CONTRIBUTIONS TO THE EIGHTH INTERNATIONAL CONFERENCE

ON PHENOMENA IN IONIZED GASES

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ABSTRACT

This report embodies the contributions by E. Gerjuoy to the Eighth International Conference on Phenomena in Ionized Gases, held at Vienna, Austria, August 27 - September 2, 1967. In particular, this report contains: (i) Summary of the Plenary Session on Collision Processes; (ii) Chairman's Introductory Remarks at the Plenary Session; (iii) the text of the first paper at this Plenary Session. The contents of this report will be published (precisely as given here) in the Conference Proceedings.

Plenary Session: Collision Processes

Chairman: E. Gerjuoy

SUMMARY

Surveys of the principal contributions to the 5th International Conference on the Physics of Electronic and Atomic Collisions at Leningrad, July, 1967, are presented. There are four individual surveys, by four different speakers, covering respectively the principal contributions at Leningrad in the four sub-fields: electron-atom collision theory, electron-atom collision experiments, atom-atom collision theory, atom-atom collision experiments. In effect these reviews cover the progress in atomic collision research in the two year period since the 1965 Belgrade Conference on Phenomena in Ionized Gases.

Plenary Session: Collision Processes

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Introductory Remarks

As you know, contributed papers on the subject of elementary atomic collision processes have not been accepted at this Conference, because such papers were the primary interest of the 5th International Conference on the Physics of Electronic and Atomic Collisions, held at Leningrad only a month ago. On the other hand, our interpretations and predictions of many phenomena in ionized gases depend strongly on collision reaction rates. Consequently, the programme for the present Conference has incorporated this plenary session, with the objective of reviewing the major accomplishments reported at Leningrad. In effect these reviews -- by the four speakers this morning -- will very largely bring this audience up to date on recent developments in the field of electronic and atomic collision research. Actually it is customary, and less awkward, to say simply "atomic collision research", although the colliding bodies may be electrons, protons, neutral atoms and molecules, positive and negative atomic and molecular ions, or even positrons and mesons. The essential feature of an atomic collision is that the only consequential interactions are Coulomb or related non-nuclear forces, such as spin-orbit or van der Waal's. Present investigations are limited to two -- or at most three -- initially colliding bodies, each of which, however, may be composed of many electrons and atomic nuclei, as just explained.

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Turning now to this morning's talks, I want to stress that the speakers deliberately are making no special effort to describe those advances which seem most relevant to phenomena in ionized gases. We are surveying atomic collision research as it is, not as this audience might like it to be. Of course, even in two hours, it is impossible to intelligibly summarize all the important experimental and theoretical contributions to the Leningrad Conference. Each of this morning's speakers -- in the four sub-fields into which the field of atomic collisions is conveniently divided -- has been forced to omit topics which deserved presentation, but which simply could not be fitted into a half hour talk including time for discussion from the floor. Abstracts of all the contributed papers at Leningrad have been published in an English language volume [1]. Comparison of this volume with the corresponding volume [2] for the previous International Conference on the Physics of Electronic and Atomic Collisions -- at Quebec in 1965 -- is an excellent way to discern the steadily increasing intensity and sophistication of work in the field. It also is useful to compare the talks in this session with the corresponding survey talks -- by Schulz [3] and by Hasted [4] -- at the 1965 Belgrade International Conference on Phenomena in Ionized Gases. A very brief report on the Quebec Conference -- by Fite and myself [5] -- also may be of interest.

In this connection, it is worth noting that, although they cover exactly the same subjects merely two years apart, the Leningrad volume contains abstracts of 309 papers to the Quebec's 180, an increase of over 70%. The number of theoretical papers at Leningrad was 140, about twice the number of theoretical papers at Quebec. In both Conferences, however, the percentage of theoretical papers devoted to electron-atom or electron-molecule collisions was almost exactly the same, about 60%. On the other hand, the percentage of experimental papers on electron-atom and electron-molecule collisions

fell from 51% at Quebec to 37% at Leningrad. The above percentages reflect the following unpleasant fact: Although improving experimental techniques increasingly are making accessible to observation the almost limitless number and variety of atom-atom and atom-molecule reactions, many details of electron-atom or electron-molecule collisions, including even electron scattering by atomic hydrogen, remain unpredicted by theory.

The sharp increase, relative to Quebec, in the number of Leningrad papers was not an unmixed blessing. The Leningrad programme was more crowded, and allowed considerably less time for discussion, than did Quebec. It well may be the case that the 6th International Conference on the Physics of Electronic and Atomic Collisions, to be held in the United States in 1969, will have to be organized like this Ionization Conference, with essentially no presentations of individual contributed papers. In other words, atomic collision experimentalists and theorists, like their colleagues in almost all fields of physics, now are absorbing worthwhile problems and emitting publications at what has become a burdensome rate. Fortunately, attempts to alleviate the difficulties of keeping up with the literature -- in the field of atomic collisions at any rate -- are under way. In particular, this audience should be informed that the United States recently has set up several atomic collision information centers, a development considered important enough to warrant two invited talks at Leningrad [6]. These centers regularly issue bibliographies and literature reviews, and will respond to requests for their reports.

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[4] J. B. Hasted, Beograd Conference, ibid, vol. 1, p. 9.

[5] W. Fite and E. Gerjuoy, Science 150, 516 (1965).

[6] "Atomic Collisions Information Centers in U.S.A.", invited talks at Leningrad by C. F. Barnett, Oak Ridge National Laboratory, Oak Ridge, Tennessee, U.S.A., and by L. J. Kieffer, Joint Institute for Laboratory Astrophysics, University of Colorado, Boulder, Colorado, U.S.A.

Plenary Session: Collision Processes

I. Recent Progress in Electron-Atom Collision Theory**

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Under the general heading of electron-atom collisions I -- and the next speaker -- include as well collisions between electrons and atomic ions, neutral molecules or molecular ions. However, of the 82 contributed papers on electron collision theory at Leningrad [1], only 16 were concerned with collisions involving molecules or molecular ions, despite the obvious practical importance of such collisions. Calculations of collision cross sections for incident electrons still are so tedious, and so questionably reliable, that theorists generally try to avoid the extra uncertainties and difficulties associated with molecular targets. Molecular wave functions are much less well known and much more complicated than atomic wave functions. Moreover, even in collisions where vibrational and rotational excitations are inconsequential, molecular vibrations and rotations often cannot be ignored. For example, in the elastic scattering of slow electrons by N_2, studied experimentally by Ehrhardt and Willmann [2], if -- speaking classically -- the

cross section is expected to depend on the orientation or magnitude of the internuclear separation, then the computed quantum mechanical cross section may be expected to depend on the initial rotational or vibrational states of the target nitrogen molecule.

As a matter of fact, for reasons of simplicity just explained, more than half the 16 aforementioned papers on electron-molecule collisions were concerned with H_2 or H_2^+. The types of reactions studied in these 16 papers include: elastic scattering, electronic excitation, rotational excitation, vibrational excitation, dissociative recombination

$$e^- + AB^+ \rightarrow A + B \quad , \tag{1}$$

dissociative attachment (also called dissociative capture)

$$e^- + AB \rightarrow A + B^- \quad , \tag{2}$$

and photoionization

$$h\nu + AB \rightarrow e^- + AB^+ \quad , \tag{3}$$

the theory of which depends on knowledge of the wave function for elastic scattering of an electron by the resultant ion AB^+. On the whole, the results of these Leningrad theoretical studies on electron-molecule collisions are not a major advance over the corresponding Quebec studies. Worth mentioning, however, are:

(a) Calculations, by Temkin and Vasavada [3], of s-wave phase shifts in the elastic scattering of electrons by H_2^+, via a generalization of the so-called method of polarized orbitals, which previously had been applied to electron-atom scattering only.

(b) An analysis, by Bardsley, Mandl and Wood [4], of other investigators' experiments on the elastic and inelastic scattering of electrons by

N_2, to determine whether the data are consistent with the hypothesis that the observed N_2 vibrational excitation proceeds via a postulated resonant -- i.e., quasistable -- state of N_2^-. The analysis is noteworthy because it shows that unequivocal inferences concerning the properties of the hypothesized molecular N_2^- state can be drawn from the data, especially from the angular distribution of the scattered electrons. Experiments already have shown that valuable information on resonant states of atomic ions can be gained from measured angular distributions of electrons scattered by atoms, as Dr. Ehrhardt will discuss.

(c) Calculations, by Dubrovsky, Ob'edkov and Janev [5], of dissociative capture by H_2, D_2 and HD, on the assumption that the capture proceeds via three resonant states, at energies between 8 and 14 eV. The results are shown in Fig. 1, the solid lines being the theoretical curves. The authors [5] first fitted the positions and widths of the three resonances -- in this case of H_2^- -- to the open circles representing the observed H_2 dissociative capture cross sections [6]. Assuming that the identical resonance energies and widths also occur in HD^- and D_2^-, the dissociative capture cross sections of HD and D_2 then could be predicted. The agreement between these predictions and the data [6] for HD and D_2 -- the closed circles and triangles respectively -- support the notion (embodied in the theory) that dissociative attachment competes with autoionization of the intermediate resonating states. The relative magnitudes of the theoretical curves reflect the fact that $H + H^-$ separate faster -- and therefore allow less time for autoionization -- than do the heavier $H^- + D$ or $H + D^-$, which in turn separate more rapidly than $D + D^-$. In this connection I remark that the dissociative attachment measurements shown have been extended to lower electron energies by Schulz and Asundi [7], who reported another resonance at 3.75 eV, with a very marked

isotope effect. At this electron energy, the cross sections for dissociative attachment in H_2 and D_2 differ by a factor of 200, corresponding to a quasistable state whose autoionization lifetime is only 10^{-15} sec. Moreover, it is possible that vibrational excitation of H_2 and D_2 proceeds via this same 3.75 eV resonant state, which suggests the need for a theoretical analysis of e-H_2 scattering along the lines of the e-N_2 analysis performed by Bardsley, Mandl and Wood [4]. Regrettably, this need is likely to be satisfied only too soon. My introductory remarks [8] should make understandable my considered use of the word "regrettably".

This concludes my survey of the Leningrad theoretical studies of electron-molecule collisions, so that I now turn to the area of electron-atom collision theory, on which the rest of this talk will concentrate. Even in this area, where molecular complications have been ruled out, theorists remain markedly reluctant to tackle any but the simplest collisions, namely collisions with one-electron systems such as H and He^+, or collisions with two-electron systems such as H^-, He and Li^+. To be specific, of the 66 contributed papers on electron-atom collision theory at Leningrad, only 55 actually were attempting numerical calculations; the remaining 11 involved purely formal considerations. Of these 55, as many as 37, or two-thirds, examined solely collisions with H, He, H^-, etc., containing at most two target electrons; only 18 papers attempted any calculations on target atoms containing three or more electrons.

In regard to the above statistics, please note that the term "electron-atom collisions" includes not only collisions with atomic ions (as I hardly need to say), but also positron scattering by neutral atoms or atomic ions. Although atomic collision cross section measurements employing incident positron beams are just beginning to receive serious consideration, theoretical

studies of positron collisions have been under way for some time. In fact, there were 10 papers on positron scattering at Leningrad. Basically, positron scattering theory is not very different from electron scattering theory, mainly because both positrons and electrons have the same mass. Certainly the theoretical procedures for positron collisions are much closer to electron collision procedures than to the proton collision procedures Dr. Smith will discuss. Nevertheless, positron collisions are of considerable theoretical interest, because of the following two compensating differences between positron and electron scattering.

(a) In one way, positron scattering is easier to treat than electron scattering because positrons are distinguishable from the electrons in the target atom. Thus the wave function describing a positron collision need have no particular symmetry under interchange of the incident particle and one of the target electrons.

(b) On the other hand, positron scattering is harder to treat than electron scattering because electrons in the target atom can be captured by the positron in bound states of positronium.

Associated with these differences between positron and electron scattering is the possibility of positron attachment to atoms, which could greatly affect the low energy behavior of positron cross sections. In particular, the scattering of positrons by hydrogen atoms depends strongly on whether or not there can be a bound state of the three-particle system composed of a proton, an electron and a positron. Similarly the scattering of positrons by helium depends strongly on whether or not a positron can be bound to a helium atom. These questions have been examined by Gertler, Snodgrass and Spruch [9], who reported on methods for obtaining rigorous lower bounds on energy eigenvalues. In other words, these authors seek a result of form

$$E > E_{min} \tag{4}$$

where E is the actual bound state energy, and E_{min} is the computed bound. If E_{min} turns out to be positive, then the system assuredly is not bound. Eq. (4) is to be contrasted with

$$E < E_{max} \tag{5}$$

which is the result yielded by the well known and commonly employed Rayleigh-Ritz. The fact that E_{max} turns out positive carries no inference that the system is not bound. In this fashion Gertler et al [9] were able to prove that He cannot bind a positron, but were not able to decide conclusively whether or not a hydrogen atom can bind a positron. However, they were able to show that the positron binding to atomic hydrogen -- if possible at all -- assuredly is very weak; the binding energy must be less than 0.08 eV. They also were able to prove that the system $H + e^+$ could not possibly be bound if the positron mass were less than 3/4 the electron mass. As a matter of fact, Drachman [10] reported that his calculations on positron scattering by atomic hydrogen indicated the positron could not be bound unless its mass exceeded 2.95 electron masses. However, Drachman's results are only indicative that the system $p + e^- + e^+$ cannot be bound; the results are not conclusive because Drachman does not employ the rigorous methods of Gertler et al [9].

I now have finished with positron reactions: from here on, therefore, I shall be concerned solely with those 56 contributed theoretical papers at Leningrad which examined collisions between actual electrons and atoms or atomic ions. Of these 56, one-third, namely 19, were largely devoted to the subject of resonances, i.e., to topics connected with the existence (or possible existence) of quasistable states of atoms and atomic ions.

More specifically, these 19 papers either computed the energies and widths of resonances, or predicted the detailed shapes of cross sections at energies near resonances, or attempted to develop procedures for treating reactions proceeding via intermediate quasistable states. There also were seven other electron-atom collision theory papers wherein resonances played a less immediate role, but to whose contents the existence of resonances was quite relevant. For example, Marriott and Rotenberg [11], whose main objective was finding a practical method for treating collisions with many-electron atoms, applied their method to low energy electron scattering by Li, in an energy range where resonances were expected; in fact, they found a resonance in the elastic cross section at an energy just 0.01 eV below the first excitation threshold, which lies at 1.8 eV and leaves the Li atom in its 2P state. Similarly, the Riverside, California group presented papers [12,13] on applications of their methods to low energy elastic collisions with atomic H, He, Ne and Ar, in all of which resonances are known to exist.

Evidently the subject of resonances has aroused the interest of many atomic collision theorists; experimentalists are interested too, as Dr. Ehrhardt's talk will attest. An immediately obvious reason for this interest is, simply, that the subject happens to be of comparatively recent origin; the first serious attempt to interpret observed structure in electron scattering cross sections as resonances was made only ten years ago [14], and the first direct observation [15] of a resonance in electron-atom elastic scattering dates only from 1963. It is quite clear, as was brought out in discussions at Leningrad, that the possibility of practical applications -- in or outside the field of atomic collisions -- is not an important present motivation for research on resonances. Just because resonances tend to have such narrow widths -- of the order of 10^{-2} electron volts at most -- their

effects are not readily manifested. In laboratory plasmas, for instance, electron energy distributions (over which resonant cross sections would have to be averaged) usually are much wider than 10^{-2} eV.

This remark about electron energy distributions is merely indicative, of course, and should not be taken to mean that consequential effects of resonances in plasmas are wholly ruled out. For example, the aforementioned feature [7] that 3.75 eV electrons dissociatively attach 200 times more strongly to H_2 than to D_2 conceivably could cause observable differences in the behavior of H_2 and D_2 laboratory plasmas. As a matter of fact, the existence of quasistable resonant states does seem to have important consequences in astrophysical plasmas, such as the solar corona and the instellar medium. The astrophysical consequences of resonances have been discussed recently by Goldberg [16] and by Burgess [17], in a book titled "Autoionization", edited by Temkin. In particular, Burgess [18], in a 1965 Astrophysical Journal paper, has given formulas for the rate of recombination of electrons with ions via dielectronic recombination, which denotes the sequence of reactions

$$e^- + A^{+(n)} \rightleftarrows A^{+(n-1)**} \rightarrow A^{+(n-1)*} + h\nu \qquad (6)$$

In dielectronic recombination $A^{+(n)}$, a stable ion of species A, n-times ionized, combines with an electron into a quasistable doubly excited state (designated by the two asterisks) of the ion $A^{+(n-1)}$. This state can autoionize back into the original $A^{+(n)}$ and free electron, as indicated by the arrow pointing to the left. But if the autoionization time is long enough, the quasistable $A^{+(n-1)**}$ may radiate a photon instead, and thereby end up in a singly excited (one asterisk) stable state of $A^{+(n-1)}$. Once the radiation occurs, true recombination has taken place, i.e., a free electron

definitely has been removed from the plasma.

It perhaps is noteworthy that -- despite this recent astrophysical interest -- the theoretical papers on resonances at Leningrad included no direct calculations on dielectronic recombination per se. There were two theoretical papers dealing with what amounts to the inverse of dielectronic recombination, namely ionization via a photon absorption raising an atom or ion to a quasi-stable doubly excited state. As it happens, both these two papers were concerned with molecular photoionization. A third related theoretical paper -- by Drukarev [19] -- estimated cross sections for photodetachment following excitation to an autoionizing state, as for instance in

$$H^-(1s^2) + h\nu \rightarrow H^-(2s,2p) \rightarrow H(1s) + e^- \qquad (7)$$

An earlier 1967 analysis -- by McGowan [20] -- of angular distribution measurements on e-H scattering, has almost certainly proved that there exists an autoionizing state of H^-, with approximate configuration 2s2p, lying 9.71 eV above the ground state of atomic hydrogen.

This work of McGowan's is a good simple illustration of the type of information one can gain from angular distribution measurements. In the neighborhood of an H^- autoionizing state, elastic scattering of electrons by atomic hydrogen presumably proceeds via

$$e^- + H(1s) \rightarrow H^{-**} \rightarrow e^- + H(1s) \qquad (8)$$

If the intermediate H^- state is an S state, i.e., has zero orbital angular momentum, then conservation of angular momentum requires that the outgoing scattered electron also has zero angular momentum, i.e., is an s-electron. In other words, if the intermediate H^- state has zero orbital angular

momentum, electrons scattered via Eq. (8) will have a spherically symmetric angular distribution. On the other hand, if the intermediate H^- state has unit orbital angular momentum, the outgoing electron will be a p-electron, and the electron angular distribution will depend on the scattering angle. Thus, the mere observation that the scattering is or is not spherically symmetric immediately distinguishes between intermediate resonant H^- S and P states. Actually, this explanation has been over simplified, even in the present almost trivial case. At energies in the vicinity of the resonance, not every electron is scattered via the intermediate resonant state. Some electrons are scattered by the same mechanisms as are operative at energies far from resonances, and the interference between the resonant and non-resonant scattering must be taken into account. But it is not difficult to do so; indeed quantitative predictions of the energy and angular dependences of scattering cross sections near an isolated resonance have been worked out years ago by the nuclear theorists, for all conceivable combinations of initial, intermediate and final states.

With this brief explanation of the utility of angular distribution measurements, I will drop the topic, leaving it up to Dr. Ehrhardt to show you some actually observed distributions. What I have not yet discussed -- and must discuss now -- is the work at Leningrad on predicting electron-atom scattering resonances. For this purpose, it is sufficient to concentrate on the theoretical papers at Leningrad dealing with resonances in scattering by one or two-electron systems only, e.g., H and He. There are reasonably useful methods of estimating resonant energies for scattering by more complex atoms, developed by Fano [21] well before the Quebec Conference. For instance, one can construct term series for the doubly excited ionic configuration energies. But these methods are admittedly approximate, and probably already

have been carried about as far as possible; at any rate, there were no contributed theoretical papers at Leningrad on Fano's methods for predicting resonant energies. It is true that there were a number of quite elaborate calculations of heavy atom resonances, based on generalizations of the techniques which presently are being employed for scattering by H and He. For example, Lipsky and Cooper [22] used close-coupling methods to compute the photoionization cross sections of neon and argon, wherein there are resonances corresponding to resonances in the scattering of electrons by the respective positive ions Ne^+ and Ar^+. Similar calculations, on nitrogen and neon, were performed by Conway, Ormonde and Smith [23], as well as by Moores [24], on Be, Mg and Ca; also there are the previously mentioned related works by Marriott and Rotenberg [11], and by the Riverside, California group [13]. For the heavier atoms, however, the utility of all such highly expensive calculations must remain questionable until we have been assured that the methods employed can yield accurate predictions for the lightest. The desire to establish such assurance very largely accounts for the aforementioned fact that two thirds of the actual electron-atom collision calculations at Leningrad involved at most two target electrons.

I now want to describe the methods which presently are being employed to predict the resonances in electron scattering by one and two-electron systems. These methods all were developed before the Quebec Conference, so that I shall explain them only just enough (I hope) to keep the discussion intelligible to those members of this audience who are unfamiliar with electron scattering theory. In general, the methods for theoretically predicting resonances fall into one of two broad classes:

(a) Methods which make predictions about the resonances only. These methods take advantage of the fact that resonances are associated with quasi-stable states, having complex energies

$$E = E_r - i\Gamma/2 \quad , \tag{9}$$

so that the probability density associated with the wave function describing a resonant state decays exponentially with time

$$\psi(t) \sim e^{\frac{-iEt}{\hbar}} = e^{\frac{-iE_r t}{\hbar}} e^{\frac{-\Gamma t}{2\hbar}} \tag{10a}$$

$$|\psi(t)|^2 \sim e^{\frac{-\Gamma t}{\hbar}} \tag{10b}$$

Evidently the lifetime τ of the state is $\hbar/\Gamma$; equally evidently, using the Uncertainty Principle, the width of the resonance is Γ.

$$\Delta E \tilde{=} \frac{\hbar}{\tau} = \Gamma \tag{11}$$

(b) Methods which compute scattering phase shifts at all incident energies, and which thereby locate the resonances as those energies, if any, at which a phase shift $\delta(E)$ suddenly increases by π as the energy E increases by the (percentagewise) very small amount Γ. The fact that the phase shift $\delta(E)$ must increase, not decrease, at a resonance is connected with some very general theorems relating the slope of the phase shift at resonance to the time delay encountered by electrons undergoing resonant scattering; this time delay is associated with the lifetime of the quasistable state in which the incident to-be-scattered electron is captured. In fact one can prove that the time delay

$$\tau \tilde{=} 2\hbar \frac{d\delta}{dE} \tag{12}$$

implying $d\delta/dE > 0$. For example, in the neighborhood of an elastic s-wave resonance, using the notation of Eq. (9)

$$\delta = \delta_o + \tan^{-1} \frac{\Gamma/2}{E-E_r} \tag{13}$$

where δ_o is the phase shift for non-resonant, i.e., potential scattering. Using Eq. (13) in Eq. (12), and averaging over the width of the resonance, yields an average lifetime

$$\langle\tau\rangle_{av} = \frac{2\hbar}{\Gamma} \tag{14}$$

corresponding to both formation and decay of a quasistable state of lifetime $\hbar/\Gamma$. An interesting theoretical paper giving close-coupling calculational results for the time delays in e-He scattering was presented by Codper [25] at Leningrad. I will note the possibility -- which does not seem to have been pointed out in the literature -- that measuring the number of scattered electrons at a function of delay time ultimately may prove to be the only feasible means of establishing the existence of very narrow resonances.

One method of the type (a) is the variational principle of Herzenberg and Mandl [26], which is a generalization -- to complex eigenvalues, Eq. (9) -- of the well-known Rayleigh-Ritz variational principle for real eigenvalues. There were no applications of this variational principle to electron-atom scattering at Leningrad, but there were two applications to electron-molecule collisions. The previously referred to analysis by Bardsley et al [4] incorporated one such application, for N_2; the second application, somewhat indirect, was by Herzenberg [27], who examined associative detachment via an intermediate resonant state. The associative detachment reaction

$$A + B^- \rightarrow AB + e^- \tag{15}$$

is the inverse of dissociative attachment, Eq. (2), discussed at the beginning of the talk. Another variational principle for complex eigenvalues, of rather novel form, was presented by Rudakov and Kutchinsky [28], in papers generalizing a variational principle for potential scattering originally described at

Quebec [29]; however, no calculations for actual electron scattering problems, using this variational principle, have been reported.

Another -- quite different -- procedure for getting at the locations of complex eigenvalues (9) is the method of projection operators, stemming from 1958 and 1962 nuclear theory papers by Feshbach [30]. The idea here is to somehow eliminate the imaginary part of the energy, after which one can estimate E_r, the real part of the complex eigenvalue, by the standard Rayleigh-Ritz variational principle. If I may say so, the method seems to have been inspired by the Biblical injunction "If thine i offend thee, pluck it out". In essence, the method projects out of the state of allowed functions all bound states to which the resonant state under investigation can decay by autoionization. In this subspace, therefore, the resonant state has infinite lifetime, i.e., zero width, i.e., its energy is purely real. The energy calculated this way is not precisely the original E_r of Eq. (9); there is a so-called "energy shift" introduced by solving Schrodinger's Equation in the subspace, rather than in the original space. But in practical applications the shifts are small, and can be estimated. Very high precision calculations of this type, on the P-wave resonances in e-H and e-He^+ scattering, were reported by Bhatia and Temkin [31]. One reason for describing the projection operator technique in this survey is that the notion of using projection operators suddenly has become very popular in atomic collision theory, even in atom-atom collisions. For instance, O'Malley [32], at Leningrad, employed projection operators in a paper on curve crossing in heavy particle collisions, a subject on which Dr. Smith surely will have lots to say. I further remark -- just to show you how wide-ranging the use of projection operators has become -- that Kleinman, Hahn and Spruch [33], in an unusual paper which computed upper and lower bounds on the coefficients

of r^{-6} in the long range interaction between an electron and the neutral atoms H, He, Li, Ne and Na, also made use of projection operators.

Now I turn to calculations of class (b) discussed above, wherein one simply calculates the phase shifts as best one can. The two predominant procedures of this type are known by the method of close-coupling (a term I already have mentioned in this talk) and the non-adiabatic theory. These methods are two alternative approaches to the problem of ordering a set of approximate scattering solutions to Schrodinger's equation in such a way that, as the order of approximation is increased, the approximate solutions converge to the exact wave function describing the scattering. Stated very loosely, the zero order approximation in the non-adiabatic theory includes only the monopole part of the interaction between the incident electron and the atom (of course, for an electron incident on a neutral atom, the monopole part vanishes more rapidly than r^{-1} at long range); successively higher approximations amount to including successively higher multiples of the interaction. In the nth approximation, after dropping all multipoles higher than n, the corresponding approximate wave function is a sum over n radial functions, which are coupled through the Schrodinger equation. These coupled equations are to be solved exactly, which is where the machine time gets used up. The method of polarized orbitals (also mentioned previously) retains only the dipole terms in this non-adiabatic expansion.

The close-coupling method expands the exact wave function, describing the coupled incident electron plus atom, in a series of eigenfunctions of the isolated atom. The expansion coefficients in this series are functions of the incident electron's coordinates; as before, these functions are coupled through the Schrodinger equation. In the zeroth approximation the expansion includes only one term, namely the initial state of the atom (its ground state

say); successive approximations include more and more atomic eigenfunctions in the series. Again, the coupled equations in any approximation are to be solved exactly, a task which is a far from trivial computing problem even if only three closely coupled eigenfunctions are employed. A very important feature of the close-coupling method is that it can give bounds on the phase shifts. It can be proved that if one already has included all the open channels in the expansion, then at any fixed incident energy E increasing the number of closed channels in the expansion can only increase the computed value of tan $\delta(E)$, δ the phase shift. Since the exact wave function presumably can be expanded as a sum over all channels, open plus closed, this theorem implies that in each approximation the close coupling approximation yields a lower bound on tan $\delta(E)$. I will remind you that a "channel" is a possible set of physically distinguishable reaction products. "Open" channels are those which are energetically accessible by the time the reaction products are infinitely separated; "closed" channels are energetically inaccessible in this sense. To illustrate, in e-H scattering at incident electron energies below 10.2 eV, the ground state of hydrogen (together with the outgoing electron, of course) forms the only open channel. Any 2s, 2p, 3s, 3p, 3d, etc., included in the close-coupling expansion would be closed channels at energies less than 10.2 eV. At energies above 10.2 eV, the 2s, 2p channels become open, and must be included in the close-coupling expansion if the calculations are to give a bound on tan δ. In actual practice, both the non-adiabatic and close-coupling methods may be combined with each other and with variational principles for the phase shifts.

I now come to the crucial question -- how good is this vast theoretical apparatus I've described? Very briefly, the situation may be summarized as follows:

(α) Already by the time of the Quebec Conference it had become believable that the close-coupling and non-adiabatic methods would be able to account for the overall -- that is to say -- the non-resonant behavior of observed e-H and e-He cross sections at incident energies below the first excitation thresholds in these atoms (10.2 eV and 19.8 eV respectively), i.e., at incident energies where only the elastic scattering channel is open. The agreement between theory and experiment hardly was exact, but it did appear that improved computers, permitting higher order approximations, would make the agreement even better [34, 35].

(β) Also by the time of Quebec, the close-coupling and non-adiabatic methods similarly seemed able to account for the observed resonances in e-H and e-He scattering at incident energies below the first excitation threshold. Moreover, at these resonances, the methods of class (a) described above yielded reasonable agreement with the close-coupling and non-adiabatic results. Helium scattering was harder to handle than hydrogen scattering, of course; moreover, predictions of the widths were notably less successful than predictions of the resonant energies. All in all, however, there was no real reason to doubt the essential validity and utility of the theoretical methods for predicting resonances. Consider, for instance, Fig. 2, taken from a 1965 publication by McGowan, Clarke and Curley [36]. Fig. 2 shows the energy dependence of the observed e-H scattering cross section at 90°, from about 9.3 eV to 10.2 eV, which covers the region below the inelastic threshold wherein resonances are observed. The smooth curve is simply a best fit to the experimental points; the plus signs below the data mark the locations of H^- singlet and triplet quasistable states, predicted by various groups using methods which have been described, including the projection operator, non-adiabatic and close-coupling procedures. The abscissas of these pluses

are their only significant feature. The different ordinates are to facilitate comparison of the different predictions for the resonant energies; predicted resonant widths are not shown. It is apparent that the theoretical predictions for the location of the lowest ^1S resonance do cluster at the energy, namely 9.5 eV, where structure first appears in the experimental cross section. There also is evidence of structure near the predictions for the location of the ^3P resonance. As I already have explained, McGowan's latest analysis [20] of the data puts this ^3P resonance at 9.71 eV. I stress that the predictions plotted in Fig. 2 all date from before the Quebec Conference. Plotting the results of the most recent calculations would bring the different theoretical predictions even closer to each other, as well as closer to the experimentally determined locations of these lowest ^1S and ^3P resonances [37]. I also note that calculations of the widths have improved recently. In particular, Chen and Rotenberg [38] at Leningrad have come very close to the observed ^1S width, using what in effect is a variational principle for a matrix element involving a projection operator. A final feature of Fig. 2 worth mentioning is the clustering of resonances at the first excitation threshold. As a matter of fact, it now is generally believed [39] that there are an infinite number of H^- resonances below 10.2 eV.

This brings me, finally, to the last Leningrad theoretical papers I shall discuss in detail, namely the close-coupling calculations of Burke and collaborators [40, 41, 42] on excitation cross sections in e-H and e-He scattering. These important papers, which drew much attention, are by far the most elaborate attempts to compute excitation cross sections ever attempted, and they make maximum use of present computer capabilities. In other words, they are as good as we are likely to be able to do for some time. In what follows I shall concentrate on the e-H calculations [40, 41], which provide

a better test of the theory because the e-He calculations obviously are more difficult to push through. Further details on these e-H calculations [40, 41] may be found in a Harwell report by Burke's group [43]. The particular objective of these papers is prediction of the atomic hydrogen 1s-2s and 1s-2p excitation cross sections, at energies from threshold at 10.2 eV to just below the threshold for excitation of the n = 4 levels (which lie 1/16 of a Ryberg below the ionization threshold). Many resonances were found in this energy range, of course, including some so-called "shape resonances", which result when the incident electron is temporarily trapped in what in effect is a potential trough. The consequent delay in leaving the atom corresponds to a resonance, just as in the autoionization lifetime delays discussed heretofore. In general the resonances had widths at most of the order of 10^{-3} eV, too narrow to have been observed experimentally, so that the absence of resonant fluctuations in the experimental cross sections is of no concern. The averaged 1s-2s cross section, on the other hand, though its general shape agreed well with experiment, was a factor of 2 above the experiment. If this disagreement with experiment were unequivocal, it would be a serious blow to our theoretical prospects of making reasonably exact cross section predictions in He and heavier atoms. Burke stresses, however, that the experiments are not really absolute; they are performed by normalizing the experiment to the Born approximation at 300 eV. Burke suggests that this normalization may be the source of the discrepancy between theory and experiment. There is no doubt that the next few years will see some very determined efforts to make truly absolute measurements of these hydrogen 1s-2s and 1s-2p cross sections.

I will close this talk with the following additional remarks concerning the Leningrad theoretical papers. While I have tried to give you a fair

picture of the main present trends in electron collision theory, I don't want you to think that theorists are totally unaware of the need for reasonably valid cross section estimates, by methods which don't require the elaborate and expensive computations I have been discussing. One such means of estimating electron collision cross sections, which did get considerable attention at Leningrad, is known as Vainshtein's method [44]; perhaps the term "methods" would be more accurate, since Vainshtein does not always use precisely the same approximating procedures. Vainshtein's method(s) are useful in excitation and ionization of atoms by electrons. In effect Vainshtein enables improvement on the Born approximation, which is unreliable at low incident electron energies, without much more numerical work than the Born approximation. An even more trivial procedure for estimating cross sections, due to Gryzinski [45], which was the subject of heated discussion at Quebec, also has received considerable study during the past two years. Gryzinski's procedures don't even involve quantum mechanics; his estimates of cross sections are obtained using nothing more than the classical Coulomb cross section, together with a few not very well-founded rules. However, Bauer and Bartly [46], in a 1965 paper, have concluded that in ionization by electrons -- and probably also in excitation by electrons -- Gryzinski's methods typically are reliable to a factor of three. Several papers at Leningrad, by a combined Pittsburgh and NASA group [47], took the obvious step of examining the utility of Gryzinski in ion-atom collisions. Their conclusions (which I quote because I know Dr. Smith won't find time to do so) were that in charge transfer to incident protons -- from noble gas and alkali atoms at any rate -- Gryzinski has dubious value. For proton ionization of the same atoms, however, Gryzinski is as good or better than for electron ionization. More importantly, perhaps, it could be shown [48] that Gryzinski's seemingly ad hoc procedures for ionization -- by electrons and protons -- actually did have a quantum mechanical basis.

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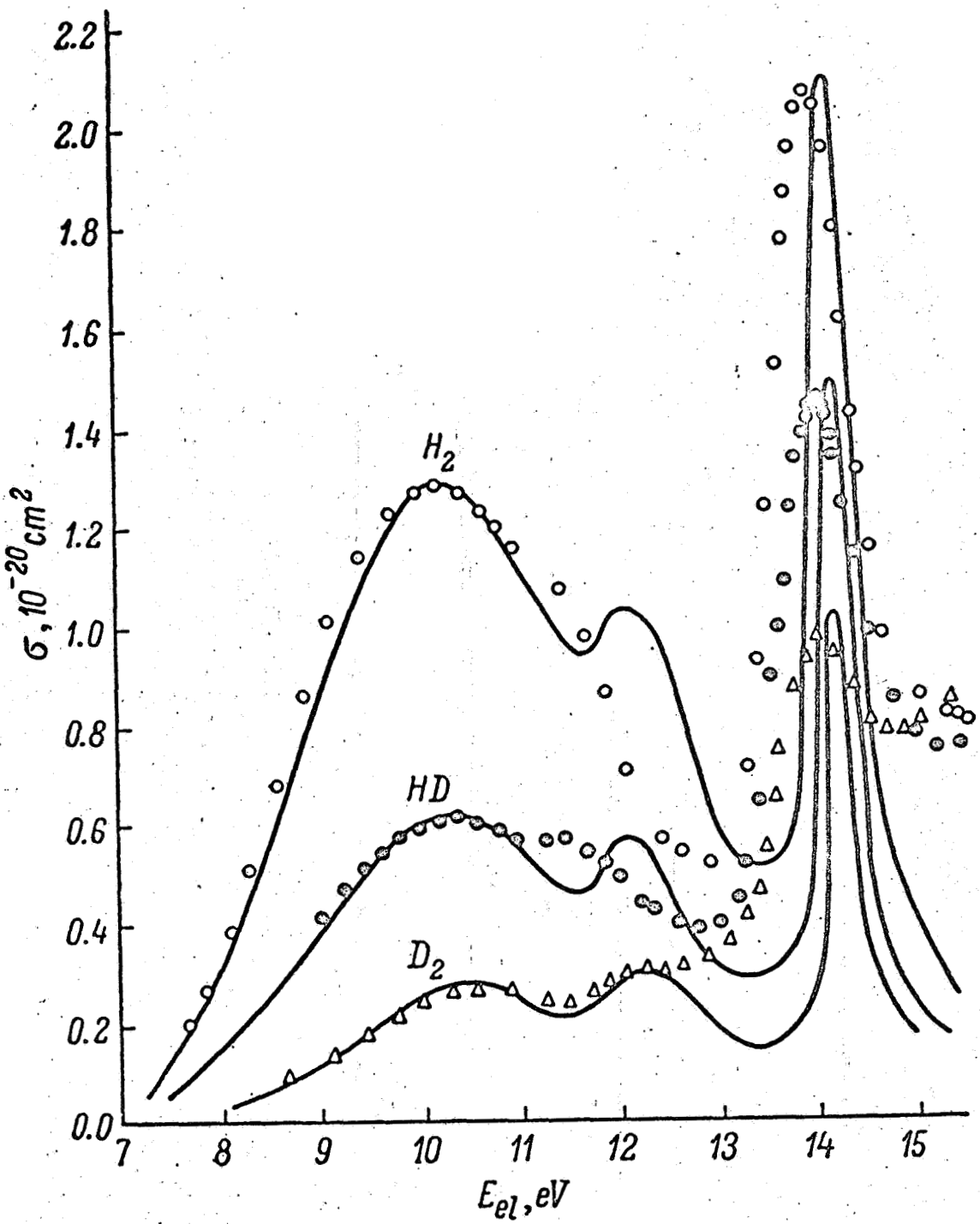
FIGURE CAPTIONS

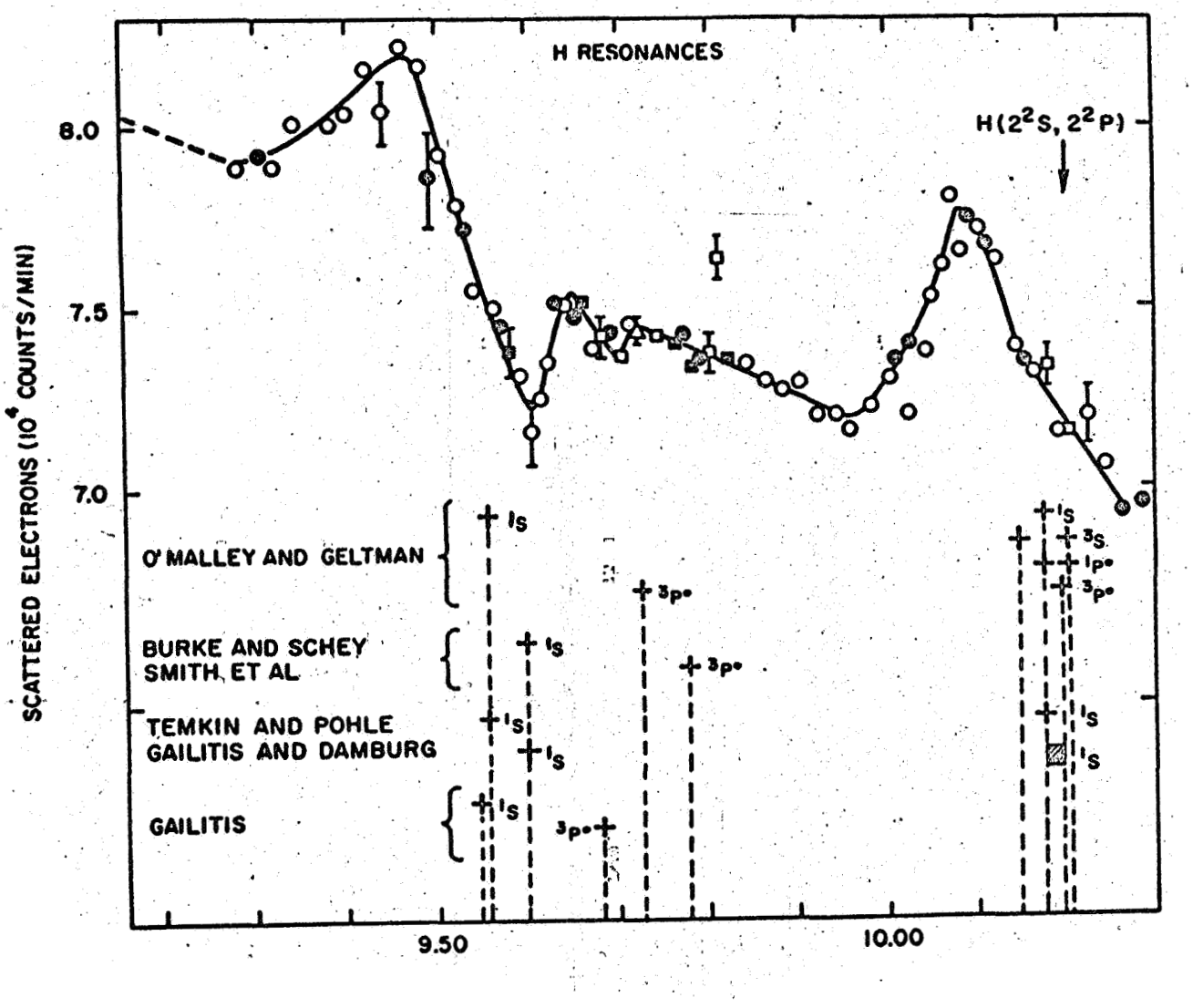
Fig. 1. The dissociative capture cross sections for the H_2, DH and D_2 molecules. The solid lines represent the present calculation, the points are the experimental data. E_{el}-electron energy.

Fig. 2. Structure in the 90° elastic scattering of electrons by atomic hydrogen. The solid line is a smooth curve through the experimental points. The abscissa is the electron energy, in eV. The vertical arrow marks the threshold for inelastic scattering. The pluses and hatched square mark the location of the resonances, as predicted by various theoretical groups.



The dissociative capture cross sections for the H_2, DH and D_2 molecules.

The solid lines represent the present calculation, the points are the experimental data. E_{el} — electron energy.


H RESONANCES
H(2²S, 2²P)
8.0
7.5
7.0
SCATTERED ELECTRONS (10⁴ COUNTS/MIN)
O'MALLEY AND GELTMAN
BURKE AND SCHEY
SMITH, ET AL
TEMKIN AND POHLE
GAILITIS AND DAMBURG
GAILITIS
1S
3P°
3S
1P°
9.50
10.00