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MANY-ELECTRON THEORY OF PHOTOEMISSION

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I. INTRODUCTION

One of the most important methods of studying the internal structure of atoms and molecules involves the absorption of a quantum of light. For example, microwave and infrared spectroscopy yield information about the rotational and vibrational degrees of freedom in a molecule, while optical and ultraviolet absorption spectroscopy probe vibrational structure as well as the electronic degrees of freedom. These techniques are very similar in that they all involve the resonant absorption of light quanta. This takes the system from an initial state, characterized by a wavefunction $\psi_i$, to a final state specified by the wavefunction $\psi_f$. The difference in energy between the two states, $E_f - E_i$, is equal to $hv$, the energy imparted by the photon. Absorption takes place only at the resonant frequencies. Thus the experimental techniques used in these types of spectroscopy generally involve exposing the sample to a known photon flux and examining the resultant flux from the sample after the interaction has taken place.

Photoelectron spectroscopy (PES) is in principle very similar to the techniques mentioned above. The major operational difference arises because the final states observed in PES lie in the ionization continuum. Absorption of a photon thus results in the ejection of at least one photoelectron from the system. These electrons are subjected to kinetic-energy analysis, and it is the kinetic-energy spectrum which contains information about the absorption process. As in the other absorption techniques, the energy conservation equation

$$hv = E_f - E_i$$

(1)
must be satisfied.

It is helpful to think of a general final state reached by absorption of the photon as a superposition of many degenerate states \( \psi_j \).

\[
\psi_f = \sum_j c_{fj} \psi_j
\] (2)

Each of these states partitions the total energy, \( E_f \), into two components:

\[
E_f = E_j + T_j
\] (3)

where \( E_j \) is the energy of an ionic state and \( T_j \) is the kinetic energy of the ionized electron. The measurement of the kinetic energy of the electron focuses our attention on a particular state \( \psi_j \), and we have:

\[
h\nu = (E_j + T_j) - E_1 = E_B^j + T_j,
\] (4)

where the quantity \( E_B^j \) is defined as the binding energy of the photoelectron.

The most commonly used experimental procedure is therefore to fix the photon frequency and scan the photoelectron kinetic energy spectrum for peaks in intensity. Observation of a peak at an energy \( T_j \) implies the existence of an excited ionic state separated from the initial state by an energy \( E_B^j \). This yields information about the ionic states of the sample, and, to some degree, about the properties of the initial state. The probability of observing an electron of energy \( T_j \), given by \( |c_{fj}|^2 \), is related to the cross-section for photoionization. This provides further information about both states involved in the transition. It is important to note
that if one simply observed the attenuation of the photon flux, the information obtained would pertain to a combination of absorption processes involving all the ionic states that are energetically accessible to the radiation. The advantage of PES is that it allows the study of specific ionic states.

This chapter will deal with the nature of these excited states, their energies, and the transition probabilities for reaching them via photon absorption. In Section II the basic theoretical formalism for the interaction of the radiation field with an N-electron system will be reviewed. The nature of the wavefunctions used to describe electronic states and the means of computing them is presented in Section III. In Section IV, the physical concepts which emerge from a study of the wavefunctions will be used to characterize the nature of the ionic states observed in PES. Section V will then analyze the photoionization cross-section in terms of the logical hierarchy of approximations commonly employed in cross-section calculations. The sum rule which relates the cross-section to the relaxation energy will also be discussed. In Section VI the origin and magnitude of the relaxation energy in a variety of systems will be examined and related to the physical and chemical properties of the species. The chapter ends with a brief discussion of the most commonly used approaches for estimating binding energies.

II. INTERACTION WITH THE RADIATION FIELD AND PHOTOIONIZATION

We begin by briefly reviewing the semiclassical treatment of the interaction of radiation with matter. As Schiff\(^1\) points out, the term "semiclassical" refers to the assumption that the radiation field may be treated classically (within the framework of Maxwell's equations), whereas the system of particles is treated quantum-mechanically. This approximation
has the advantage of simplicity and, for the absorption of radiation, gives the same results as quantum field theory.

A. Time Dependent Perturbations and Fermi's Golden Rule

Consider a system of particles in a stationary state of a time-independent electrostatic Hamiltonian $H_0$. At some time $t_1$, a time-dependent term is introduced which represents the electromagnetic field. The field is assumed to be weak enough to be considered a small perturbation, but this disturbance may induce transitions to other stationary states of the particle Hamiltonian. The methods of time-dependent perturbation theory can be used to learn the probability that the system will be found in one of these states at some later time $t_2$.

The stationary states, $\psi_n$, of $H_0$ satisfy the Schrödinger equation

$$H_0 \psi_n = E_n \psi_n$$

and have a simple oscillatory evolution in time

$$\psi_n(t) = e^{-i/E_n t} \psi_n.$$  

A general solution of the equations of motion

$$i\hbar \frac{d\psi(t)}{dt} = H_0 \psi(t)$$

for some arbitrary state $\psi(t)$ can be written

$$\psi(t) = \sum_n c_n e^{-i/E_n t} \psi_n.$$  

The square modulus of the coefficient, $|c_n|^2$, is independent of
time. It gives the probability of observing the superposition state, \( \psi(t) \), in some eigenstate \( \psi_n \).

If a time dependence is present in the Hamiltonian; i.e., if

\[
H = H_0 + V(t)
\]  

(9)

then Eq. (8) is no longer a general solution of the wave equation. In fact there are no longer actually any stationary states. However, the form of the Hamiltonian we have chosen [Eq. (9)] implies that it still may be useful to expand the general solution in terms of the complete set of stationary states associated with \( H_0 \). Thus the solution is still given by Eq. (8), but we must now consider the expansion coefficients to be time-dependent.

Substitution of (8) into the Schrödinger equation

\[
\frac{i}{\hbar} \frac{d\psi(t)}{dt} = H \psi(t)
\]  

(10)

yields equations of motion governing the expansion coefficients:

\[
\frac{i}{\hbar} \frac{dc_k(t)}{dt} = \sum_n c_n(t) V_{kn} e^{i \omega_{kn} t}
\]  

(11)

where \( V_{kn} \) is the matrix element of the perturbation between the unperturbed states,

\[
V_{kn} = \langle \psi_k | V | \psi_n \rangle
\]  

(12)

and

\[
\hbar \omega_{kn} = E_k - E_n
\]  

(13)

From this point we proceed as usual in perturbation theory. The
coefficients for which we wish to solve are expressed as a power series in the perturbation, usually taken only to first order. Integration of this equation yields a probability amplitude for observing the arbitrary state $\psi_k$.

In anticipation of the nature of the specific perturbation to be considered later, we note that if the system is originally in some eigenstate, $\psi_1$, of $H_0$, and if the perturbation depends harmonically on the time,

$$V(t) = V_0 e^{i\omega t},$$

then the probability of finding the system in some other eigenstate $\psi_k$, i.e., $|c_k(t)|^2$, is directly proportional to the time that the perturbation has been active. This implies we should convert our attention to a transition probability per unit time, which finally leads to Fermi's "Golden Rule":

$$P_{k+1} = \frac{2\pi}{\hbar} \rho(E_k) \left| \langle \psi_k | V | \psi_1 \rangle \right|^2. \quad (15)$$

Here $P_{k+1}$ is the transition probability per unit time for the process $\psi_1 \rightarrow \psi_k$. The term $\rho(E_k)$ is the energy density of final states in the neighborhood about $\psi_k$.

B. The Classical Radiation Field and the Photoemission Cross Section

In order to use Eq. (15) to calculate the transition probabilities induced by the electromagnetic field, we must decide upon the form of the perturbation $V$. It is possible to show by correspondence arguments
that the Hamiltonian describing a system of spinless particles of charge \( e \) and mass \( m \) in an electromagnetic field is given by

\[
H = H_0 + \left( -\frac{i\hbar e}{2mc} \mathbf{\nabla} \cdot \mathbf{A} - \frac{i\hbar e}{mc} \mathbf{A} \cdot \mathbf{\nabla} + \frac{e^2}{2mc^2} |\mathbf{A}|^2 \right) + e\phi . \tag{16}
\]

Although we are not specifically interested in spinless particles, the interaction between the spin of the electron and the incident light wave is negligible. The operator \( H_0 \) represents the Hamiltonian describing the particles in the absence of the field. The vector \(-i\hbar \mathbf{\nabla}\) is a sum of momentum operators for the individual particles

\[
\mathbf{\nabla} = \sum_i (\mathbf{\nabla}_i) . \tag{17}
\]

The radiation field itself is described by the vector potential \( \mathbf{A} \) and a scalar potential \( \phi \). These are related to the electric and magnetic field strengths, \( \mathbf{E} \) and \( \mathbf{H} \), by

\[
\mathbf{E} = -\frac{1}{c} \frac{\partial}{\partial t} \mathbf{A} - \mathbf{\nabla}\phi
\]

\[
\mathbf{H} = \mathbf{\nabla} \times \mathbf{A} . \tag{18}
\]

There is some flexibility in choosing the potentials which define the field, and, for fields such as those associated with a light wave, it is common to work in the coulomb gauge. In this case we have

\[
\mathbf{\nabla} \cdot \mathbf{A} = 0 ,
\]

\[
\phi = 0 . \tag{19}
\]
Since we have assumed that the field is weak, we furthermore neglect the term in \(|A|^2\), and finally obtain:

\[
H = H_0 - \frac{\hat{\mathbf{e}}}{mc} \mathbf{A} \cdot \mathbf{v} \tag{20}
\]

or

\[
V(t) = -\frac{\hat{\mathbf{e}}}{mc} \mathbf{A} \cdot \mathbf{v} . \tag{21}
\]

Now the vector potential for radiation propagating in the form of a plane wave of wave vector \(\mathbf{q}\) and frequency \(\omega\) can be written

\[
\mathbf{A} = \mathbf{u} A_0 \left( e^{-i\mathbf{q} \cdot \mathbf{r} - i\omega t} + e^{+i\mathbf{q} \cdot \mathbf{r} - i\omega t} \right) \tag{22}
\]

where \(\mathbf{u}\) is a unit vector specifying the direction of the electric field vector (the polarization), and \(A_0\) is the amplitude of the potential. The intensity associated with this plane wave is:

\[
I = \frac{\omega^2}{2\pi c} A_0^2 . \tag{23}
\]

Since the perturbation is harmonic and we are considering a final state \(\psi_k\) which lies in the continuum, we can substitute Eqs. (21, 22, 23) into Eq. (15) and find that

\[
P_{k+i} = \frac{4\pi^2 \hbar e^2 I}{m^2 c^2 \omega^2} \rho(E_k) \left| \mathbf{u} \cdot \langle \psi_k | e^{-i\mathbf{q} \cdot \mathbf{r} - i\omega t} | \psi_i \rangle \right|^2 . \tag{24}
\]
This is an expression for the transition probability per unit time from state $\psi_i$ to state $\psi_k$ with $E_k > E_i$. Only the second component of the vector potential [Eq. (22)] has contributed to this probability.

This probability is generally expressed in a somewhat different form. The cross section, $\sigma$, is defined as the total transition probability per unit time divided by the incident photon flux. This flux is simply the intensity of the electromagnetic field divided by the photon energy. A more convenient quantity, however, is the differential cross section for ejection of an electron in a small solid angle, $d\Omega$, with respect to some axis, e.g., that of the electric field vector. This is given by

$$\frac{d\sigma_{k+i}}{d\Omega} = \frac{\pi \hbar^2 e}{m^2 c \omega} \rho(E_k) \left| u \cdot \langle \psi_k | e^{i \hat{q} \cdot r} \psi_i \rangle \right|^2,$$

(25)

where $\rho(E_k)$ is the density of final states corresponding to the given solid angle.

This completes the development of the cross section for photo-emission in a purely formal way. The major assumption which has been made thus far is that the interaction between the electrons and the electromagnetic field is small enough that it can be treated in first order. The final assumption about the field which we have not discussed thus far, but is generally made, involves the exponential factor in the matrix element [Eq. (25)]. It can be expanded in the series
\[ e^{i \mathbf{q} \cdot \mathbf{r}} = 1 + i \mathbf{q} \cdot \mathbf{r} + \frac{1}{2} (i \mathbf{q} \cdot \mathbf{r})^2 + \ldots \]  

(26)

If only the first term in this sum is retained, the resulting simplification is known as the "dipole approximation". Since the momentum of the photon is directly proportional to \( q \), it is sometimes referred to as the neglect of photon momentum; this omission will obviously become less acceptable as the photon energy increases. For the purposes of PES, the dipole approximation should be rather good as long as \( q \ll k \), where \( k \) is the wavevector of the photoelectron.\(^3\)

III. THE WAVEFUNCTIONS

Let us now consider the wavefunctions \( \Psi_k \) and \( \Psi_\text{i} \), which describe eigenstates of an electrostatic Hamiltonian in the absence of perturbation. In systems containing two or more electrons, exact solutions for these wavefunctions do not exist, and we are forced to seek appropriate approximations. As the structure of the final ionic states and the mechanisms from which they derive oscillator strength are usually interpreted in the language of these approximations, it is helpful to examine in some detail what they imply about the electronic structure of the system and the nature of the ionization process.

The Hamiltonian for which we seek solutions of the Schrödinger equation will be of the non-relativistic electrostatic form for an \( N \)-electron system in the field of a nucleus of charge \( Z \),

\[ H_0 = \sum_{i=1}^{N} \left[ -\frac{\hbar^2}{2m} \nabla_i^2 - \frac{Z}{r_i} \right] + \sum_{i=1}^{N} \sum_{j>i}^{N} \frac{1}{r_{ij}} \]  

(27)
The first term in brackets represents the kinetic energy and nuclear attraction operators for the $i^{th}$ electron and the last term is the coulombic interaction between electrons $i$ and $j$.

Nearly all work on this problem involves the use of the Variation Principle. This approach employs an approximate form for the $N$-electron wavefunction which contains adjustable parameters that are varied to minimize the expectation value of the Hamiltonian. Because the energy found in this way must be an upper bound to the actual energy, the optimized parameters define the best approximation to the true wavefunction available using a particular model.

A. One-Electron Models

The one-electron approximation is nearly always employed to calculate electronic structure. It is assumed that the $N$-electron wavefunction can be expressed in a form which involves $N$ one-electron functions. The simplest wavefunction of this type is the Hartree product, in which the motion of any one electron is assumed to be completely independent of the others, i.e.,

$$
\psi_0(1,2, \ldots N) = \phi_1(1) \phi_2(2) \ldots \phi_N(N).
$$

The spin orbital $\phi_j(1)$ is a function of the coordinates of electron 1, and is the product of a spatial function, $\chi_1(r_1, \theta_1, \phi_1)$, and a one-electron spin function, $\alpha(1)$ or $\beta(1)$, where $\alpha$ corresponds to $m_s = +\frac{1}{2}$ and $\beta$ to $m_s = -\frac{1}{2}$. 
If we assume the motion of each electron is governed by a central field, the one-electron functions will be hydrogen-like. The \( \{ \chi \} \) are thus products of a radial function and a spherical harmonic,

\[
\chi_n(l) = R_{n\ell}(r_1) Y_{\ell m}(\theta_1, \phi_1)
\]

(29)

The quantum numbers \( n, \ell \) and \( m \) are the same as those in the hydrogen problem and we therefore speak of the orbitals as being \( s, p, \) or \( d \)-like, etc. The radial function \( R_{n\ell}(r) \) is regarded as adjustable and application of the variational technique (subject to the constraint that the radial function should remain normalized to unity) leads to a set of \( N \) integro-differential equations which determine the optimum set of orbitals \( \{ \phi \} \). Each such orbital must satisfy a pseudo-Schrödinger equation for an effective Hamiltonian in which the potential is provided by the nuclear attraction and the spherically-averaged Coulombic interaction with all the other electrons. These equations are solved iteratively, since the potential in which a specific electron moves depends on the other, as yet undetermined, orbitals. One originally guesses a set of radial functions. These orbitals are used to generate a potential, which leads to an improved set of functions. These new functions generate a new field, etc. This is continued until all the orbitals change by less than some acceptable threshold from one iteration to the next, and this final potential is known as the self-consistent field.
The Hartree product [Eq. (28)] suffers from the serious drawback that it does not satisfy the requirement of antisymmetry the exact wavefunction must obey; interchange of the coordinates of two electrons does not result in a change in the sign of the wavefunction. The simplest wavefunction for a closed shell atom which preserves the product form of Hartree but satisfies the antisymmetry requirement is given by Eq. (30):

\[ \psi_0(1, 2, \ldots, N) = \mathcal{A}(N) \left\{ \phi_1(1) \phi_2(2) \ldots \phi_N(N) \right\} \cdot \]  

\( \mathcal{A}(N) \) is called the N-electron antisymmetrizer and permutes the coordinates of the electrons in the direct product. Its effect is more explicitly seen in the equivalent form of the Slater determinant:

\[ \psi_0(N) = \frac{1}{(N!)^{1/2}} \begin{vmatrix} \phi_1(1) & \phi_2(1) & \ldots & \phi_N(1) \\ \phi_1(2) & \phi_2(2) & \ldots & \phi_N(2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_1(N) & \phi_2(N) & \ldots & \phi_N(N) \end{vmatrix} \]  

When the determinantal function above is subjected to the variational technique (constraining the \( \{ \phi \} \) to remain normalized and orthogonal), the familiar Hartree-Fock equations result:

\[ \left[ -\frac{1}{2} \nabla_i^2 - \frac{Z}{r_1} \right] \phi_1(1) + \sum_{j \neq 1} \left[ \int \phi_j^*(2) \frac{1}{r_{12}} \phi_j(2) d\tau_2 \right] \phi_1(1) \]

\[ \sum_{j \neq 1} \delta(m_{s_i}, m_{s_j}) \left[ \int \phi_i^*(2) \frac{1}{r_{12}} \phi_j(2) d\tau_2 \right] \phi_j(1) = \sum_j \epsilon_{ij} \phi_j(1) . \]
The first two terms in brackets arise in Hartree's formulation, but the last one is strictly a result of the antisymmetric form of the wavefunction. This exchange term is too well-known to warrant discussion.

The reason we have written out the Fock equations explicitly is to point out the presence of the Lagrangian multipliers, $\epsilon_{ij}$. It can be shown that if the one-electron spin orbitals are subjected to a unitary transformation, the total wavefunction is unchanged, and the form of the Hartree-Fock equations is also invariant. Therefore the spin-orbitals are not uniquely determined, and caution should be employed in placing too great an importance on the "physical nature" of these one-electron functions.

The fact that many of the final ionic states important in PES can be described in terms of the ionization of an electron from a specific orbital rests on the success of Koopmans' Theorem as a fairly accurate first approximation to the ionic state. Koopmans, however, realized that there is an optimum set of spin orbitals for describing ionization; the canonical set which result from that particular unitary transformation of the $\phi$'s which diagonalizes the Lagrangian multiplier matrix $\epsilon_{ij}$. It is fortunate that Koopmans' assumption works as well as it does; however, situations arise for which one-electron descriptions are no longer adequate (as is true for the case of satellite structure in PES, to be discussed later).

Rigorously, we can only say that photoionization takes a system described by one many-body wavefunction to a final state characterized by another many-body wavefunction. The canonical Hartree-Fock orbitals are "special" for describing this process because they happen to lump most of the "many-body" effects into one orbital.

To illustrate this point, consider the transition from the ground
state of the molecule carbon monoxide (\(^{1}\Sigma^+\)) to its first ionic state possessing \(^{2}\Pi\) character. This transition can be described fairly accurately in terms of the ionization of an electron from the canonical orbital \(^{1}\pi\). This "molecular orbital" extends over both atomic centers; however, the delocalized molecular orbitals of CO can be transformed into a completely equivalent set which are largely localized and correspond to the classical concepts of bonding pairs of electrons. A description of the same transition in terms of these localized orbitals would necessitate talking of ionization of "part of an electron" from a carbon-oxygen "bonding" orbital, another fraction of an electron from the carbon "lone pair", etc. In this representation the transition must be referred to as a many-body process whereas it is adequately described as a one-electron process in the canonical representation. The same arguments apply to Bloch vs. Wannier functions when discussing a solid. Although it reduces to a question of semantics, the point has largely been unappreciated by photoelectron spectroscopists, and the question of what constitutes "many body" effects in ionization is meaningful only within the context of a specific representation.

B. Correlation and Configuration Interaction

We now turn to the final refinement in the form of the wavefunction which allows one, in principle, to approach the exact wavefunction to any degree of accuracy desired. The particular method we shall describe is not the only one available for correcting the shortcomings of the Hartree-Fock function, but it is the one in most common use by quantum chemists. This model is termed configuration interaction (CI), so-called
because in the early days of quantum mechanics it was felt that the Hartree-Fock wavefunction was not exact because of its interaction with low-lying excited states. It has since been recognized that this is not the case. The assumption of the central field and the spherically-averaged potential, while accounting for the long range portion of the Coulombic interaction, does not allow for the description of the instantaneous repulsion between electrons. The CI concepts introduced below will be used in the discussion of the cross section in Section IV. After the formalism is developed, the types of configurations important for correlating various systems will be discussed.

There are an infinite number of solutions to the Hartree-Fock equations (32) in addition to those which are occupied in the Hartree-Fock determinant. These unoccupied solutions are termed the virtual orbitals. Obviously, an infinite number of Slater determinants can be formed by "exciting" electrons from one or more of the Hartree-Fock orbitals into virtual orbitals, and the exact wavefunction can therefore be expanded in this series of Slater determinants. Thus the exact wavefunction can be written

\[ \psi_0(N) = \sum_k C_k \phi_k , \]  

(33)

where the \( C_k \) are the expansion coefficients (again generally determined variationally) and \( \phi_k \) represents a specific Slater determinant. This added flexibility usually results in a decrease in the energy of the wavefunction of less than 1%, but even this is often large compared to electron affinities, reaction energetics, and other properties of interest.
to the chemist. Furthermore, the changes in the charge density brought about by CI are often very important in the computation of dipole moments, the electrostatic field at the nucleus, etc. A recent review of the effects of correlation on many properties of interest has been given by Schaefer.12

The exact form and convergence properties of the CI wavefunction (33) are, of course, dependent on the orbital basis employed. For closed-shell systems such as the neon atom, the Hartree-Fock determinant dominates all others. The remaining corrections have been termed "dynamical correlations" by Sinanoğlu13 and can be shown to primarily reflect short-range correlations in the motion of two electrons. The inclusion of such effects thus keeps the electrons farther apart and reduces the energy. In the \( ^1S \) ground state of the neon atom, e.g., this correlation energy has been estimated14 to be 10.37 eV compared to the Hartree-Fock energy of 3497.73 eV; a difference of approximately 0.3%.

In open-shell atoms and molecules, fundamentally different types of CI occur. In many cases, it is not even possible (within the usual assumptions of doubly-occupied spatial orbitals) to write a single determinant which possesses the correct symmetry for the state in question.15 Even at this level, the concept of one electron in a particular orbital must be abandoned. The asymmetry of the Coulomb field means that it is no longer even roughly accurate to speak of individual electrons possessing specific angular momenta as was the case for the closed-shell central field. In addition, relatively large CI effects appear which are characterized by excitations from the Hartree-Fock orbitals into virtual orbitals that are "nearly degenerate" with them.
For example, the $2s^2 + 2p^2$ excitation is very important for correlating the ground state of Be.

The two factors mentioned above fall into the general category of "internal" and "semi-internal" correlation as discussed by Silverstone and Sinanoğlu. In addition to them, the "all-external" or dynamical correlation present in closed-shell systems is also important. Because of these problems it is sometimes hazardous, even in the Hartree-Fock approximation, to speak of the "ionization of the $1s$ electron" in an open-shell atom or molecule. The phenomenon of multiplet splitting in PES is a dramatic example of this.

IV. THE FINAL STATE IN PHOTOEMISSION

In Section II we emphasized the fact that photoionization is a transition between two states characterized by N-electron wavefunctions. In order to obtain some physical insight into the processes leading to the final states observed in PES, we must at least begin by discussing the transition in terms of a one-electron orbital model. The particular failures of the one-electron picture will become apparent later.

A. The Primary State

The most intense peaks, or "primary" states, observed in photoelectron spectroscopy involve, to first approximation, the ionization of an electron from a specific canonical spin-orbital in the atom or molecule. These primary states are the ones roughly describable by Koopmans' assumption, in the sense that the electron density in the ionic state resembles the original system with a "hole" in the region of space which characterized
the orbital. The most probable continuum function is the one which results when the photoelectron accepts the unit of angular momentum transferred in the absorption process. Thus ionization of the 1s electron in neon is well described by a final ionic state of $^2S$ symmetry, coupled to a continuum function of $p$ symmetry, which gives $^1P$ symmetry for the entire system. The most important channels in the ionization of the 2p electron involve $d$ and $s$-symmetry continuum functions, etc.\textsuperscript{19}

Although these one-electron descriptions are often qualitatively satisfying, the "passive" electrons in the final state have actually relaxed; they are not optimally described by the same spin-orbitals as in the ground state.\textsuperscript{20} This relaxation, even without explicitly involving CI, constitutes a many-body effect in the sense that the motion of those electrons not directly involved in the ionization are coupled to the influence of the departing photoelectron. This relaxation phenomenon has important consequences for both the energy and intensity of the primary states and will be discussed later.

B. Correlation States

Toward higher binding energy from each of these primary peaks there are generally satellites which have come to be known as reflecting the presence of "shake-up" states. There are, in general, an infinite number of such states associated with each primary state, but only a few of them have observable intensities. They can, in favorable circumstances, be 20\textsuperscript{-}30\% as intense as the primary peak. In an orbital description they are usually described as one-electron excitations accompanying ionization. The excitations which lead to the most intense satellites
generally follow monopole selection rules, e.g., ionization of the neon ls electron accompanied by the excitation of a 2p electron into a 3p orbital. This monopole mechanism results in an ionic state of the same angular momentum ($^2S$) as the primary hole state and a continuum function of p character, yielding the overall $^1P$ symmetry required by the dipole selection rules.

Although the orbital picture described above is commonly used, compared to the primary states these "shakeup" states are much less favorably described in terms of one-electron transitions. First of all, there are usually two or more final states of the proper symmetry which can be derived from a given one-electron transition. This follows because each one-electron excitation may result in two (or more) unpaired valence electrons which can couple to the unpaired core electron to give two (or more) final states having the same symmetry as the primary state. Each one-electron excitation thus splits, a result analogous to the multiplet splitting phenomenon in the primary states of paramagnetic species. Furthermore, the assumptions of one-electron, one orbital often have to be discarded. This is due to the possibility of configuration mixing in the final state, which can lead to many one-electron processes being involved in reaching a given final state. As an example, the 2p → np and 2p → n'p processes may both become important in reaching a particular shakeup state in neon. Bagus and Gelius\textsuperscript{21} have shown that the energies of the Ne ls satellites are fairly well described in terms of an (optimized orbital) multi-determinantal wavefunction corresponding to a specific (2p → np) orbital excitation. This would seem to imply that in this case mixing among the various excited configurations is small. The intensities
computed in the sudden approximation\textsuperscript{22} from these wavefunctions, however, are in poor agreement with experiment.\textsuperscript{23} Recent calculations on the F 1s satellites in hydrogen fluoride have shown that the most intense satellite state in the spectrum involves strong mixing of both $3\sigma \rightarrow 5\sigma$ [roughly $F 2p_\sigma \rightarrow F 3s$] and $1\pi \rightarrow 2\pi$ [$F 2p_\pi \rightarrow F 3p_\pi$] excitations.\textsuperscript{24} Any attempt to describe this state as being reached by a single one-electron excitation would require, at the least, removal of the restrictions of specific angular momenta for every orbital. We would be forced to speak of the excitation as involving orbitals which have both $\sigma$ and $\pi$ character.

Finally, in addition to the relaxation processes important in primary states, there are additional rearrangements involved even in a state which can be well described in the "monopole excitation" model. As a result, the orbitals which electrons are "shaken up to" often bear little relationship to the excited state orbitals of the neutral system. It can also be shown that, in the absence of these many-body relaxation effects, there would be no satellites at all observed in photoelectron spectroscopy. For this variety of reasons the satellites are also referred to as "correlation peaks".

The third type of state observed arises from what is called the "conjugate shakeup" mechanism. The transition moments to these states are generally much smaller than the previous two types mentioned. As an example, a conjugate shakeup process accompanying 1s ionization in neon might lead to the $^2P$ final ionic state of Ne$^+$ ($1s^2 2s^2 2p^5 3s$). The continuum function would then have either $s$ or $d$ symmetry, resulting in the overall $^1P$ character necessary from the dipole selection rules. This path is termed "conjugate shakeup" since it appears that the one-electron excitation
is $2p \rightarrow 3s$, which does not follow the monopole rules proposed for the normal shakeup process.\textsuperscript{25}

The more common conjugate shakeup situation occurs when ionization and excitation occur in the same shell. For example, the final state $1s^22s^22p^43s(\epsilon p)$, reached in the one-electron model through the transitions $2p \rightarrow \epsilon p$, $2p \rightarrow 3s$, cannot be reached via the usual monopole selection rules. Wuillemin and Krause\textsuperscript{26} have estimated that an upper limit for the intensity of this process relative to the normal case (final electron configuration $1s^22s^22p^43p$) is of the order of 25%. States of this type have also been identified in the He(I) and He(II) spectra of gaseous cadmium,\textsuperscript{27} mercury,\textsuperscript{28} and lead.\textsuperscript{29} The ground state of Hg, e.g., is described by the Hartree-Fock determinant

$$[\text{core}] \ 6s^2 \ \left( ^1S \right) .$$

The 6s level primary ionic state

$$[\text{core}] \ 6s^1 \ \left( ^2S \right)$$

is observed as well as the conjugate state

$$[\text{core}] \ 6p^1 \ \left( ^2P \right) .$$

The latter is roughly 1% as intense as the primary peak (at the He(I) photon energy). The conjugate excitation $6s \rightarrow 6p$ is invoked in the one-electron model to explain this final state. Berkowitz et al.\textsuperscript{28} have shown that a great deal of the transition moment to this state is caused by admixture of the "nearly degenerate" configuration

$$[\text{core}] \ 6p^2 \ \left( ^1S \right) .$$
into the ground state wavefunction. Thus the inclusion of correlation in the ground state of Hg is a very important mechanism for contributing to the observed satellite structure.

V. MANY-ELECTRON EFFECTS ON THE CROSS SECTION

In this section we examine the specific mathematical form of many-body effects on the photoionization transition moment. The terms which arise in a single-determinantal description of both initial and final state will be dealt with first, followed by the effects of configuration interaction.

A. Relaxation in the Primary State

Let us begin with the single Slater determinants

$$\psi_i(N) = \frac{1}{(N!)^{1/2}} |\phi_1(1) \phi_2(2) \cdots \phi_N(N)|$$  \hspace{1cm} (34a)

and

$$\psi_f(N) = \frac{1}{(N!)^{1/2}} |x(1) \phi_2'(2) \cdots \phi_N'(N)| .$$  \hspace{1cm} (34b)

The orbitals of the final state have been primed to emphasize that they are not necessarily identical to the initial state functions. We have also associated the continuum function, x(1), with the orbital \( \phi_1 \); i.e., if the set \( \{ \phi_2', \phi_3', \ldots \} \) closely resembles \( \{ \phi_2, \phi_3, \ldots \} \) except for the effects of relaxation, then \( \psi_f \) corresponds to the primary state associated with the orbital \( \phi_1 \).

When these wavefunctions are substituted into the transition moment, the result is given by
The notation $\psi_f(N-1,x,1)$ refers to an $N-1$ electron Slater determinant which is formed from the $N$-electron determinant by deleting the column containing the orbital $x$ and the row denoting electron 1; i.e.,

$$\psi_f(N-1,x,1) = \frac{1}{[(N-1)!]^\frac{1}{2}} \begin{vmatrix} \phi'_2(2) & \phi'_3(2) \cdots & \phi'_N(2) \\ \phi'_2(3) & \phi'_3(3) \cdots & \phi'_N(3) \\ \vdots & \vdots & \vdots \\ \phi'_2(N) & \phi'_3(N) \cdots & \phi'_N(N) \end{vmatrix}$$

The same notation applies to the wavefunction $\psi_i(N-1,\phi_j,1)$. It is formed by striking the column containing $\phi_j$ and the row containing electron 1 from $\psi_i(N)$. The sums over the index $j$ are over all spin orbitals. Since $x$ has either $\alpha$ or $\beta$ spin (depending on the nature of $\phi_j$), certain terms in the sums over $j$ in Eq. (35) vanish by spin orthogonality. For the present, however, we will retain the full expression, but simplify its appearance with the following definitions:

$$s^{1j} = \langle \psi_f(N-1,x,1) | \psi_i(N-1,\phi_j,1) \rangle$$

$$p^{1j} = \langle \psi_f(N-1,x,1) | \sum_{k=2}^{N} \psi_k | \psi_i(N-1,\phi_j,1) \rangle .$$

Equation (35) is then given by
The first term of (37) is related to the usual one-electron interpretation. An electron in orbital $\phi_1$ makes a dipole transition to the continuum. If the orbital angular momentum of $\phi_1$ is given by $\lambda$, then $\langle x|\phi_1 \rangle$ can be non-zero only if $x$ has $\lambda+1$ or $\lambda-1$ symmetry.

The factor $S^{11}$ multiplying this one-electron moment is the overlap of the "passive orbitals", i.e., those not directly involved in the ionization. This overlap factor is generally between .9 and 1.0 for primary states, but much smaller for satellite states. Its effect is to introduce the many-body aspects of relaxation into the cross-section. In fact, it is easy to show that if we had made Koopmans' assumption -- i.e., $\phi_2 = \phi'_2$, $\phi_3 = \phi'_3$, etc. -- all the sums in Eq. (37) would vanish, $S^{11}$ would be unity, and we would be left with the active electron approximation

$$T_{f \leftrightarrow i} = \langle x|\psi_1|\phi_1 \rangle .$$

Relaxation thus introduces a multiplicative factor which reduces the contribution of the one-electron moment. It is also the source of the additive corrections in Eq. (37).

The first sum over $j$ in Eq. (37) arises from the antisymmetry requirements on the initial state wavefunction, and brings components into the total transition moment which arise from dipole transitions.
involving the other orbitals of the initial state. It will be shown in a later example to be interpretable as an ionization accompanied by monopole excitation.

The second line in Eq. (37) arises from the action of the remaining momentum operators, $\mathbf{\nabla}_2$ through $\mathbf{\nabla}_N$. Here an electron appears to make a monopole transition ($\phi_j \rightarrow \chi$) and the passive orbitals have rearranged themselves through a dipole excitation. The form of this term is very similar to that of the conjugate shakeup mechanism proposed by Berkowitz et al.\textsuperscript{28}

Each of these three types of processes contribute to the transition moment even in a primary state. For example, consider the neon (1s) primary hole state reached by absorption of soft x-ray radiation. The ionic state has $^2S$ character and the continuum function is $p$-like. The first term in Eq. (37)

$$\langle \phi_p \mathbf{\nabla} | 1s \rangle S_{1,1s}$$

will dominate. The normal shakeup mechanism is involved in the non-vanishing term

$$\langle \phi_p \mathbf{\nabla} | 2s \rangle S_{1,2s}.$$ 

An electron appears to be ionized from the 2s orbital accompanied by the monopole transition $1s \rightarrow 2s$. Finally, a nonvanishing contribution

$$\langle \phi_p | 2p \rangle p_{1,2p}$$

involves ionization of the 2p electron, accompanied (roughly speaking) by the excitation $1s \rightarrow 2p$. All three mechanisms reach the same final
state and reflect the many-body nature of photoionization.

In the particular example used here, the second term should be negligible with respect to the first. This can be seen from examination of the ratio

\[ R_2 = \frac{\langle x_p | v | 2s \rangle s^{1,2s}}{\langle x_p | v | 1s \rangle s^{1,1s}}. \] (39)

If \( R_2 \) is substantial compared to unity, retention of the second term is warranted. Now \( \frac{s^{1,2s}}{s^{1,1s}} << 1 \); in fact a rough estimate for this term based on Bagus' results\(^{20} \) is \( 10^{-3} \). Furthermore \( \langle x_p | v | 2s \rangle / \langle x_p | v | 1s \rangle \) is of the order of magnitude of \( 10^{-1} \) for x-rays of approximately 1 keV energy. Thus the second term makes a contribution approximately \( 10^{-4} \) that of the first. As a general rule, the ratio of the overlap factors will always be small for any primary state, thereby decreasing the importance of this term. Certain situations might arise, however, when this small factor would be counterbalanced by a large ratio in the one-electron moments and this mechanism could then conceivably make a sizable contribution to the total cross section.

It is much more difficult to estimate the importance of the third term. Its effect is governed by the ratio

\[ R_3 = \frac{\langle x_p | 2p \rangle p^{1,2p}}{\langle x_p | v | 1s \rangle s^{1,1s}}. \] (40)

To estimate the factor \( \langle x_p | 2p \rangle / \langle x_p | v | 1s \rangle \) we note that if we choose a plane wave for \( x_p \), i.e., \( x_p = e^{i\mathbf{k} \cdot \mathbf{r}} \), then \( \langle x_p | v | 2p \rangle = ik \langle x_p | 2p \rangle \), and
Qualitatively, one would thus expect this term to be very dependent on the photon energy due to the presence of both the $1/k^2$ factor and the ratio of the transition moments. The $P^{1,2p}/S^{1,1s}$ ratio, however, is energy independent. $P^{1,2p}$ is the complex conjugate of the $x$-ray emission transition moment -- in the approximation in which relaxed orbitals are used for the initial (1s hole) state and the neutral atom ground state functions are used to describe the final (2p hole) state. $P^{1,2p}$ in neon is of the order of $10^{-1}$ bohr$^{-1}$, while $S^{1,1s}$ is nearly unity. In the general case, the emission transition moment will be dependent on the specifics of the atomic or molecular structure. A ratio of this type has been examined for the F(1s) hole state of HF and been found to be negligible. More work is needed, however, to be able to assess the significance of this term. At this time it seems probable that this third type of contribution is of minor importance except possibly in the region near threshold.

To summarize, the major many-body effect brought about by relaxation is a reduction of the active electron transition moment by the multiplicative factor $S^{11}$. Neglect of relaxation would therefore result in a predicted cross section which is higher than the experimental result by a factor of $(S^{11})^2$. In fact, this tendency toward overestimation has been noted by Wuiellemier and Krause in a recent comparison of experimental data for neon with theoretical predictions which disregard relaxation. They have found that the discrepancy is greatest in those
cases where relaxation effects should be more important, e.g., for nearly all incident photon energies the calculated 2s orbital cross section is \(20\%\) greater than experiment, whereas the 2p orbital cross section is in much better agreement. More theoretical work is needed to determine if this discrepancy is due to the relaxation effect, or is primarily a result of the need for a more sophisticated wavefunction which explicitly includes configuration interaction.\(^{33,34}\)

B. Configuration Interaction

Thus far we have examined the consequences of relaxation on the photoionization cross section. This was done within the assumption of single-determinantal wavefunctions for both the initial and final states. Such wavefunctions suffer from the inadequacies pointed out in Section III, and inclusion of configuration interaction can have significant effects on the cross section. CI in the initial state appears to be the prime contributor to the observed intensity of the conjugate shakeup peaks in Hg and Cd.\(^{27,28}\) The importance of correlation in determining the intensity of normal shakeup peaks in which ionization and excitation occur in the same valence shell has been noted by Åberg,\(^{35}\) Carlson et al,\(^{36}\) and Byron and Joachain.\(^{37}\) The importance of both initial and final state correlation in core-level satellite spectra has recently been studied by Martin, Mills, and Shirley.\(^{24,30}\) In the following discussion we will concentrate on the qualitative aspects of CI as it affects core level satellite structure.

Suppose that the initial state is described by a multiconfiguration wavefunction \(\psi_0(N)\)

\[
\psi_0(N) = \sum_m D_{0m} \phi_m(N),
\]  

(41)
where $D_{0n}$ is the coefficient of the configuration $\phi_n$ in the wavefunction $\psi_0$. The configurations may be single Slater determinants expanded in the occupied and virtual orbital set $\{\phi\}$ or, if necessary, sums of determinants chosen to possess the symmetry properties of the ground state. As discussed previously, the coefficient of the Hartree-Fock configuration, $D_{00}$, will be the leading term in the expansion. For closed-shell atoms or molecules it will usually have a value between 0.9 and 1.0, the rest of the coefficients being 0.2 or less.

Each final state is expanded similarly,

$$\psi_{f',(N)} = \sum_n D_{f'n} \phi_n^{(N)}$$

(42)

where the primes on the configurations denote that they have been formed using the continuum function and a set of occupied and virtual orbitals appropriate for the final state. Although several virtual continuum functions should, in principle, be included and allowed to be occupied in the CI calculation, we will assume each configuration contains the one electron function $\chi_{f'}$, and perform the CI on the ion alone. Thus

$$\psi_{f',(N)} = \chi_{f',(1)} \sum_n C_{f'n} \phi_n^{(N-1)}$$

(43)

Again, the primary hole state, $f' = 0$, is characterized by a large $C_{00}$ where $\phi_0^{(N-1)}$ is the hole state Hartree-Fock configuration. For the satellite states $f'$, there may be several configurations which mix strongly. This will be dependent to some extent upon the virtual orbitals used to define the excited configurations, but in most cases there will
be a small number (~1 to 3) of configurations with coefficients greater than 0.5.

Insertion of Eqs. (41) and (43) into the expression for the transition moment (35) yields

\[ T_{f'0} = \sum_{m,n} C^*_{f'0} D_{0m} \langle x_{f'}, |\psi| \phi_1 \rangle S_{nn}^{11} + \ldots \]  

(44)

We have again assumed that the final state predominantly involves ionization from orbital \( \phi_1 \). \( S_{nn} \) is the \((N-1)\) electron overlap integral between configurations \( n \) and \( m \) and the dots represent the other terms obtained. In view of the previous discussion they should be small for core-level ionization and will be neglected.\(^{38}\)

The ratio of the transition moments to the primary state and a satellite is thus given by:

\[ \frac{T_{00}}{T_{f'0}} \approx \frac{\langle x_0 |\psi| \phi_1 \rangle}{\langle x_{f'} |\psi| \phi_1 \rangle} \frac{\sum_{m,n} C^*_{0n} D_{0m} S_{nm}^{11}}{\sum_{m,n} C_{f'n} D_{0m} S_{nm}^{11}} \]  

(45)

If the final states are close in energy, then the one-electron matrix elements should be very nearly the same. The density of final states which enters into the cross section [Eq. (25)] should also be similar for the two states. These two assumptions lead to the relative intensities of the two states in the overlap approximation,\(^{39}\)

\[ \frac{I_{00}}{I_{f'0}} \approx \frac{\left| \sum_{m,n} C^*_{0n} D_{0m} S_{nm}^{11} \right|^2}{\left| \sum_{m,n} C_{f'n} D_{0m} S_{nm}^{11} \right|^2} \]  

(46)
To illustrate these CI effects, we have drawn a state diagram for a four-electron system in Fig. 1. On the left is the Hartree-Fock level for the ground state and some of its excited configurations; above these are the primary hole state configuration and the pair of configurations which are the first approximations to the shakeup states. In the middle of the diagram we have allowed the ionic configurations to interact, forming the observable states of the ion. The ground state function has also been allowed to mix with its excited configurations. On the far right we have assigned hypothetical CI wavefunctions for the ionic states. The wavefunction for the ground state is the analog of \( \psi_0(N-1,1s,1) \) -- the 1s orbital has been projected out of the wavefunction.

The effective intensity of the primary hole state is given in our example by the four contributions to the overlap integral denoted by A, B, C, and D. The total overlap integral for the primary hole state is dominated by the contribution from A because it is a product of two large coefficients and a large determinantal overlap. Contributions B and C are smaller because they involve a small product of coefficients together with a small overlap integral. This integral is not zero, since the orbitals of the hole state have relaxed somewhat. Finally, the contribution from D is small because, although the determinantal overlap is large, the product of the coefficients is very small.

In the case of the satellites, however, the total overlap is a fraction of that for the primary state and configuration interaction contributions are much more important. A main contributor may be the analog to path B, since the coefficients are both large. Within this
overlap picture, the small intensity of the satellites is due to the small determinantal overlap between the shakeup configurations and the ground state. Path A might also contribute an amount of the same order of magnitude since, although the product of coefficients is small, the determinantal overlap is large. The two contributions mentioned thus far could be termed a CI effect in the final state. For similar reasons, the analog of path D is also important for the satellites and it arises through an initial state CI mechanism. The contribution from path C is obviously smaller than the others.

Because the ratio of the intensity of satellite to primary peaks is given by the ratio of the total overlaps, configuration interaction is expected to be very important in understanding even the qualitative nature of the satellites. Contributions to the total overlap enter with a phase, and omission of CI can result in intensities which are either too high or too low.

To summarize this section, many-body effects on the cross section arise from two somewhat artificially separate phenomena. The cross section to a primary hole state is affected predominantly by relaxation in the passive orbitals. This results in an apparent reduction in the cross section from that computed assuming no relaxation. Additional relaxation effects and the inclusion of CI is expected to be of lesser importance for most primary states, although there may arise situations where it becomes significant (multiplet splitting, closely spaced primary states, etc.). The intensities of satellite peaks, on the other hand, depend entirely upon relaxation and configuration interaction contributions. In a strictly formal vein, of course, there exist only eigenstates of the
electrostatic Hamiltonian. The concepts of relaxation and CI arise only when we attempt to form better approximations to those eigenstates than are available within the confines of an independent electron model.

Thus far, we have examined relaxation as it affects peak intensities. It is well known that it also has important consequences for the energies of the final states. The latter part of this chapter will be concerned with the qualitative aspects of the final state stabilization which comes about through the rearrangement of the passive electrons. This relaxation energy can be related to the intensity of the satellite peaks through an approximate sum rule derived by Manne and Åberg. Although these authors obtained the result from an application of the sudden approximation, it can also be derived in the dipole approximation. We shall not show this, but simply note that it follows from the neglect of an energy dependence in the ratio of the cross section for the primary state vs. its satellites.

In our notation, the sum rule is given by

$$E_R = \frac{\sum \frac{I_f}{I_0} \Delta_f}{\sum \frac{I_f}{I_0}}$$

(47)

where $E_R$ is the relaxation energy, $(I_f/I_0)$ is the intensity of the satellite peak relative to the main peak and $\Delta_f$ is the separation in energy between the satellite and the primary state. The denominator simply reflects a normalization condition so that the intensity units are arbitrary. The summations are taken over discrete satellites; they convert to an integration over any continua.
From Eq. (47) we see that there exists a "lever arm" relationship between the satellite intensities and the relaxation energy. If $E_R$ were zero, no satellites would be observed. In the case that $E_R$ is large, the relaxation manifests itself either as an intense set of satellites "near the main peak", or weak satellites "far from the main peak", or of course, something in between. The sum rule provides a great deal of qualitative information about the relaxation process. For example, it is a common misconception that there are no satellites in the core level photoelectron spectrum of metals. It is known, however, that there is a large relaxation energy involved in core ionization in these species, so there must be a fairly large probability for multiple excitation processes. In metals the shakeup (as well as the multiple ionization or shakeoff) spectrum is essentially continuous because the excitations are into the conduction band. Thus while no discrete peaks are observed, the relaxation energy is manifested as a broad background on the high-binding-energy side of the main peak.

VI. RELAXATION EFFECTS ON BINDING ENERGY

The foregoing discussion related the photoemission spectrum to the photoelectric process per se. Two features that were emphasized -- the many-electron nature of the process and the multiplicity of final states -- should make it clear that "relaxation energy" is a concept without a unique meaning. In a strictly formalistic, many-electron description of the photoemission problem this concept need never arise. However, in most discussions that focus on the properties of real systems, a one-electron description is adopted at some point. "Relaxation energy"
(or "polarization energy") then becomes a useful term for describing the energy reduction of the passive electrons in the final state. The relaxation energy, $E_R(j)$, accompanying photoemission from one-electron level $j$ is usually defined by

$$E_B(j) = E_f^0(N-1) - E_i^0(N)$$

$$= -\varepsilon_j(N) - E_R(j) + \Delta E_{\text{corr}} + \Delta E_{\text{mult}} + \Delta E_{\text{rel}}. \quad (48)$$

Here $E_f^0(N-1)$ and $E_i^0(N)$ are respectively the total energies of the primary final state and the initial state. The orbital energy $\varepsilon_j(N)$ is the energy assigned to the $j^{th}$ orbital in the initial state; by Koopmans' Theorem, $-\varepsilon_j(N)$ is the binding energy that orbital $j$ would have if the passive orbitals were unchanged during photoemission (i.e., no relaxation). In referring to $-\varepsilon$ we usually automatically neglect multiplet structure and correlation energy. The former is important only for open-shell systems, and can be corrected in a straightforward way, through the term

$$\Delta E_{\text{mult}} = (E_f - \overline{E}_f) - (E_i - \overline{E}_i).$$

Here $E_f - \overline{E}_f$ is the multiplet energy separation of the final state from the average energy of that configuration, within a single-determinant description, and $E_i - \overline{E}_i$ is defined similarly. For most simple atomic configurations these quantities have been tabulated in terms of Slater integrals. The correlation-energy correction, $\Delta E_{\text{corr}}$, accounts for the difference in the energy stabilization of the final and initial
states through configuration interaction. Clearly $\Delta E_{\text{mult}}$ and $\Delta E_{\text{corr}}$ must be considered together for open-shell systems, in which $\Delta E_{\text{mult}}$ is non-zero. The last term, $\Delta E_{\text{rel}}$, is an artifact, necessary only if a non-relativistic theory has been used. We shall ignore $\Delta E_{\text{rel}}$ in the following discussion, as it is only an avoidable complication. The terms $\Delta E_{\text{mult}}$ and $\Delta E_{\text{corr}}$ are sometimes important. No unexceptionable general statement can be made about these terms, but they may have either sign and are usually small in magnitude ($\approx 1$ eV). By contrast the relaxation energy term always lowers the binding energy ($E_R > 0$), and it is large ($> 1$ eV) for core levels. This section treats relaxation energy in atoms, molecules, solids, adsorbates, and solutes. In each case the physical origin of $E_R$ will be discussed, its magnitude considered (with examples where available), and relevant applications mentioned.

A. Atoms

Removal of an electron from an atomic orbital creates a positive hole toward which the passive electrons' orbitals relax to minimize the system's total energy. Within the constraint of a one-determinant wavefunction this relaxation takes place adiabatically; i.e., the electrons' quantum numbers do not change. Hedin and Johansson$^{42}$ showed that the relaxation energy, $E_R(j)$, accompanying ionization from orbital $j$ can be treated conveniently as the sum of inner-shell, intra-shell, and outer-shell contributions,

$$E_R(j,n) = E_R(n' < n) + E_R(n' = n) + E_R(n' > n). \quad (49)$$

Here $n$ is the principal quantum number of orbital $j$ and $n'$ is that
of the passive electrons.

The inner-shell term $E_R(n' < n)$ is negligible. Hedin and Johansson obtained this result by direct calculation for Na, K, and their ions. To obtain some physical insight into why this is true, we note that the potential inside a hollow charged sphere is constant. Thus the presence of an electron in shell $n$ has little influence on a wavefunction in shell $n' < n$.

Intra-shell relaxation is intermediate in magnitude, usually $\lesssim 5$ eV. It arises through a reduction, during removal of an electron from orbital $j$, in the average electrostatic repulsion among the passive electrons in shell $n$. The leading term in $E_R(n' = n)$ involves a decrease in the Slater integral $F^0_{nn}$, not a change in the coefficient of this integral (which would appear in the orbital energy). The physical picture in this case is that the electrons in shell $n$ are all constrained to lie at essentially the same radius but may distribute themselves on a sphere of that radius to minimize their repulsive interaction. A simple classical model shows that the loss of an electron from an eight-electron $s,p$ shell will lead to a reduction of $\sim 3\%$ in the average pair repulsion between the remaining electrons. If $F^0$ is reduced by 3%, the value of $E_R(n' = n)$ would be 3.3 eV for the $n = 2$ shell in sodium and 1.9 eV for the $n = 3$ shell in potassium, in rough agreement with the values 2.9 eV and 1.2 eV, respectively, calculated by Hedin and Johansson.

Outer-shell relaxation is easy to understand, and $E_R(n' > n)$ may be very large. An electron in the $n$ shell shields orbitals in the $n' > n$ shells almost completely. Removal of an $n$-shell electron therefore increases the effective nuclear charge experienced by the $n'$ shell by
practically one unit. This essentially quantitative shielding has led to simplified estimates of $E_R(n' > n)$ based on "equivalent core" models, which have proved to be quite accurate. For core-electron binding energies, outer-shell relaxation is by far the largest contributor to $E_R(j,n)$ provided that several electrons occupy a shell with $n' > n$.

Thus for atomic potassium, Hedin and Johansson found values of $E_R$ (and percentage arising from $E_R(n' > n)$) of 32.8 eV (96%), 10.8 eV (82%), and 2.2 eV (40%), respectively, for the 1s, 2s, and 3s orbitals.

A number of estimates of $E_R(j,n)$ for light atoms are available. Bagus did early hole-state calculations. Rosén and Lindgren developed an optimized relativistic Hartree-Fock-Slater method which has been applied by Gelius and Siegbahn to the hole states of elements through Cu ($Z = 29$). Outer-shell relaxation energies can also be calculated by a method that combines the polarization potential approach of Hedin and Johansson with the equivalent-cores model. Table I gives a summary of the total calculated relaxation energies of the orbitals in selected light atoms. Most of the values were taken from ref. 45 for consistency, but many of them are also available in other sources and the agreement between different calculations is very good.
Table I. Calculated atomic relaxation energies for the orbitals of light atoms (eV)$^a$

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<th>1s</th>
<th>2s</th>
<th>2p</th>
<th>3s</th>
<th>3p</th>
<th>3d</th>
<th>4s</th>
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</table>

$^a$Values are mostly from ref. 45. Some are interpolated.

Table I shows that $E_R(j,n)$ decreases monotonically with increasing $n$, as expected because of the dominance of outer-shell relaxation. For the same reason, $E_R(j,n)$ increases monotonically with $Z$ for a given
orbital. In valence orbitals only intra-shell relaxation is important, and it is fairly small in most cases. For s,p shells the value of $E_R$ increases as the shell is filled within a given period but decreases from one period to the next higher one. This is a consequence of the 2p shell, for example, being smaller than the 3p shell, and consequently having a greater average electron-electron repulsion energy. $E_R$ is slightly larger for ns electrons than for np electrons. These observations will all be valuable below in discussing relaxation in molecules. Even in atoms these results are useful, because they indicate that relaxation energies in valence shells should decrease somewhat in going to heavy atoms.

B. Molecules

The relaxation energy accompanying photoemission from core levels in molecules is nearly always larger than in atoms, because additional electronic charge can flow toward the positive hole. It is convenient, though arbitrary, to consider the total relaxation energy as the sum of atomic plus "extra-atomic" contributions,

$$E_R(j) = E_R^a(j) + E_R^{ea}(j).$$

(50)

Naturally the exact partitioning of $E_R(j)$ in this way can be neither unambiguous nor unique, but it can be meaningful within any particular molecular orbital model. To gain physical insight into $E_R^{ea}$ we can envision it as arising through polarization of electrons toward the hole. Alternatively, we may think of one unit of positive charge having been added to the molecule. It would naturally expand repulsively to the
outside of the molecule to minimize repulsive interaction. A homonuclear
diatomic molecule would be expected to acquire a net charge of approxi-
mately $+e/2$ on each atom, because the core hole from atom A would be
screened by transfer of $\sim -e/2$ of electronic charge through polarization
of the valence orbitals. Similarly, in methane, ionization of the C 1s
orbital would be accompanied by transfer of charge $\sim -e/4$ from each
hydrogen. That these expectations are approximately borne out is shown
in Table II, which gives final-state atomic charges calculated in the
"RPM" approach. This is a model that uses CNDO/2 molecular orbitals and
accounts for relaxation.

<table>
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<tr>
<th>Atom</th>
<th>Orbital</th>
<th>q(initial)</th>
<th>q(final)</th>
<th>$\Delta q$(bond)</th>
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<td>C in CH$_4$</td>
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<td>C 1s</td>
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<td>+0.26</td>
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<td>N$_2$(passive N)</td>
<td>N 1s</td>
<td>0</td>
<td>+0.62</td>
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</tbody>
</table>

$^a$From ref. 46.
$^b$Charge transfer along each bond.

From this discussion, $E_R$ for a given core level would be expected
to increase substantially from the free atom to the diatomic molecule.
Since the single additional atom will not provide more than $\sim e/2$ of
screening charge, however, this increase in $E_R$ is limited. Experimental
results on second-row elements have shown that the 1s binding energies are (2 - 3 eV) lower than the value calculated for free atoms. This is probably the approximate size of the extra-atomic relaxation energy in these molecules. Additional ligands allow further enhancement of $E_R$ because more electrons are available for screening, and the charge buildup on any ligand is small. Even in the second-row hydrides of C, N, and O the 1s binding energies are about 6 eV lower than in the free atoms: again most of this difference can be attributed to the $E_{\text{ea}}^R$ term. Nearly all the total possible extra-atomic relaxation energy is already realized for these small molecules. Increase of the molecular size even to infinity (a solid) adds only $\sim 2 - 3$ eV additional relaxation energy.

This is to be expected on the argument that screening leaves a positive charge of $+e$ distributed on the outside of a molecule of radius $R$ where it exerts a repulsive potential of $e/R$. The largest change in $R^{-1}$ with increasing molecular size has already been realized for the hydrides.

In molecular orbitals relaxation energies must be considered in two classes. Delocalized orbitals, in which the electronic charge is distributed more or less uniformly around the molecule, can be treated in the same terms as were valence shells in atoms. Consider, for example, a diatomic molecule in the second row. Ionization from a molecular orbital made up of atomic 2p functions will entail essentially the same relaxation among the passive $n = 2$ orbitals that was obtained in the free atom. This implies that $E_R$ terms in molecular orbitals can be estimated by summing over atomic orbital population $P_{ij}$ times appropriate intra-shell relaxation energies for those orbitals:
where the $E_R^{ij}(A0)$ values could be taken from Table I. This approach was used by Banna et al.\textsuperscript{48} for molecular orbitals in fluorinated methanes with considerable success. It is conceptually preferable to the common practice of estimating binding energies in molecules simply by reducing the calculated orbital energies by a constant factor. The use of Eq. (51) should yield rather good estimates of molecular-orbital binding energies, although errors due to correlation-energy differences will still be present.

In localized molecular orbitals; i.e., lone-pairs or highly-polarized orbitals, additional contributions to $E_R$ can arise through extra-atomic relaxation. Atomic (intrashell) relaxation would still be present, and a relation like Eq. (50) would be applicable. The $E_{R\alpha}^{ea}$ term is not readily calculable, but it is both important and useful, as it is closely related to conventional chemical properties, as discussed below. We note that the presence of additional relaxation in localized molecular orbitals should be of some value in identifying these orbitals, although no applications of this feature have been tested as yet.

Variations in core-level and lone-pair binding energies are closely related to variations in chemical reactivity. In fact, the lone-pair binding energy is essentially the Lewis basicity within a constant additive factor. By extending the concept of Lewis basicity to include core lone pairs, core-level binding energies can be included in this statement. The physical significance of this connection can be
appreciated by considering the following two reactions of an alcohol molecule in the gas phase:

\[
\begin{align*}
\text{ROH} + \text{H}^+ & \rightarrow \text{ROH}_2^+ \quad E = PA \\
\text{ROH} & \rightarrow \text{RO}^* + \text{e}^- \quad E = E_B(0 \text{ 1s}) .
\end{align*}
\]

In Eq. (52a) a proton approaches the OH group and becomes bound. An 0 1s electron is lost in Eq. (52b), leaving a positive hole on the oxygen atom. In both cases the system must respond to the addition of a positive point charge, located either within or very near the oxygen atom. The absolute magnitudes of the energies of these two reactions are very different but their variation as the R group is altered is nearly identical,

\[
\Delta(PA) \approx -\Delta E_B .
\]

This relationship was first observed for alcohols and amines; it has been confirmed and extended to a large number of other molecules, thereby establishing the relationship between Brönsted basicity and core-level binding energy for a given functional group. While not all of the variation in \(E_B\) arises from variation of \(E_{ea}^R\), calculations show that this is the main contributor.

The Lewis basicity is a more general concept. It does not refer to reactions with any particular acid, but rather to the system's tendency to give up an electron from a lone pair in the valence shell. Now core electron binding energies and those of lone-pair valence electrons on the same atom have been shown to vary together. This is expected, because both variations result from a combination of the initial-state
potential and the polarization of this potential during photoemission, measured at the orbital in question. The concept of Lewis basicity can therefore be extended (at least to within a proportionality factor close to unity) to include the variation in binding energy of core electron "lone pairs". A stringent test of the transferability of ligand function is then afforded by comparing the variation of $E_B$ for core levels of two functional groups when the ligands are changed together. In comparing the series RI and ROH for alkyl iodides and alcohols, the $I \ 3d_{5/2}$ and $O \ 1s$ binding energies were found to vary linearly.\footnote{Even HI and water lay on the straight line.}

The chemical "message" of these results is simple: Reactivity, like binding energy, depends not only on the properties of the initial state but on those of the final state as well. In working with the formalism of extra-atomic relaxation, we say that the binding energy depends on both the effective potential of a given core level in the initial state and on the change in this potential on photoionization. The chemical-reactivity description would use the terms inductive and polarization effects. It is a mistake to discuss chemical properties in terms of ground-state properties (such as dipole moments) alone: the same is true of binding energies. Since both basicity and binding-energy variation depend on the same combinations of inductive and polarization phenomena, it is fortunate that this additional complication is present. Binding-energy shifts appear to possess considerable diagnostic value for the determination of chemically interesting properties, and extensive future application can be expected.
One immediate application of these ideas can be made in the interpretation of the variation of the "ionization potential" of the alkyl alcohols. This is the binding energy of the oxygen lone pair. In sign and approximately in magnitude it is equal (see Fig. 2) to the extra-atomic relaxation energy as predicted by the RPM model.\(^49\) Thus extra-atomic relaxation appears to account for a phenomenon that has received a variety of explanations in the last 30 years.

C. Solids

Relaxation energies in solids are best discussed separately for insulators and conductors. We shall treat insulators first.

When a molecule or a multiatomic ion is present in a molecular or ionic solid, respectively, the binding energy of an orbital in that moiety is naturally considered as the sum of its local and lattice contributors.\(^53\) The relaxation energy accompanying loss of an electron from orbital \(i\) will have a (molecular or ionic) local contribution plus a contribution due to lattice polarization,

\[
E_R(i) = E_{R,\text{loc}}(i) + E_{R,\text{latt}}(i) \quad .
\]

The \(E_{R,\text{loc}}(i)\) term has been dealt with in Sections A and B. For large molecules or ions \(E_R(i)\) consists mainly of this term and \(E_{R,\text{latt}}(i)\) can be neglected. Little evidence is available on the \(E_{R,\text{latt}}(i)\) term in molecular crystals. We may safely assume that it is small (<1 eV) on theoretical grounds.

In the ionic crystal case the experimental situation is reasonably clear. Fadley et al.\(^53\) first discussed the polarization energy term for
an ionic lattice. They used a model described by Mott and Gurney\textsuperscript{54} to conclude that this term is of the order 1 eV or less for a series of potassium salts. The largest $E_R(i,\text{latt})$ terms would, of course, be expected in monatomic ions, and on balance, the alkali halides appear to present the most suitable salts for study of $E_R(i,\text{latt})$ terms. Citrin and Thomas\textsuperscript{55} carried out a careful study of core-level binding energies in eleven alkali halides. By comparing observed binding energies with predictions of a simple theory, they were able to obtain evidence for the existence of an $E_R(i,\text{latt})$ term, plus an estimate of its size. They avoided the troublesome problem of the reference level for an insulator by comparing cation and anion core-levels with free-ion binding energies. Uncertainties in the reference energy shift all the levels in the crystal together. This analysis followed that of Fadley et al.,\textsuperscript{53} including both a Madelung and an electronic\textsuperscript{56} relaxation energy, but, adding a repulsive term $E(i,\text{REP})$, they gave the equation (in our notation)

$$E_B(i) = E_B(i,\text{FI}) + \phi \frac{e^2}{R} - E(i,\text{REP}) - E_R(i,\text{latt}). \quad (55)$$

Here $E_B(i)$ and $E_B(i,\text{FI})$ are respectively the binding energy of orbital $i$ in the alkali halide lattice and the free ion, while $\phi \frac{e^2}{R}$ is the Madelung potential energy. Since this latter term is of the order of 10 eV in magnitude, it might appear that errors of $\sim 1$ eV are incurred in this model by neglecting the $\sim 10\%$ covalency of alkali halide lattices.\textsuperscript{57} In fact this is not a serious problem, because the Madelung term tends to cancel the change in core-level binding energy on forming the alkali or halide ion.\textsuperscript{58}
Citrin and Thomas calculated $E_R(i,\text{latt})$ using a method given by Mott and Littleton\textsuperscript{59} for estimating the polarization energy around a lattice vacancy. This probably represents an upper limit for $E_R(i,\text{latt})$, because the nearest neighbors' polarizabilities must be smaller in a lattice with no vacancy. At any rate, the differences between calculated values of $E_R(i,\text{latt})$ for cations and anions in the same lattice ranged up to 1.2 eV. Inclusion of this term in Eq. (55) improved the differences between calculated and measured cation and anion binding energies. This gives somewhat indirect evidence that their calculated values of $E_R(i,\text{latt})$ -- which range between 1.45 eV and 2.69 eV -- are at least approximately correct. Thus extra-ionic relaxation energies in alkali halide lattices may be taken to vary around 2 eV.

Another rather indirect measure of extra-atomic relaxation energy in alkali halides is given by the relative differences between core-level peak energies and Auger energies in photoemission spectra in free atoms and crystal lattices. The additional electron hole in the Auger final state polarizes neighboring ions more strongly than the photoemission final states. Hence the Auger transition entails additional extra-atomic relaxation. In going from atomic sodium to sodium salts, Kowalczyk et al\textsuperscript{60} found that the Na(KLL) Auger transition energy increased by 4.3 eV in NaI and 3.7 eV in Na\textsubscript{2}O. A simple lattice-polarization model indicates that the additional extra-atomic relaxation in an Auger transition should be about twice that accompanying photoemission.\textsuperscript{60} Thus half these observed differences, or $\sim 2$ eV, can be attributed to $E_R(i,\text{latt})$ in NaI, for example, in good agreement with the results of Citrin and Thomas. We may conclude that the lattice contribution to extra-atomic relaxation
energies accompanying core-level ionization in alkali halide crystals is of the order of 2 eV, as the model of Mott et al.\textsuperscript{54,59} would predict.

Uncertainty about reference energies has thus far precluded a definite discussion of the $E_R(i,\text{latt})$ term in semiconductors. In a semi-metal -- graphite -- it has been possible to calculate the $E_R(i,\text{latt})$ term quantitatively by using empirical binding energies in hydrocarbon molecules as calibration points. Davis and Shirley\textsuperscript{46} used a relaxation model with CNDO wavefunctions to calculate C 1s relaxation energies for trigonally-bonded carbons in benzene and larger planar hydrocarbons, extrapolated to an infinite lattice, and obtained a C 1s binding energy (284.4 eV) in excellent agreement with experiment (284.7 eV). This theory did not start from first principles but used the experimental C 1s binding energy in benzene as an anchor point. It appears that graphite is one lattice for which an accurate core-level binding energy can be predicted.

Extra-atomic relaxation energy terms in metals are often large, and they can be treated in a straightforward way because there is no reference energy problem. On photoemission of a core electron from an atom in a metallic lattice, the itinerant valence electrons are attracted toward the positive hole thus created. In contrast to the insulator case, screening charge can actually be transferred to the atom from which the photoelectron is ejected. This phenomenon is conveniently discussed in terms of positive phase shifts, $\delta_\ell$, in the partial $\ell$ waves that describe the itinerant electrons. Friedel's allow theory\textsuperscript{61} is useful here: the photo-excited atom can be treated as an impurity of one unit higher atomic number than the lattice. The Friedel sum rule in the form
would apply. This relation states that the excess charge of +e present on the impurity will be screened through phase shifts that lead to a net charge of -e being attracted toward the hole. The \( \ell \)-character of this charge depends on the character of the conduction bands immediately above the Fermi energy. Thus in the 3d transition metals, most of the shielding is by the d wave, while in copper the s and p waves are important. Figure 3 shows a dramatic decrease in the quantity

\[
\Delta E_B(3p) = E_B(3p, \text{free atom}) - E_B(3p, \text{metal})
\]

for the 3d metals at the end of the d shell. Ley et al.\(^6\) explained this behavior in terms of a potential model similar to that of Hedin and Johansson.\(^4\) For the 3d metals through Ni, d-wave state density lies just above the Fermi energy, and the resultant d-wave screening is similar to that expected for a 3d electron. The potential model gives

\[
\Delta E_B(3p) \approx \frac{1}{2} F^0(3p, 3d)
\]

where \( F^0 \) is a Slater integral. The 3p,3d repulsive interaction \( F^0 \) is large because the 3d orbital is relatively small. In Cu and Zn the 3d shell is full, there is little d-wave density above \( E_F \), and the corresponding \( F^0(3p, 4s) \) and \( F^0(3p, 4p) \) integrals that approximately describe \( \Delta E_B(3b) \) for s and p wave screening are much smaller. Hence the sudden drop in \( \Delta E_B \) between Ni and Cu. Figure 3 shows experimental values of
ΔE_B as well as theoretical estimates based on Eq. (57). This relation overestimates ΔE_B because the shielding charge is, of course, not completely localized. Another treatment of extra-atomic relaxation in metals, based on polarizability of the lattice, has been given by Citrin and Hamann. Neither approach is in quantitative agreement with experiment, but the basic physics of extra-atomic relaxation energies accompanying core-level photoemission in metals is now well understood. It appears that this phenomenon can now profitably be applied to the elucidation of electronic structure problems, such as those related to phase shifts of the partial waves.

Valence electrons in metals also experience a substantial E_{R}^{ea} term. This fact can be obscured by making an oversimplified interpretation of the delocalized nature of these electrons. In fact, the mean binding energies of electrons in the valence bands, \( \bar{E}_B^{(VB)} \), is lower than binding energies of the corresponding orbitals in the free atoms, \( E_A^{(VA)} \), mainly because of the \( E_R^{ea} \) term. Wigner and Bardeen, in their classic paper on the work function in alkali metals, derived an expression that can be rearranged to

\[
\bar{E}_B^{(VB)} = E_A + E_C - \left[ \frac{3e^2}{5r_s} - \frac{0.458e^2}{r_s} \right].
\]

(59)

Here \( E_C \) is the cohesive energy. The quantity in brackets can be interpreted as the coulomb and exchange energy differences imposed by creation of a hole in the valence bands (\( r_s \) is the radius of the Wigner-Seitz sphere). A common misinterpretation of the Wigner-Bardeen theory is based on the idea that valence orbitals should show little relaxation
because Koopmans' Theorem can be used. It is, of course, true that little intra-shell relaxation would be expected, as in atoms or molecules (see Table I). However, the presence of itinerant valence electrons assures that the analogue of extra-atomic relaxation is also present, in the form of polarization of the electron gas toward the "Coulomb hole" (for Coulomb energy) or "Fermi hole" (for exchange). Unfortunately, the magnitude of $E_{ea}^R$ is quite insensitive to the degree of localization of the final-state hole. It is clear, however, that substantial relaxation does take place on photoemission of a valence electron from a metal, in contrast to an atom or molecule.

D. Adsorbates

The power of electron spectroscopy for solving problems in surface science and catalysis has led to many applications of photoemission to adsorbed species on metallic substrates, usually with the intention of studying adsorbate-catalyst interactions. Relaxation energy shifts play a rather crucial role in these studies.

In physical adsorption, the adsorbate photoemission peaks have the same structure observed in the free atom or molecule. The binding energy of each peak is lowered relative to the gas-phase value by an additional relaxation energy that arises through polarization of the substrate valence electrons to screen the adsorbate hole state, i.e.,

$$E_{B}^{F}(ads) = E_{B}^{V}(gas) - \phi - E_{R}^{F}(ads) \quad (60)$$

Here the work function $\phi$ is retained because while it is the vacuum-referenced binding energy, $E_{B}^{V}(ads) = E_{B}^{F}(ads) + \phi$, that should be compared
to $E_B^{(\text{gas})}$, the work function may be altered by the adsorbate's presence. Yates and Erickson\(^66\) have studied xenon adsorbed on a clean tungsten surface, finding an $E_R$ value of 2.6 eV for the $3d_{5/2}$ levels, similar to the value observed for xenon embedded in a metallic lattice.

Core-level binding energies in adsorbed molecules are generally substantially smaller than the gas-phase values. The presence of a valence-electron reservoir in the metal allows the molecular equivalent of outer-shell relaxation, as electron charge is transferred into the molecule's valence orbitals during photoemission. Thus Barber et al\(^67\) reported an O 1s binding energy of 532 eV for oxygen adsorbed on graphite. This corresponds to 537 eV relative to the vacuum level after a work-function correction. This is still some 9 eV lower than the value $E_B \approx 546$ eV expected for free atomic oxygen, indicating a substantial $E_R$. For oxygen in adsorbed CO the 1s binding energies show some relaxation energy relative to gaseous CO,\(^68,69\) but the experimental situation is generally unclear as yet.

Adsorbate molecules show molecular orbital peaks in photoemission spectra that yield detailed adsorbate-substrate bonding information. Thus Demuth and Eastman\(^70\) found that most of the molecular orbitals shifted to lower binding energy in adsorption of $\text{C}_2\text{H}_2$, $\text{C}_2\text{H}_4$, and $\text{C}_6\text{H}_6$ on nickel. The average shifts of all the $\sigma$ orbitals were 3.2, 2.1, and 1.7 eV, respectively. It should be noted that these shifts are smaller than core-level shifts on adsorption, because they arise from the molecular analogue of intrashell relaxation. Two other observations should be made. These additional values of $E_R$ from extra-molecular relaxation decrease with increasing molecular size because the hole
charge tends to be screened already within the molecule. Also, close examination of the photoemission spectra of adsorbates in this work and elsewhere shows that the strongly bound \( \sigma \) orbitals show larger relaxation shifts than more weakly-bound \( \pi \) orbitals, as is the case for molecular orbitals in free molecules, discussed above.

Orbitals that form chemisorption bonds to the substrate tend to oppose the trend and shift to higher binding energy. This is an initial state effect. It has been observed for the least-bound \( \pi \) orbitals in \( \text{C}_2\text{H}_2, \text{C}_2\text{H}_4, \) and \( \text{C}_6\text{H}_6 \) by Demuth and Eastman.\(^{70}\) In \( \text{CO} \), a similar shift has been observed for the 5\( \sigma \) orbital, which merges with the 1\( \pi \) orbital, yielding an intense combined peak.\(^{71}\) The 5\( \sigma \) peak is the carbon "lone pair" orbital. It should be perturbed, as \( \text{CO} \) is believed to stand up as an adsorbate, with the carbon atom bonded to the substrate. Additional evidence for this orientation is provided by the relative oxygen and carbon core-level shifts.\(^{72}\) The various changes expected in molecular photoemission spectra on adsorption are illustrated in Fig. 3.

In an earlier section it was emphasized that binding energies, and particularly relaxation energies, are good indices to chemical reactivity. Chemical properties cannot be understood in terms of initial-state properties alone: the final state (following reaction) or an intermediate state must also be considered. The same is true for binding energies. In adsorbates the chemical reactivity vs. binding energy parallelism is not so easily made. It would appear, however, that the same polarization effects that lower the binding energy in an adsorbate molecule should serve to stabilize any activated complex formed by this molecule, thus speeding up the reaction. It would be as naive to attempt...
to explain catalytic reactions in terms of properties of the reactants alone as it would for any other reactions. Relaxation effects appear to hold one of the keys to an understanding of the complex problem of heterogeneous catalysis. 72

E. Solutes

Solvation has the effect of providing a reservoir of electrons for screening holes created by photoemission from solute molecules. For this reason the binding energy of a given orbital should be lower if the molecule is in solution than it would be in the gas phase. Liquid-vapor shifts in this direction have been observed. 73 The few data available as yet appear to support the expectation that dielectric liquids will show relaxation-energy shifts about equal to those found in dielectric solids. Enhanced relaxation energies in solutes are well worth study. They are related, for example, to variations in the order of reactivity between gaseous and dissolved molecules. Thus the difference in basicity between methanol and t-butanol should be reduced or even reversed in solution, because the solvent can more easily assist in lowering the energy of the protonated methanol ion. Such a reversal is already known for the acidity of alcohols. 74 Further connections of this type between $E_B$ and reactivity provide motivation for photoemission studies on solutes.
VII. APPROXIMATE BINDING-ENERGY METHODS

The last section dealt with the theory of electron binding energies. For completeness, some approximate methods are mentioned below. Only fairly rigorous methods fall within the scope of this discussion. Other methods are discussed in appropriate chapters.

Any attempt to calculate binding energies quantitatively must include relaxation effects. The potential energy of the active orbital due to the entire charge distribution of the molecule must also be considered, not just the local "atomic charge". Beyond these constraints the model employed for a given study will depend on the parameters of that study. The most straightforward approach is an accurate SCF-CI calculation on both initial and final states. Unfortunately, this is seldom feasible for large molecules or large numbers of molecules. More approximate models are therefore nearly always employed. In comparing these models a few simple points can be made:

1. There is little to be gained in practice by using "polarization potential" theories; since \textit{ab initio} hole-state calculations are still required, one may well compare total energies of initial and final states.

2. For large molecules or for problems involving many types of molecules, even single-determinantal \textit{ab initio} calculations are likely to become impractical. Less exact molecular-orbital models such as CNDO, INDO, etc., must then be employed.

3. In applying "intermediate-level" molecular orbital models, it is inadvisable to compare total energies of hole states
and ground states. The errors entailed in these models preclude reasonable accuracy via this approach.

Binding energies of molecular orbitals can probably be estimated to sufficient accuracy by using orbital energies from \textit{ab initio} calculations on molecular ground states, with relaxation corrections as discussed in Section VI-B. Orbital energies from intermediate-level models are less satisfactory in predicting the order of orbital binding energies.\textsuperscript{48}

Core-level binding energies cannot, of course, be calculated using CNDO, etc. models because they do not explicitly consider core orbitals. However, Basch\textsuperscript{75} and Schwartz\textsuperscript{76} showed that core-level orbital energy shifts (i.e., shifts in the orbital energy of a given orbital, say carbon 1s, from one molecule to another) are nearly equal to (minus) shifts in the potential at the nucleus,

\[ \Delta \varepsilon \cong -\Delta V_n. \]

Since \( \Delta V_n \) is easily (and even rather accurately) calculable from CNDO wavefunctions, it is possible to calculate orbital-energy shifts at the CNDO level, a great simplification compared to using \textit{ab-initio} calculations. This approach was first used in a predictive fashion by Davis et al,\textsuperscript{77} who found quite good agreement with experimental binding energies in small molecules. It is termed a "potential model" because the electrostatic potential, rather than the total energy, is used to estimate shifts in binding energy. This specific approach was later termed GPM, because only the ground state potential was calculated.\textsuperscript{78,46}

Relaxation effects can be taken into account by extending this model, applying the "equivalent cores" approximation of Jolly\textsuperscript{79} and
modifying Hedin and Johansson's polarization potential theory to apply to the potential at the nucleus. Davis and Shirley found that this "relaxation potential model" (RPM) gave somewhat better agreement with experiment than the GPM approach. The essential feature of the RPM is that binding energy shifts are given by

\[ \Delta E_B = -\Delta V_n - \Delta V_R. \]

The relaxation term is given by

\[ \Delta V_R = \frac{1}{2} \left[ V_n(Z+1) - V_n \right]; \]

that is, the change in potential at the nucleus on ionization of a core electron due to outer electron relaxation is approximated by the change that would occur if the nuclear charge were increased by one unit. This RPM approach is both accurate and easy to use. It gives results in good agreement with experiment and yields \( \Delta V_R \) values in fairly good agreement with \textit{ab initio} estimates. It has been observed that RPM gives systematic differences in both \( \Delta E_B \) and \( \Delta V_R \) compared to \textit{ab initio} values. The very good overall agreement of RPM predictions with experiment offers encouragement that these differences could be reduced by adjustments in the CNDO parameters.

We close this chapter by noting that further discussions of various models for binding energy shifts are given in the appropriate chapter. In particular, Jolly discusses the equivalent-cores approximation in Chapter . The essential equivalence of this approximation and the potential model has been shown. Finally, two additional techniques
for estimating binding energies are being evaluated as this is written: the $X_{ab}$ method$^{83}$ and a propagator approach.$^{84}$ Both are promising but it is too early to evaluate them.
FOOTNOTES AND REFERENCES

1. Nearly every introductory quantum mechanics text presents a discussion of the semiclassical treatment. Many also include sections on quantum field theory. See, e.g., Schiff, Quantum Mechanics, McGraw-Hill Book Co., New York, N.Y.; Merzbacher, Quantum Mechanics, John Wiley & Sons, Inc., New York, N.Y.

2. Here, and elsewhere, the summation sign indicates a summation over discrete states and, when appropriate, integration over continuous variables.

3. The two most common expressions for the transition moment in the dipole approximation are the velocity and length forms. For exact wavefunctions, the two are equivalent and related by

\[ \langle \psi_k | \mathbf{r} | \psi_i \rangle = \frac{-m(E_k - E_i)}{\hbar^2} \langle \psi_k | \mathbf{v} | \psi_i \rangle \]

4. We have used the atomic units for which \( e = \hbar = m = 1 \). The unit of energy is given by the Hartree (27.2097 eV) and distance is measured in bohrs (0.5292 Å).

5. This is true as long as certain conditions are met. See J. K. McDonald, Phys. Rev. 43 (1933) 830.

6. For an excellent discussion of these topics, the reader is referred to the two volumes by Slater, Quantum Theory of Atomic Structure, McGraw-Hill Book Co., New York, N.Y. (1960).

7. T. Koopmans, Physica 1 (1933) 104.

8. Although we have been discussing the Fock equations for an atomic system, upon the assumption of the Born-Oppenheimer approximation all principles carry over into the molecular case. The only
modification is that numerical integration of the Fock equations becomes very impractical and we are generally forced to resort to still another expansion.

\[ \phi_i = \sum_k C_{ik} n_k \]

The functions \( \{n\} \) make up what is known as the basis set. It is generally regarded as fixed, and the variation is performed on the expansion coefficients \( \{C\} \). This leads to the Hartree-Fock-Roothaan equations. In the limit of a complete basis set, the orbitals found by this method approach the Hartree-Fock orbitals. In actual practice, however, the basis set must be of a very limited size and thus selection of a basis which is flexible enough to describe all the \( \{\phi\} \) accurately is a very important step in the calculation.

15. Many methods exist for bypassing this problem without specifically resorting to a CI calculation (spin unrestricted Hartree-Fock, spin-extended Hartree-Fock, etc.). They all involve removing certain restrictions from the standard closed-shell formalism and are discussed
in reference 12.


See also D. W. Davis, R. L. Martin, M. S. Banna, and D. A. Shirley, J. Chem. Phys. 59 (1973) 4235, and references therein.


23. P. S. Bagus, private communication.


25. The distinction in this case is complicated again when the many-electron nature of the wavefunction is considered. The same ionic state could be imagined to occur through ionization of the 2p electron accompanied by the monopole excitation 1s → 3s. As long as the total wavefunction was used in computing the cross section, no differentiation between the two one-electron models could be made.


29. S. Süzer, private communication.

31. For the purposes of illustrating many-body effects, \( x \) could be any of the common forms in use: a plane wave, a plane wave orthogonal to the set \( \{ \phi' \} \), a Hartree-Fock continuum function, etc. The form of the final state given here does not necessarily imply that \( x \) was found through a calculation which explicitly considers exchange, etc.

32. This has also recently been pointed out by C. S. Fadley, Chem. Phys. Letters 25 (1974) 225.

33. Amus'ya et al.\(^{34}\) have computed the neon orbital cross sections within a many-body formalism and the results are in much better agreement with experiment. Their particular method, however, does not distinguish between relaxation and CI effects as we have defined them and it is difficult to know the relative importances of the two.


38. There may exist configurations in the ground state CI expansion in which the orbital \( \phi_1 \) is not occupied. In that case, the sum over \( m \) will not always contain a matrix element involving the orbital and we should therefore regard expression (44) as a sum over only
those determinants which contain the function $\phi_1$.

39. All variations in the intensity due to the angular distribution in
the differential cross section have been neglected.


41. J. C. Slater, Quantum Theory of Atomic Structure, McGraw-Hill (1960),


46. D. W. Davis and D. A. Shirley, J. Electr. Spectr. and Related
Phenomena 3 (1974) 137.

47. J. A. Pople and D. L. Beveridge, Approximate Molecular Orbital


50. T. D. Thomas, private communication.

51. B. E. Mills, unpublished data (private communication).

52. J. E. Hashmall, B. E. Mills, D. A. Shirley, and A. Streitwieser, Jr.,
J. Amer. Chem. Soc. 94 (1972) 4445.

53. C. S. Fadley, S. B. M. Hagstrom, M. P. Klein, and D. A. Shirley,

54. N. F. Mott and R. W. Gurney, Electronic Processes in Ionic Crystals,

56. Nuclear relaxation is slower and need not be considered. See reference 53.


58. Reference 53, p. 3788. See also reference 55.


64. E. Wigner and J. Bardeen, Phys. Rev. 48 (1935) 84.


71. D. Menzel observed this spectrum (private communication) as did D. E. Eastman. The interpretation is not universally accepted.
72. A more detailed discussion is available in "X-Ray Photoemission and Surface Structure", by D. A. Shirley, J. Vac. Sci. Technol. 12 (1975) 175.
81. M. E. Schwartz (private communication).
FIGURE CAPTIONS

Fig. 1. A hypothetical state diagram for a beryllium-like system. At the bottom left is the Hartree-Fock determinant for the ground state and two of its excited configurations of $^1S$ symmetry; above them is the $1s$ hole state determinant and the two configurations of $^2S$ character which arise from the $2s \rightarrow 3s$ excitation (the coupling of the valence electrons is denoted parenthetically). In the center portion the effects of CI are shown. To the right of each state is a hypothetical wavefunction for it (see text).

Fig. 2. Comparison between the (oxygen lone pair) first ionization potential in aliphatic alcohols and the relaxation energy due to screening of a positive charge on the oxygen atom. The line has a slope of 0.9. This agreement suggests that the variation in ionization potential, which has been variously attributed to "hyperconjugation" and other effects, is in fact largely a consequence of extra-atomic relaxation.

Fig. 3. Reduction in the 3p binding energy of 3d elements from gas to metal (points) and estimates based on the simple extra-atomic relaxation model (line). The dramatic decrease between nickel and copper is a consequence of the filling of the 3d shell.

Fig. 4. Energy level diagram for photoemission from an adsorbate molecule, showing ground state $M$, core-hole state $M^+(c)$, and hole states $M^+(VBS)$ and $M^+(VNBS)$ of valence orbitals that do and do not bond to the substrate, respectively. Vacuum reference levels are used. Hole state energies (and binding energies) are lowered on physisorption because of screening by the substrate's valence electrons. The
core-hole relaxation energy $\Delta E_{RC}$ is greater than that of the valence-level hole states, $\Delta E_{RV}$. On chemisorption, the adsorbate-to-substrate bonding orbital is identified by an increase in its hole-state (and binding) energy, $\Delta E_{BOND}$. 
\[ \Psi_2(N-1) = 0.1 \ (1s2s^2) + \{0.5(A)-0.8(B)\} + \cdots \]
\[ \Psi_1(N-1) = 0.1 \ (1s2s^2) + \{0.8(A)+0.5(B)\} + \cdots \]
\[ \Psi_0(N-1) = 0.9 \ (1s2s^2) + \{0.1(A)+0.1(B)\} + \cdots \]

\[ \Psi_{g.s.(N-1)} = 0.9 \ (1s2s^2) + 0.1 \ (1s2s3s) + \cdots \]

Fig. 1
Fig. 2
Fig. 3

The graph shows the relationship between the first ionization potential (eV) and $E_R$ (eV) for various molecules. The molecules are marked as:

- $(CH_3)_3 COH$
- $(CH_3)_2 CHOH$
- $CH_3 CH_2 OH$
- $CH_3 OH$
- $H_2O$

The line on the graph indicates a linear relationship between these two variables.
Free molecule  Physisorbate  Chemisorbate

Fig. 4
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