THE EXCITED STATE
IN CHEMICAL PHYSICS

PART 2

Edited by J. Wm. McGowan
Department of Physics and the Centre for Interdisciplinary Studies in Chemical Physics
The University of Ontario
London, Ontario, Canada

Volume XLV

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INTRODUCTION

This volume of the Advances in Chemical Physics is the second to be devoted entirely to studies of the excited states of molecules. Since the publication of the first volume, there has been continued expansion of the subject. The contributions in this volume, which cover a variety of topics, supplement the earlier articles and report the results and interpretations based upon later technology. Just as for the earlier volume it is hoped that this and succeeding volumes will supplement the rather broadly scattered literature and provide an introduction both for the interested student and the working scientist.

S. Rice
PREFACE

Following the direction established by its predecessor, this second volume of *The Excited State in Chemical Physics* further summarizes theoretical and experimental information available from a variety of sources. It deals with the production of excited atoms, ions, and molecules; the elastic and inelastic scattering of these species; and the production of excited products following collision.

In the five years since the first volume was published, there has been increased interest in the chemistry within gas lasers and the chemistry induced by laser radiation, the kinetics and photochemistry within fusion and industrial plasmas, as well as in the normal and perturbed lower and upper atmosphere. And, since the Three Mile Island accident there has been renewed interest in radiation damage to living and nonliving things. This state of affairs has not only precipitated a variety of spectroscopic studies, but has also brought more attention to the nonspectroscopic aspects of excited state production and the interaction of excited species. The latter topic was stressed in the earlier volume and the emphasis is retained here.

Each chapter was prepared by one or more authorities in excited state chemistry and physics, who summarize much of the latest work and new technology and review research in their areas of expertise. The choice of material and approach is as timeless as it is timely, since the experimental and theoretical techniques reviewed can be applied much more broadly than just within the immediate context.

The combination of theory with experiments dealing mainly with the excited state makes this volume invaluable for the research student as well as for the seasoned scientist, especially in such areas as laser development and laser chemistry, the chemical physics and kinetics of the atmosphere, studies of flames, and related topics.

This project has continued to receive the support of many groups and has been completed largely because of the assistance granted by the Office of Standard Reference Data, National Bureau of Standards. To this office and to many others we owe much.

As editor of this volume I must express my most sincere appreciation to those who have worked hard on the various chapters, who have reviewed the material with me, and who have been patient as this volume has slowly come together.

J. William McGowan

London, Ontario
February 1981
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CHAPTER ONE

CONTINUUM OPTICAL OSCILLATOR-STRENGTH MEASUREMENTS BY ELECTRON SPECTROSCOPY IN THE GAS PHASE

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I. INTRODUCTION

A. Oscillator Strengths and Electron Spectroscopy

The absolute intensity of dipole-allowed transitions is conveniently expressed in terms of $f(0)$, the optical (dipole) oscillator strength. The quantity $f(0)$ is simply related to the absorption coefficient and also to the cross section for absorption or emission of radiation (see Section II). The concept of oscillator strength developed from the classical picture of the atom in which the electrons were envisaged to be in free oscillation at given frequencies about an equilibrium position with respect to the massive nucleus. The oscillator strength $f(0)$ was defined as the number of electrons in free oscillation at a given frequency and was thus considered to be related to the intensity of absorption at a given frequency. The total oscillator strength was thus equal to the total number of electrons in the atom. Subsequently, the quantum theory of atomic structure emerged, giving a description of the atom involving both bound (discrete) and continuum (ionized) states. A very large number of transitions can occur between these states—far in excess of the number of atomic electrons. Nevertheless, the historical oscillator strength terminology has been retained in assigning an absolute scale for the probability of transition between two energy states. Thus for all possible processes $n$, the total sum of oscillator strengths is such that $\sum_n f_n(0)$ equals the total number of electrons in the atom. The sum is over all discrete and continuum states and is discussed further in Section II.

Optical oscillator strengths have traditionally been measured by optical absorption and lifetime methods. Such measurements have of necessity been restricted to those regions of the electromagnetic spectrum where suitable exciting photon sources are available. Consequently, relatively few measurements have been made in the vacuum ultraviolet (UV) and soft-X-ray regions since sufficiently intense tunable (continuum) light sources have not generally been available, at least above 20 eV. It is now apparent that electron storage rings will, in principle, supply sufficiently intense continuum radiation to allow a wide range of such measurements to be made. However, even with the increasing availability of synchrotron radiation to date, such information is scarce and many experiments, particularly those involving photoionization phenomena, are extremely difficult to carry out. Quantitative spectroscopy at ultraviolet UV and X-ray energies is of fundamental chemical interest since it involves many of the higher electronic states of valence electrons and all inner-shell excitations as well as all ionization processes. This type of quantitative information is necessary for a more complete understanding of processes such as those that occur in radiation-induced decomposition, aeronomy, high-temperature
chemistry, and discharge phenomena. Furthermore, such experimental data are urgently needed for the formulation and evaluation of quantum-mechanical procedures.

In the last decade electron spectroscopy in its various forms has been proven a valuable spectroscopic tool for determining the bound and ionized energy levels of atoms and molecules. The principal achievements of photoelectron, electron impact, and Auger and Penning ionization electron spectroscopy are given in a number of recent publications. Of these methods, gas-phase photoelectron spectroscopy (PES) has provided by far the largest amount of data. However, the attention of photoelectron spectrosocists has been primarily focused on the energies of the ejected electron, and little quantitative work on absolute intensities has been reported, in part because of the paucity of calibrated tunable light sources in the far UV, as discussed earlier. Another problem has been that, for ease of construction, most PES spectrometers have been designed to sample ejected electron spectra at 90° to the photon beam. The intensity is thus modulated by the variation of the (usually unknown) asymmetry parameter, \( \beta \), for each state, with energy. Although this effect can be avoided by sampling at the so-called magic angle (54.7° for unpolarized radiation), few spectrometers have been constructed in this configuration. However, the most serious problem in PES is that little attempt has been made to correct for the electron-transmission efficiency of the analyzer. As discussed in Section IV, such corrections may be very significant, even over a few electron volts, but it has been only recently that such corrections have been considered. The few quantitative PES experiments that have been reported are discussed in Section V.

By contrast, a growing number of quantitative fast-electron-impact experiments have been used in recent years as an alternative method of obtaining optical oscillator strengths. One of the major aims of this chapter is to draw attention to these methods, to review their principal achievements and potentialities, and, where possible, to make comparisons with directly determined optical data. Using the Born approximation, Bethe laid the theoretical groundwork in 1930, showing that a quantitative relationship exists between photon absorption and the scattering of fast charged particles (see Section II). More recently, these ideas have been discussed in depth by Inokuti and Kim. The early work of Franck and Hertz had shown in many ways the qualitative similarity between electron impact and photon absorption. For example, the processes of excitation, ionization, and dissociation could all be induced by electron bombardment of molecules. The first quantitative evidence demonstrating this relationship came from the total cross-section measurements by Miller and Platzmann. However, it was the pioneering differential electron-scattering studies by Lassettre and his co-workers that gave the main impetus
leading to the development of modern quantitative electron-impact spectroscopy. Lassettre and his group at the Mellon Institute have subsequently made the dominant contribution to the measurement of optical oscillator strengths for discrete transitions by electron-energy-loss spectroscopy. This work has involved the extrapolation of generalized oscillator strengths to zero momentum transfer to obtain the optical oscillator strength (see Section II).

More recently these ideas have been extended very effectively by van der Wiel and his co-workers, 12-17 giving rise to the development of a variety of "photon-simulation" experiments using high-energy, small-angle electron scattering. These studies are significant in that the chosen experimental conditions approach the optical limit (see Section II) sufficiently closely so that dipole oscillator strengths are measured directly. These experiments have provided the major portion of the continuum oscillator strength data that are available in the literature to date. Much of this work is discussed in Sections IV and V.

B. Energy Transfer In Electron and Photon Experiments

The ability of fast electrons to excite dipole-allowed (optical) transitions can be qualitatively understood in terms of what has been called "pseudo-photons" or the "virtual photonfield." Figure 1 illustrates the principal effects occurring when a fast electron interacts with a target molecule via a distant collision (large impact parameter and thus small scattering angle). As the electron passes by, the target experiences a sharply pulsed electric field of which the perpendicular component is significant. Ideally, in the limit the $E$ field will approach a $\delta$ function that, if Fourier transformed into the frequency domain, would afford the perfect spectroscopic "light" source consisting of a continuum composed of all frequencies at equal intensities. In practice, the pulse will have a narrow but finite width, and there will be a falloff in intensity of "pseudophotons" at high frequencies. (It should be stressed that this method does not simulate photons; rather, under the appropriate conditions, the electron-impact differential cross section is related to the optical cross section by kinematic factors alone.\textsuperscript{5,14}) Nevertheless, a sufficiently wide spectral range can readily be achieved in the laboratory, and the effective high-energy transfer limit in electron-scattering experiments is usually determined by other factors (see Section II).

For a molecule AB, we may compare the processes of photoabsorption and electron-impact excitation as follows:

\begin{align*}
    \text{Photoabsorption} & \\
    \text{Electron-impact excitation} & \\

    h\nu(E) + AB \rightarrow AB^* & \quad (1.1) \\
    e(E_0) + AB \rightarrow AB^* + e(E_0 - E) & \quad (1.2)
\end{align*}
Figure 1. Electric field, \( E(t) \), and corresponding frequency spectrum, \( I(\nu) \), associated with distant collision of fast electron and molecular target: (a) collision parameters—\( v \), electron velocity and \( b \), impact parameters; (b) idealized case for very fast electron; (c, d) realistic picture.

where \( E \) is the energy of quantum state \( \text{AB}^* \) and \( E_0 \) is the impact energy of the electron. From these expressions it is apparent that the resonant photon energy \( E \) in photoabsorption is analogous to the energy loss of the incident electron when scattered by the target in the electron-impact process. In other words, we may “equate” the photon energy with energy loss.

It should be noted that the electron-impact process is nonresonant; the important consequences of this are discussed in the text that follows. In effect, a fast electron \( (E_0) \) offers the target a “white-light” continuum of “pseudophotons” that are absorbed with a frequency-dependent probability that can be quantitatively related to the optical oscillator strength via the Bethe-Born relation (see Section II). The net result is that under the appropriate experimental conditions we may perform quantitative measurements equivalent to photoabsorption and so on using techniques of fast-electron-impact and electron-energy-loss spectroscopy (see Section III). As discussed earlier,\(^4\) it is of particular advantage to exploit this relationship in the UV and soft-X-ray regions of the spectrum where continuum light-source availability is very restricted, with the exception of synchrotron radiation. However, the latter source is only available at a few locations and is of enormous expense. Even where synchrotron radiation is available, use of the photons is still subject to the well-known difficulties of
optical spectroscopy at short wavelengths,\textsuperscript{14} which include low reflectivity, order overlapping, and efficient monochromation. Dispersion of synchrotron radiation leads to changes in polarization and also modifications of photon flux that necessitate calibration of the effective photon intensity for ionization oscillator-strength measurements.\textsuperscript{18} It has been pointed out by Inokuti\textsuperscript{5} that use of electron impact instead of photons can have some additional advantage because of the nonresonant nature of electron-impact excitation. This property eliminates line-saturation effects that occur when the natural line width is narrower than the experimental photon bandwidth.

Since ionization is only a special case of excitation it is also possible to simulate the photoionization process using fast electrons. We may compare the processes

\begin{align*}
h r(E) + AB &\rightarrow [AB^+ + e_{ej}] & \text{Photoionization} \\
e (E_o) + AB &\rightarrow [AB^+ + e_{ej}] + e_{sc} (E_0 - E) & \text{Electron-Impact ionization}
\end{align*}

where $e_{ej}$ is the electron ejected from AB on ionization and $e_{sc}$ is the fast-scattered electron.

It is apparent that in both cases energy $E$ is deposited in $[AB^+ + e_{ej}]$ and that, as in the case of excitation, the photon energy is analogous to the electron energy loss. However, since there are now two electrons sharing the excess energy in electron-impact ionization, it is necessary to use time correlation (coincidence techniques) for the simulation of photoionization

\begin{table}
\centering
\caption{Photon-Simulation Experiments\textsuperscript{a}}
\begin{tabular}{lll}
\hline
PHOTON EXPERIMENT & ELECTRON-IMPACT EQUIVALENT & TYPICAL REFERENCES \\
\hline
Photoabsorption & Electron-energy-loss spectroscopy & 25 \\
Photoionization mass spectrometry (\textit{fragmentation}) & Electron–ion coincidence (e–ion) & 149,166 \\
Total photoionization & Electron energy loss—total ejected electron, coincidence (e,2e) & 24 \\
Photoelectron spectroscopy & Electron energy loss—selected ejected electron, coincidence (e,2e) & 23,194 \\
Photofluorescence (of ionic states) & Electron-energy-loss—electron–ion–photon (triple) coincidence & 191 \\
\hline
\end{tabular}
\end{table}

\textsuperscript{a}Various aspects of the instrumentation and techniques used in these experiments as well as conventional PES are discussed in Section IV.
experiments. The possible photoexcitation and ionization experiments that have been simulated are summarized in Table I.

C. Scope of This Review

This article is essentially restricted to a consideration of the measurement of optical oscillator strengths by methods employing various forms of electron spectroscopy. Targets are restricted to atoms and molecules in the gas phase, and only absolute or relative *quantitative* measurements are generally included (i.e., only those experiments in which electron transmission and ion kinetic energy are accounted for, at least on a relative basis). Generalized oscillator strengths are discussed only insofar as they relate to the derivation of optical oscillator strengths. Detailed accounts of generalized oscillator strength measurements can be found in the work of Lassettre et al.\textsuperscript{9-11} and Bonham and Fink,\textsuperscript{19} who have studied various aspects of the Bethe surface. Oscillator-strength measurements for discrete transitions using electron-impact spectroscopy have been the subject of two recent detailed reviews by Lassettre.\textsuperscript{10,11} Some notable studies have also been made by Geiger.\textsuperscript{20} Therefore, this chapter emphasizes optical oscillator-strength measurements for continuum processes involving energy transfers in excess of $\sim 10$ eV. Attention is focused on: (1) photoabsorption $f(0)$ measurements by electron-impact spectroscopy, (2) partial ionization (electronic state) $f(0)$ measurements using photoelectron spectroscopy and electron–electron coincidence, (3) total ionization $f(0)$ measurements using total (e,2e) and (e–ion) coincidence with mass analysis, and (4) partial ionization (fragmentation) $f(0)$ measurements using (e–ion) coincidence with mass analysis.

Attention is given to results for the noble gases (including multiple ionization processes) as well as energy transfer and fragmentation in diatomic and small polyatomic molecules. In Section II the theoretical background of the methods is discussed and a sufficient framework developed to enable the laboratory worker to design experiments as well as to understand and interpret the data. The current status of oscillator-strength calculations is discussed in Section III. Section IV discusses some aspects of the experimental methods used in oscillator-strength measurements by electron spectroscopy. Finally, a discussion is given in Section V illustrating some of the more significant oscillator-strength measurements that have been made to date using electron-spectroscopic techniques. No attempt has been made to give tables of oscillator-strength data in this review. In many cases this most useful form of data is available in the original published articles. We would like to take this opportunity to exhort authors of forthcoming publications to provide such tables of data
in addition to diagrams since this greatly facilitates the use and comparison of oscillator strengths.

II. THEORETICAL BACKGROUND

A. Introduction

In optical experiments the absorption of radiation is governed by the Beer–Lambert law. If \( I_0(E) \) is the measured intensity of a beam of electromagnetic radiation of energy \( E \) and \( I(E) \) that following absorption by a gas of thickness \( L \) containing \( n \) molecules per unit volume, then:

\[
I(E) = I_0(E) \exp[-\sigma(E)nL]
\]

where \( \sigma(E) \) is the optical cross section for absorption that has units of area.

An analogous expression holds for electron scattering, except that in such an experiment we usually desire to measure that proportion of the incident beam (of impact energy \( E_0 \)) that has lost energy \( E \). In general, the intensity of such an inelastically scattered beam will depend on the polar angles \( \theta, \phi \) (with respect to the main beam) at which it is measured. If the incident electron beam has an intensity \( I_0 \), the inelastically scattered beam will have an intensity

\[
I_{sc}(\theta, \phi, E, E_0) = \int_{\Delta \Omega} I_0 nL \frac{d^2 \sigma_{el}}{d \Omega} (\theta, \phi, E, E_0) d\Omega
\]

where \( \Delta \Omega \) is the solid angle subtended by the detector at the scattering region and \( \sigma_{el} \) is the electron-impact cross section. Both expressions (II.1) and (II.2) are idealized in that corrections are usually needed in practice for pressure-dependent effects. These corrections are especially significant in optical work in the near UV since \( \sigma \ll \sigma_{el} \).

The cross section \( \sigma \) is a fundamental property of the molecule and as such is related to the molecular wave functions for the two states between which a transition is induced. Hence it is desirable to separate the contributions to \( \sigma \) that arise from purely kinematic quantities such as the impact energy of the electron beam from those that depend solely on the properties of the molecule. To this end, a dimensionless quantity, the oscillator strength, is introduced in optical absorption spectroscopy, defined by the relation:

\[
j_{0\alpha}(0) = 2E \sum_{\alpha} A_{\beta} \left| \langle \Psi_{m\alpha} | \sum_{i=1}^{N} r_i | \Psi_{0\beta} \rangle \right|^2
\]

(II.3)
in which $\sum A_{\beta}$ denotes a summation over the degenerate excited states $\psi_{ma}$ and an average over the degenerate initial states $\Psi_{0\beta}$. $\hat{e}$ is a unit vector in the direction of the electric field, and the equation is written, for convenience, in atomic units. The summation within the bracket is over the $N$ electrons in the molecule.

An analogous quantity, the generalized oscillator strength, is found to be useful in electron-scattering theory. It is a function of the momentum $\mathbf{K}$ transferred from the incident electron to the molecule and has the form:

$$f_{om}(\mathbf{K}) = \frac{2E}{|\mathbf{K}|^2} \sum_{\alpha} A_{\beta} \left| \left\langle \psi_{ma} \left| \sum_{i=1}^{N} e^{i\mathbf{K} \cdot \mathbf{r}_i} \right| \psi_{0\beta} \right\rangle \right|^2$$  \hspace{1cm} (II.4)

The cross sections $\sigma_i(E)$ and $\sigma_{el}(\theta_s, \phi_s, E, E_0)$ are related to those two oscillator strengths through the equations:

$$\sigma_i(E) = \frac{\pi}{c^2} \cdot f(0)$$  \hspace{1cm} (II.5)

and

$$\sigma_{el}(\theta_s, \phi_s, E, E_0) = \frac{2}{E} \cdot \frac{|k_f|}{|k_i|} \cdot \frac{|f(\mathbf{K})|}{|\mathbf{K}|^2}$$  \hspace{1cm} (II.6)

where $k_i$ and $k_f$ are the incident and scattered electron momenta, respectively. It is clear from equation (II.4) that

$$\lim_{|\mathbf{K}| \to 0} f_{om}(\mathbf{K}) = 2E \sum_{\alpha} A_{\beta} \cdot \hat{\mathbf{K}} \cdot \left\langle \psi_{ma} \left| \sum_{i=1}^{N} \mathbf{r}_i \right| \psi_{0\beta} \right\rangle$$  \hspace{1cm} (II.7)

where $\hat{\mathbf{K}}$ is unit vector in the direction $\mathbf{K}$. Comparison of equations (II.7) and (II.3) shows that they are numerically identical, and thus in low-momentum-transfer scattering experiments we may replace the unit electric vector by the unit vector $\mathbf{K}$. It is this close analogy between electron scattering and optical absorption spectra that we wish to exploit in the simulation experiments (see Table I).

If the energy transfer $E$ is sufficiently large, ionization occurs and the oscillator strength and cross section become continuous functions of $E$. To preserve the simplicity of equations (II.1) and (II.2), relationships (II.5) and (II.6) must be modified such that:

$$\sigma_i(E) = \frac{\pi}{c^2} \cdot \frac{df(0)}{dE}$$  \hspace{1cm} (II.8)

$$\sigma(\theta_s, \phi_s, E, E_0) = \frac{2}{E} \cdot \frac{|k_f|}{|k_i|} \cdot \frac{1}{|\mathbf{K}|^2} \cdot \frac{df(\mathbf{K})}{dE}$$  \hspace{1cm} (II.9)
Although the oscillator strengths are dimensionless, their derivatives with respect to $E$ are not, and units become a significant problem in continuum absorption. In cgs (electrostatic) units, equation (11.8) reads

$$\frac{df(0)}{dE} = \frac{mc}{\epsilon^2 \pi \hbar} \sigma_i(E) \quad (\text{II.10})$$

where $\sigma_i(E)$ is expressed in square centimeters and $E$ in ergs. More normally, $E$ is expressed as a frequency $\bar{\nu}$ in wave numbers, when we have

$$\frac{df(0)}{d\bar{\nu}} = \frac{mc^2}{\epsilon^2 \pi} \sigma_i(\bar{\nu}) \quad (\text{II.11})$$

The cross section $\sigma_i(E)$ may also be expressed in units of megabarns ($1 \text{ Mbarn} = 10^{-18} \text{ cm}^2$). Under these circumstances, inverting (II.10) we have

$$\sigma(\text{Mbarns}) = 1.76 \times 10^{-10} \frac{df}{dE(\text{ergs})} \quad (\text{II.12})$$

If $E$ is expressed in electron volts (eV), we find

$$\sigma(\text{Mbarns}) = 109.75 \frac{df}{dE(\text{eV})} \quad (\text{II.13})$$

It should be noted that these expressions hold only for excitation to the continuum and that comparison of electron scattering and optical absorption for discrete transitions is only possible if the resolution of both types of experiment is known.

The problem with equations (II.8) and (II.9) is that the definitions of the two cross sections appear to change abruptly with passage through the ionization threshold. A full discussion of this has been given by Fano and Cooper, and it suffices here to point out that we may define differential cross sections

$$\frac{d\sigma_i(E)}{dE} = \frac{\pi}{\epsilon^2} \frac{df(0)}{dE} \quad (\text{II.14})$$

$$\frac{d\sigma_{el}(\theta, \phi, E, E_0)}{dE} = \frac{2}{E} \left| \frac{k_f}{k_l} \right| \frac{1}{|K|^2} \frac{df(K)}{dE} \quad (\text{II.15})$$

The cross section defined in (II.15) is related to the observed intensity of
the scattered beam by the expression

$$
\int_{E}^{E+\Delta E} \frac{dI_{sc}(\theta, \phi, E, E_0)}{dE} dE = \int_{E}^{E+\Delta E} \int_{\Delta \Omega d} L n I_0 \frac{d^3 \sigma}{dE d\Omega}(\theta, \phi, E, E_0) dE d\Omega
$$

(II.16)

A similar expression may be written for optical absorption when the exponent in (II.1) is sufficiently small. Substituting equation (II.15) in (II.16), we may obtain the generalized oscillator strength over some region $\Delta E$ by simple integration.

B. Molecular Processes

The energy transferred by the photon or electron to the molecule may be lost by the latter in a number of different ways. If this energy is lower than the ionization threshold, the usual pathways are (1) reradiation or (2) dissociation into neutral fragments or charged fragments (from ion-pair processes); in other words:

$$
A - B \rightarrow (AB)^* \rightarrow (AB) \rightarrow A^+ + B^-, A^- + B^+, \cdots
$$

If $A'$ or $B'$ are not in their ground state, further fragmentation or radiation may occur. Radiation from $AB^*$ may not give the ground state, and further fluorescence may take place. In the target region energy may also be lost by collision with other molecules or with the walls of the target chamber.

If the energy is higher than the ionization threshold, the preceding processes may still occur, but we also have the possibility of two types of ionization process:

$$
AB \rightarrow AB^+ + e_{ej} \quad \text{Molecular ionization}
$$

$$
A^++B^+ + e_{ej} \quad \text{Dissociative ionization}
$$

In energy transfers above the ionization threshold, it is usual for several different ionization processes to occur with probabilities depending on $E$. The measured optical oscillator strength for absorption is thus a sum corresponding to a variety of different processes. Denoting this total optical oscillator (ionization potential): strength by $df(0)/dE$, we have, for
where we have partitioned the oscillator strength into two sets of processes, those involving ionization \((i)\) and those involving neutral processes \((n)\). The ionization efficiency \(\eta\) is then given by

\[
\eta = \left( \sum_i \frac{df'(0)}{dE} \right) \left( \frac{df(0)}{dE} \right)^{-1}
\] (II.18)

The individual partial oscillator strengths \(df'(0)/dE\) for each ionization process are individual functions of \(E\). It is usual to define the branching ratio \(b_i\) as

\[
b_i = \left[ \frac{df'(0)}{dE} \right] \left[ \sum_i \frac{df'(0)}{dE} \right]^{-1} \quad \text{and} \quad \sum b_i = 1
\] (II.19)

Characterization of the neutral processes is far more difficult, and little information is available at present. However, studies on some simple molecules (see Section V) have indicated that the ionization efficiency approaches unity quite rapidly as the energy loss increases above threshold, suggesting that, except where transitions to Rydberg states just below a new ionization threshold are significant, the dominant mode of energy loss in the far UV is by ionization often accompanied by molecular fragmentation.

**C. Born Approximation**

Consider a beam of electrons incident along the \(+z\) direction. The wave function is of the form \(\exp(ik_i z)\), and the current is given by\(^{26}\)

\[
j_i(r) = Re \left( \psi^* \frac{\nabla}{i} \psi \right) = |k_i| \hat{z}
\] (II.20)

where \(\hat{z}\) is a unit vector in the \(+z\) direction. This corresponds to a current of one electron per second with momentum \(k_i\). If the electron is scattered inelastically, the outgoing wave function will be a spherical wave, emanating from the scattering center. Such a wave function may be represented by a function that behaves asymptotically at large values of \(r\) as

\[
\psi_f = \frac{\exp(ik_f r)}{r} \cdot f(\theta, \phi)
\] (II.21)
where \( f(\theta, \phi) \) is some angular function. The scattered current may be calculated using equation (11.20) and is

\[
J_{sc}(r) dA = |k_i| |\tilde{r}| f(\theta, \phi)^2 \frac{dA}{r^2}
\]

(II.22)

where \( dA \) is the area of the detector.

The cross section \( \sigma_{el}(\theta, \phi, E, E_0) \) is measured using the detectors, and since we expect it to be proportional to both the solid angle subtended by the detector and to the incident current, we have

\[
J_{sc}(r) dA = J_s(r) \sigma_{el}(\theta, \phi, E, E_0) \frac{dA}{r^2}
\]

(II.23)

where \( \sigma_{el}(\theta, \phi, E, E_0) \) is introduced as a proportionality constant. We have, comparing (II.22) and (II.23) and using (II.20),

\[
\sigma_{el}(\theta, \phi, E, E_0) = \frac{|k_i|}{|k_i|} |f(\theta, \phi)|^2
\]

(II.24)

Thus to calculate the cross section, we need only calculate the asymptotic part of the scattered electron wave function. This is straightforward, at least for first-order perturbation theory. Provided that the time scale during which the perturbation of the molecule by the impact electron occurs is small compared to the time scale for electronic motion, we find

\[
f(\theta, \phi) = \frac{-1}{2\pi} \int \exp(iK \cdot r) \langle \Psi_m | V | \Psi_0 \rangle dr
\]

(II.25)

where the perturbing potential \( V \) is given by

\[
V = -\frac{\sum_{p=1}^{M} Z_p}{|r - R_p|} + \sum_{i=1}^{N} \left( \frac{1}{|r - r_i|} \right)
\]

(II.26)

in atomic units, \( R_p \) are the nuclear coordinates, and \( r_i \) are those of the electrons.

In addition to the assumptions underlying the use of first-order perturbation theory, a number of other assumptions underlie equation (II.25).

1. In effect, the equation has been derived under the assumption of infinite nuclear mass. This is accurate enough for electron scattering, but for proton and atom scattering a coordinate transformation is needed, the details of which are given in Mott and Massey.26
2. All relativistic effects have been ignored. Corrections for impact energies of less than 10 keV are very small, but above this level a careful distinction must be drawn between the velocity and energy of the electron. Corrections to first order have been given by Inokuti.\textsuperscript{5}

3. All exchange effects have been neglected. For fast incident electrons inducing discrete transitions, this is a very accurate assumption, but if ionization occurs, and especially if the energies of the two outgoing electrons are comparable, such effects are likely to be of great importance. For the most part we are concerned here with ionization to energy levels only a few tens of volts into the continuum using electron energies of very high incidence and, under these circumstances, the effects of exchange are practically negligible.\textsuperscript{26-28}

To derive an expression for the oscillator strength, we must consider equation (II.25) more closely. Assuming that the electronic part of the wavefunctions $\Psi_m$ and $\Psi_0$ are orthogonal, integration over the nuclear attraction part of $V(\text{II.26})$ will vanish. The electron-repulsion part may be simplified by interchanging the order of integration in (II.25) and considering first the integration over $r$. We find

$$\sum_i \int \exp(iK \cdot r) \int \cdots \int \Psi^*_m \left( \frac{1}{|r - r_i|} \right) \Psi_0 dr_1 \cdots dR_M dr$$

$$= \sum_i \int \cdots \int \Psi^*_m \left( \int \frac{\exp(iK \cdot r)}{|r - r_i|} dr \right) \Psi_0 dr_1 \cdots dR_M dr \quad (\text{II.27})$$

The integral in brackets is well known to have the value $(4\pi/|K|^2)\exp(iK \cdot r_i)$, so\textsuperscript{26}

$$f(\theta, \phi) = \left( -2/|K|^2 \right) \sum_i \langle \Psi_m | \exp(iK \cdot r_i) | \Psi_0 \rangle \quad (\text{II.28})$$

Recalling the definition of the generalized oscillator strength (II.4) and using equation (II.24), we find

$$\sigma_{el}(\theta, \phi, E, E_0) = \frac{2}{E} \left| k_f \right| \frac{1}{|K|^2} \cdot f_{om}(K) \quad (\text{II.29})$$

provided we sum and average equation (II.28) in the usual way.

The generalized oscillator strength defined by (II.4) has a number of important properties that have been listed by Inokuti.\textsuperscript{5} Of great importance practically are the sum rules

$$S(\mu, K) = \left( \sum_m + \int_m \right) E^\mu_m f_{om}(K) \quad (\text{II.30})$$
where \( S(\mu, K) \) is convergent for \(-1 < \mu < +2\) and \( E_m \) is the energy loss associated with the transition \( 0 \rightarrow m \). For our purpose the most significant is

\[
S(0, K) = \left( \sum_m + \int_m \right) f_{0m}(K) = N \tag{II.31}
\]

where \( N \) is the total number of electrons in the molecular system. This is an analogue of the well-known optical sum rule

\[
S(0, 0) = \left( \sum_m + \int_m \right) f_{0m}(0) = N \tag{II.32}
\]

Its importance lies in the fact that it may be used, at least for simple molecules, to place the measured photoabsorption spectrum on an absolute scale. However, great care should be exercised in the use of (II.31) and (II.32) since the summation includes transitions from valence orbitals to inner orbitals already occupied. Such transitions cannot be seen, of course, and thus calibration of subshell photoabsorption spectra by this method will give results that are only approximate.\(^{123}\)

Clearly, if \(|K| \) is small, the exponential term in (II.4) may be expanded and we obtain a series of the form\(^9,30\)

\[
f_{0m}(K) = 2E\left[ \epsilon_1^2 + (\epsilon_2^2 - 2\epsilon_1\epsilon_3)|K|^2 + (\epsilon_3^2 - 2\epsilon_2 + 2\epsilon_1\epsilon_5)|K|^4 + \cdots \right] \tag{II.33}
\]

\[
= f_{0m}(0) + |K|^2 f_{0m}^{(1)}(0) + |K|^4 f_{0m}^{(2)}(0) + \cdots + \tag{II.34}
\]

where

\[
\epsilon_n = \frac{1}{n!} \sum_i \langle \Psi_m | (\hat{K} \cdot r_i)^n | \Psi_0 \rangle
\]

and the unit vector \( \hat{K} \) is defined as previously. Two things are important here. The first is that, as foreshadowed earlier, the limiting value of \( f_{0m}(K) \) as \( K \rightarrow 0 \) is indeed the optical value. The second is that, as a consequence of sum rules (II.31) and (II.32), we have, at once

\[
\left( \int_m + \sum_m \right) f_{0m}^{(1)}(0) = 0 \tag{II.35}
\]

The sum rule has been checked by Backx et al., who found, in addition that \( K^2 f_{0m}^{(1)}(0) \) was much smaller than \( f_{0m}(0) \) for the molecules studied.\(^{31}\)