\alpha_1 = zZe^2/\hbar v$. Nigam et al.,[7] use Dalitz's[8] relativistic expression for the single scattering cross section derived in the second Born approximation for the scattering of a spin-half-charged particle by the screened Coulomb field of an atom, and the dis-

tribution function for multiple scattering was calculated in powers of α_1 in a consistent manner. They obtained satisfactory agreement with the experimental results of Hanson, Lanzl, Lyman, and Scott[9] for the $1/e$ widths of the distribution function for the scattering of 15.6 MeV electrons by Au and Be. Further the work of Nigam, Sundaresan and Wu,[7] (hereafter to be referred as paper A), in contrast to Molière's[3] theory, predicts different screening angles for electron and positron scattering and consequently, different distribution functions for multiple scattering. Nigam and Mathur[10] have applied the results of paper A and calculated the difference in multiple scattering of electron and positron and found good agreement with the experiment of Henderson and Scott.[11]

The method of estimating the energy of fast ionizing particles in photographic emulsion by measuring the deviations in their tracks produced by multiple scattering was first suggested by Bose and Choudhuri.[12] Gottstein, Menon, Mulvey, O'Ceallaigh, and Rochat[13] have shown that the mean deviation of a charged particle passing through a given layer of matter is directly proportional to the charge and inversely proportional to the product (momentum $\times$ velocity) the constant of proportionality depending on the composition of the scattering medium. They calculated the "scattering constant" using Molière's theory. In this paper, the mean angle of multiple scattering, spatial and pro-

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