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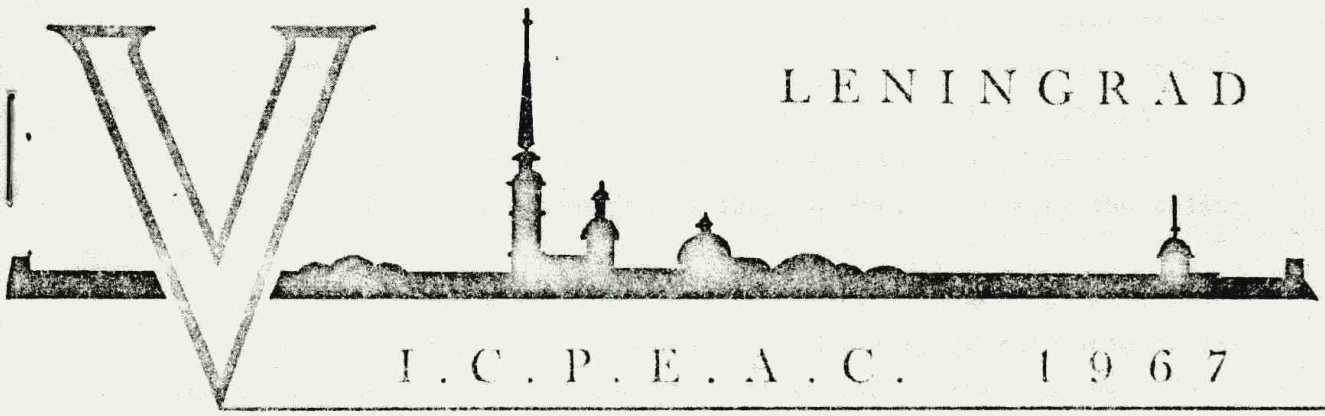
THE PHYSICS OF ELECTRONIC AND ATOMIC COLLISIONS:

Invited Papers from the Fifth International Conference

Leningrad, July 17-23, 1967



Theoretical Aspects of Atomic Collisions: Heavy Particle Collisions

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The variety of processes for heavy particle collisions is considerably larger than for electronic collisions.

At the same time the atomic collisions allow more distinct classification than the electronic ones, due to the large mass difference between electrons and nuclei.

The relation between the two kinds of collision processes is similar to that between atomic and molecular radiation processes; the spectra of molecules are much more complicated, but they can be divided into rotational, vibrational, and electronic spectra. In fact, the theory of electronic and atomic collisions is simply the extension of the theory of atomic and molecular spectra into the region of positive energies.

The first question which the theory has to answer is why inelastic atomic collisions occur at all. In fact, up to some KeV energies (and for heavy particles up to some tens of KeV), the velocity of relative motion of atoms is considerably less than that of the electrons in the atomic shells. Therefore, the condition $T\Delta E/h \gg 1$ is fulfilled, T being the duration of collision and ΔE being the change of internal energy of atomic particles. The left side of this inequality is usually called the Massey parameter. When the inequality is satisfied, the adiabatic approximation is valid. The electrons continually adjust to the position of nuclei and the atomic particles relax to the same states they had been in before the collision.

But experiment gives the opposite result. In most cases inelastic processes occur with considerable probability at slow velocities, sometimes even near to the energetic threshold of the process. For instance, such results are presented in [1]. This general result

means that for some internuclear distances R, the quantity ΔE becomes very small or even vanishes.

So we have to consider the potential curves of the quasi-molecule composed of the colliding atoms. It is the language of potential curves that is the most adequate one in the theory of slow atomic collisions.

We have to distinguish two cases, depending on whether the two electronic states under consideration have or do not have the same symmetry.

In the first case, the potential curves, according to the Neumann-Wigner theorem, do not intersect; i.e., ΔE cannot vanish. But ΔE can reach a very small value if there exists some additional approximate symmetry group which produces some additional approximate quantum numbers characterizing each state.

Lichten has supposed [2] that these additional quantum numbers are the quantum numbers for each electron if we consider the molecular orbital approximation to be sufficiently adequate, i.e., if we attribute some definite wave function to each electron. It is well known from molecular calculations that this approximation is valid for small and intermediate internuclear distances. Then the curves corresponding to the states of the same symmetry, but having different symmetries for some one-electron states, can intersect in this approximation. More precise calculation eliminates this intersection and leads to a small but finite ΔE. Therefore the adiabaticity condition can fail even at small velocities.

It is very important to carry out reliable and detailed calculations illustrating this pseudo-crossing at least for the relatively simple systems.

In the second case, when the symmetry of both states is different (for instance, Σ and Π states), the curve crossing is allowed and ΔE can vanish, but the inelastic processes occur only because of the rotation of the internuclear axis. In this case the intersections at small values of R are of special importance. The simplest limiting case of degeneration at $R = 0$ is considered in [2].

It is very important to continue the experimental investigation of the transition from the elastic collisions to the inelastic ones in the intermediate region of tens and hundreds of eV, measuring the

energy losses and the scattering angles. Using the coincidence techniques which allow us to pick out the process with a definite energy loss, we now have an opportunity to observe all these values.

The behavior of the potential curves is generally so complicated that apparently one cannot avoid using some averaging approaches to the problem. Perhaps, it is possible to introduce the phenomenological "friction" describing the inelastic processes. It is interesting to note that the two types of processes considered above lead to various kinds of "friction": a radial one proportional to V_R, and an azimuthal one, proportional to V_ϕ (i.e., to the radial and to the azimuthal components of the velocity). The relation between the two types of processes can be connected to the peculiarities of the total differential cross section curve.

So we can ask whether the electronic shells are "elastic" or "viscous " (reflecting the role of radial friction), and "slippery" or "rough" (reflecting the role of azimuthal friction). Of course, some other statistical approaches to the problem are possible. We can, perhaps, introduce the density of the pseudo-crossing points on the (E,R) plane, using the Thomas-Fermi model, the Wigner-Dyson statistical ensemble of S-matrices, and so on.

In this connection it is worthwhile to consider collective vibrations which became important as a result of the striking discovery of discrete inelastic losses in atomic collisions.

Now two possible explanations of this phenomenon are proposed. The first one was proposed by Fano and Lichten [2] who suggested that these states are formed by pushing out the electrons from the L-shell into the outer shells of the atoms; i.e., the usual one-body approximation is used. The second explanation [5] involves the excitation of specific, collective vibrations of the entire electronic core or some electronic shell of the atom.

It is hardly probable that the controversy between the adherents of each point of view could be resolved definitely by proposing some critical experiment. Rather it should be found out which method is more convenient for describing these states.

In particular, it is important to know whether allowing for the collective effects leads only to the corrections (even though sub-

stantial, as in the case of photoeffect [5]) to the one-particle model or gives substantially new results which can be obtained in the one-particle model only by using a superposition of a great number of configurations.

It should be noted that the adiabatic approximation is valid for the collective excited states, too. Meanwhile, the Massey parameter for excitations of the order of 200 eV is much more than unity under the usual assumptions. Therefore the question arises, How can this state be excited at comparatively slow collisions?

Among the other problems connected with the adiabatic approximation for the bound states, the nonuniformity of this approximation is worth mentioning. When the depth and the shape of the potential well changes, the wave function changes first inside the well and only after that under the barrier, far from the well. Therefore, for the deep tunneling processes, such as resonant charge exchange, the adiabatic approximation ceases to be valid at lower velocities than usual. The Schrödinger equation is similar to the heat transfer equation, so this effect can be compared to the smoothing and the delay of an underground temperature change relative to a surface temperature change.

The potential curves for quasi-molecules are analytic functions of the internuclear distance R. Therefore all the potential curves for the states of the same symmetry give us different values of one multivalued function. We can pass from one value of this function to the other, rounding the branching points on the complex plane R. It is known from the theory, that in slow collisions the most important branching points are those which lie near the real axis, i.e., the pseudo-crossing points. It is no use, therefore, to make the calculation too accurately, defining the shape of the potential curves as precisely as possible, if we are dealing with only two-state approximations. It is better to consider the positions of the branching points and the general analytical properties of the functions $U(R)$. Until now these properties were not sufficiently known. In principle, it is possible to construct various dispersion relations using the analyticity of $U(R)$.

Such a general approach is especially important if we consider

the highly excited states of the quasi-molecule and the transition into the continuous spectrum. The energy then becomes complex at real R; unstable quasi-stationary states with definite lifetimes are formed; the branching point lies just on the real axis, and we pass on to the so-called unphysical sheets of U(R). The dynamics of such a process of transition into the continuous spectrum are being intensively studied, so we now know a little about quasi-stationary states of the molecules, of their widths, situations, and so on. Here the measurements of detached electron energy distributions are extremely important. Pioneering work of this kind was presented at the conference [6]. The presence of energetically discrete groups of electrons indicates that pseudo-crossings of the quasi-stationary potential curves, which have not been previously observed, are possible. These crossings are very interesting from the point of view of general theory.

Much attention was paid at the conference to the various resonance processes in the continuous spectrum, such as the resonant dissociative capture of electrons. A pronounced isotope effect in this case can be easily explained theoretically and is very useful for the determination of the lifetime and the energy of the unstable molecular states [7].

The theoretical description of these processes is based on the natural extension of the adiabatic approximation to unstable states. According to this approximation the time-dependence of the wave function is given by

$$\exp\left(-\frac{i}{h}\int E\,dt\right) \quad .$$

For the complex energy $E_o - i\frac{\Gamma}{2}$ we obtain for the probability of decay

$$w = 1 - \exp\left(-\frac{1}{h}\int \Gamma\,dt\right) \quad .$$

However, the conditions of applicability of such a quasi-adiabatic approximation are still unknown, and it would be very interesting to investigate this problem.

Thirteen papers dealing with these questions were presented at the conference, and one of the sessions was entirely dedicated to this problem [8]. Thus it appears that ionization and other processes related to the continuous spectrum of electronic states can be treated by the same (or slightly modified) methods of adiabatic approximation, which were successfully applied to the description of charge exchange and excitation.

In this connection the calculations of the complex energies of the quasi-stationary states as well as the development of new methods for such calculations are very important. In particular, the variational method giving the complex energy as a stationary state of a certain functional is of interest [9].

A number of papers are devoted to various interference processes, i.e., to various oscillations of cross sections. This interference can be connected with charge exchange [10], with identity of nuclei [11], with hard core forces in the interaction between atomic particles [12], with the precession of angular momentum [13], and so on. In all these cases, by measuring the positions of maxima and the amplitudes of oscillations, we can obtain the shape of the potential curves, the positions of the pseudo-crossing points [14], and so on. This direction in the investigation of atomic interactions will, no doubt, develop very rapidly. It could be called "collisional spectroscopy" [15] or, better, "collisional spectrometry," and in case of investigation of the oscillatory structure of cross sections, "collisional interferometry."

These methods allow us to obtain in principle much more information about the potential curves than we can, for example, from various observations of molecular phenomena.

From the point of view of the relative motion of the nuclei, atomic collisions belong to the intermediate region between classical and quantum mechanics. Usually the de Broglie wave length for atoms is much less than their dimensions and so the classical description is valid. (Just as in atomic collisions, we find the same effect as in the scattering of light by raindrops in such phenomena as the rainbow, glory, halo, and so on.)

More detailed consideration of the classical approximation shows

that it can be used in cases where it is apparently inapplicable. For instance, in symmetrical charge exchange we can consider the interference between two classical trajectories corresponding to the scattering of particles at the given angle by two different potentials. If the transitions from one potential curve to the other occur only in the close vicinity of the pseudo-crossing point, the trajectory can branch (with each branch weighted). The phase can be calculated as a classical action integral and the trajectories, being parallel before and after collision, can produce interference [16]. At low energies many phenomena, especially those due to interference, require the wave treatment of the relative motion of the atoms. This is particularly the case when the energy of electronic transition is comparable to the energy of relative motion of atoms. In this connection various semiclassical methods, such as the eikonal method, have been developed.

In conclusion it should be noted that triple collisions have hardly been investigated at all. In some cases these processes are of a resonant nature and therefore their probability is great. For example, in the collision between two atoms and an electron a considerable energy exchange between the electron and the atoms can take place which cannot be attained in the electron-single atom collision [16]. Up to now only the processes of the type $(3 \rightarrow 2)$ have been considered, these processes being the inverse ones of the two-particle collisions followed by detachment of an electron. Their probability can be obtained from the principle of detailed balance, if the cross section for the two-body collision is known. Without doubt the theory of triple collisions will develop more intensively in the future.

The number of theoretical papers on electronic-atomic collisions submitted to this conference exceeds the number of papers on heavy particle collisions. However, this is due to the complexity of heavy particle collisions rather than the greater importance of electronic collisions. In this case the theorist can be likened to the man who looked for the lost purse under the street lamp only because there was more light there. I believe that at the next conference this ratio must change. Just as it was true at the recent conference that twice as many experimental papers dealt with atomic collisions as dealt with electronic ones, so it must be for theoretical work.

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