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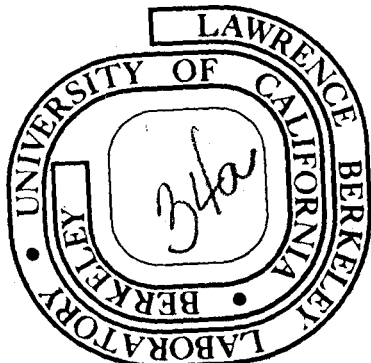
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# Theory of Core-Level Photoemission Correlation State Spectra

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## Abstract

A theoretical framework is given for calculating satellite spectra (sometimes called "shake-up" or "monopole" spectra) that accompany core-level photoemission peaks. Photoemission is regarded as a special case of optical excitation in an N-electron system. The sudden approximation (SA) is applied in a way that expresses the photoelectric cross section as a product of a one-electron transition term and an overlap determinant, plus correction terms. The dipole approximation (DA) is applied similarly. Relationships between the SA and DA results are noted. Configuration interaction (CI) in the final state is discussed. It is emphasized that the main core-level peak and satellites do not really arise from one- and two-electron excitations, respectively, but from qualitatively identical transitions. The importance of initial-state CI in determining satellite intensities in molecular x-ray photoelectron spectra is pointed out for the first time.

## I. INTRODUCTION

The growing application of x-ray photoemission spectroscopy, in which atomic core levels are photo-ionized with monochromatic x rays and the orbital binding energies measured through spectrometric analysis of the photoelectrons' kinetic energies, has led to renewed interest in calculations of photoemission spectra for atomic and molecular core levels. Most work has been focussed on the lowest-binding-energy peak observed in the characteristic spectrum from each core level; i.e., the "adiabatic"<sup>1</sup> or "primary" peak. The relaxation energy,

$$E_R^j = -\epsilon_j - E_B^j, \quad (1)$$

has received considerable attention recently; enough indeed to exaggerate the significance of the primary peak at the expense of the rest of the characteristic spectrum. Here  $\epsilon_j$  is the orbital energy and  $E_B^j$  the binding energy of orbital  $j$ .

In this paper we describe a theory of the satellite structure encountered in x-ray photoemission from core levels. Emphasis is laid on the fact that photoemission is a many-body process, carrying an  $N$ -electron system from an initial to a final state (Section II). Several levels of approximation are discussed. In Section III an  $N$ -electron sudden approximation is derived, which estimates relative cross-sections with fair accuracy. Section IV treats the dipole approximation, retaining and evaluating terms that are usually neglected. The two approximations are compared and shown to be equivalent when certain approximations have been made.

Section V shows that configuration interaction (CI) in the final state should be very important in determining the intensities of the "shake-up"

peaks, which are therefore not adequately described as arising from two-electron excitations. Ground-state CI is introduced in Section VI. It is shown to be nearly as important as final-state CI in determining the intensities of shake-up satellite peaks.

## II. PHOTOEMISSION AS AN N-ELECTRON PROCESS

In photoemission an N-electron system in an initial state  $\psi_i(1, 2, \dots, N)$  interacts with the radiation field. A photon is absorbed, taking the system to a final state  $\psi_f(1, 2, \dots, N)$ , in which at least one electron has been ejected into a continuum state. We shall restrict the discussion below to those events in which only one electron is ejected. This is done for brevity only, and no serious loss of generality is entailed: extension of this treatment to multiple-free-electron final states is straightforward.

Kinetic-energy analysis of the photoelectron spectrum reveals peaks at energies

$$K_j = \hbar\omega + E_i(N) - E_f^j(N-1) \quad (2)$$

where  $E_i(N)$  is the initial-state energy and  $E_f^j(N-1)$  is the total energy of the remnant N-1 electron system. The spectrum is usually dominated by states at the "one-electron binding energies",

$$E_B^j \equiv E_f^j(N-1) - E_i(N), \quad (3)$$

each of which corresponds approximately to the orbital energy  $\epsilon_j$  of a one-electron atomic or molecular orbital - the simplest one-determinant

description of the initial state [Eq. (2)]. Closer inspection of the spectrum reveals a set of satellite states, at higher energies  $E_{f, (N-1)}^j$ , associated with each main peak. In the literature on the subject these satellites have been variously termed "shake-up", "monopole-excitation", and "correlation" states. Unfortunately they have also been treated as if they were qualitatively different from, or were reached in a different way than, the primary N-1 electron state. The apparent differences are in fact an artificial consequence of using certain one-electron orbitals as a basis set to describe the initial and final systems, together with the assumption of <sup>single</sup> determinantal wave functions. While these heuristic descriptions have certain pedagogic value, they must not be taken literally. The satellites do not arise through a two-step process, and they do not correspond to one electron being ejected as a photoelectron and a second electron being "excited" to a higher bound orbital. Such descriptions are intuitively appealing but fundamentally incorrect. They confuse the eigenstates of the (N-1)-electron Hamiltonian with a particular set of basis orbitals.

A photoemission experiment is just a special case of optical absorption in which the N-electron system absorbs a photon of energy  $\hbar\omega$  and is raised from its initial state to a final state with one unbound electron. The act of observing the kinetic energy of the photoelectron (the N<sup>th</sup> electron), in anticipation of using Eq. (2) to study the N-1 electron system, should also focus our attention on the fact that the final state is really that of an N-electron system. If dipole selection rules are operative, which is often the case, they apply to the total N-electron system. This means, for example, that a  $^1S \rightarrow ^1P$  transition is allowed for the total system; any combination of (N-1)-electron

final state plus photoelectron final state symmetries that couple to  $^1P$  (e.g.,  $^2S + p$ ,  $^2P + s$ , etc.) would satisfy this criterion. Among the  $^2S$  final states of the N-1 electron system none has preference *a priori*. The main lines and the satellites are fundamentally exactly equivalent. Each is reached directly via a one-step, "one-electron" dipole transition.<sup>2</sup> The intensity differences arise, as shown below, because of quantitative differences in cross-sections.

The above general comments are valid without reference to basis sets, configuration interaction, or even electron correlation. We emphasize their basis-set independence. While one-electron molecular orbitals provide a convenient basis set, which we shall use below, they are in no way necessary.

### III. THE N-ELECTRON SUDDEN APPROXIMATION

The first application of the sudden approximation to hole-state excitation was made by Bloch.<sup>3</sup> Many authors have contributed to the literature on this subject. Åberg has given a recent comprehensive discussion of the sudden approximation in connection with x-ray satellite spectra.<sup>4-6</sup> Åberg's work is now the standard reference in the field of inner-shell ionization phenomena, especially in connection with x-ray spectra. For general use in photoelectron spectroscopy it is not directly applicable, however, because in inner-shell ionization, per se, attention is focused on the ionic N-1 electron system, and the photoelectron is disposed of quickly by taking the high-energy limit  $k \rightarrow \infty$ . We are, however, interested primarily in the behavior of the N-electron system under the constraint of constant total energy; i.e., the photoelectron has a finite energy determined by Eq. (2). We present below



an application of the sudden approximation to photoemission in which this high energy limit is not taken.<sup>7</sup> The essential new feature is that it can be used to estimate relative cross sections for all states observed in photoelectron spectroscopy, not just the satellites of a given primary peak.

In the sudden approximation, we assert that the interaction between the radiation field and the electronic system can be described as a delta function in time. For times  $t < t_0$ , we assume the system is in an eigenstate,  $|\psi_i(N)\rangle$ , of a time-independent Hamiltonian,  $H_1$ . For times  $t > t_0$ , it is assumed that the evolution of the wavefunction is governed by a different time-independent Hamiltonian  $H_2$ . At  $t = t_0$ , the Hamiltonian changes discontinuously from  $H_1$  to  $H_2$ , but we require that the wavefunction be continuous across this interval. This treatment then leads to the well-known result that the probability of observing the system in some eigenstate,  $|\psi_f(N)\rangle$ , of  $H_2$  at times  $t > t_0$  is simply given by

$$P_{f \leftarrow i} = \left| \langle \psi_f(N) | \psi_i(N) \rangle \right|^2. \quad (4)$$

In applying this result to photoemission, we assume that  $H_1$  is just the  $N$  electron electrostatic Hamiltonian for the atom (or molecule) in its ground state, and that  $H_2$  is separable into an  $(N-1)$ -electron electrostatic term plus a free-electron operator. The final state is thus described by the product function (5)

$$\psi_f(N) = \chi_f(1) \Psi_f(N-1), \quad (5)$$

Where  $\chi_f(1)$  is the solution of the free-particle operator for electron 1 (a plane wave), and  $\Psi_f(N-1)$  is the wavefunction for the ionic state.

It is, of course, possible to attain any degree of accuracy desired for the ground-state and ionic-state wavefunctions through the techniques of configuration interaction, but for the present let us represent each state as a single Slater determinant;

$$\psi_i(N) = (N!)^{-1/2} \left| \phi_1(1) \phi_2(2) \cdots \phi_N(N) \right|, \quad (6)$$

$$\psi_f(N-1) = [(N-1)!]^{-1/2} \left| \phi'_2(2) \phi'_3(3) \cdots \phi'_N(N) \right|. \quad (7)$$

where  $\{\phi_i\}$  is some appropriate basis of one electron orbitals,<sup>8</sup> and the orbitals  $\phi'_i$  are primed to note that they are similar, but not identical, to the initial-state basis functions. We have written the final state orbitals in this way to imply that it's possible (qualitatively) to assign  $\phi_1$  as the orbital involved in ionization.

We are interested in the matrix element  $\langle \psi_f(N) | \psi_i(N) \rangle$ . If the passive orbitals remained frozen during photoemission (i. e., if  $\phi'_i = \phi_i$  for all  $i$ ), in the spirit of Koopmans' theorem, it is easy to show by expanding Eq. (6) in minors, e. g.,

$$\psi_i(N) = (N!)^{-1/2} \sum_{j=1}^N \phi_j(1) (-1)^{j+1} \psi_i(N-1; \phi_j, 1) \quad (8)$$

that

$$\langle \psi_f(N) | \psi_i(N) \rangle = N^{-1/2} \langle \chi_f | \phi_1 \rangle. \quad (9)$$

The quantity  $\psi_i(N-1; \phi_j, 1)$  denotes the minor of  $\phi_j(1)$  in  $\psi_i(N)$ . Thus according to the usual sudden-approximation and golden-rule arguments, the cross section for photoemission would vary as

$$\sigma_1 = N^{-1} \left| \langle \chi_f | \phi_1 \rangle \right|^2 \rho(E_f), \quad (10)$$

where  $\rho(E_f)$  is the density of plane wave continuum states at the photoelectron energy  $E_f$ . The relative cross sections for photoemission

from two orbitals would vary as

$$\frac{\sigma_i}{\sigma_j} = \frac{|\langle \chi_f | \phi_i \rangle|^2 \rho(E_f)}{|\langle \chi_f | \phi_j \rangle|^2 \rho(E_f)} \quad (11)$$

It is of course clear that this approach is extremely crude, but it will give a qualitative idea of the variation of cross section ratios with energies, provided that it is not applied near threshold, even using this plane-wave approximation for  $\chi$ . In comparing this result with Åberg's derivation we note that he obtained  $N^{-1}$  as the probability of exciting a given orbital. The reason for the difference is that Åberg was doing a different problem -- x-ray satellites -- for which the emphasis was on the production of hole states with high-energy x-rays, whereas we are specifically interested in the photoelectron.

Relaxing the frozen-orbital restriction, we can write

$$\begin{aligned} \langle \psi_f(N) | \psi_i(N) \rangle &= (N!)^{1/2} \langle \chi_f(1) \prod_{k=2}^N \phi_k'(k) | \psi_i(N) \rangle \\ &= (N!)^{1/2} \sum_{j=1}^N (-1)^{j+1} \langle \chi_f(1) \prod_{k=2}^N \phi_k'(k) | \phi_j(1) \psi_i(N-1; \phi_j, 1) \rangle \end{aligned} \quad (12)$$

Here we have used a relation given by Löwdin<sup>9</sup> to write a symmetric product function (times  $(N!)^{1/2}$ ) in place of  $\psi_f(N)$  in the matrix element. Without loss of generality we may consider only the case in which electron "1" goes into the continuum final state  $\chi_f$ . The entire (antisymmetric) N-electron initial state  $\psi_i(N)$  must be used, and it is expanded across the first row.

Many-electron effects are apparent even in the crude level of theory (SA; one-determinant function) employed thus far: the transition matrix element is not separable into an "active" times a "passive" electron part. Expansion of the RHS of Eq. (12) yields

$$\langle \psi_f(N) | \psi_i(N) \rangle = N^{-1/2} \langle \chi_f | \phi_1 \rangle \begin{vmatrix} \langle 2' | 2 \rangle & \langle 2' | 3' \rangle & \cdots & \langle 2' | N \rangle \\ \langle 3' | 2 \rangle & \langle 3' | 3' \rangle & & \langle 3' | N \rangle \\ \vdots & \vdots & & \vdots \\ \langle N' | 2 \rangle & \langle N' | 3 \rangle & \cdots & \langle N' | N \rangle \end{vmatrix} \\ + N^{-1/2} \sum_{j=2}^N (-1)^{j+1} \langle \chi_f | \phi_j \rangle \begin{vmatrix} \langle 2' | 1 \rangle \langle 2' | 2 \rangle \cdots \langle 2' | j-1 \rangle \langle 2' | j+1 \rangle \cdots \langle 2' | N \rangle \\ \langle 3' | 1 \rangle \langle 3' | 2 \rangle \cdots \langle 3' | j-1 \rangle \langle 3' | j+1 \rangle \cdots \langle 3' | N \rangle \\ \vdots & \vdots & & \vdots & \vdots \\ \langle N' | 1 \rangle \langle N' | 2 \rangle \cdots \langle N' | j-1 \rangle \langle N' | j+1 \rangle \cdots \langle N' | N \rangle \end{vmatrix} \quad (13)$$

Here the abbreviated notation  $\langle 2' | 2 \rangle = \langle \phi_2^i | \phi_2 \rangle$  has been used in the determinants. If unrelaxed orbitals were used to describe the passive electrons in the final state, we would have  $\langle i' | j \rangle = \delta_{ij}$ , and Eq. (13) would reduce to Eq. (9). Using real (relaxed) orbitals, the first term will usually be altered somewhat. The product of the diagonal elements  $\langle j' | j \rangle$  is typically of the order of 5 to 10 percent less than unity, while the off-diagonal elements are very small (.05-.2). Thus the first term might be  $\sim .9 \langle \chi_f | \phi_1 \rangle$  which, when squared, is only 10 - 20% different from the frozen-orbital approximation.

The second term in Eq. (13) is more problematical. To assess its importance, note that it is possible to interchange rows and columns of the determinant so that all of the largest elements (for which  $k' = k$ ) are along the diagonal. We will still be left, however, with one term

along the diagonal of the form  $\langle j' | 1 \rangle$ , where  $j'$  is the final state orbital that most closely resembles  $\phi_j$ , the orbital which has been expanded out. This particular element will effectively dictate the magnitude of the diagonal product (since all others are nearly unity, and the diagonal products will yield the largest term by far in each determinant). We thus have additional terms which are roughly given by

$$\langle \chi_f | j \rangle \langle j' | 1 \rangle.$$

Dividing this by the first term, which is approximately  $\langle \chi_f | 1 \rangle$ , gives

$$\text{Ratio} = \frac{\langle \chi_f | j \rangle \langle j' | 1 \rangle}{\langle \chi_f | 1 \rangle}.$$

It is safe to assume  $\langle j' | 1 \rangle \ll 1$  for all  $j'$ ,<sup>10</sup> but the ratio  $\langle \chi_f | j \rangle / \langle \chi_f | 1 \rangle$  may be significantly larger than unity, thereby necessitating the retention of the sum in Eq. (13). For example, if we consider ionization of a neon 2s electron by soft x-rays ( $\hbar\omega \sim 1.5$  keV), the overlap of the 1s orbital in the hole state with the 2s orbital in the ground state is very small. However,  $\langle \chi_f | 1s \rangle$  is much larger than  $\langle \chi_f | 2s \rangle$  at these photon energies.

This sum can be regarded as arising from an "internal shakeup" mechanism: in fact it is rather similar in structure to "conjugate shakeup".<sup>11</sup> An electron appears to be ejected from the  $j^{\text{th}}$  orbital into the continuum and replaced by an electron from orbital  $\phi_1$ . This mechanism requires both exchange in the initial state (to make the product  $\langle j' | 1 \rangle \langle \chi | j \rangle$ ) and relaxation in the final state (to make  $\langle j' | 1 \rangle \neq 0$ ). Further discussion of this interesting term lies outside the scope of this paper, but we note that it was not apparent in Åberg's

treatment because the photoelectron was not explicitly included in the final state.

The cross-section for photoemission from core level  $\phi_1$  can now be written as

$$\sigma_{SA} = N^{-1} \left| \langle \chi_f | 1 \rangle S^{11} + \sum_{j=2}^N (-1)^{1+j} \langle \chi_f | j \rangle S^{1j} \right|^2 \rho(E_f) \quad (14a)$$

$$= \left\{ N^{-1} \langle \chi_f | 1 \rangle^2 (S^{11})^2 + 2N^{-1} \langle \chi_f | 1 \rangle S^{11} \sum_{j=2}^N (-1)^{1+j} \langle \chi_f | j \rangle S^{1j} + N^{-1} \left[ \sum_{j=2}^N (-1)^{1+j} \langle \chi_f | j \rangle S^{1j} \right]^2 \right\} \rho(E_f) \quad (14b)$$

where  $S^{11}$  denotes the first  $(N-1) \times (N-1)$  determinant in Eq. (13) and  $S^{1j}$  is the determinant under the sum; i. e., the determinant with the first row and  $j^{\text{th}}$  column stricken. In the frozen-orbital approximation the second and third terms would vanish,  $S^{11}$  would have a value of unity, and Eq. (14) would reduce to Eq. (10). If the second and third terms can be neglected by virtue of the product  $\langle \chi_f | j \rangle S^{1j}$  being sufficiently small for all  $j$ , but if relaxation is not neglected, then  $(S^{11})^2$  will typically be in the range  $\sim .7$  to  $.95$  and  $\sigma_{SA}$  will be reduced by this factor relative to the estimate in Eq. (10). Equation (11) will still be approximately valid because the  $(S^{11})^2$  type terms should have similar values for different photoemission transitions, and the various cross-sections will show similar reductions.

An important advantage of the present  $N$ -electron formulation of the SA is that the factor  $\langle \chi_f | \phi_1 \rangle$  contains an explicit dependence of the photoemission cross-section on the orbital symmetry of  $\phi_1$  and the

photon energy.<sup>12</sup> By using these plane waves (of the right wavelength) for  $\chi_f$  and Slater orbitals for  $\phi_1$ , most of the crudest physical features of photoemission cross-section ratios could be derived using this approach. Thus, for example, we can easily deduce the well-known result that  $\sigma(2s)/\sigma(2p)$  for second-row elements is small for very soft ( $\sim 100$  eV) photons but larger for harder ( $\sim 1000$  eV) photons, which is readily understandable in terms of the deBroglie wavelength of the final state  $\chi_f$ .<sup>13</sup>

The above discussion has argued that the SA can give qualitatively reasonable results for photoemission cross-sections when applied properly. We do not, of course, advocate using the SA when other methods are available, as described below.

#### IV. THE N-ELECTRON DIPOLE APPROXIMATION

The dipole approximation is derived by taking account of the photon field explicitly by adding a term

$$\vec{p}_i \rightarrow \vec{p}_i - \frac{e}{c} \vec{A}$$

to the momentum operator of each electron. Here  $\vec{A}$  is the vector potential of the photon field. After making the dipole approximation and carrying out several standard manipulations, it can be shown that the introduction of  $H_\phi$  inserts an operator  $\sum_{k=1}^N \vec{p}_k$  into the transition matrix element and adds a multiplicative factor of  $(\hbar\omega)^{-1}$ . The cross-section thus becomes

$$\sigma_{DA} \propto (\hbar\omega)^{-1} \left| \vec{u} \cdot \langle \psi_f(N) \left| \sum_{k=1}^N \vec{p}_k \right| \psi_i(N) \rangle \right|^2 \rho(E_f) \quad (15)$$

where  $\vec{u}$  is the polarization vector of the radiation. At this point we shall suppress the vector notation and concentrate on the momentum matrix element. Angular distribution effects lie outside the scope of our discussions. Expansion of the matrix element in Eq. (15) yields terms that differ from those in the sudden approximation only in including a matrix element of the momentum operator  $p_1$ . There are also additional terms arising from the rest of the momenta,  $\sum_{k=2}^N p_k$ . This result can be arranged in the form

$$\langle \psi_f(N) | \sum_{k=1}^N p_k | \psi_i(N) \rangle = \langle \psi_f(N) | p_1 | \psi_i(N) \rangle + \langle \psi_f(N) | \sum_{k=2}^N p_k | \psi_i(N) \rangle \quad (16)$$

$$= \langle \chi_f | p | 1 \rangle S^{11} + \sum_{j=2}^N (-1)^{1+j} \langle \chi_f | p | j \rangle S^{1j}$$

$$+ \sum_{j=1}^N (-1)^{1+j} \langle \chi_f | j \rangle \langle \Pi_{\ell} \phi_{\ell} | \sum_{k=2}^N p_k | \psi_i(N-1, \phi_j, 1) \rangle. \quad (17)$$

The first two terms of (17) arise from the  $p_1$  operator, and the rest from the  $\sum_{k=2}^N p_k$  sum. We have written (17) in this form to point out that the transition moment has two major terms. In the first an electron makes a dipole transition from orbital 1 (or j) to the continuum function. In the second, an electron in orbital 1 (or j) makes a monopole transition to  $\chi_f$ , while the passive electrons make a dipole transition to the final ionic state. Thus this last term, which is present to some extent in all photoemission processes, represents a component of a "conjugate" transition. It is very important to point out that we do not have to make the drastic assumptions about  $\chi_f$  that were made in the sudden approximation. The continuum function may be of any accuracy



desired, and, specifically, is not required to be a plane wave.

It is interesting to note the connection between this form of the cross-section and the N-electron sudden approximation. One finds that the cross section implied by Eq. (17) approaches the RHS of Eq. (14) if only the first two terms of (17) are retained and p is replaced by unity. Another comparison with the SA is obtained by approximating  $\chi_f$  with a plane wave. In this case we may replace  $\langle \chi_f | p | j \rangle$  by  $\hbar k_f \langle \chi_f | j \rangle$  and Eq. (17) becomes

$$\begin{aligned} \langle \psi_f(N) | \sum_{k=1}^N p_k | \psi_i(N) \rangle_{PW} = & \left\{ \hbar k_f \langle \chi_f | 1 \rangle S^{11} + \sum_{j=2}^N (-1)^{1+j} \hbar k_f \langle \chi_f | j \rangle S^{1j} \right. \\ & \left. + \left[ \sum_{j=1}^N (-1)^{1+j} \langle \chi_f | j \rangle \langle \prod_{\ell=2}^N \phi_{\ell}^{\dagger} | \sum_{k=2}^N p_k | \psi_i(N-1); \phi_j, 1 \rangle \right] \right\} \end{aligned} \quad (18)$$

Since by energy conservation

$$\hbar \omega = E_B + \frac{\hbar^2 k_f^2}{2m}$$

it follows that<sup>14</sup>

$$\begin{aligned} \sigma_{DA} \propto & \left( \frac{k_f^2}{k_f^2 + 2m E_B / \hbar^2} \right) \left| \left\{ \langle \chi_f | 1 \rangle S^{11} + \sum_{j=2}^N (-1)^{1+j} \langle \chi_f | j \rangle S^{1j} \right\} \right|^2 \\ & + (\hbar k_f)^{-1} \sum [p] \left| \rho(E_f) \right|^2 \end{aligned} \quad (19)$$

Here  $\sum [p]$  denotes the sum over momentum terms in square brackets in Eq. (18). As  $k \rightarrow \infty$  the coefficient in Eq. (19) approaches unity,

the last term goes to zero, and Eq. (19) approaches Eq.(14a); i.e., the energy dependence of the dipole cross section approaches the SA result. Again, however, the form given here contains an explicit expression for the momentum matrix elements of the active electrons.

The results given in Eqs. (11), (14a), and (16-19) are straightforward, but to our knowledge they have not been given explicitly before, and most molecular core-level photoemission spectra are interpreted using even more approximate expressions. The deficiencies of the SA, the DA, and the plane-wave (or OPW) approximations are too well-known to require discussion. Nevertheless, for the purposes at hand -- the calculation of core-level correlation-peak relative intensities -- any of these approaches is usually adequate provided that configuration interaction is treated properly. We turn to this subject in the next section.

## V. FINAL-STATE CONFIGURATION INTERACTION

Correlation ("shake-up") lines arise through transitions to higher-energy states of the same symmetry as the "primary" hole state. The energies of the satellite lines can conveniently be obtained from a configuration-interaction calculation on the final state. Let us consider the excited determinants  $\psi_f^{(n)}(N)$  of a molecular-ion primary determinant  $\psi_f^{(0)}(N)$  that are described by single excitations. After the configuration-interaction calculation has been carried out, the eigenstates  $\bar{\psi}_{fn'}(N)$  are given by

$$\bar{\psi}_{fn'}(N) = \sum_n C_{n'n} \psi_f^{(n)}(N) \quad (20)$$

where  $C_{n'n}$  are coefficients that describe the extent of configuration mixing. In each of the (single-) determinantal basis states  $\psi_f^{(n)}(N)$

a photoelectron continuum function  $\chi^{(n)}$  is included as one of the  $N$  one-electron functions. In principle  $\chi^{(n)}$  should therefore be included in the configuration-interaction calculation, which would be carried out on the full  $N$ -electron system. In practice, this will often not be feasible, and the CI calculation will be done only on the  $N-1$  electron molecular ion core. Aside from the continuum function  $\chi$ , the other  $N-1$  orbitals in  $\psi_f^{(0)}(N)$  are generated by deleting the appropriate core orbital  $\phi_1$  from the molecular ground-state function, and allowing all the orbitals to relax, as in the previous sections. Thus  $\psi_f^{(0)}(N)$ , the reference configuration, is just the determinant formed from the functions  $\chi_f, \phi_2', \phi_3', \dots, \phi_N'$ , as before. If the virtual orbitals are numbered  $\phi_{N+1}', \phi_{N+2}'$ , etc., then typical low-lying configurations would be the determinants formed from  $\left\{ \chi_f, \phi_2', \phi_3', \dots, \phi_{N-1}', \phi_{N+1}' \right\}$ ,  $\left\{ \chi_f, \phi_2', \phi_3', \dots, \phi_{N-1}', \phi_{N+2}' \right\}$ , etc. In forming the  $N$ -electron basis states the usual angular momentum coupling and symmetry rules must, of course, be obeyed.<sup>15</sup>

The matrix element for a transition to the final eigenstate  $\Psi_{fn'}(N)$  has the form

$$\langle \Psi_{fn'}(N) | \sum_{k=1}^N p_k | \psi_i(N) \rangle = \sum_n C_{n'n}^* \langle \Psi_{fn'}(N) | \sum_{k=1}^N p_k | \psi_i(N) \rangle. \quad (21)$$

Combining Eq. (21) with Eq. (17) we obtain

$$\langle \Psi_{fn'}(N) | \sum_{k=1}^N p_k | \psi_i(N) \rangle = \sum_n C_{n'n}^* \langle \chi_{n'} | p | 1 \rangle S_n^{11} + \dots \quad (22)$$

The terms indicated by dots are those additional terms on the RHS of Eq. (17). If we neglect them (on the basis that they are often very small

for core-level ionization), the leading term given above yields a simple expression for transition cross-sections to the correlation states. The momentum matrix element factors, giving

$$\langle \Psi_{fn'}(N) | \sum_{k=1}^N p_k | \psi_i(N) \rangle \approx \langle \chi_{n'} | p | 1 \rangle \sum_n C_{n'n}^* S_n^{11}. \quad (23)$$

The intensity ratio of the  $n'$  correlation peak to the main peak is thus

$$\frac{I(n')}{I(0)} \approx \frac{|\langle \chi_{n'} | p | 1 \rangle|^2}{|\langle \chi_0 | p | 1 \rangle|^2} \frac{\left| \sum_n C_{n'n} S_n^{11} \right|^2}{\left| \sum_n C_{0n} S_n^{11} \right|^2} \frac{\rho(E_{n'})}{\rho(E_0)}, \quad (24a)$$

$$\left( \frac{I(n')}{I(0)} \right)_{\text{PWA}} \approx \left[ \frac{k_{n'}^2 \rho(E_{n'}) |\langle \chi_{n'} | 1 \rangle|^2}{k_0^2 \rho(E_0) |\langle \chi_0 | 1 \rangle|^2} \right] \frac{\left| \sum_n C_{n'n} S_n^{11} \right|^2}{\left| \sum_n C_{0n} S_n^{11} \right|^2}, \quad (24b)$$

$$\left( \frac{I(n')}{I(0)} \right)_{\text{OA}} \approx \frac{\left| \sum_n C_{n'n} S_n^{11} \right|^2}{\left| \sum_n C_{0n} S_n^{11} \right|^2}. \quad (24c)$$

Equation (24a) is general: the only approximations that it entails are a single-determinant initial state, neglect of some terms in Eq. (17) as described above, and of course the DA. Equation (24b) is based on a plane-wave continuum state -- cf Eq. (18). In Eq. (24c) we have assumed a constant matrix element  $\langle \chi | p | 1 \rangle$  (and density of final states) between transitions to state  $n'$  and the main line. This does not require the plane wave approximation, but requires only that  $\langle \chi_0 | p | 1 \rangle$  and  $\rho(E)$  change little with energy over the range  $\Delta E$  spanning the main line and its satellites. Since  $\Delta E$  is usually  $\sim 10$ -30 eV, and small compared to the total kinetic

energy accompanying x-ray photoemission ( $\sim 1$  keV), this "overlap approximation" is usually quite a good approximation to the more exact Eq. (24a).

Application of Eqs. (24) to a real molecule would be expected to show correlation-state peaks at energies corresponding to the experimental spectrum. The intensities would be the right order of magnitude on the whole, but would probably not agree in detail with experiment. An important factor has been left out until now -- configuration interaction in the initial state. This will be treated below.

## VI. INITIAL-STATE CONFIGURATION INTERACTION

Up to this point we have treated the initial and final states of the  $N$ -electron system in an unsymmetrical way, using a single-determinant wave function for the initial state, but including configuration-admixed final eigenstates. This approach is appropriate for relative correlation-peak energies, because only the lowest electronic level is thermally populated in the ground state. In treating intensities, however, initial-state configuration interaction must be considered explicitly. It turns out to be of equal importance to CI in the final state, for reasons given below.

In the CI expansion [Eq. (20)] the coefficient  $C_{00}$  will usually be rather large; i. e., 0.9 to 1.0. This is expected because the lowest core-hole state of the molecular ion is substantially separated in energy from the correlation states. The latter may be substantially mixed by CI, since the configurations from which they are derived may be nearly degenerate in energy. Thus in the typical transformation matrix in Eq. (20),

- a)  $C_{00}$  is large ( $\sim 0.9$  to  $1.0$ ).
- b)  $C_{n'0}$  and  $C_{0n'}$  are small ( $\approx 0.1$  or less).
- c) The  $C_{n'n}$  are less predictable. However for any given correlation state  $n'$  a small number ( $\sim 1$  to  $3$ ) of elements  $C_{n'n}$  will usually be rather large ( $\geq 0.5$ ).

If configuration-interaction in the initial state is considered, an equation similar to Eq. (20) can be written,

$$\bar{\psi}_{im'}(N) = \sum_m D_{m'm} \psi_i^{(m)}(N), \quad (25)$$

and the statements (a)-(c) will also hold for the coefficients  $D_{m'm}$ .

The correlation-peak intensities in Eq. (24) may be understood qualitatively if we recognize that the overlap determinants  $S_n^{11}$  are not all of similar size. In fact,  $S_0^{11}$  is much larger than all the rest, because it gives the overlap of the passive orbitals in the main configuration of the initial and primary final state; i. e., the orbitals  $(\phi_2 \dots \phi_N)$  and  $(\phi'_2 \dots \phi'_N)$  are the same except for adiabatic relaxation. In every other  $S_n^{11}$  at least one orbital  $\phi'_j$  is changed and the overlap is greatly reduced. Thus an important term in  $I(n')$  comes from the admixture of the ground-state like configuration into each correlation state  $n'$ . In this approximation CI distributes the initial-state configuration of the passive orbitals among the various final states of the molecular ion, with most of it going to the lowest ( $n' = 0$ ) state. The photoelectric transition thus "picks out" the initial-state configuration in each final state, with relative strength  $\sim |C_{n'0}|^2$ , from Eq. (24c). The second major contributor to  $I(n')$  is the overlap between the ground state determinant and the dominant excited-state configuration,  $\psi_f^{(n)}$ , in the state  $n'$ . In this

contribution the coefficient  $C_{n'n}$  is large, but the overlap  $S_n^{11}$  is small. This term actually provides the major part of  $I(n')$ , but the first factor is not necessarily negligible. In summary, the main peak is intense because both  $C_{00}$  and  $S_0^{11}$  are large, while the low intensities of the correlation peaks are due to the small coefficient  $C_{n'0}$  (which is multiplied by a large overlap) and the small overlap  $S_n^{11}$  (which is multiplied by a large coefficient  $C_{n'n}$ ).

When initial-state CI is introduced, Eq. (23) must be modified by substituting  $\Psi_{im'}(N)$  for  $\psi_i(N)$ . Using Eqs. (20) and (25)

$$\langle \Psi_{fn'}(N) | \sum_{j=1}^N p_j | \Psi_{im'}(N) \rangle \approx \langle \chi_{n'} | P | 1 \rangle \sum_{n,m} C_{n'n}^* D_{m'm} S_{nm}^{11}, \quad (26)$$

where  $S_{nm}^{11}$  denotes the overlap determinant of the  $n^{\text{th}}$  final state configuration and the  $m^{\text{th}}$  initial state configuration, with the first row and column omitted. Referring to statements (a)-(c), and noting that only the  $m' = 0$  case is of practical interest for photoemission, we find that three kinds of terms are expected to be dominant in Eq. (26):

- i)  $C_{00}^* D_{00} S_{00}^{11}$ . This accounts for most of the intensity in the main peak. This is analogous to  $C_{n'0}^* D_{00} S_{00}^{11}$ , in which the main configuration of the initial ground state ( $|D_{00}| \sim 0.9$  to  $1.0$ ) "picks out" its counterpart in the final correlation states ( $|C_{n'0}| \sim 0.1$ ). This could be termed "CI in the final state".
- ii)  $C_{n'n}^* D_{00} S_{n0}^{11}$ , also a "final state CI" effect. These first two contributions were discussed in the previous section.
- iii)  $C_{n'n}^* D_{0m} S_{nm}^{11}$ , in which the configurations that are admixed into the initial state to a small extent ( $|D_{0m}| \sim 0.1$ ) pick out

their counterparts which form the major portions of the final correlation states ( $C_{n'n} \sim 0.5 - 1.0$  for some  $n$ ). This could be termed "CI in the initial state". Like  $S_{00}^{11}$ ,  $S_{nm}^{11}$  is of the order of unity.

The symmetry between (ii) and (iii) is obvious. Clearly CI in the ground state is potentially as important for intensity calculations as is final-state CI. Since both contribute to the same transitions, they add in phase before the matrix element is squared, and omission of (iii) can therefore yield transition intensity estimates that are either too high or too low. We did indeed find this to be the case in the calculations on HF described in the next paper. Without initial-state CI the intensities were about right in the aggregate but very wrong in detail; with it the agreement with experiment was essentially perfect.

We now give a set of equations for relating core-level correlation-peak intensities to the intensity of the main line. The equations are similar to Eqs. (24) but include initial-state CI.

$$\frac{I(n')}{I(0)} = \frac{|\langle \chi_{n'} | p | 1 \rangle|^2}{|\langle \chi_0 | p | 1 \rangle|^2} \frac{\left| \sum_{n,m} C_{n'n}^* D_{0m} S_{nm}^{11} \right|^2}{\left| \sum_{n,m} C_{0n}^* D_{0m} S_{nm}^{11} \right|^2} \frac{\rho(E_{n'})}{\rho(E_0)} \quad (27a)$$

$$\left( \frac{I(n')}{I(0)} \right)_{\text{PWA}} \approx \left[ \frac{k_{n'}^2 \rho(E_{n'}) |\langle \chi_{n'} | 1 \rangle|^2}{k_0^2 \rho(E_0) |\langle \chi_0 | 1 \rangle|^2} \right] \frac{\left| \sum_{n,m} C_{n'n}^* D_{0m} S_{nm}^{11} \right|^2}{\left| \sum_{n,m} C_{0n}^* D_{0m} S_{nm}^{11} \right|^2} \quad (27b)$$

$$\left( \frac{I(n')}{I(0)} \right)_{\text{OA}} \approx \frac{\left| \sum_{n,m} C_{n'n}^* D_{0m} S_{nm}^{11} \right|^2}{\left| \sum_{r,m} C_{0n}^* D_{0m} S_{nm}^{11} \right|^2} \quad (27c)$$



Equations (27) should serve as an adequate theoretical basis for the calculation of correlation-peak (or "shake-up") spectra accompanying core-level peaks in atoms and molecules. The first application to a molecule is reported in the next paper.

## FOOTNOTES AND REFERENCES

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1. We mean adiabatic here in a statistical mechanical sense; i. e., the one electron quantum numbers specifying the state do not change. It is not meant to imply anything about the time scale of the ionization process.
2. Semantic confusion is possible here. By a one-electron transition we mean a transition caused in first order by a one-electron operator or a linear combination of one-electron operators. Thus  $\sum \vec{p}_i$  would qualify, but not  $\vec{s}_i \cdot \vec{s}_j$ .
3. F. Bloch, Phys. Rev. 48, 187 (1935).
4. T. Åberg Phys. Rev. 156, 35 (1967).
5. T. Åberg Am. Acad. Sci. Fenn. AVI 308, 1 (1969).
6. T. Åberg Phys. Rev. A2, 1726 (1970).
7. This result was also obtained by Åberg,<sup>5</sup> as an intermediate step in his derivation of the high energy limit. Its implications were not discussed. To avoid confusion, we felt a new derivation was required.
8. The orbitals can be imagined to be spin-orbitals - a spatial function times a spin function. E. g.  $\phi_1(1) = \phi_{1s}(\vec{r}_1) \alpha(1)$ .
9. Per-Olov Löwdin, Phys. Rev., 97, 1474 (1955).
10. These can be estimated from results reported by P. S. Bagus, Phys. Rev., 139, A619 (1965).
11. J. Berkowitz, J. L. Dehmer, Y. K. Kim, and J. P. Desclaux, J. Chem. Phys. 61, 2556 (1974).

12. The selection rules operative here are monopole. If  $\phi_1$  has s symmetry, then the overlap integral will "pick out" that component of the plane wave function which has s symmetry. This result is obtained because we have not included the photon field in our treatment. In more rigorous approaches the photon field is included explicitly. In that case one finds that absorption of the photon transfers one unit of angular momentum to the final state, and the dipole selection rules discussed in Section II apply.

13. W. C. Price, A. W. Potts, and D. G. Streets, Electron Spectroscopy, edited by D. A. Shirley, North-Holland Publishing Co., 1972.

14. In this step, we have assumed that the dot product of  $\vec{u}$  with the transition moment introduces a multiplicative constant into the cross section. This factor will depend on the specific nature of a given experiment, but for the purpose of showing the connection with the SA need not be examined in detail.

15. For the sake of simplicity we have employed single determinantal basis states. In actual practice, it is usually more convenient to define the configurations as linear combinations of Slater determinants which are eigenfunctions of some appropriate operator for the state.

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