Molecular Wave Functions and Inelastic Atomic Collisions*

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A theoretical interpretation is given of inelastic atomic collisions, especially violent cases where the atomic electron shells deeply interpenetrate. The basis set consists of a product of single-particle, hydrogen-molecular-ion orbital wave functions. The occurrence of large energy losses at critical internuclear distances can be seen as a result of the promotion of inner-shell electrons predicted by molecular-orbital (MO) theory. Energy losses, multiple ionization, and fast-electron ejection happen as a result of transitions between MO single-particle energy levels at crossings. A list is given of the mechanisms which cause an avoidance of diabatic crossings. After the collision, the atoms are left in narrow, discrete states with several electrons simultaneously, highly excited. This type of excitation occurs in heavy-particle collisions or in nuclear fission, but not in photon or electron bombardment. The presence of fast electrons at definite energies is seen as a unique prediction of the present model. The lack of correlation between the charge states of the separating atoms after the collision is seen to result from the weakness of correlation energy among electrons in highly excited, outer shells. The consistency of the MO model with the details of energy losses, fast-electron spectra, and positions of critical internuclear distances indicates the insufficiency of purely statistical models and the lack of necessity of the assumption of plasma oscillations or other *ad hoc* mechanisms. A noteworthy feature of this analysis is that the Born-Oppenheimer approximation has been extended to collisions which involve nuclear kinetic energies of several hundred kV.

I. INTRODUCTION

WHEN atomic projectiles suffer hard (wide deflection angle, small impact parameter) collisions with other atoms, the electron shells deeply interpenetrate. In these violent encounters, large energy losses occur at characteristic internuclear distances. Showers of electrons are thrown out at velocities which are far different from those of the electrons in the original projectile. Thus the mechanism of electron ejection cannot have a simple classical origin. It is the purpose of this discussion to show that we can understand these phenomena in terms of some familiar ideas of atomic physics: the molecular-orbital (MO) model, the Auger effect, and the Landau-Zener theory of level crossing.

Afrosimov and Federenko[1] and Morgan and Everhart[2] have studied inelastic energy losses in hard collisions between rare-gas ions and atoms. The application of coincidence techniques by Afrosimov *et al.*[3] and Everhart and co-workers[4] has given the charge states of each particle in addition to the total energy loss. Figures 1 and 2 show the average energy losses and number of ejected electrons, respectively, as a function of the smallest internuclear distance[5] during the collision of Ar and Ar^+. We can note the remarkable features of energy losses which run up to kV and ejected electrons ranging to a dozen in number. Both energy loss and number of ejected electrons rise sharply at certain critical internuclear distances [$R_0 \sim 0.5$, 0.2 atomic units (a.u.)].

In a recent letter, Fano and the author[6] proposed a mechanism for the large energy losses, multiple ionization, and the sharp rises at certain internuclear distances. It was based on the old ideas of promotion of MO's arising from inner-shell atomic electrons,[7,8] the theory of level crossing,[9] and the Auger effect

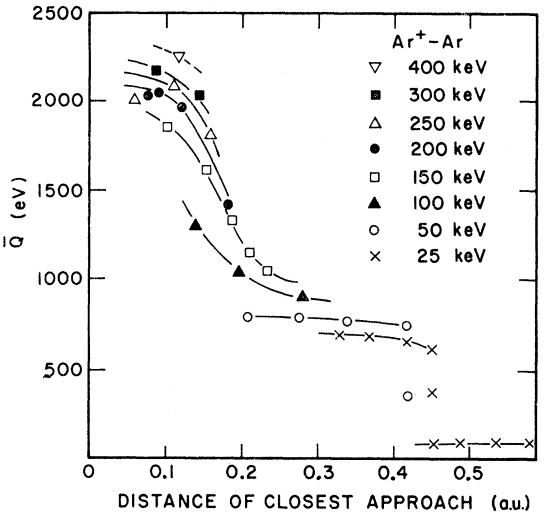

FIG. 1. Average energy losses $\bar{Q}$ in Ar-Ar^+ collisions as a function of distance of closest approach. Source: See Ref. 4.

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[1] V. V. Afrosimov and N. V. Fedorenko, Zh. Tekhn. Fiz. **27**, 2557 (1957) [English transl.: Soviet Phys.—Tech. Phys. **2**, 2378 (1957)].

[2] G. H. Morgan and E. Everhart, Phys. Rev. **128**, 667 (1962).

[3] V. V. Afrosimov, Yu. S. Gordeev, M. N. Panov, and N. V. Fedorenko, Zh. Tekhn. Fiz. **34**, 1613 (1964); **34**, 1624 (1964); **34**, 1637 (1964); **36**, 123 (1966) [English transls.: Soviet Phys.—Tech. Phys. **9**, 1248 (1965); **9**, 1256 (1965); **9**, 1265 (1965); **11**, 89 (1966)].

[4] E. Everhart and Q. C. Kessel, Phys. Rev. Letters **14**, 247 (1965); Q. C. Kessel, A. Russek and E. Everhart, *ibid.* **14**, 484 (1965); Q. C. Kessel and E. Everhart, Phys. Rev. **146**, 16 (1966).

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

[6] U. Fano and W. Lichten, Phys. Rev. Letters **14**, 627 (1965).

[7] F. Hund, Z. Physik **40**, 742 (1927).

[8] R. S. Mulliken, Phys. Rev. **32**, 186 (1928).

[9] 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).

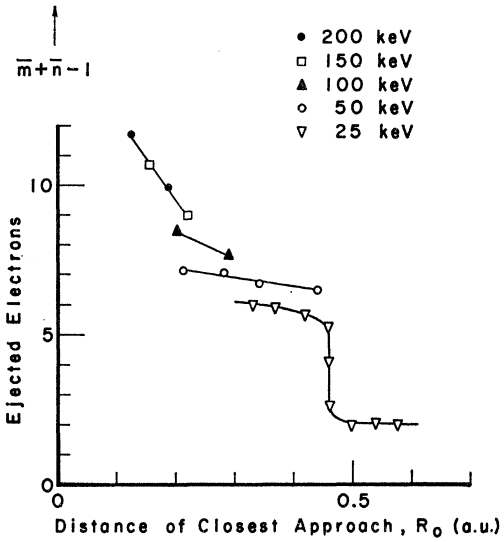

FIG. 2. Number of ejected electrons in Ar-Ar$^+$ collisions as a function of distance of closest approach. Source: See Ref. 4.

(autoionization).[10] A prediction was made[6] that fast electrons would be emitted in hard collisions. This prediction was later confirmed in several laboratories.[11–13] This paper gives a more detailed account of the theory of energy losses and ionization in hard atomic collisions.

II. GENERAL PRINCIPLES

In this Section we shall give a resumé of the principles required to relate the theory of molecular energy levels to collision problems. Applications will then be made to specific pairs of colliding atoms.

A. Energy Levels of Diatomic Molecules

Our first objective is to review the molecular-orbital (MO), independent-particle model of molecular wave functions.

Figure 3 shows a correlation diagram for the MO energy levels of a single electron in the field of two identical nuclei, as in H_2^+. Note that energy levels of the same orbital angular momentum,[14] m_l, ($m_l=0$ for σ orbitals, $m_l=1$ for π orbitals, $m_l=2$ for δ, etc.) do cross in this case. m_l denotes the projection of the orbital angular momentum of a single electron along the internuclear axis. (The usual notation for this, λ, is not used to avoid confusion with the present use of λ for effective range.) This diagram shows the electron promotion mechanism of Hund[7] and Mulliken,[8] in which electrons can have a higher principal quantum number in going from separated atoms to united atom. Promotion is important in atomic collisions because:

(1) Energy levels from the same shell and of comparable energy before collision can be widely separated after promotion. The promotion energy can be many atomic units, or several hundred eV. These are the largest energies which affect the electron dynamics of heavy-particle collisions.

(2) There are many crossings of energy levels. (Loosely speaking, degeneracies at $R=0$ or $R=\infty$ can be called "crossings".)

(3) Transitions between MO's at crossings can leave a promoted electron stranded in a higher level after the collision. Thus promotion plus level crossing can be a cause of very high excitation of atoms in collisions.

B. Molecular Orbital Energies

The energy ϵ_i of the ith molecular orbital is operationally defined as the ith eigenvalue of the Hartree-Fock equations for the system at a given internuclear distance. These energies can be computed to within a few percent by the self-consistent-field method of Roothaan.[15]

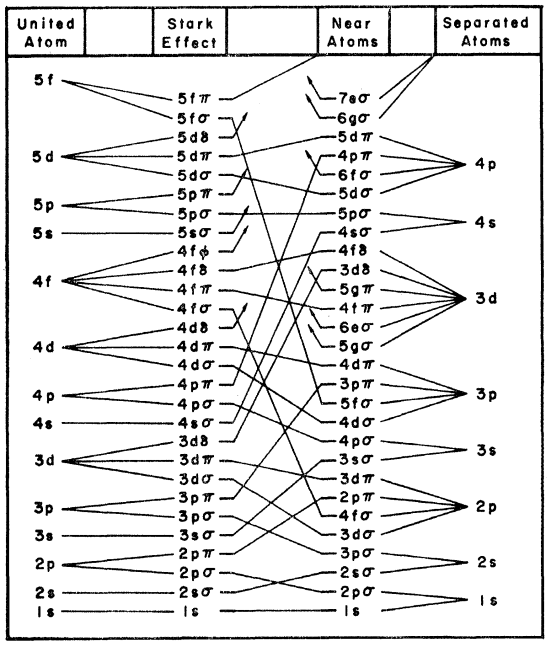

FIG. 3. Correlation diagram for molecular orbitals of a hydrogen molecular ion, or any other one-electron homonuclear, diatomic, molecular ion. Source: W. Weizel, *Bandenspektren* (Akademische Verlags-gesellschaft M.B.H., Leipzig, 1931).

[10] For a concise history of the Auger effect and for references to the original papers, see E. V. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, New York, 1935), Chap. 15.

[11] C. Snoek, R. Geballe, W. F. v.d. Weg, P. K. Rol, and D. J. Bierman, Physica **31**, 1553 (1965).

[12] Q. C. Kessel, M. P. McCaughey, and E. Everhart, Phys. Rev. Letters **16**, 1189 (1966); **17**, 1170 (1966).

[13] M. E. Rudd, T. Jorgensen, Jr. and D. J. Volk, Phys. Rev. **151**, 28 (1966).

[14] m_l denotes the projection of the orbital angular momentum of a single electron along the internuclear axis. The usual notation for this, λ, is not used to avoid confusion with the present use of λ for effective range.

[15] This discussion is based largely on the treatment of C. C. J. Roothaan, Rev. Mod. Phys. **23**, 69 (1951).

In the lowest-order approximation, each electron moves in the sum of two Coulomb fields of the shielded nuclei. It is of interest to compare this diatomic case with the corresponding atomic approximation, in which the central field has a $1/R^2$ dependence. This arises when there is complete shielding by inner shells. In a completely shielded atom, all the atomic orbitals of the same principal quantum number have the same energy, i.e., $\epsilon(ns)\sim\epsilon(np)\sim\epsilon(nd)$. In real atoms, the shielding is incomplete, each shell partially penetrates into inner shells, and the degeneracy within the shell is removed. We shall call the resultant intervals the *subshell splitting*.

In the molecular case, the assumption of complete shielding leads to an energy-level diagram which resembles the correlation diagram of Fig. 3. Figures 4 and 5 show such diagrams for diatomic systems formed from two rare-gas atoms, neon and argon. These diagrams show the subshell splitting in the united and separated atoms.

The incomplete shielding produces additional penetration effect in molecules. This lifts the degeneracy and causes avoidance of crossing of MO's with the same parity and angular momentum. [Even (gerade, or g) orbitals correlate with the united atom levels of even parity (s,d,g). Odd (ungerade, or u) orbitals correlate with levels of odd parity (p,f,h)]. For example (see Figs. 3, 4, or 5), the crossing of $3d\sigma$ with $3s\sigma$ is avoided and the correlations $3s$(Ca) $\leftrightarrow$ $2p$(Ne) and $3d$(Ca) $\leftrightarrow$ $3s$(Ne) replace the hydrogenic correlation of Fig. 3. The splitting of united or separated atomic energy levels can be viewed as special cases of level crossings at $R=0$ or $R=\infty$, respectively.

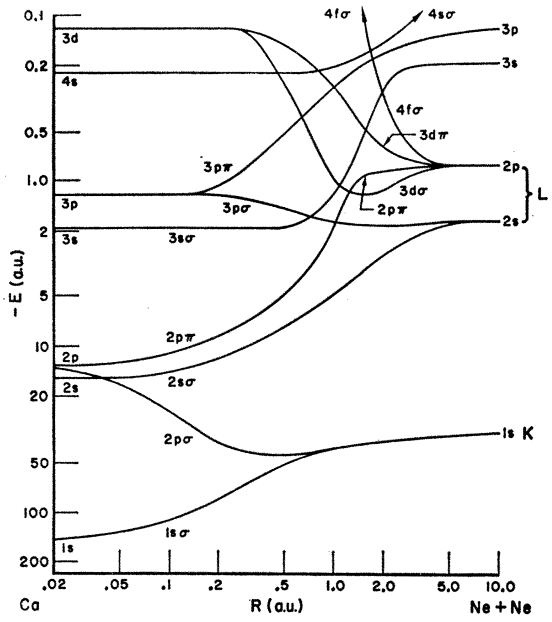

FIG. 5. Energy levels of the diabatic (H_2^+-like) molecular orbitals of the Ne-Ne system. Energies at $R=0$ and $R=\infty$ are taken from tables of atomic energy levels (see caption to Fig. 4). Values of orbital energies for R greater than 1.5 a.u. are taken from unpublished calculations of T. L. Gilbert and A. C. Wahl, Bull. Am. Phys. Soc. **10**, 1097 (1965). Other values are estimated by the author.

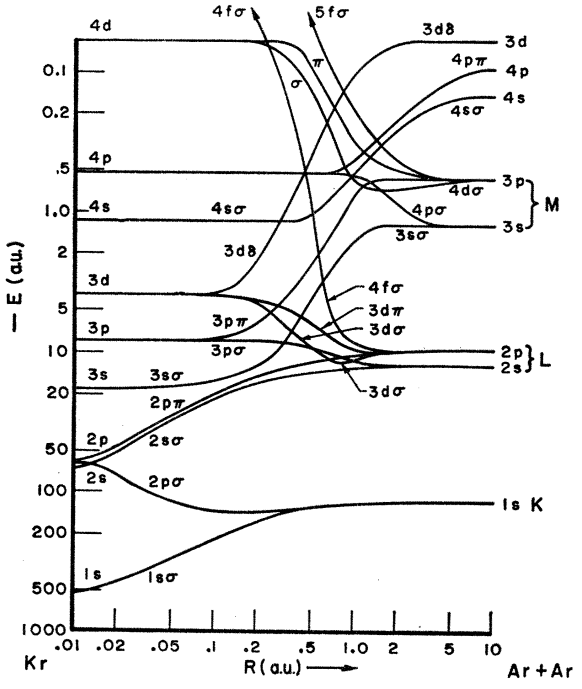

FIG. 4. Energy levels of diabatic (H_2^+-like) molecular orbitals of the Ar-Ar system. Energies at $R=0$ and $R=\infty$ are known from Moore (Ref. 51, Vol. I and II). Inner-shell terms are taken from J. C. Slater, Phys. Rev. **98**, 1039 (1955). Energies at $3.8\leq R$ are obtained from T. L. Gilbert and A. C. Wahl, Bull. Am. Phys. Soc. **10**, 1097 (1965). Energies at other internuclear distances are estimated by the author.

To estimate the size of the interaction which prevents diabatic (hydrogen molecular ionlike) MO's from crossing, we can assume it is of the same order of magnitude as the subshell splitting of the united or separated atomic levels which correspond most closely. Since the subshell energy splitting is small compared to the energy difference between shells of different principal quantum number, it is useful to refer to "crossing" of diabatic MO's whenever promotion occurs. For example, in Ar+Ar, the promotion energy of the $4f\sigma$ electron is $\sim$10 a.u. (see Fig. 4). The interaction between it and the $4p\sigma$ MO would not be likely to be more than the $4p$-$4f$ splitting in Ca, which is about 0.5 a.u. Thus it is reasonable to treat this as a crossing between diabatic MO's.

The idea of crossing loses its validity when the interaction which causes avoidance is comparable to the largest separation of the levels. Then the "crossing" region is no longer well localized. Thus, it seems questionable whether the concept of "crossing" is useful when the promotion energy is comparable to, or smaller than, the subshell splitting. A look at the diagrams (Figs. 4 and 5) reveals that this is the case

for outer-shell electrons. Thus, the present discussion will be largely limited to cases of inner-shell promotion.

At present, accurate MO calculations have been limited to relatively large internuclear separations, outside the interesting range where electron promotion occurs.[16] Therefore we must rely on estimates to give the diabatic MO energies at smaller internuclear distances. It should be emphasized that the energy levels in Figs. 4 and 5 do not show penetration effects. A correct computation would show the avoidance of crossings of MO's of the same parity and angular momentum.

C. Applications of Orbital Energies

We now review the question of how to apply the orbital energies ϵ_i to an understanding of the energy levels of the entire molecular system.

Koopmans's theorem[15,17] predicts that the energy of the singly charged molecular ion, AB^+, is equal to the energy of the neutral AB, minus the orbital energy of the missing electron:

$$E(AB^+,\phi_i^{-1})=E(AB)-\epsilon_i,$$

where ϕ_i and ϵ_i denote the ith MO and eigenvalue, respectively.

It immediately follows that to raise the system to the state with a missing jth electron takes an energy

$$E(AB^+,\phi_j^{-1})-E(AB^+,\phi_i^{-1})=\epsilon_i-\epsilon_j.$$

Also, it follows that crossings occur when the MO eigenvalues are equal. Thus Koopmans's theorem gives both the excitation energies and locations of crossings of states of the ion which are obtained by removing an electron from a MO. This theorem has proven quite useful in the analysis of inelastic and charge-exchange collisions of He^+ on He.[6,17–21] It also should prove helpful in the analysis of other collisions between a like rare-gas atom and ion, where the closed-shell MO structure of the parent molecule is present from $R=\infty$ down to small internuclear distances.

[16] However the energy levels from these calculations are useful for the less penetrating atomic collisions. See Figs. 3, 4, and 5 for references.

[17] T. Koopmans, Physica **1**, 104 (1933); see also, F. Seitz, *The Modern Theory of Soilds* (McGraw-Hill Book Company, Inc., New York, 1940), p. 313.

[18] W. Lichten, Phys. Rev. **131**, 229 (1963). This paper gives a convenient conversion from atomic to practical units.

[19] R. P. Marchi and F. T. Smith, Phys. Rev. **139**, A1025 (1965); F. T. Smith, D. C. Lorents, W. Aberth, and R. P. Marchi, Phys. Rev. Letters **15**, 742 (1965).

[20] Yu. N. Demkov and Yu. E. Murakhver, in *Proceedings of the IVth International Conference on the Physics of Electronic and Atomic Collisions* (Science Bookcrafters, Hastings-on-Hudson, New York, 1965), p. 332.

[21] It should be pointed out that many excited states do not fall in this category. In particular, if the ith or jth orbital is degenerate $(\pi,\delta,\gamma,\cdots)$ Koopmans's theorem cannot be used to find excitation energies in the ion. Also the theorem is likely to be less accurate when used to find energies of states of the ion which are not obtained by removing an electron from the ground state of the molecule. See Sec. III.A of this paper for applications of Koopmans's theorem.

It should be pointed out that calculation of the *state* wave functions and energies would be very difficult in the case of promotion of inner-shell electrons. As in the case of He^+-He collisions,[18] there is an infinite number of crossings of states, and a great simplification is made by considering individual diabatic MO's (independent-particle model).

D. Causes of Transitions Among Diabatic MO's

We have seen that, within the independent-particle (MO) model, electron-penetration effects cause transitions among diabatic MO's at crossings. Now we shall inquire into other effects.

1. *Electron Correlation (Configuration Interaction)*

Finer interactions can cause one or more electrons[22] to change MO assignments during a collision. For example, near the crossing of the $4f\sigma$ curve with that of $3p\pi$ (Figs. 4 and 5) we can expect transitions of the form $(4f\sigma)^2\rightarrow(3p\pi)^2$ or $(4f\sigma)^2\rightarrow(3s\sigma)^2$. Single-particle interactions can not cause such transitions; electron correlation is effective if the symmetries of the *total* wave functions of both states are the same. Since electron correlation is relatively weak ($\sim$0.1 a.u. or less),[18] we can expect such transitions to count in the outer shells at slow collision velocities ($v/\lambda\sim$0.1 a.u. or less).[18] The orbital selection rules are only that the *sum* $\sum m_l$ is unchanged; i.e., $\sum\Delta m_l=0$, and that the parity of the *product* of the MO's is the same.

2. *Electronic Interaction with Nuclear Motion*

The effects which we have discussed all are consistent with the Born-Oppenheimer approximation,[23] which calculates the electronic energy levels in the field of the clamped nuclei. The concept of "crossings" arose as we made finer and finer approximations in proceeding from diabatic MO's to adiabatic MO's and finally to adiabatic states, as we admitted the perturbations of electron penetration and then electron correlation. Next we shall go outside the Born-Oppenheimer approximation and discuss the effect of the perturbation due to nuclear motion on the electronic states.

It is convenient to divide collisions into two classes. In the first, the impact parameter b is small compared to the effective range λ of the electronic interactions; in the second case $b\approx\lambda$. For $b\ll\lambda$, the effect of the nuclear rotation is negligible, except for a sudden 180° flip at $R\approx0$. This sudden flip only causes a phase change of 180° in the *ungerade* orbital wave functions and there is a phase shift in resonant charge-exchange proba-

[22] It might be thought that Brillouin's theorem precludes one-electron jumps. This is not the case, since the theorem assumes the nonjumping MO's to be identical in both states. There is no obvious reason to make this assumption. For a discussion of Brillouin's theorem and for original references see J. C. Slater, *Quantum Theory of Molecules and Solids* (McGraw-Hill Book Company, Inc., New York, 1963), Vol. I, pp. 141, 259.

[23] M. Born and J. R. Oppenheimer, Ann. Physik, **84**, 457 (1927).

TABLE I. Interactions causing transitions between diabatic MO's at crossings. b=impact parameter (a.u.); v=ion velocity (a.u.); λ=effective range of molecular wave function.

Interaction or effect	Selection rules for transition Number of electrons jumping	Δm_l	MO parity conservation	Order of magnitude of perturbation (in atomic units[a])	Most effective range
Electron penetration	1	0	Yes	Same as subshell splitting	All shells
Nuclear motion, including rotational interaction	1	0	Yes	$v/2\lambda \approx \Delta E$	$b \ll \lambda$, for all shells
		± 1	Yes	$v/2\lambda \approx \Delta E$	$b \approx \lambda$, for all shells
Electron correlation (configuration interaction)	1 or more	any	not necessary	$\Delta E \lesssim 0.1$ a.u. perhaps much less.	outer shells, slow collisions ($v/\lambda \lesssim 0.1$), perhaps much less.

[a] See Ref. 18 for conversion of atomic to practical units.

bility.[20,24] Transitions between MO's do result from small-impact-parameter collisions. These transitions, which are caused by the radial motion, have the selection rules $\Delta m_l=0$, $g \leftrightarrow g$, $u \leftrightarrow u$, $u \leftrightarrow g$.

Rotation of the internuclear axis is most effective for $b \sim \lambda$, since promotion and level crossing occurs in this region. The selection rules for this type of rotation induced transition are $\Delta m_l=\pm 1$, $g \leftrightarrow g$, $u \leftrightarrow u$, $g \leftrightarrow u$. (Forbidden transitions with $\Delta m_l=\pm 2, \pm 3, \cdots$ can occur in higher order.)

In both cases, the perturbation is of order of magnitude (in a.u.)[18] $\Delta E \sim 1/T \sim v/2\lambda$, which is typical of time-dependent perturbations.[25]

A summary of the interactions which cause transitions among diabatic MO's is given in Table I. It must be noted that these rules and the energy-level diagrams (Figs. 4 and 5) only can be used as rough guides in an area where no exact knowledge exists because of the complexity of the subject.

3. *Other Interactions*

Other interactions, such as magnetic fine structure, magnetic hyperfine structure, electric quadrupole and many other magnetic perturbations usually are too small to cause transitions in atomic collisions. In heavy atoms, the spin-orbit interaction could be comparable to the subshell splitting. In this case, the quantum number $\Omega=m_l+m_s=m_j$ should be substituted in place of m_l in Table I.

E. Level Crossings and Energy Losses

We have seen that transitions between diabatic MO's occur at crossings, and that the selection rules in Table I are obeyed. We also have seen that, if such a crossing involves a promoted electron, the system can be left in a highly excited, auto-ionizing state after the collision. The well-known Landau-Zener theory[9] gives a simple model of these processes at crossings. These assumptions provide a plausible mechanism of energy losses which brings accepted concepts of atomic and molecular physics in line with experimental facts.

The new thing about these collisions is the nature of the multiply excited states that result. These states are only weakly excited in photon and electron impact experiments. It appears that, in small-impact-parameter collisions, excitation of these levels is almost statistically certain.

The reason for this is that many successive crossings occur in collisions with highly promoted electrons. The probability P of a transition to such a state is given by the expression[9] (in a.u.)[18] $P=e^{-w}$, where $w=2\pi H^2/v(d\epsilon/dR)$, where H is the off-diagonal matrix element coupling the crossing states, v the collision velocity and ϵ the energy splitting between unperturbed states. In collisions involving heavy atoms in the multi-keV range of energy, w can be of the right order of magnitude to produce a good transition probability, which becomes almost a certainty when several crossings occur.

F. Auto-ionization

The mechanism of auto-ionization is well understood. Accurate calculations of fluorescence yields[26] and Auger transition probabilities have been made.[27–29] The lifetimes for KLL auto-ionization are typically the order of 10^2 a.u. (1 a.u.$=2\times10^{-17}$ sec^{-1}); Coster-Kronig

[24] The author's hypothesis as to the origin of this phase shift, as given in Ref. 18, appears to be incorrect.

[25] See Ref. 18, Sec. II.A. See also the "Massey criterion" for example, in H. S. W. Massey and E. H. S. Burhap, *Electronic and Ionic Impact Phenomena* (Oxford University Press, Oxford, England, 1952), p. 441.

[26] For a review of the subject, see R. W. Fink, R. C. Jopson, H. Mark, and C. D. Swift, Rev. Mod. Phys. **38**, 513 (1966).

[27] For KLL yields and probabilities, recent papers are by F. J. Callen, Phys. Rev. **124**, 793 (1961); W. N. Asaad, Nucl. Phys. **44**, 399 (1963); **66**, 494 (1965).

[28] For Coster-Kronig yields and probabilities (LLM processes), recent papers are by E. J. Callen, Rev. Mod. Phys. **35**, 524 (1963) and W. N. Asaad, Nucl. Phys. **63**, 337 (1965).

[29] Extremely accurate results have been obtained for two electron systems. See, for example, P. G. Burke, D. D. McVicar, and K. Smith, Phys. Rev. Letters **11**, 559 (1963).

(*LLM*) transitions tend to be much faster, with lifetimes of the order of 10^1 a.u. In general, we can expect that auto-ionization which involves inner-shell vacancies will be relatively slow, because of low overlap of wave functions; auto-ionization involving transitions within an inner shell or among outer shells is likely to be relatively fast, because of larger overlap among wave functions. Finally, we should note that in light atoms in the keV energy range, collision times are small compared to auto-ionization lifetimes; virtual states of the system can be treated as stable during the collision; auto-ionization can be assumed to occur *after* the collision from discrete states.[18] In collisions among heavy atoms in the keV range, the lifetimes of the faster auto-ionizing states begin to border on the range of collision lifetimes; on the other hand, inner-shell vacancies can be expected to last until after the collision.

Thus we can make a distinction between two types of auto-ionization processes. Multiple excitations in outer shells are of a very complex nature. These Auger processes occur rapidly immediately after, and perhaps during the slowest collisions with heavy atoms. The energy spectrum of electron emission from these levels is expected to be very complex and ill-defined. Except for nonstatistical peaks from long-lived discrete states,[6,13] a statistical model may be the only practical way of handling the energy spectrum theoretically[30] for this type of collision.

On the other hand, excitation of inner-shell vacancies is expected to lead to auto-ionization from discrete, well-defined states, after the collision is over and after auto-ionization is complete in outer shells. Well-defined peaks of a nonstatistical nature are to be expected[6] and are observed.[11–13] The energy of these peaks can be calculated from the well-known relationship[10]:

$$E=-\epsilon_1+\epsilon_2+\epsilon_3,$$

where E is the energy of the Auger electron, ϵ_1 is the energy of the inner-shell vacancy, ϵ_2 and ϵ_3 are the energies of the two electrons which are ejected and fill the inner shell, respectively. It should be emphasized that the energies are those of the atom, after the excitation in outer shells has been dissipated by Auger processes.[31] Also, it should be pointed out that the expression is an approximation which does not satisfy Koopmans's theorem. Finally, the "promotion energy," $\epsilon_2-\epsilon_1$, is roughly independent of the state of ionization of the outer shells of the atom. This can be shown to follow from classical electrostatics and the shell structure of the atom. Also it can be verified empirically by examination of energy levels of isoelectronic atoms.

Because the atom can be in a variety of auto-ionizing states which correspond to differing values of ϵ_1 and ϵ_2, there is a statistical broadening of the high-energy Auger peak. Rudd *et al.*[13] have partially resolved this broadened Auger peak into discrete, sharp lines.

The number of electrons ejected can be estimated by a simple recipe, which is in accordance with the known facts of auto-ionization. For each *pair* of electrons promoted from the valence shell (shell of largest principal quantum number) to outer shells, one Auger electron is ejected and one falls back to the valence shell. Then one fast electron is ejected for each inner-shell vacancy.[31]

III. APPLICATIONS

In this Section we shall consider the application of the ideas of inner-shell promotion, level crossing, and the Auger effect to specific examples of ion-atom collisions. Since digital computer calculations of MO energy levels are generally not available, we shall restrict our discussion to symmetric collisions, where estimation of the energies and location of crossings is relatively simple.

A. H-H$^+$; He-He$^+$

Hydrogen and helium atoms are unique in that all electrons start in $1s$, K orbitals. These orbitals act in many ways like "inner shells," in that promotion energies are relatively large.

The energy levels of H_2^+ are known exactly. Some low-lying levels are shown in Fig. 6. Bates and Williams[32] considered the theory of collisions between $H(1s)$ and H^+ ions. They took into account coupling between $2p\sigma$ and $2p\pi$ states of the quasimolecule H_2^+. They found a "remarkably large" cross section for excitation of the $2p$ state at proton energies as low as 30 eV. These predictions were verified by subsequent experiments,[33] which were in agreement with the molecular model up to the highest calculated energy, 3 keV.

It is worthwhile to examine this basic system in some detail. The reason for the unusually large excitation cross section can be understood by an examination of the molecular states. (See Fig. 6). At $R=0$, a level crossing of the $2p\sigma$ and $2p\pi$ MO's occurs. The $2p\sigma$ MO is promoted from the $1s$ state of the separated H atom. The initial wave function is an equal mixture of $1s\sigma_g$

[30] A. Russek and M. T. Thomas, Phys. Rev. **109**, 2015 (1958); **114**, 1538 (1959); J. B. Bulman, and A. Russek, Phys. Rev. **122**, 506 (1961); A. Russek, *ibid.* **132**, 246 (1963).

[31] There is also the possibility of direct ejection of electrons at the instant of collision. It is not easy to distinguish between directly ejected electrons and those which are auto-ionized from outer shells very rapidly. It seems unlikely that direct electrons would occur for $v\ll 1$ a.u. The actual number of ejected electrons can be expected to be somewhat larger than estimates, by about 10%, because of electron shake-off. For a more complete discussion, see T. A. Carlson, W. E. Hunt, and M. O. Krause, Phys. Rev. **151**, 41 (1966).

[32] D. R. Bates and D. A. Williams, Proc. Phys. Soc. (London) **83**, 425 (1964). See also the calculation by L. Wilets and D. F. Gallaher, Phys. Rev. **147**, 13 (1966). Note: In the latter paper, in Fig. 2, the $2s$ and $2p$ exchange probabilities are in error. They should be reduced by a factor of 10.

[33] R. F. Stebbings, R. A. Young, C. L. Oxley, and H. Ehrhardt, Phys. Rev. **138**, A1312 (1965).

and $2p\sigma_u$ MO's [18]

$$\psi_{\text{init.}}=\frac{1s\sigma_g \pm 2p\sigma_u}{\sqrt{2}}.$$

The great energy gap between $1s\sigma_g$ and all other states precludes $1s\sigma_g$ excitation, except at nuclear velocities which are high enough to cause a complete breakdown of the molecular model. The "crossing" at $R=0$ allows transitions from $2p\sigma$ to $2p\pi$ levels. The final wave function in this case is

$$\psi_{\text{final}}=\frac{1s\sigma_g}{\sqrt{2}}+\frac{c2p\sigma_u+d2p\pi_u}{\sqrt{2}},$$

where c and d are complex numbers, $|c|^2+|d|^2=1$. The probability of excitation of $2p\pi$ states is $|d|^2/2$.

From this molecular model, several conclusions follow:

(1) The maximum probability of excitation of $2p$ is 0.5.

(2) The probabilities are equal for electron capture and excitation to the $2p$ state.

(3) The $2p$ states are polarized; that is the magnetic substates $2p\pi_{\pm 1}$ are excited. The resultant polarization of the light can be calculated by a Clebsch-Gordan expansion of the $2p\pi_{\pm 1}$ levels into the appropriate magnetic substates of the fine-structure levels of $H(^2p_{3/2},^2p_{1/2})$.

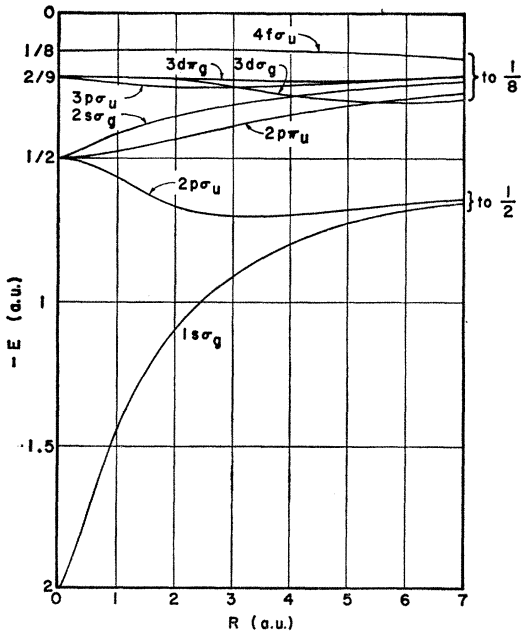

FIG. 6. Energy levels of the molecular orbitals of H_2^+. Source: D. R. Bates, K. Ledsham, and A. L. Stewart, Phil. Trans. Roy. Soc. (London) A246, 215 (1953).

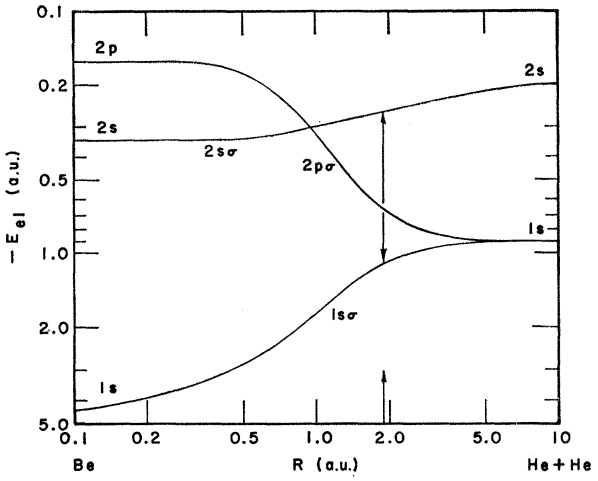

FIG. 7. Molecular orbital energy levels for the He-He system. Sources: For $R=0$ and $R=\infty$, see caption to Fig. 4. $1s\sigma$ and $2p\sigma$, $R\geq 0.5$ a.u. [P. Phillipson, Phys. Rev. 125, 1981 (1962)]. Other values are estimated by the author.

These conclusions are valid as long as nuclear velocities are low enough to avoid interference by other states, such as $4f\sigma_u$. The calculation of Wilets and Gallaher[32] indicates that conclusion (2) holds roughly up to $v\approx 0.5$ a.u. ($E\approx 5$ keV).

We can use a rough method to estimate the most effective impact parameter for $2p$ excitation for a given proton energy. For the interaction to have frequency components in resonance with the excitation energy

$$\Delta E(b)=E(2p\sigma)-E(2p\pi)\sim 1/T\sim v/2b,$$

where $\Delta E(b)$ is the splitting of the $2p$ sublevels at $R\sim b$, T is the time of interaction, and b is the impact parameter. This equation is readily solved graphically by means of the energy-level diagram (Fig. 6). For example, at a proton energy of 2 keV, which corresponds to a velocity of 0.28 a.u., we find the impact parameter is given approximately by the equation $\Delta E(b)=0.14/b$. This gives $b=0.9$ a.u. A more detailed analysis[32] shows a broad maximum excitation probability of 0.3 at $b=1.0$ a.u. Bates and Williams[32] also find the probability is not strongly energy-dependent.

We have seen that a fairly crude model can be used to estimate the impact parameter b for maximum rotational excitation and therefore the cross section $\sigma\sim\pi b^2$. Also the dependence on nuclear kinetic energy is not critical. These results will be used later in this paper. H_2^+ has furnished us with our first, and most basic, example of the effect of MO promotion and level crossing in inelastic collisions.

In the case of $He\text{-}He^+$ collisions, we again have promotion from the atomic inner K ($1s$) shell and level crossing. An energy-level diagram is shown for the MO's

of $(He)_2$ (Fig. 7).[34,35] The initial wave function is

$$\psi_{\text{init}}=[(1s\sigma_g)^2(2p\sigma_u)\pm(1s\sigma_g)(2p\sigma_u)^2]/\sqrt{2}.$$

The $(1s\sigma_g)(2p\sigma_u)^2$ part of the wave function corresponds to a promotion of two of the three electrons with an energy level which rises rapidly at smaller internuclear distances. A previous discussion has given the position of crossings[18] of this state with excited states. A "perturbation" in the elastic-scattering cross section has been attributed to these crossings by Smith, Lorents, Aberth and Marchi.[19]

The position of the first crossing can be estimated from the curves in Fig. 7. The lowest excited state has an orbital assignment $(1s\sigma_g)^2(2s\sigma_g)\ ^2\Sigma_g^+$. Excitation of this state leads to equal probability of excitation of or capture into the metastable $^3S_1$ state of He. This is a two-electron jump and involves electron correlation. The splitting between crossing states is small, at most only a few eV[18]; such transitions occur at low velocities. The MO transitions are $(2p\sigma_u)^2\rightarrow(1\sigma_g)(2s\sigma_g)$. The energy deficit is approximately $\Delta E=\epsilon(2s\sigma_g)+\epsilon(1s\sigma_g)-2\epsilon(2p\sigma)$. This goes to zero at the internuclear distance where $\epsilon(2p\sigma)$ is midway between $\epsilon(2s\sigma_g)$ and $\epsilon(1s\sigma_g)$, as is shown in Fig. 7. This occurs at an internuclear distance of $R\sim1.9$ a.u., in good agreement with the analysis of experimental perturbations[19,35] by Smith *et al.*

As the internuclear distance becomes smaller, an infinite number of successive crossings leads to higher excited states of the atom, until at 1.4 a.u. the diabatic curve $(1s\sigma_g)(2p\sigma_u)^2$ crosses the $(He)_2^{++}$ curve and enters the continuum of $(He)_2^+$. At smaller internuclear distances it crosses curves leading to more highly excited states, as $He^+(2s)$ and $He(2s,2p)$.[36] Again, we can expect equal probability of capture or excitation cross sections in inelastic collisions, as we have shown in the case of $H\text{-}H^+$ collisions. The arguments here are completely analogous.

The experiments of De Heer *et al.*[37] show that the low-energy capture and excitation cross sections are the same for the same state in He^+-He collisions, and thus verify the predictions of the molecular-orbital treatment. The complex structure of the cross sections[37] is likely to be related to a complicated chain of competing reactions which arise at the position of successive crossings of curves. In order to understand these events in more detail, it is helpful to measure inelastic differential scattering cross sections.[38]

[34] It would be advisable for the reader also to consult Ref. 18, Fig. 4, for a *state* energy-level diagram, which is very helpful for an understanding of this discussion.

[35] It should be pointed out that the *orbital* energies in Fig. 7 were previously used to obtain the *state* energies of Fig. 4, Ref. 18, by use of Koopmans's theorem.

[36] For a discussion of highly excited states, see the results of R. B. Barker and H. W. Berry, Phys. Rev. **151**, 14 (1966).

[37] F. J. DeHeer, L. Wolterbeek Muller, and R. Geballe, Physica **31**, 1745 (1965). Similar results have been obtained by S. Dworetsky, R. Novick, W. W. Smith, and N. Tolk [Phys. Rev. Letters **18**, 939 (1967)] at very low energies.

[38] D. C. Lorents, W. Aberth, and V. W. Hesterman, Phys. Rev. Letters **17**, 849 (1966), have reported oscillatory differential-scattering cross sections for excitation of He by He^+ ions. Similar results have been obtained by Dworetsky *et al.* on total cross sections (see Ref. 37).

B. Heavy-Particle Collisions

We shall now discuss collisions between heavy atoms, where a definite inner- and outer-shell structure plays an important role. We can best study these collisions as one peels an onion.

First, we shall discuss soft collisions which occur at low energy and small deflection angles. These consist of only mildly penetrating encounters. Then, as the energy is raised and/or the angle of scattering goes up, the hardest collisions penetrate deeply into inner shells.

1. Ne-Ne$^+$ Collisions

Figure 5 shows the energy levels of $(Ne)_2$. At large internuclear distances, $(Ne)_2$ has the ground-state, closed-shell MO configuration

$$(1s\sigma_g)^2(2p\sigma_u)^2(2s\sigma_g)^2(3p\sigma_u)^2(3d\sigma_g)^2(2p\pi_u)^4(3d\pi_g)^4\times(4f\sigma_u)^2.$$

If we assume the collision occurs between an atom and an ion which are both in ground states (no metastable ions[39] in the primary beam), the initial state of the system is $Ne(1s)^2(2s)^2(2p)^6\ ^1S$ and $Ne^+(1s)^2(2s)^2(2p)^5\ ^2P$. Because the spin-orbit splitting is small in Ne, we can ignore the electron spin. An atom in a p state can orient itself in three possible ways in a diatomic molecule. Two correspond to a doubly degenerate Π state and one corresponds to a Σ state.[40,41] In each case, a resonant charge exchange occurs. The over-all charge-exchange probability is a weighted sum of the two probabilities.

The work of Jones *et al.*[41] on Ne-Ne$^+$ collisions is a definitive, high-resolution study of resonant charge exchange and energy loss. In these measurements, the location of critical internuclear distances is pinpointed accurately.

Let us first consider the collisions which occur in Σ states. The initial molecular wave function can be written as $(1s\sigma_g)^2(2p\sigma_u)^2(2s\sigma_g)^2(3p\sigma_u)^2(2p\pi_u)^4(3d\pi_g)^4\times[(3d\sigma_g)^2(4f\sigma_u)\pm(3d\sigma_g)(4f\sigma_u)^2]/\sqrt{2}$. Note that this is completely analogous (except for several closed shells) with the wave function for He-He^+ crossings. The first crossing capable of causing a perturbation of elastic scattering[19] or inelastic events occurs at $R\sim2.5$ a.u. The transition in question is $(3d\sigma_g)(4f\sigma_u)^2\rightarrow(3d\sigma_g)^2(3s\sigma_g)$, which again is analogous to the helium case. No evidence has been found[41] for the 16.7 eV $2p$-$3s$ excitation which would result from failure to

[39] H. D. Hagstrum, Phys. Rev. **104**, 309 (1956).

[40] This argument presupposes equal *a priori* probabilities among the three possible Π, Π_{-1}, and Σ_0 states, and random phases. The same holds if electron spin is taken into account, if the states of various J and J_Z are equally probable and have random phases. This assumption holds unless there is some mechanism such as optical pumping which selectively populates certain substates of the ion beam. Such a mechanism can exist in electron-bombardment sources.

[41] P. R. Jones, T. L. Batra, and H. A. Ranga, Phys. Rev. Letters **17**, 281 (1966); P. R. Jones, N. W. Eddy, H. P. Gilman, A. K. Jhaveri, and G. Van Dyk, Phys. Rev. **147**, 76 (1966); P. R. Jones, P. Costigan, and G. Van Dyk, *ibid.* **129**, 211 (1963).

cross at this point. It thus appears that this crossing is diabatic in the experimental energy range of $E>500$ eV. Perhaps the matrix element for this transition is very small because it is a configuration interaction type. If this is the case, it might be possible to see the inelastic energy loss of 16.7 eV at *lower* ion energies or smaller scattering angles.

On the other hand, both the 18.9 eV energy loss and disappearance of resonant charge exchange occur at $R<1.3$ a.u.[41] It is plausible to attribute these events to the rotationally induced transition $4f\sigma_u \rightarrow 3p\pi_u$. There is no reason to expect this crossing to be weak. It is strong and is the first observed transition.

The single transition $(4f\sigma_u) \rightarrow (3s\sigma_g)$ is forbidden by the parity rule. Thus the 16.6 eV energy loss does not occur.

A number of mechanisms may account for the 48.4 ± 2.0 eV energy loss.[42] One possibility is a double transition $(4f\sigma_u)^2 \rightarrow (3s\sigma_g)^2$, which would excite two electrons in the system from $2p$ to $3s$. However this transition appears at the wrong internuclear distance to support this possibility. Thus electron correlation appears too weak to permit this transition.

A more plausible transition is $3p\sigma_u$ to $2p\pi_u$, which only can occur at $R\sim1.0$ a.u. in the π collisions, which have "half a vacancy" in the $2p\pi_u$ orbital. The wave function in the π states can be written

$$\frac{(2p\pi_u)^{-1}\pm(3d\pi_g)^{-1}}{\sqrt{2}}.$$

This transition would leave a $2s$ electron promoted to fill a $2p$ vacancy. It is interesting to note that this excitation never occurs by itself, since the corresponding 27.0-eV energy loss is never observed. Thus it appears to be a statistical certainty that one or more $4f\sigma_u$ electrons are promoted if the system goes through the many crossings at $R\lesssim1.3$ a.u.

Transitions induced by electron correlation are again not found in collisions in π states. For example, the transition $(2p\pi)^3(3d\pi)^4 \rightarrow (2p\pi)^4(3d\pi)^2(3p\pi)$, which would occur at the crossing $R\sim2$ a.u., does not seem to appear. If it did, it would damp out the π oscillations of charge-exchange probability in the experiments of Jones *et al.*[41] This is another example of diabatic crossings of states which involve relatively weak interactions.

In summary, all the energy losses and processes in the soft collisions of Jones *et al.*,[41,42] can be accounted for by the promotion of the $4f\sigma_u$ and $3p\sigma_u$ orbitals. The *double* promotion of the $4f\sigma_u$ orbital seems to lead to a virtual certainty of inelastic collisions for small enough minimum internuclear distances. These results will be useful in the interpretation of hard collisions involving Ar and Ar^+.

We have seen that relatively soft collisions ($E\ll25$ keV, $v\ll1$ a.u.), which involve only penetration of outer electron shells, tend to be diabatic when electron correlation is concerned, but that one-electron transitions can occur when penetration or nuclear-rotation effects are involved. In particular we have pointed out that certain promotions, such as the $4f\sigma$ orbital, lead to statistically, very probable transitions.

We now ask what happens in harder collisions, when inner-shell electrons can be promoted. A remarkable experiment has been performed recently by Kessel, McCaughy and Everhart[43] and by Rudd.[44] A prominent peak is found at 750 eV in the energy distribution of backward-scattered electrons from Ne-Ne^+ and Ne-Ne^{++} collisions in the ion energy range 150–400 keV ($v\sim1$ a.u.). The authors interpret their results as a promotion of the inner K-shell electron.

We now give a detailed account of this collision in terms of molecular states (Fig. 5). It is clear that promotion of K electrons can occur only at crossings of $2p\sigma$ and $2p\pi$ MO's at small internuclear separations. (The crossing with $2s\sigma$ is diabatic, because electron correlation is the only possible matrix element. Also, since $2s\sigma$ is doubly occupied, there are no vacancies available. Thus the $2s\sigma$ crossing can be ignored.) Transitions from $2p\sigma$ to $2p\pi$ can occur via rotational excitation, if a prior vacancy exists in the π MO. We have seen that two thirds of Ne-Ne^+ collisions are in the Π states with a "hole" of the form $\frac{1}{2}\sqrt{2}(2p\pi_u\pm3d\pi_g)^{-1}$. If we assume the 30% maximum transition probability from the $2p\sigma$ MO to the vacant $2p\pi$ MO, then at most 20% of the total Ne-Ne^+ collisions could lead to Ne ions or atoms with a K-shell vacancy. The experimental result[43,45] shows a maximum probability of 10% for emission of fast electrons. This is in striking contrast to the near certainty of excitation of an electron in a $4f\sigma$ MO. The difference is clearly a statistical one. In the case of the $2p\sigma$ MO, only a fraction of a "hole" exists in the $2p\pi$ MO. In the $4f\sigma$ case, many vacancies exist in numerous MO's.

If the incoming projectile is Ne^{++}, then there are twice as many p-shell vacancies. Therefore there should be twice as many "holes," on the average,[46] in the $2p\pi$ MO, and therefore twice as many fast electrons ejected as in Ne-Ne^+ collisions at the same energy. If the projectile is Ne in its ground state, there should be no vacancies, no K-shell promotions, and therefore no fast electrons.

The dependence of excitation on internuclear distance can be estimated by scaling the hydrogenic results for 200-keV Ne atoms. The predicted result is a broad maximum of excitation probability at $R_0=0.06$ a.u. The experimental results begin to rise at $R_0=0.12$ a.u.,

[42] P. R. Jones, T. L. Batra, and H. A. Ranga, in *Proceedings of the IVth International Conference on the Physics of Electronic and Atomic Collisions* (Science Bookcrafters, Hastings-on-Hudson, New York, 1965), p. 292, and private communication.

[43] Q. C. Kessel, M. P. McCaughy, and E. Everhart, Phys. Rev. **153**, 57 (1967); see also Ref. 12.

[44] M. E. Rudd (private communication).

[45] The agreement appears to be fortuitous, however, since the experimental results are partially based on results obtained with Ne^{++}. [E. Everhart (private communication).]

[46] It can be shown by a Clebsch-Gordan expansion of the ^3P, ^1D, or ^1S wave functions into products of MO's, that this is indeed true.

reach a plateau at 0.08 a.u. and remain level to $R_0=0.05$ a.u., the smallest experimental value.

The 840-eV energy loss and the 750-eV ejection energy can be related to the promotion hypothesis.[6] The energy-loss results[43] show an excitation of approximately 350 eV (13 a.u.) per atom *before* the K-shell excitation occurs. This represents the energy required to remove *completely* 9 L electrons from the system of $Ne+Ne^+$. Of the $8+7=15$ L electrons in the system, $9\frac{1}{2}$ are in the promotable $4f\sigma$, $3d\pi$, $3d\sigma$ and $3p\sigma$ MO's. It appears likely, therefore, *that virtually all of the promotable electrons are raised to excited levels during hard collisions.*[47]

In Sec. II a distinction was made between the relatively fast Auger processes involving outer shells and the slower inner-shell processes. We assume for simplicity here that the highly excited Ne^+ (or Ne) atom has 5 or 6 electrons in outer shells, 3 in the L shell and 1 in the K shell. A typical configuration would be $Ne(1s)(2s)(2p)^2(M,N\cdots)^6$, which would be expected to give 3 Auger electrons and drop 3 into the L shell, according to the recipe of Sec. II. After the outer-shell de-excitation is over, a possible state could be $Ne^{3+}(1s)(2s)^2(2p)^4$. Similarly, a typical Auger sequence in $(Ne)^{+*****}$ might lead to $Ne^{3+}(1s)(2s)^2(2p)^4$. It also should be noted that these are only *typical* Auger sequences. Many other paths doubtlessly are followed. Each of these states would de-excite by ejecting a fast electron.

The experimental value for total number of ejected electrons can be obtained from Fig. 5 of Ref. 43. It can be seen that, on the average, both the scattered and recoiling atoms are Ne^{3+}, but that one additional (fast) electron is ejected in the second peak, which has been identified as an inner-shell excitation.[43] These results are again in excellent agreement with the simple recipe given at the end of Sec. II. It should be pointed out that the model given here is highly oversimplified, most likely fortuitous, and only gives the over-all features of an *average* process. A complete statistical analysis of all the level crossings, charge partition among outer shells during separation and of all the many possible Auger channels would be necessary to give the widths and shapes of the various distributions.

We now can estimate the excitation energy and the energy of the ejected electron. The promotion energy[48] is given by $\epsilon(2p)-\epsilon(1s)=874-22=852$ eV. The ejection energy is given[49] by $2\epsilon(2p)-\epsilon(1s)=\epsilon(2p)+[\epsilon(2p)-\epsilon(1s)]=-97+852=755$ eV. These results are in excellent agreement with the experimental values[43] for these two quantities, which are 840 eV and 750 ± 20 eV for the promotion and ejection energies, respectively.

The qualitative agreement between theory and experiment as to the size of transition probability, the dependence on internuclear distance, and the quantitative agreement in the case of the energy loss, the number and the energy of ejected electrons can be taken as confirmation of the promotion hypothesis of Fano and the author.[6] It should be emphasized that the experimental facts are entirely in accord with a reasonable interpretation based on accepted concepts of molecular energy levels[7,8] and Auger processes.[10,26–28]

2. *Ar-Ar$^+$ Collisions*

We have seen in the case of Ne-Ne^+ collisions that promotable L-shell electrons are excited in turn with statistical certainty, as the internuclear separation is decreased. Let us focus our attention on the features of Ar-Ar^+ collisions which show these processes most clearly. (Figs. 1 and 2). At the critical internuclear distance of $R_0\sim0.5$ a.u. a rapid rise occurs in energy loss and in the number of ejected electrons. Both measures of excitation then rise gradually until $R_0\sim0.2$ a.u. where both again rise rapidly. Figure 4 shows that the sharp rise at $R_0\sim0.5$ a.u. can be linked with the promotion of two $4f\sigma$ electrons from the L shell. We have seen in the case of Ne that excitation of at least one $4f\sigma$ electron is virtually certain within a certain critical internuclear distance. In argon, it appears this is the case for both $4f\sigma$ electrons for $R_0<0.5$ a.u.

It should be noted in Fig. 1 that the maximum energy loss for smaller R_0 does not vary much with energy; however the curve does broaden at higher ion kinetic energy. This is typical of rotational excitation at a crossing at zero internuclear separation. It is reasonable to attribute the rise at $R_0\sim0.2$ a.u. to such excitations, as $3d\sigma$ and $3d\pi$ to $3d\delta$, or $3p\sigma$ to $3p\pi$. However, other possible promotion mechanisms at small R_0 cannot be ruled out.

Rudd *et al.*[13] and Snoek *et al.*[11] have observed fast electrons emitted by Ar atoms and/or ions after collisions with various atoms, molecules and solids. The fast electron peak was at an energy of about 190 eV, with a width of about 50 eV.[50] We shall analyze this collision in the same way that we treated the K-shell excitation in Ne.

Everhart *et al.*[4] find three discrete energy losses Q, at an ion energy $T=25$ keV, deflection angle $\theta=16°$: $Q=90\pm17$, 379 ± 10, 613 ± 14 eV.

A careful study of isoelectronic ions[51] shows that any excitation of the M shell in Ar, such as $3s\rightarrow3p$ or $3p\rightarrow3f$ or $3p\rightarrow4s$, has an energy of about 15 eV.

[47] It is possible that a small number of these electrons are promoted directly into the continuum. There is no evidence to exclude this possibility.

[48] Strictly speaking, one should use the orbital energies in the multiply charged ion. However, if we follow the arguments given at the close of Sec. II, we can use the values of the ionization potential of Ne for $\epsilon(2p)$ and the x-ray term value for $\epsilon(1s)$.

[49] To find the ejection energy, the ionization potential of Ne^{+3} was used to give $\epsilon(2p)$. For simplicity, it was assumed that both the captured and ejected electrons were $2p$. Actually, some of the electrons are $2s$. The effect of including $2s$ electrons in a theoretical calculation would lower the estimated ejection energy by a small amount.

[50] Rudd *et al.*, (Ref. 13) have shown that the peak actually consists of numerous sharp peaks ranging from 120 to 220 eV, which result from the large number of possible states from which the atom or ion can eject fast electrons.

[51] C. E. Moore, Natl. Bur. Std. Circ. No. 467 (1949).

Thus, by the same argument which was used in the case of Ne in the preceding paragraph, we can assume the 90-eV energy loss to correspond to an average excitation of about 6 M-shell electrons. Therefore the first loss corresponds to an excitation of most of the $9\frac{1}{2}$ "promotable" M-shell electrons. This "characteristic energy loss," which Afrosimov *et al.*[3] call R_I*, owes its apparent constancy to the fact that there are few M-shell electrons left to be promoted. The experiments of Jones *et al.*[42] show that R_I* is indeed not a characteristic energy loss, but is only a limiting case of losses which become smaller in more gentle collisions.

The second and third losses correspond to an additional excitation of one or two $2p$ electrons out of the L shell, via $4f\sigma$ crossings with other MO's.[4,6] The promotion energy has two individual values 289±27 eV and 234±24 eV. It is unclear why the experimental promotion energies differ so much from each other.

The second excitation would lead to a typical auto-ionizing state, such as

$$\mathrm{Ar}^{+}(1s)^2(2s)^2(2p)^5(3s)^2(3p)^6$$

or

$$\mathrm{Ar}^{++}(1s)^2(2s)^2(2p)^5(3s)^2(3p)^5.$$

The estimated promotion energy is

$$\epsilon(3p)-\epsilon(2p)=-16+244=228\ \mathrm{eV},$$

and the ejection energy is

$$\epsilon(3p)+[\epsilon(3p)-\epsilon(2p)]=-34+228=194\ \mathrm{eV},$$

where $\epsilon(3p)$ is the average for Ne^+ and Ne^{++}. These results are in good agreement with the experimental results of 234±24 eV and 190±25 eV, respectively. The predicted values are in disagreement with the second energy loss of 289±27 eV. The reason for this disagreement is not understood. Except for this isolated case, the over-all good agreement of experimental results[4,11,13,43] with theoretical prediction[6] indicate that the promotion mechanism is capable of accounting for the general nature of the process.

It should be pointed out again that hard atomic collisions excite states which have many electrons promoted. These states are unlike those seen in the excitation by photons or electrons, where one electron usually, and two electrons occasionally, are excited. Therefore, it will be a difficult matter to make unique assignments of the many discrete energies of the ejected electrons.

IV. CHARGE CORRELATION BETWEEN ATOMS

Everhart and co-workers[4] pointed out the lack of correlation between the charges of each atom. That is, for a given ion kinetic energy and impact parameter, the relative probability of one atom having a charge m was independent of the charge n of the other collision partner.

The reason for this can be found in the independent-particle-model (MO) nature of molecular electrons. The correlation energy of electronic wave functions is too small to affect the relative positions of the electrons during the short collision time. This is especially true for the electrons promoted to the loosely bound, outer-electron shells. How these electrons divide up after the collision is purely a matter of chance.

One striking exception to this rule is when the excitation of a single electron dominates the energy losses of the system. This occurs at the $R_0=0.5$ a.u. crossing in $(Ar)_2$, where only one or two L-shell electrons can be promoted, and where each inner-shell vacancy causes a large effect on the auto-ionization. In the case of a *single* promotion, it is obvious that the L-shell vacancy must be in one atom only. Therefore strong charge-correlation will exist.

V. OTHER EVENTS AT CHARACTERISTIC INTERNUCLEAR DISTANCES

Multiple ionization and large energy losses are two phenomena which show sharp changes at characteristic internuclear distances. Afrosimov *et al.*[3] find a third type of event. The curve for the total (inelastic plus elastic) differential scattering cross section deviates from the smooth curve calculated from a screened Coulomb interaction. The deviation is in the form of bumps, which also occur at the same characteristic internuclear distances.

Smith *et al.*[52] have discovered similar "perturbations" in the elastic scattering of He^+ on He. Smith *et al.* claim these perturbations occur at the crossing of energy levels in the molecular complex $(He)_2^+$. Although the theory of scattering in the presence of level crossings is not yet complete, it appears reasonable to interpret the bumps in heavy-atom differential cross sections as further indications of crossings of molecular energy levels.

VI. COMPARISON WITH OTHER MODELS

Russek and co-workers[30] have proposed a model in which the excitation energy of collision is distributed statistically among the outer-shell electrons. Fano and the author[6] have pointed out that the Russek model is inconsistent with the shell structure of atoms and the discrete, sharp nature of the auto-ionizing states of atoms. In particular the prediction[6] of emission of fast electrons has been sufficiently well verified[11–13] to disprove a purely statistical model for the ejected-electron energy distribution. A more definitive test will be given by observation of coincidences between ejected electrons and atoms scattered by a particular angle.

Afrosimov *et al.*[3] considered a promotion mechanism, but rejected it for the interpretation of a series of collective oscillations in the colliding system. Their argument was based on the constancy of a set of quantities they named R*, which were claimed to be characteristic energy losses. Everhart and co-workers have repeated

[52] F. T. Smith, D. C. Lorents, W. Aberth, and R. P. Marchi, Phys. Rev. Letters **15**, 742 (1965).

the experiments of Afrosimov *et al.* and claim that the R^* only appear to be constant over a narrow range of experimental variables. Thus the factual basis of the collective oscillations is under dispute. (See par. III. B.2).

Brandt and Lundqvist,[53] suggested the possibility of plasma oscillations of atomic electrons and estimated the energies to be of the order of $[\frac{1}{2}$(atomic number)] a.u. which would be of the order of 200 eV in Ar. Wieder and Borowitz[54] have calculated the lowest frequencies for plasma oscillations for the Ar atom, and found an energy $E=h\nu\sim60$ eV. Amusia[55] has calculated separate energies of 40–70 eV for M shell and 220–320 eV for L-shell oscillations.

However, such collective oscillations never have been independently observed in the predicted x-ray absorption. Furthermore, there is no way of predicting at what internuclear distance such oscillations should be excited in collisions, nor does the collective model make specific predictions about the velocity distribution of ejected electrons. Also, the presence of discrete excitations (inner-shell promotions) near the hypothesized plasma states is inconsistent with the theoretical assumptions of the theory.[54]

Nikulin,[56] an author from the same laboratory as Afrosimov *et al.*,[1,3] recently has discussed the Ar-Ar$^+$ collision. He states that the analysis of Ref. 6 in terms of shell structure and inner-shell promotion is satisfactory for the interpretation of the second and third discrete energy losses in Ar-Ar$^+$. He attributes the first energy loss to excitation of inner d shells of the Kr$^+$-like $(Ar)_2^+$ molecular ion. As a test of this hypothesis, he predicts a discrete ejected-electron peak in the neighborhood of $\sim$50 eV, which arises from auto-ionization of the compound ion $(Ar)_2^+$. The experiments[13,50] fail to find the predicted peak.

The promotion of the $3d$ MO's probably occurs at $R_0\sim0.2$ a.u. (see Sec. III.B.2 of the present paper), where energy losses beyond the third discrete excitation occur. Thus, according to the present viewpoint, $3d$ MO's cannot account for the first energy loss. The first energy loss is viewed in this paper as an excitation of many outer-shell electrons.

In a recent article, Amusia, Afrosimov, Gordeev, Cherepkov and Sheftel[57] have proposed searching for evidence of many-body effects by observation of cross sections for inelastic proton and electron scattering from atoms. Furthermore, the authors have abandoned the position that heavy-particle atomic collisions show evidence of collective excitations.

The promotion model has the advantages that the energy losses and kinetic energies of ejected electrons are in agreement with experiment, that the position of critical internuclear distances is accounted for, and that a consistent interpretation is made of experiments ranging from the simplest to most complex systems. Therefore it seems unnecessary to postulate a radically new mechanism of excitation to reconcile the experimental facts with atomic and molecular theory.

On the other hand, the Landau-Zener theory is a statistical one. Since level crossing lies at the roots of the promotion model of inelastic collisions, some form of statistical model is needed to interpret the experimental data on excitation. In addition, we have seen in Sec. IV that lack of electron correlation leads to a statistical distribution of the charge state of separating atoms. Finally, the Auger de-excitation can follow many alternative paths. Thus the statistical approach[30] has a certain validity. Everhart and Kessel[58] have developed a purely phenomenological statistical model which seems to be a satisfactory way of summarizing a large body of experimental data. Their model takes into account the promotion of inner-shell electrons. It appears that any successful, detailed theory must take into account both the molecular states and the statistical nature of the transitions at level crossings, in the outer shells when the molecular complex breaks up, and in the Auger decay processes.

VII. CONCLUSIONS

The present paper rests on two basic assumptions: Molecular states can be used in the analysis of atomic collisions and that electrons are emitted from discrete states of the system. These statements are equivalent to saying that certain interaction energies are large compared to the widths of the states. In the collision complex, the interactions are the promotion energies of inner-shell electrons; the widths are the range of possible energies of the outer-shell electrons. In the electron-energy spectra, the energies are the separations between quasistationary states; the widths are the broadening caused by the auto-ionization lifetimes. It appears that these assumptions are supported by experimental facts.

The Born-Oppenheimer molecular states were originally formulated to explain the facts of molecular spectroscopy, where energies of nuclear motion are but a few eV. It is remarkable that these states serve in analyses of collisions with nuclear kinetic energies which range up to hundreds of keV.

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