

CONF-9009267-2

A paper for the DOE-OHER Conference on the Physical and Chemical Mechanisms in Molecular Radiation Biology, Woods Hole, Massachusetts, 4-7 September 1990.

ATOMIC AND MOLECULAR THEORY*

Received by [unclear]

Mitio Inokuti

DEC 04 1990

Argonne National Laboratory, Argonne, Illinois 60439

CONF-9009267--2

DE91 004475

Abstract

The multifaceted role of theoretical physics in understanding the earliest stages of radiation action is discussed. Scientific topics chosen for the present discourse include photoabsorption, electron collisions, and ionic collisions, and electron transport theory. Connections of atomic and molecular physics with condensed-matter physics are also discussed. The present article includes some historical perspective and an outlook for the future.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

* Work supported in part by the U.S. Department of Energy, Assistant Secretary for Energy Research, Office of Health and Environmental Research, under Contract W-31-109-ENG-38.

The submitted manuscript has been authored by a contractor of the U.S. Government under contract No. W-31-109-ENG-38. Accordingly, the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for U.S. Government purposes.

MASTER 

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

1. Introduction

1.1. Role of theoretical physics

My assignment is to discuss the role of theoretical physics in understanding the initial stages of radiation interactions with atoms and molecules in the context of radiation biology. At the outset, let us consider the role of physics in general in the same context. In three respects physics has contributed materially and will undoubtedly continue to do so.

First, physics provides instrumentation necessary for research in radiation biology. By "instrumentation" I mean a broad class of devices for the generation of radiations, for the measurement of radiations, and for the identification and analysis of radiation effects. This role of physics has long been well recognized; indeed, it is so obvious that we often fail to point it out.

Second, physics provides principles that are crucial for establishing a framework of sound reasoning. To cite an example in our context, it is the role of physics to tell how different radiations are absorbed in different materials.

Third, physics provides data basic to the considerations of chemical and biological effects of radiation. Elementary examples in our context are the stopping powers of various materials for particles of various energies and related quantities such as the linear energy transfer (LET). Any serious discussion of physical and chemical mechanisms of radiation effects requires knowledge of at least the stopping powers, and often more, e.g., of cross sections for individual energy transfer processes.

Theoretical physics in particular contributes in the same three respects: instrumentation, principles, and data. A recent example of theoretical physical contributions to instrumentation development is seen in computerized tomography, which originated in the mathematical problem^{1,2} of determining electron density in matter from measurements of photon beam attenuation in various directions. (Although computerized tomography is primarily used in medical diagnosis and radiotherapy planning and is only indirectly related to radiation biology, I cite this example because of its great importance and to illustrate the wide-ranging significance of theoretical physics.) Contributions of theoretical physics in providing principles and data are plentiful and too well known to be enumerated.

1.2. Subfields of physics relevant to the theme of the conference

Several subfields of physics play different roles in our context. They include particle and nuclear physics, atomic and molecular physics, condensed-matter physics, and statistical physics.

The role of particle and nuclear physics primarily concerns characterizing charged-particle spectra resulting from the incidence of baryons (e.g., pions, neutrons, and energetic heavy ions) with matter. Besides causing electromagnetic interactions, baryons strongly interact with nuclei at short distances, causing nuclear transformation and generating various charged particles. An example of excellent work on charged-particle spectra in materials of interest to radiation biology and radiological dosimetry is seen in the papers by Caswell and Coyne.³⁻⁶

In the main part of this present paper I will discuss the role of atomic and molecular physics in some depth and also touch upon some areas of condensed-matter physics. As an introduction, I wish to make a single remark.

Since radiation biology concerns the cell, which consists of condensed matter with many component molecules, condensed-matter physics is actually more relevant than atomic and molecular physics. However, atomic and molecular physics are basic and are more advanced in treating details and thus serve as an underpinning for condensed-matter physics. In other words, any concept in condensed-matter physics must be consistent with the knowledge of atomic and molecular physics. Moreover, under certain circumstances, radiation interactions in condensed matter occur virtually in the same way as in individual atoms and molecules, the influence of atomic and molecular aggregation playing only a minor role. This circumstance occurs, for instance, for energy transfer far exceeding the binding energy of an electron in the relevant shell; more precisely, an electron of kinetic energy much higher than the binding energy sees individual atoms or molecules in condensed matter almost as if they were isolated. In contrast, an electron of lower energy interacts with condensed matter in a notably different way.

The role of statistical physics in our context arises because radiation interactions with matter cause a multitude of collision processes. In order to evaluate the cumulative consequences of all these processes to the incident radiation and to matter, we must use some elements of the particle transport theory, either in the form of an analytic method or a Monte Carlo simulation. This topic belongs to statistical physics⁷ and physical kinetics,⁸ in the words of the Landau school.

1.3. Historical Perspective

In my view, the present conference in effect belongs to a series that began at Oberlin, Ohio.⁹ Subsequent meetings were at Highland Park, Illinois,¹⁰ and Airlie, Virginia.¹¹

The Oberlin conference marked the beginning of the modern inquiry into our theme. The physics part of the discussion at Oberlin was presented by Morrison, Fano, Platzman, Evans, and others. Fano¹² discussed secondary electron spectra and the total ionization yield. Platzman gave two papers, one¹³ on the earliest processes in radiation chemistry and biology and the other¹⁴ on the stopping power with particular emphasis on the influence of chemical binding and molecular aggregation in condensed matter. The papers by Fano and by Platzman were most stimulating to me (then a graduate student at the University of Tokyo) and indeed posed many of the problems that have been pursued seriously by many workers including myself. The knowledge now obtained about some of the problems then raised is extensive and solid. An example of such a problem is secondary-electron spectra, discussed here by Toburen.¹⁵ Another example concerns the total ionization yield; progress in this topic up to the early 1970s is seen in the ICRU Report 31.¹⁶

A few points made in the Oberlin proceedings warrant mention as examples of the remarkable foresight of Platzman. In the discussion following Fano's presentation, Platzman¹⁸ pointed out the incorrectness of the then standard notion that a heavy particle of speeds comparable to $e^2/\hbar = c/137$ does not ionize atoms or molecules with appreciable probability. This remark later led to the discovery of the electron promotion mechanism by Fano and Lichten,¹⁷ which in turn led to extensive studies that continue even now. Another noteworthy point made by Platzman¹⁴ concerns the importance of studying the spectra of water and other substances in the far-ultraviolet and soft X-ray regions, which eventually led to current research using synchrotron radiation.

The Highland Park conference was most noteworthy because of Platzman's prediction of the hydrated electron, whose presence was firmly established through the absorption spectrum first reported by Hart and Boag.¹⁹

spectroscopic studies thus initiated have led to many important results in basic physics, e.g., the understanding of doubly excited and other autoionizing states of atoms and molecules or, more generally, of electron correlation effects.²⁴

In this sense, DOE-OHER deserves a great deal of credit.

2. Atomic and Molecular Collisions

2.1. Preamble

Knowledge about individual collisions of energetic charged particles and photons with atoms and molecules is fundamental to the full understanding of radiation actions on matter, as was recognized at the Oberlin conference. For considerations of radiation energy absorption in some depth, e.g., for analyzing track structure or calculating yields of excitation and ionization, we need cross sections for individual collisions of various kinds and for various particles.

Research on those individual collisions has a long history and continues to be pursued by many workers. However, not every result of this research is relevant to our theme. As I have been stressing for years,^{25,26} cross-section data must fulfill what I call the trinity of requirements in order to be useful for the analysis of radiation actions and indeed for many other applications. In other words, they must be absolute, correct, and comprehensive in order to be useful for the analysis of radiation actions and indeed for most other applications such as astrophysics, atmospheric physics, and fusion research. The meaning of the term "absolute" is plain; cross-section values must be given in cm^2 or any other absolute scale. The meaning of the term "correct" is clear; cross-section values must be right, although

the degree of required accuracy depends upon the specific application. The meaning of the term "comprehensive" may call for explanation. In the analysis of radiation actions, we need cross-section values for a wide range of particle kinetic energy, energy transfer, and other variables characterizing a collision process such as scattering angle. This is true because particles of widely different energies exist in irradiated matter and because the outcome of a single collision is by no means unique. Therefore, we need cross-section values for a wide range of collision variables and for a variety of atomic and molecular species. However, the cross-section data in the literature are often relative as opposed to absolute, discordant as opposed to correct, or fragmentary as opposed to comprehensive. (This is because studies on atomic collision physics are largely carried out for purposes other than ours, most notably for advances in basic physics. To prove a point in physics, it is indeed sufficient and expedient to generate relative cross-section values over a crucial, limited range of variables, either in theory or experiment, although the requirement of correctness is crucial in all scientific contexts.)

In what follows, I shall discuss several topics selected in part from the point of view of the trinity of requirements and in part for their importance in other respects.

2.2. Photoabsorption

Let me begin with the photoabsorption cross section and related matters. The importance of the photoabsorption cross section in far vacuum ultraviolet and soft X-ray regions, i.e., for photon energies between about 10 eV and several keV, is twofold. First, photons in these regions interact most strongly with materials of low and modest atomic numbers (including most of

the materials in the biological cell) and therefore have a special role in the study of mechanisms in radiation biology. Second, there are close relations between the photoabsorption cross section and the cross section for glancing collisions of charged particles, which occur frequently when the particles are fast, as first pointed out by Bethe²⁷ and discussed fully in the literature as exemplified by Refs. 28-30. It is precisely because of these relations that Platzman¹⁸ at Oberlin called for studies on oscillator strength spectra (which are the same as photoabsorption cross sections as functions of photon energy, apart from a universal constant) of water and other materials basic to radiation biology. In 1966, Platzman³¹ also surveyed fragmentary data then available and gave his "educated guesses."

Now our knowledge of the oscillator strength spectra is incomparably more extensive and reliable, as illustrated by reviews of data by Samson³² on atoms and by Gallagher et al.³³ on molecules. These reviews focus on experimental data, but concomitant progress in theory is crucial. The 1968 review by Fano and Cooper³⁴ was a landmark in the modern theory of photoabsorption cross sections of atoms. Progress since then is seen the reviews by Starace³⁵ and by Amusia.³⁶

The theory of photoabsorption cross sections of molecules has seen considerable developments, although it has not yet reached the level of rigor that has been attained for the corresponding theory for atoms. Among other methods, the multiple-scattering method, pioneered by Dehmer and Dill,³⁷ is particularly notable for its general applicability to polyatomic molecules. Major accomplishments are the demonstration of the possibility of realistic calculations fully taking into account the crucial effects of nonspherical molecular fields experienced by outgoing electrons and the elucidation of commonly occurring phenomena such as shape resonances and barrier effects.

Full treatment of these topics is beyond the scope of the present discussion because a great deal of physics is involved in the transition of an electron from a bound orbit into an unbound orbit, especially from a molecule, which has a geometric structure as well as internal degrees of freedom.

Indeed, a great deal of physics and chemistry waits to be discovered concerning excited and ionized states of polyatomic molecules. As we see in the review of data by Gallagher et al.,³³ the result of photoabsorption or energy transfer from any other agent in excess of the first ionization threshold energy may or may not be ionization; molecular dissociation into fragments is a competing process. Full elucidation of the competition between ionization, dissociation, and other relaxation processes of polyatomic molecules along the lines outlined by Henriksen³⁸ among others, will be an important task left for the future.

2.3. Electron collisions

The importance to our theme of electron collisions with molecules is clear, because the absorption of any ionizing radiation in any matter produces many electrons whose kinetic energies are widely distributed.

Considered from the point of view of the trinity of requirements, the most significant development in the last two decades is the advent of cross-section compilations³⁹⁻⁴¹ for simpler molecules such as N_2 , O_2 , and H_2O . The compiled and recommended data are based in part on experiment and in part on theory.

The role of theory in cross-section determination, not only for electron collisions but also for all atomic and molecular collisions, is manifold. First, theory provides principles, i.e., a general framework of understanding applicable to all atoms and molecules. An example of this role is seen in the

Bethe theory²⁷⁻³⁰ and its major conclusions such as the relations between the photoabsorption and glancing collisions of charged particles. In my view, this role is the most important of all. Second, the principles found through theoretical study often point to the general systematics that correct cross sections should obey. For example, the principles tell us in general how cross sections for different atoms or molecules should depend on the electronic structure. Third, in certain exceptionally simple cases, theory leads to numerical calculations of sufficient reliability to be taken seriously. Finally, in rarer cases, theory opens up a novel perspective.

The theory of electron-molecule collisions has seen notable progress in the past two decades, as seen in recent monographs.⁴²⁻⁴⁴ Here I choose to point out one development that seems to be especially important, i.e., the application of the multiple-scattering method.^{37,38} For instance, Sato et al.⁴⁵ used this method and obtained cross sections in excellent agreement with experiment for elastic scattering by H₂O of electrons at 2-200 eV.

2.4. Ionic collisions

Progress in the understanding of ion-atom and ion-molecule collisions pertinent to our theme is likewise noteworthy.⁴⁶⁻⁴⁹ This progress started with the Fano-Lichten discovery of what we now call the electron-promotion mechanism, which accounts for the inelasticity of close collisions between particles carrying electrons.

For convenience, let me discuss separately collisions in different energy regions. First, at very high energies, i.e., at energies of many MeV/u and higher, the first Born approximation is adequate for most of the collisions, as has long been recognized.²⁷⁻²⁹ Next, at energies between a few MeV/u and many keV/u, various perturbative methods⁴⁶ were developed in the

past two decades, with partial success. Yet classical-trajectory Monte-Carlo simulations⁴⁷ have turned out to be most successful for explaining many experimental results. None of the methods is fully justifiable for a wide range of energies and for a wide variety of collisions. Among the challenging problems are spectra of convoy electrons (i.e., secondary electrons that are ejected in the forward direction at speeds comparable to the speed of an incident ion), the recoil of target atoms, multiple electron ejection and multiple electron capture by an incident ion, and fragmentation of molecules. All these matters have been studied experimentally and await full theoretical treatment.

For collisions at intermediate energies, i.e., at energies of several keV/u, progress in theory has been considerable.⁴⁸ Electron capture by an incident ion and the excitation of a target atom are reasonably well understood within present theories. However, details of ionization processes such as ejected-electron spectra need further theoretical study. Ionic collisions with molecules have been treated only for simpler molecules such as H₂, N₂, and O₂. Furthermore, theoretical work on ionic collisions with polyatomic molecules, molecular clusters,⁴⁹ or solid surfaces⁵⁰ is in an early stage of exploration. These topics are evidently more relevant to radiation effect studies. In particular, some understanding seems most urgently needed of the general characteristics and systematics of collisional ionization and dissociation of polyatomic molecules such as hydrocarbons.

Collisions of ions at low energies, i.e., at energies of several eV/u are relevant to radiation chemistry and hot-atom chemistry. Knowledge in this area is mainly experimental, and theoretical studies are highly desirable. With the advent of supercomputers, reasonably realistic determination of adiabatic-potential surfaces is becoming feasible for collision systems

involving a considerable number of atoms, and this determination will provide a sound starting point for analysis. The next decade will see developments in theories of low-energy ionic collisions with polyatomic molecules, molecular clusters,⁴⁹ and solid surfaces.⁵⁰

Efforts toward data compilation to satisfy the trinity of requirements are underway also for ionic collisions, as Toburen¹⁵ discusses. An excellent example is seen in the recent work of Phelps,⁵¹ who studied the collisions of a proton with molecular hydrogen with exceptional thoroughness. Inspection of the work gives a good impression of the level of current understanding and an appreciation of the rich physics involved.

2.5. General remarks on atomic collision theory

I wish to make a few points that seem to be essential for eventual theories of atomic and molecular collisions in general. My first point is the need for what I call the Wigner policy.⁵² The idea is to distinguish at least two regions of space: one in which colliding partners are well separated and the other in which they temporarily form a combined dynamical system that allows full exchanges of energy, angular momentum, and other quantities describing the internal motion. Explicitly distinct treatment of the two regions is necessary because different physics is involved. Figures 1 and 2 illustrate the idea. Moreover, distinction of more than two spatial regions may be necessary.

This idea of distinguishing regions of space has been implemented in several formulations including the R-matrix theory, the quantum defect theory, and the frame transformation theory, as seen in the monograph by Fano and Rau.⁵³ However, the general importance of the idea, apart from the technicalities necessary for implementation in specific applications, does not

seem to be fully appreciated. Indeed, the multiple-scattering method, to which I referred in connection with photoabsorption and electron collisions with molecules, may be viewed as a minimal version of the Wigner policy applied to electron problems. I believe that the Wigner policy needs to be incorporated into bound-state calculations of molecules in quantum chemistry.

Much too often, I find that theoretical calculations, formulated from the point of view of analytical expediency, use the same wave function form for the entire space. It is true that under certain simple circumstances a single-form wave function is sufficient to yield a basically correct result. However, this simplification should be clearly justified in advance from full consideration of the physics. In general, we need to be prepared to start with the Wigner idea.

As a second point, I stress the need for theoretical work to establish methods for data representation and systematization. This kind of work is extremely important from the point of view of the trinity of requirements. An example is seen in the Bethe theory,²⁷⁻²⁹ which gives a general analytic form for a cross section, and hence the stopping power, as a function of the charged-particle speed (though it is limited to high speeds). A more elementary example is the quantum-defect theory,⁵³ which gives the Rydberg formula for energy levels of highly excited states of simpler atoms and molecules and its generalizations for more complicated cases. According to this theory, individual energy levels as observed in experiments need not be tabulated; only a few key indices (i.e., the ionization threshold and the quantum defect in the simplest case) summarize all the information and thus are subjects of theoretical study.

Returning to the cross-section study, I point out another example of work in the same spirit. This example concerns the analytic representation of

oscillator strength spectra and secondary-electron spectra,⁵⁴⁻⁵⁸ based on studies of these spectra from the point of view of the theory of functions of a complex variable. I strongly suspect that work in this direction will be much more fruitful than we have so far appreciated.

3. Atoms and Molecules versus Condensed Matter

The connection of atomic and molecular physics with condensed-matter physics is an important topic in our context. Indeed, in the present conference, Christophorou⁵⁹ will discuss high-pressure gases as a prelude to condensed matter, and Ritchie⁶⁰ will focus on problems specific to condensed matter. Therefore, I intend to present a few introductory remarks. A more extensive account⁶¹ of my views on this subject has been published. (I intend to write a comprehensive article in the near future; therefore, I should most appreciate receiving remarks on Ref. 61.)

Let me focus on the complex dielectric-response function $\epsilon(E)$, viz., the electric displacement generated in matter by an external electric field of unit strength that is spatially uniform and oscillates at angular frequency $\omega = E/\hbar$. Basic properties of $\epsilon(E)$ are fully discussed in textbooks such as that of Landau and Lifshitz.⁶² The real part $\epsilon_1(E)$ describes the dispersion, and the imaginary part $\epsilon_2(E)$ describes the absorption, both of light at angular frequency ω . The probability that a glancing collision of a fast charged particle results in transfer of energy E to matter is proportional to

$$\Pi(E) = \text{Im} \left[\frac{-1}{\epsilon(E)} \right] = \frac{\epsilon_2(E)}{\epsilon_1^2(E) + \epsilon_2^2(E)}$$

In a low-density material, e.g., in a dilute gas, $\epsilon_1(E)$ is close to unity, and $\epsilon_2(E)$ is much smaller than unity at all E . Then, $\Pi(E)$ is virtually the same as $\epsilon_2(E)$, which means that the spectrum of energy transfer in a glancing collision of a fast charged particle is the same as that for photoabsorption. In a high-density material, e.g., in condensed matter, $\Pi(E)$ may differ appreciably from $\epsilon_2(E)$. An extreme case occurs if $\epsilon_1(E) = 0$ at a value of E ; then $\Pi(E) = 1/\epsilon_2(E)$ has a high value. This case is plasma excitation, well known in metals.

There are many other kinds of condensed-matter effects. A general criterion for the occurrence of molecular-aggregation effects has been given by Fano.⁶³ (For fuller discussions, see his other related papers.^{28,64,65}) Application of the Fano criterion led to the conclusion⁶¹ that the influence of molecular aggregation in water and organic materials of interest to radiation biology is certainly non-negligible at $E \lesssim 25$ eV (corresponding to valence shell excitation) but is less spectacular than in metals, in agreement with an earlier assessment.³¹

Various effects have been recognized in the past two decades. A full discussion of these effects is given in Ref. 61. Here I present in Table 1 a summary of our understanding. Although the knowledge summarized there is extensive, much remains to be done in the future. I strongly suspect that the coming decade will see the recognition of a few more crucial items to be included in Table 1.

An extremely important development in the past two decades is the work of Sanche and co-workers,⁶⁶⁻⁷³ who conducted a series of experiments to study collisions of electrons between tens of eV and about 1 eV with molecules of interest in the solid phase. The work has led to theoretical studies on the

interactions of slow electrons in condensed matter, as exemplified in Refs. 74-79.

A major conclusion we have thus drawn may be summarized as follows. Recall the distinction between the long-range interactions and the short-range interactions of an electron with a molecule in condensed matter (see Figs. 1 and 2). Molecular aggregation certainly affects the long-range interactions but leaves the short-range interactions intact. In technical terms, the long-range transition matrix $T^{(L)}$ incorporates all molecular-aggregation effects. In contrast, the short-range transition matrix $T^{(S)}$ for electron interactions with an isolated molecule remains applicable to the analysis of the electron behavior in condensed matter. This example illustrates the general strategy of approach, to be fully implemented in the coming decade.

4. Electron Transport Theory

4.1. Preamble

Absorption of any ionizing radiation by matter invariably results in the production of many electrons having a wide range of kinetic energy T . These electrons in turn collide with molecules and thereby degrade in energy and possibly produce further electrons by ionization. The description of the cumulative consequences of many collisions for the electrons and the medium is the goal of the electron transport theory. This topic is important because it provides a link between the knowledge of individual collision processes and the earliest events in radiation biology.

The electron transport theory in a broad sense belongs to statistical physics⁷ and physical kinetics,⁸ and it has been studied for many years in various contexts such as the electrical conductivity of ordinary matter as

well as of partially ionized gases, i.e., plasmas. In the context of radiation actions, modern work began with a paper by Spencer and Fano.⁸⁰

To present an overview of this topic, it is convenient to use a graph, shown in Fig. 3, in which the horizontal axis represents the electron kinetic energy T and the vertical axis the energy transfer E upon a single collision. The figure is meant to apply to water, organics, or other ordinary molecular substances (as opposed to metals or semiconductors)..

The vertical broken line indicates the first electronic excitation threshold E_1 , which is several eV. Electrons with $T > E_1$ are capable of exciting electronic levels of molecules. The cross section for electronic excitation (or for ionization if T exceeds the ionization threshold I) is appreciable at T within a few multiples of E_1 and declines gradually at higher T , as indicated by the shades in the figure. More importantly, energy transfer E is greater than E_1 for excitation and greater than I for ionization. Consequently, the moderation of an electron in the electronic excitation domain ($T > E_1$) is extremely rapid.

At $T < E_1$, cross sections are usually somewhat smaller, as indicated by lighter shades in the figure. More importantly, energy transfer E upon a single collision is much smaller because electrons in the subexcitation domain can give energies only in smaller quanta to the vibrational, rotational, and translational degrees of molecules. Thus, this domain warrants a treatment separate from that of the electronic excitation domain.

The subexcitation domain is delimited at lower T . At T comparable to thermal energy E_{th} or below, electrons not only lose energy to molecules but also may gain energy from a molecule upon a collision. Therefore, the treatment of electrons in the thermal domain is still another subject.

4.2. Electronic excitation domain

The past two decades saw notable progress in several respects. The advent of modern computers made it practical to carry out Monte Carlo simulations of electron transport first at high energies as pioneered by Berger.⁸¹ Developments since then have been extensive and show that Monte Carlo simulations are highly effective in treating problems involving complicated geometry such as dose distributions in non-uniform media, as seen in a recent workshop proceedings.⁸² Applications have been extended to lower electron energies with the use of realistic cross sections, as seen for instance in the work by Paretzke.^{83,84}

Progress in analytic treatments has been also considerable. The Spencer-Fano theory has been extended in several directions, i.e., for treating time-dependent cases, media consisting of mixtures, and stochastic aspects.⁸⁵⁻⁹¹ A major merit of the analytic theory is to elucidate principles governing electron degradation phenomena, i.e., to answer questions such as how radiation energy absorbed in a mixture might be apportioned to each component of the mixture and how stochastic aspects, e.g., yield fluctuations, can be precisely evaluated. All our experience shows that the Monte Carlo simulation and the analytic theory complement each other in deepening our understanding.

4.3. Subexcitation domain

More recently the behavior of electrons in the subexcitation domain has been studied extensively.⁹²⁻¹⁰¹ A general message resulting from the study is that subexcitation electron behavior depends upon the electronic structure of the individual medium and permits no simple scaling, for instance, in terms of

the atomic number (which is valid to some extent in the electronic excitation domain).

4.4. Thermal domain

Recent advances in the thermal domain are exemplified by the work by Shizgal and co-workers.¹⁰²⁻¹⁰⁴ Among other achievements, they have interpreted the thermalization times of electrons in simpler gases and thus have shown principles governing the thermalization process in unprecedented clarity.

4.5. Additional remarks and outlook

Although progress in electron transport theory in the past two decades is notable, as even the above cursory summary indicates, much remains to be done in the future.

In order to treat fully electron transport in condensed matter, we should incorporate quantum-mechanical effects. Even in the electronic excitation domain, quantum-mechanical effects may be appreciable for electron energies below about 100 eV. Recall that the de Broglie wavelength of an electron at 150 eV is about 10^{-8} cm, i.e., comparable to the atomic size. The de Broglie wavelength of an electron in the subexcitation domain is longer, and that of an electron in the thermal domain is even longer.

Indeed, fully quantum-mechanical treatments have been carried out on the eventual stage of a thermal electron, i.e., the solvation in water clusters and liquids, as exemplified by work of Berne and co-workers,¹⁰⁵⁻¹⁰⁷ Jonah et al.,¹⁰⁸ and Barnett et al.^{109,110} It is extremely desirable to extend work of this kind to higher energies, i.e., energies of a few eV, although methods used in the studies of Refs. 108-110 require prohibitive resources even with a

super computer. A successful resolution of this difficulty will establish a link between the traditional electron transport theory and the earliest stage of radiation chemistry.

Another related topic in radiation chemistry is the geminate-ion recombination in organic liquids, which leads to excited states of molecules that are important in the kinetics. This is an old subject discussed since the times of the conferences at Oberlin. Traditionally, it has been treated with the use of the classical trajectory and of the diffusion equation. I find it questionable to approach this problem in this way. For electron-ion recombination, there is no doubt that some quantum-mechanical effects are decisive. I have long held an idea that a more realistic approach to the electron-ion recombination will be to consider the process from the point of view of the Fermi theory¹¹¹ of perturbed Rydberg states. Virtually the same idea has recently been expressed by Schiller.¹¹² The modern theory of Rydberg states is the quantum-defect theory as fully discussed by Fano and Rau.⁵³ A prototype of the approach I envision is seen in the recent work of Du and Greene,¹¹³ who treated Rydberg states of clusters in which the competition between autoionization (i.e., electron escape) and dissociation is especially crucial. This topic is also closely related to the relaxation phenomena, such as the photofragmentation of molecules,³⁸ as I earlier mentioned, and as more generally treated by Dattagupta.¹¹⁴ I sincerely hope to discuss my views in greater technical details at a suitable occasion in the near future.

Acknowledgements

I thank Ugo Fano, M. A. Dillon, and Mineo Kimura for generously providing ideas and information of great value during the writing of the present article.

References

1. A. M. Cormack, Representation of a function by its line integrals, with some radiological applications. *J. Appl. Phys.* **34**, 2722-2727 (1963).
2. A. M. Cormack, Representation of a function by its line integrals, with some radiological applications: II. *J. Appl. Phys.* **35**, 2908-2913 (1964).
3. R. S. Caswell, Deposition of energy by neutrons in spherical cavities. *Radiat. Res.* **27**, 92-107 (1966).
4. R. S. Caswell, J. J. Coyne, H. M. Gerstenberg, and E. J. Axton, Basic data necessary for neutron dosimetry. *Radiat. Prot. Dosim.* **23**, 41-44 (1988).
5. R. S. Caswell and J. J. Coyne, Effects of track structure on neutron microdosimetry and nanodosimetry. *Nucl. Tracks Radiat. Meas.* **16**, 187-195 (1989).
6. J. J. Coyne, R. S. Caswell, J. Zoetelief, and B. R. L. Siebert, Improved calculations of microdosimetric spectra for low-energy neutrons. *Radiat. Prot. Dosim.*, in press.
7. L. D. Landau and E. M. Lifshitz, Statistical Physics, translated by J. B. Sykes and M. J. Kearsley (Pergamon Press, Oxford, 1969).
8. E. M. Lifshitz and L. P. Pitaevskii, Physical Kinetics, translated by J. B. Sykes and R. N. Franklin (Pergamon Press, Oxford, 1981).
9. J. J. Nickson (ed.), Symposium on Radiobiology. The Basic Aspects of Radiation Effects on Living Cells, Oberlin College, June 14-18, 1950 (John Wiley and Sons, Inc., New York, 1952).
10. J. L. Magee, M. D. Kamen, and R. L. Platzman (eds.), Physical and Chemical Aspects of Basic Mechanisms in Radiobiology. Proceedings of an Informal Conference, Highland Park, Illinois, 1953, Publication No. 305

(National Academy of Sciences -- National Research Council, Washington, D.C., 1953).

11. R. D. Cooper and R. W. Wood (eds.), Physical Mechanisms in Radiation Biology. Proceedings of a Conference held at Airlie, Virginia, Oct. 11-14, 1972 (USAEC Technical Information Center, Oak Ridge, Tennessee, 1974).
12. U. Fano, Secondary electrons: Average energy loss per ionization, pp. 13-24 of Ref. 9.
13. R. L. Platzman, On the primary process in radiation chemistry and biology, pp. 97-116 of Ref. 9.
14. R. L. Platzman, Influence of details of electronic binding on penetration phenomena, and the penetration of energetic charged particles through liquid water, pp. 139-176 of Ref. 9.
15. L. H. Toburen, the proceedings of the present conference.
16. International Commission on Radiation Units and Measurements, Average Energy Required to Form an Ion Pair, ICRU Report 31 (Washington, D.C., 1974).
17. U. Fano and W. Lichten, Interpretation of Ar^+ -Ar collisions at 50 keV. Phys. Rev. Lett. 14, 627-629 (1965).
18. R. L. Platzman, remarks on pp. 20-21 of Ref. 9.
19. E. J. Hart and J. W. Boag, Absorption spectrum of the hydrated electron in water and in aqueous solutions. J. Am. Chem. Soc. 84, 4090-4095 (1962).
20. W. Brandt and R. H. Ritchie, Primary processes in the physical stage, pp. 20-46 of Ref. 11.
21. M. Inokuti, Critique of cross-section data governing the physical stage of radiation action, pp. 51-67 of Ref. 11.

22. A. E. S. Green and J. H. Miller, Atomic and molecular effects in the physical stage, pp. 68-111 of Ref. 11.
23. H. H. Rossi and A. M. Kellerer, Effects of spatial-temporal distribution of primary events, pp. 224-243 of Ref. 11.
24. U. Fano, Correlations of two excited electrons. Rep. Prog. Phys. 46, 97 (1983).
25. M. Inokuti, Foreword to the Proceedings of the Workshop on Electronic and Ionic Collision Cross Sections Needed in the Modeling of Radiation Interactions with Matter, held on 6-8 December 1983 at Argonne National Laboratory, pp. iii-iv, Report ANL-84-28 (1984).
26. M. Inokuti, Cross sections for inelastic collisions of fast charged particles with atoms and molecules. Proceedings of an Advisory Group Meeting on Nuclear and Atomic Data for Radiotherapy and Related Radiobiology, Rijswijk, The Netherlands, 16-20 September 1987, pp. 357-365, (International Atomic Energy Agency, Vienna, 1987).
27. H. Bethe, Zur Theorie des Durchgangs schneller Korpuskularstrahlen durch Materie. Ann. Physik 5, 325-400 (1930).
28. U. Fano, Penetration of protons, alpha particles, and mesons. Ann. Rev. Nucl. Sci. 13, 1-66 (1963).
29. M. Inokuti, Inelastic collisions of fast charged particles with atoms and molecules -- The Bethe theory revisited. Rev. Mod. Phys. 43, 297-347 (1971).
30. M. Inokuti, VUV absorption and its relation to the effects of ionizing corpuscular radiation. Photochem. Photobiol. 44, 297-285 (1985).
31. R. L. Platzman, Energy spectrum of primary activations in the action of ionizing radiation, in Proceedings of the Fourth International Congress

- of Radiation Research, Cortina d'Ampezzo, June-July 1966, edited by G. Silini, pp. 20-42, (North-Holland, Amsterdam, 1967).
32. J. A. R. Samson, Atomic photoionization, in Handbuch der Physik, edited by S. Flügge, Vol. 31, pp. 123-213, (Springer Verlag, Berlin, 1982).
33. J. W. Gallagher, C. E. Brion, J. A. R. Samson, and P. W. Langhoff, Absolute cross sections for molecular photoabsorption, partial photoionization, and ionic photofragmentation processes. *J. Phys. Chem. Ref. Data* 17, 9-153 (1988).
34. U. Fano and J. W. Cooper, Spectral distribution of atomic oscillator strengths. *Rev. Mod. Phys.* 40, 441-507 (1968); 41, 724-725 (1969).
35. A. F. Starace, Theory of atomic photoionization, in Handbuch der Physik, edited by S. Flügge, Vol. 31, pp. 1-121, (Springer Verlag, Berlin, 1982).
36. M. Y. Amusia, Atomic Photoeffect (Plenum Press, New York, 1990).
37. J. L. Dehmer and D. Dill, The continuum multiple-scattering approach to electron-molecule scattering and molecular photoionization, in Electron-Molecule and Photon-Molecule Collisions, edited by T. Rescigno, V. McKoy, and B. Schneider, pp. 225-265, (Plenum Press, New York, 1979).
38. N. E. Henrikson, On the evaluation of branching ratios in molecular photofragmentation. *Chem. Phys. Lett.* 169, 229-235 (1990).
39. Y. Itikawa, M. Hayashi, A. Ichimura, K. Onda, K. Sakimoto, and K. Takayanagi, Cross sections for collisions of electrons and photons with nitrogen molecules. *J. Phys. Chem. Ref. Data* 15, 985-1010 (1986).
40. Y. Itikawa, K. Ichimura, K. Onda, K. Sakimoto, K. Takayanagi, Y. Hatano, M. Hayash, H. Nishimura, and S. Tsurubuchi, Cross sections for collisions of electrons and photons with oxygen molecules. *J. Phys. Chem. Ref. Data* 18, 23-42 (1989).

41. M. Hayashi, Electron collision cross sections for atoms and molecules determined from beam and swarm data, in Atomic and Molecular Data for Radiotherapy: Proceedings of an Advisory Group Meeting Organized by the International Atomic Energy Agency and Held in Vienna, 13-16 June 1988, IAEA-TECDOC-506, pp. 193-199, (International Atomic Energy Agency, Vienna, 1989).
42. I. Shimamura and K. Takayanagi (eds.), Electron-Molecule Collisions, (Plenum Press, New York, 1984).
43. L. G. Christophorou (ed.), Electron-Molecule Interactions and Their Applications, Vols. 1 and 2 (Academic Press, New York, 1983-1984).
44. E. W. McDaniel, Atomic Collisions: Electron and Photon Projectiles, (John Wiley & Sons, New York, 1939).
45. H. Sato, M. Kimura, and K. Fujima, Elastic and momentum transfer cross sections in electron scattering by water molecules. Chem. Phys. Lett. 145, 21-25 (1988).
46. R. H. Bransden, Charge transfer and ionization in fast collisions, in Electronic and Atomic Collisions: Invited papers of the XV International Conference on the Physics of Electronic and Atomic Collisions, Brighton, UK, July 1987, edited by H. B. Gilbody, W. R. Newell, F. H. Read, and A. C. H. Smith, pp. 255-269 (North-Holland, Amsterdam, 1988).
47. R. E. Olson, Multiple electron capture and ionization in ion-atom collisions, in Electronic and Atomic Collisions: Invited papers of the XV International Conference on the Physics of Electronic and Atomic Collisions, Brighton, UK, July 1987, edited by H. B. Gilbody, W. R. Newell, F. H. Read, and A. C. H. Smith, pp. 271-285 (North-Holland, Amsterdam, 1988).

48. M. Kimura and N. F. Lane, "The low-energy, heavy-particle collisions -- A close-coupling treatment, in Advances in Atomic, Molecular, and Optical Physics, Vol. 26, edited by D. Bates and B. Bederson, pp. 80-160 (Academic Press, Boston, 1990).
49. E. R. Bernstein (ed.), Atomic and Molecular Clusters (Elsevier, Amsterdam, 1990).
50. J. Los and J. J. C. Geerlings, Charge exchange in atom-surface collisions, Phys. Rep. 190, 133-190 (1990).
51. A. V. Phelps, Cross sections and swarm coefficients for H^+ , H_2^+ , H_3^+ , H , H_2 , and H^- in H_2 for energies from 0.1 eV to 10 keV. J. Phys. Chem. Ref. Data 19, 653-675 (1990).
52. M. Inokuti, The future of atomic collision theory, Comments At. Mol. Phys. 10, 99-106 (1981).
53. U. Fano and A. R. P. Rau, Atomic Collisions and Spectra, (Academic Press, Orlando, Florida, 1986).
54. M. A. Dillon and M. Inokuti, Analytic representation of the dipole oscillator-strength distribution. J. Chem. Phys. 74, 6271-6277 (1981).
55. M. A. Dillon and M. Inokuti, Analytic representation of the dipole oscillator-strength distribution: II. The normalization factor for electron continuum states in atomic fields. J. Chem. Phys. 82, 4415-4424 (1985).
56. M. A. Dillon, M. Inokuti, and Z.-W. Wang, Analytic representation of the generalized oscillator strength for ionization. Radiat. Res. 102, 151-164 (1985).
57. M. Inokuti and M. A. Dillon, What formulas are good for representing dipole and generalized oscillator-strength spectra?, in Physics of Ionized Gases. Proceedings of the Twelfth Yugoslav Summer School and

- International Symposium on the Physics of Ionized Gases, Sibenik, 3-7 September 1984, edited by M. M. Popvic and P. Krstic, pp. 3-22 (World Scientific, Singapore, 1986).
58. M. Inokuti, M. A. Dillon, J. H. Miller, and K. Omidvar, Analytic representation of secondary-electron spectra. *J. Chem. Phys.* 87, 6967-6972 (1987).
59. L. G. Christophorou, the proceedings of the present conference.
60. R. H. Ritchie, the proceedings of the present conference.
61. M. Inokuti, How is radiation energy absorption different in the condensed phase and in the gas? *Hoshasen Kagaku (Radiation Chemistry)* 49, 2-14 (1990). [In Japanese] English translation is available upon request to the author.
62. L. D. Landau and E. M. Lifshitz, Electrodynamics of Continuous Media, translated by J. B. Sykes and J. S. Bell, Chapter IX (Pergamon Press, Oxford, 1960).
63. U. Fano, Normal modes of a lattice of oscillators with many resonances and dipolar coupling. *Phys. Rev.* 118, 451-455 (1960).
64. U. Fano, Atomic interactions in dense materials, *Phys. Rev.* 103, 1202-1218 (1956).
65. U. Fano, A mechanism of collective phenomena, a preprint of an article to be published.
66. L. Sanche, Transmission of 0-15 eV monoenergetic electrons through thin-film molecular solids. *J. Chem. Phys.* 71, 4860-4882 (1979).
67. G. Bader, G. Perluzzo, L. G. Caron, and L. Sanche, Structural-order effects in low-energy electron transmission spectra of condensed Ar, Kr, Xe, N₂, CO, and CO₂. *Phys. Rev. B* 30, 78-84 (1984).

68. G. Perluzzo, L. Sanche, C. Gaubert, and R. Baudoing, Thickness-dependent interference structure in the 0—15-eV electron transmission spectra of rare-gas films. *Phys. Rev. B* 30, 4292-4296 (1984).
69. M. Michaud and L. Sanche, Interactions of low-energy electrons (1—30 eV) with condensed molecules: I. Multiple scattering theory. *Phys. Rev. B* 30, 6067-6077 (1984).
70. L. Sanche and M. Michaud, Interactions of low-energy electrons (1—30 eV) with condensed molecules: Vibrational-librational excitation and shape resonances in N₂ and CO films. *Phys. Rev. B* 30, 6078-6092 (1984).
71. M. Michaud and L. Sanche, Total cross sections for slow-electron (1—20 eV) scattering in solid H₂O. *Phys. Rev. A* 36, 4672-4683 (1987).
72. M. Michaud and L. Sanche, Absolute vibrational excitation cross sections for slow-electron (1—18 eV) scattering in solid H₂O. *Phys. Rev. A* 36, 4684-4699 (1987).
73. L. Sanche, Primary interactions of low-energy electrons in condensed matter, in Excess Electrons in Dielectric Media, edited by C. Ferrandini and J.-P. Jay-Gerin, to appear as a CRC Uniscience Book. (This review article summarizes the work of the author's group. Refs. 66-72 are representative of dozens of papers published by the group.)
74. U. Fano, J. A. Stephens, and M. Inokuti, Absence of resonances in the elastic scattering of electrons in molecular solids. *J. Chem. Phys.* 85, 6239-6240 (1986).
75. U. Fano and J. A. Stephens, Slow electrons in condensed matter. *Phys. Rev. B* 34, 438-441 (1986).
76. U. Fano, Studies of slow electron action on condensed media. *Radiat. Phys. Chem.* 32, 95-97 (1988).

77. J. A. Stephens and U. Fano, Slow electrons in condensed matter. The large polaron. Phys. Rev. A 38, 3372-3376 (1988).
78. P. Knipp, Interaction of slow electrons with density fluctuations in condensed materials: Calculation of stopping power. Phys. Rev. B 37, 12-17 (1988).
79. U. Fano and N.-Y. Du, Dissipative polarization by slow electrons. Appl. Radiat. Isotopes XX, XXX-XXXX (199X).
80. L. V. Spencer and U. Fano, Energy spectrum resulting from electron slowing down. Phys. Rev. 93, 1172-1181 (1954).
81. M. J. Berger, Monte Carlo calculation of the penetration and diffusion of fast charged particles, in Methods in Computational Physics, Vol. 1, edited by B. Adler, S. Fernbach, and M. Rotenberg, pp. 135-215 (Academic Press, New York, 1963).
82. T. M. Jenkins, W. R. Nelson, and A. Rindi (eds.), Monte Carlo Transport of Electrons and Photons (Plenum Press, New York, 1988).
83. H. G. Paretzke, Radiation track structure theory, in Kinetics of Non-Homogeneous Processes, edited by G. R. Freeman, pp. 89-170 (John Wiley & Sons, New York, 1987).
84. H. G. Paretzke, in the proceedings of the present conference.
85. A. R. P. Rau, M. Inokuti, and D. A. Douthat, Variational treatment of electron degradation and yields of initial molecular species. Phys. Rev. A 18, 971-988 (1978).
86. M. Inokuti, D. A. Douthat, and A. R. P. Rau, Statistical fluctuations in the ionization yield and their relation to the degradation spectrum. Phys. Rev. A 22, 445-453 (1983).

87. M. Inokuti and E. Eggarter, Theory of initial yields of ions generated by electrons in binary mixtures: II. J. Chem. Phys. 86, 3870-3875 (1987).
88. M. Inokuti, M. A. Dillon, and M. Kimura, Theory of electron degradation and yields of initial molecular species. Int. J. Quantum Chem. Symp. Series 21, 251-266 (1987).
89. M. Inokuti, M. Kimura, and M. A. Dillon, Time-dependent aspects of electron degradation: II. General theory. Phys. Rev. A 38, 1217-1224 (1988).
90. K. Kowari, M. Kimura, and M. Inokuti, Electron degradation and yields of initial products: V. Degradation spectra and the Fano factor for argon under electron degradation. Phys. Rev. A 39, 5545-5553 (1989).
91. K. Kowari, M. Inokuti, and M. Kimura, Time-dependent aspects of electron degradation: V. Ar - H₂ mixtures. Phys. Rev. A 42, 795-802 (1990).
92. M. A. Dillon, M. Inokuti, and M. Kimura, Time-dependent aspects of electron degradation: I. Subexcitation electrons in helium or neon admixed with nitrogen. Radiat. Phys. Chem. 32, 43-48 (1988).
93. A. Pagnamenta, M. Kimura, M. Inokuti, and K. Kowari, Electron degradation and yields of initial products: III. Dissociative attachment in carbon dioxide. J. Chem. Phys. 89, 6220-6225 (1988).
94. K. Kowari, M. Kimura, and M. Inokuti, Electron degradation and yields of initial products: II. Subexcitation electrons in molecular nitrogen. J. Chem. Phys. 89, 7229-7237 (1988).
95. M. Kimura, M. Inokuti, K. Kowari, M. A. Dillon, and A. Pagnamenta, Time-dependent aspects of electron degradation: IV. Subexcitation electrons in nitrogen and carbon dioxide. Radiat. Phys. Chem. 34, 481-485 (1989).

96. M. A. Ishii, Mineo Kimura, Mitio Inokuti, and Ken-ichi Kowari, Electron degradation and yields of initial products: IV. Subexcitation electrons in molecular oxygen. *J. Chem. Phys.* 90, 3081-3086 (1989).
97. M. Kimura, M. Inokuti, and K. Kowari, Electron degradation and yields of initial products: VI. Energy spectra of subexcitation electrons in argon and molecular hydrogen. *Phys. Rev. A* 40, 2316-2320 (1989).
98. M. Inokuti, Subexcitation electrons in gases, in Molecular Processes in Space, edited by T. Watanabe, I. Shimamura, M. Shimizu, and Y. Itikawa, pp. 65-86, (Plenum, London, 1990).
99. M. Kimura and M. Inokuti, Subexcitation electrons in molecular gases. *Comments At. Mol. Phys.*, in press.
100. M. A. Ishii, M. Kimura, and M. Inokuti, Electron degradation and yields of initial products: VII. Subexcitation electrons in gaseous and solid H₂O. *Phys. Rev. A*, in press.
101. M. Inokuti, Subexcitation electrons: An appraisal of our understanding. *Appl. Radiat. Isotopes*, in press.
102. B. Shizgal and D. R. A. McMahon, Electric field dependence of transient electron transport in rare-gas moderators. *Phys. Rev. A* 32, 3669-3680 (1985).
103. B. Shizgal, D. R. A. McMahon, and L. A. Viehland, Thermalization of electrons in gases. *Radiat. Phys. Chem.* 34, 35-50 (1989).
104. K. Kowari and B. Shizgal, Time dependent electron energy distribution functions and degradation spectra: A comparison of the Spencer-Fano equation and the Boltzmann equation. *Appl. Radiat. Isotopes*, in press.
105. A. Wallqvist, D. Thirumalai, and B. J. Berne, Localization of an excess electron in water clusters. *J. Chem. Phys.* 85, 1583-1591 (1986).

106. D. F. Coker, B. J. Berne, and D. Thirumalai, Path integral Monte Carlo studies of the behavior of excess electrons in simple fluids. *J. Chem. Phys.* **86**, 5689-5702 (1987).
107. A. Wallqvist, D. Thirumalai, and B. J. Berne, Path integral Monte Carlo study of the hydrated electron. *J. Chem. Phys.* **86**, 6404-6418 (1987).
108. C. D. Jonah, C. Romero, and A. Rahman, Hydrated electron revisited via the Feynman path integral route. *Chem. Phys. Lett.* **123**, 209-214 (1986).
109. R. N. Barnett, U. Landman, C. L. Cleveland, and J. Jortner, Electron localization in water clusters: I. Electron-water pseudopotential. *J. Chem. Phys.* **88**, 4421-4428 (1988).
110. R. N. Barnett, U. Landman, C. L. Cleveland, and J. Jortner, Electron localization in water clusters: II. Surface and internal states. *J. Chem. Phys.* **88**, 4429-4447 (1988).
111. E. Fermi, Sopra lo spostamento per pressione delle righe elevate delle serie spettrali. [On the pressure shift of the higher-order lines of the spectral series] *Nuovo Cimento* **11**, 157-166 (1934). English translation is available as NTC-TRANS-II-580.
112. R. Schiller, Ion-electron pairs in condensed polar media treated as H-like atoms. *J. Chem. Phys.* **92**, 5527-5532 (1990).
113. N.-Y. Du and C. H. Greene, Multichannel Rydberg spectra of rare gas dimers. *J. Chem. Phys.* **90**, 6347-6360 (1989).
114. S. Dattagupta, Relaxion Phenomena in Condensed Matter Physics, (Academic Press, Orlando, Florida, 1987).

Table 1. Condensed-phase effects on the oscillator strength spectrum.

Classification	Example	Remarks on Characteristics
Shift of the strength toward higher energies	Water, hydrocarbons, and organics	Occurs over wide ranges of excitation energies
Excitation of special modes of motion	Plasmons in metals	Occurs at specific energies and carries considerable strength
	Excitons in molecular crystals and ionic crystals	Occurs at specific energies and at minor strengths
Interaction of ejected electrons with other atoms and molecules	EXAFS (extended X-ray absorption fine structure)	Occurs at energies 100 eV above the pertinent threshold and at weak strengths, chiefly due to elastic scattering
Resonances	N ₂ , C ₂ H ₄ , C ₂ H ₂ , and other unsaturated hydrocarbons	Occurs at energies slightly above the threshold or even lower; influences on the strength are appreciable and lead to inelasticity

Figure Captions

Fig. 1. Schematic view of a collision of a particle with an atom or molecule. The particle, presumed for simplicity as structureless (i.e., as carrying no electrons), approaches from the right. The contribution of the approach at large distances to the scattering amplitude A is represented by a transition matrix $T_c^{(\ell, a)}$. In the superscript, " ℓ " signifies long range and "a" approach. The subscript c represents a set of quantum numbers that specify a channel. The contribution of the close encounter, in which the particle in effect merges with the target, is represented by another transition matrix $T_c^{(s)}$, where the superscript "s" signifies short range. The contribution of the departure to large distances is represented by still another transition matrix $T_c^{(\ell, d)}$, where "d" stands for departure. Consequently, we express the scattering amplitude as

$$A = \sum_c T_c^{(\ell, d)} T_c^{(s)} T_c^{(\ell, a)}.$$

The long-range transition matrices $T_c^{(\ell, d)}$ and $T_c^{(\ell, a)}$ are modified in condensed matter, while the short-range transition matrix $T_c^{(s)}$ is the same in gas and in condensed matter.

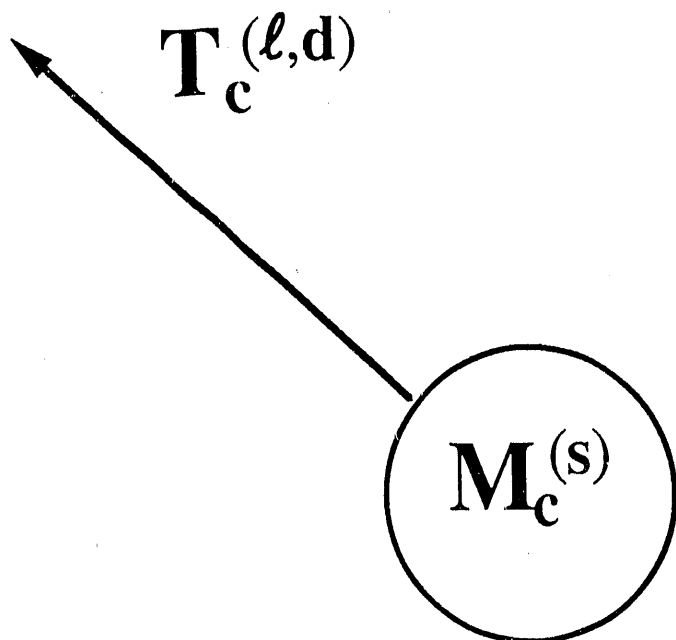
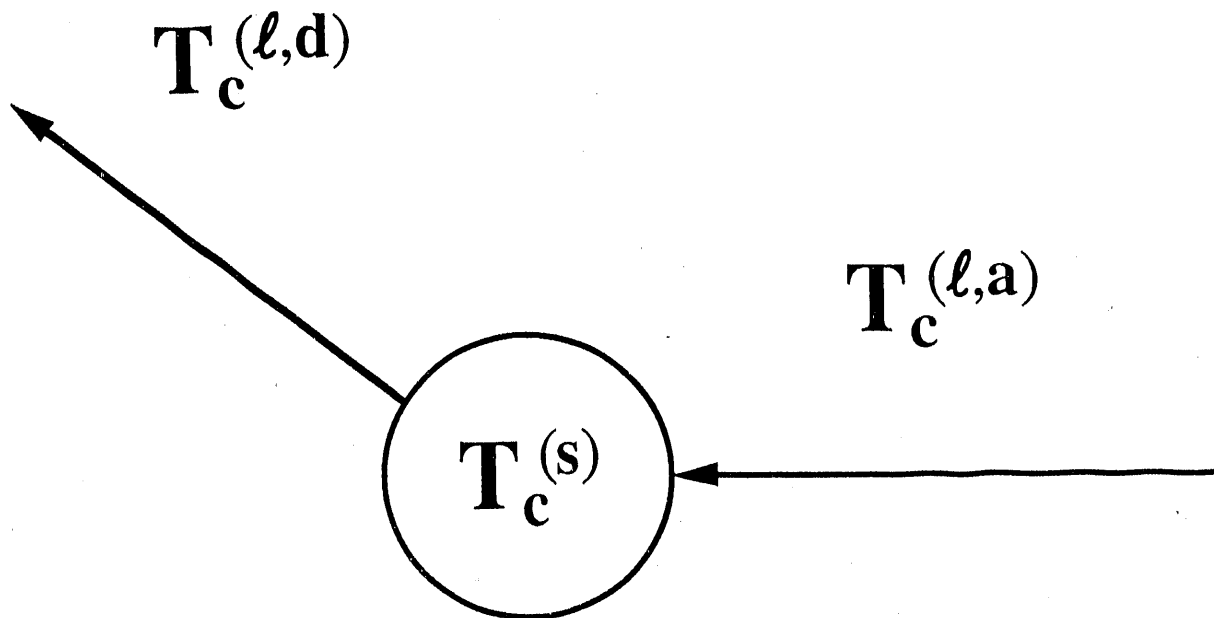
Fig. 2. Schematic view of photoabsorption. The immediate result of photoabsorption is the transition of an electron to a state of higher energy while it remains confined to the spatial domain of the initial state. The contribution of this stage to the dipole matrix element may be written as $M_c^{(s)}$, where superscript "s" signifies short range and subscript "c" a set of quantum numbers that specify a channel. The energetic electron later departs toward large distances. The contribution of this stage may be represented by a

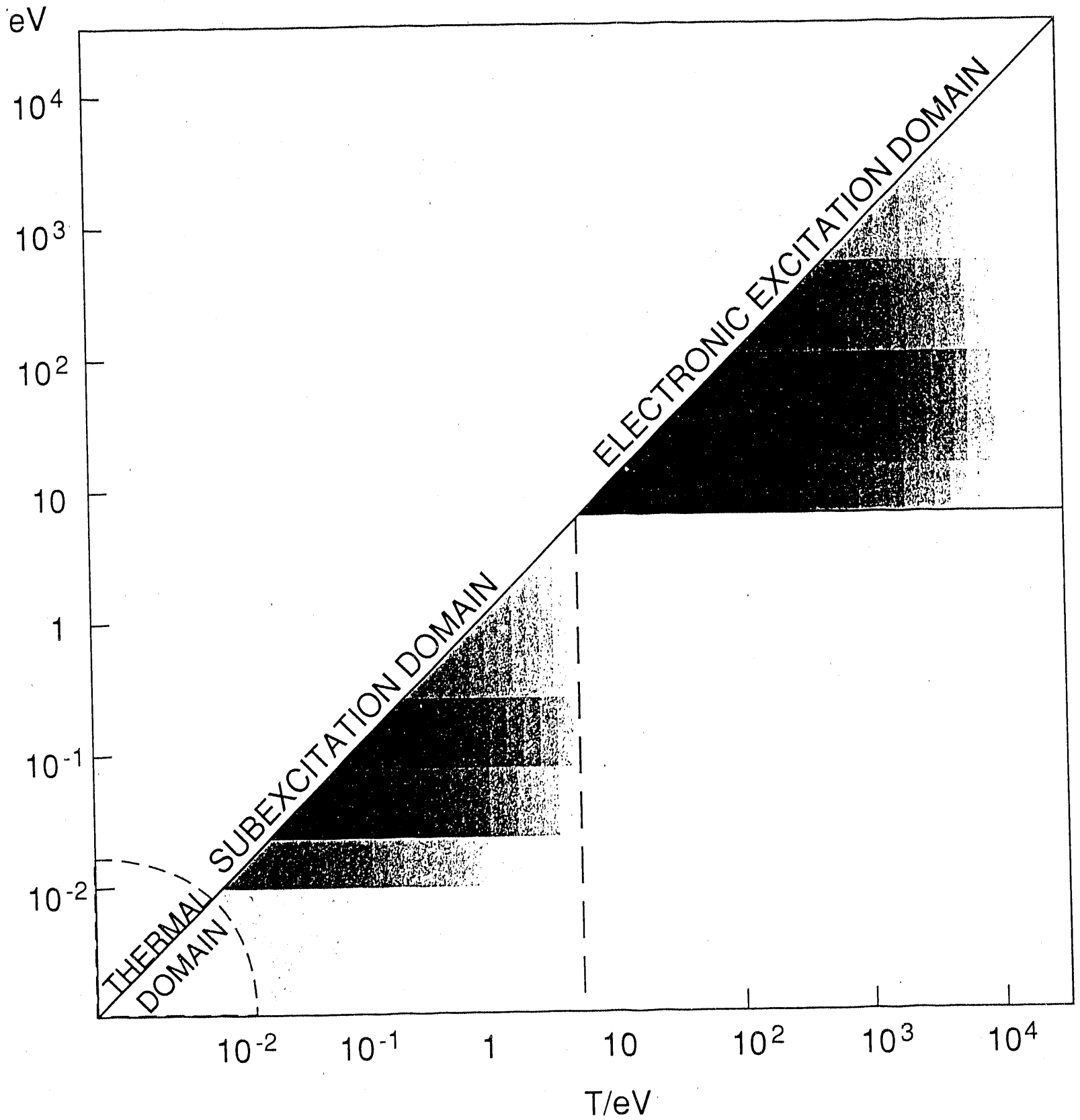
transition matrix $T_c^{(\ell, d)}$. Consequently, we express the total dipole matrix element D as

$$D = \sum_c T_c^{(\ell, d)} M_c^{(s)}.$$

The long-range transition matrix $T_c^{(\ell, d)}$ is modified in condensed matter, while the short-range matrix element $M_c^{(s)}$ is the same in gas and in condensed matter.

Fig. 3. Schematic diagram for showing three distinct domains of electron transport in a molecular substance. The horizontal axis represents the kinetic energy T of an electron. The vertical axis represents the energy transfer E upon a single collision with a molecule. The vertical broken line indicates the first electronic excitation threshold E_1 . The shade and fade roughly show the magnitudes of cross sections.





END

DATE FILMED

12 / 14 / 90

