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# MANY-ELECTRON EFFECTS IN PHOTOELECTRON SPECTROSCOPY

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# MANY-ELECTRON EFFECTS IN PHOTOELECTRON SPECTROSCOPY

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## ABSTRACT

The deviations from Koopmans' one-electron model of photoionization which lead to satellite structure in the photoelectron spectrum are examined within the formalism of configuration interaction (CI). The mechanisms which contribute to satellite intensity may be classified as continuum state configuration interaction, final ionic state configuration interaction, and initial state configuration interaction. The discussion centers around the last two mechanisms, these being the prime contributors to the satellite intensity well above threshold. Specific examples of theoretical "spectra" are presented for the F(1s) region of HF and the 1s region of neon. The agreement between theory and experiment is found to be excellent. In these two instances, initial state configuration interaction contributions increase the satellite intensity and are of nearly equal importance to the final ionic state mixing.

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# I. INTRODUCTION

Photoelectron spectroscopy (PES) provides a very powerful means of studying the internal structure of atoms, molecules, and solids. In a very general sense PES is no different from, for example, optical absorption spectroscopy: the resonant absorption of light takes the system from sone initial state, characterized by the wavefunction $\Psi_i$, to a final state specified by the wavefunction $\Psi_f$. An important difference, however, between PES and many of the other absorption spectroscopies arises because the final states observed in PES lie in the continuum with respect to ionization. Absorption of a photon thus results in the ejection of at least one electron from the system, and it is the kinetic energy and number of these "photo-electrons" (rather than the attenuation of the photon beam) which is experimentally determined. The technique in this respect is therefore akin to an emission spectroscopy.

In the photoionization process the familiar energy conservation equation

$$h\nu = E_f - E_i \tag{1}$$

must, of course, be satisfied. It is helpful to define a general final state reached by absorption of the photon as a superposition of many <u>degenerate</u> states $\psi_j$,

$$\Psi_f = \sum_j c_{fj}\psi_j \quad . \tag{2}$$

In this general description we should recognize that there may be a "quasi-bound" state embedded in the continuum at this energy, but

most of the available states partition the total energy, $E_f$, into two components:

$$E_f = E_j + T_j \quad , \tag{3}$$

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:

$$h\nu = (E_j + T_j) - E_i \equiv E_B^j + T_j \quad , \tag{4}$$

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 average of PES is that it allows the study of specific ionic states.

Although an experimental technique which permits one to "catalog" the energies of the ionic states of chemical species would certainly

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be of some interest to some people some of the time, this feature alone could obviously not generate the activity that has characterized this field in the past 10 years. The interest stems from the fact that the binding energies measured are related, via Koopmans' Theorem,[1] to the Hartree-Fock orbital energies in the initial state. These one-electron energies play a central role in our understanding of the properties of atoms, molecules, and solids. Thus, in a first approximation, PES allows one to study "atomic orbitals", "molecular orbitals", and the "one-electron density of states".[2] As the field matures, however, more and more examples of strictly many-electron effects are being discovered. Perhaps the most dramatic example is the observation of satellite structure associated with each "one-electron" (primary) peak. These satellites are strictly forbidden within Koopmans' one-electron model, but are sometimes as intense as the primary peak.

This thesis will deal primarily with the theoretical description of these satellite states in free atoms and molecules; i.e., their energies, the transition probabilities for reaching them via photon absorption, and the additional information they provide about the electronic structure of the system under study. Many of the results which emerge are also applicable to other experimental techniques which deal with ionic states--electron impact ionization (e,2e), and X-ray emission, for example. In Chapter 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 is presented in Chapter III, along with a discussion of Koopmans' Theorem and "hole state" Hartree-Fock calculations.

In Chapter IV, the physical concepts which emerge from a study of these wavefunctions will be used to characterize the ionic states observed in PES, as well as to provide qualitative guidelines as to the mechanisms through which they acquire intensity. Chapter V analyzes many-electron effects in the photoionization cross-section in terms of the logical hierarchy of approximations commonly employed in electronic structure calculations. Sum rules which relate intensities and energies are also discussed. Specific cases of satellite structure in HF and neon are presented in the final two chapters, VI and VIII.

REFERENCES

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

2. To be more specific, the binding energies of the primary peaks are approximately given by the one-electron eigenvalues of the canonical Hartree-Fock equations for closed shell (and some classes of open shell) systems. The canonical eigenvalues are but one of an infinite number of equally acceptable solutions to the Hartree-Fock equations. In practice, with the exception of atomic species, one usually furthermore expands the solutions in a finite basis set. To summarize: the binding energies are approximately given by the approximate eigenvalues of an approximately correct Hamiltonian. The most casual reader should now have no problem in understanding many of the advantages of PES vs other spectroscopic techniques.

## 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. The Dependent Perturbations and Fermi's Golden Rule

Consider a system of particles in a stationary state of a time-independent electrostatic Hamiltonian $\mathcal{H}_0$. 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 $\mathcal{H}_0$ satisfy the Schrodinger equation

$$\mathcal{H}_0 \Psi_n = E_n \Psi_n \tag{5}$$

and have a simple oscillatory evolution in time

$$\Psi_n(t) = e^{-(i/\hbar)\, E_n t}\, \Psi_n \quad . \tag{6}$$

A general solution of the equations of motion

$$i\hbar \frac{d\Psi(t)}{dt} = \mathcal{H}_0 \Psi(t) \tag{7}$$

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

$$\Psi(t) = \sum_n c_n e^{-(i/\hbar) E_n t} \Psi_n \quad . \tag{8}$$

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

$$\mathcal{H} = \mathcal{H}_0 + V(t) \tag{9}$$

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 $\mathcal{H}_0$. Thus the solution is still given by Eq. (8), but we must now consider the expansion coefficients to be time-dependent.

Substitution of Eq. (8) into the Schrödinger equation

$$i\hbar \frac{d\Psi(t)}{dt} = \mathcal{H}\Psi(t) \tag{10}$$

yields equations of motion governing the expansion coefficients.[2]

$$i\hbar \frac{dc_k(t)}{dt} = \sum_n c_n(t)\, V_{kn} e^{i\omega_{kn} t} \quad , \tag{11}$$

where $V_{kn}$ is the matrix element of the perturbation between the unperturbed states,

$$V_{kn} = \langle \Psi_k | V | \Psi_n \rangle \quad , \tag{12}$$

and

$$\hbar \omega_{kn} \equiv E_k - E_n \quad . \tag{13}$$

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, $\Psi_i$, of $\mathcal{H}_0$, and if the perturbation depends harmonically on the time,

$$V(t) = V_0 e^{i\omega t} \quad , \tag{14}$$

then the probability of finding the system in an eigenstate $\Psi_k$ which <u>lies in the continuum</u>, i.e., $|c_k(t)|^2$, is directly proportional to the time that the perturbation has been active. It is also known that because the Hamiltonian is time-dependent, there is a finite probability that transitions will take place to final states $\Psi_k$ for which the energy conservation equation $\omega = E_k - E_i$ is not satisfied. As t increases, however, the transition probability sharply "peaks" about that state or group of states for which the energy conservation equation is satisfied. For the photoionization problems we are

interested in we may safely assume the latter condition, which finally leads us to a transition probability per unit time:

$$P_{k\leftarrow i} = \frac{2\pi}{\hbar} \rho(E_k) |\langle\psi_k|V|\Psi_i\rangle|^2 \tag{15}$$

This expression is known as Fermi's "Golden Rule No. 2". Here $P_{k\leftarrow i}$ is the transition probability per unit time for the process $\Psi_i \rightarrow \Psi_k$ (with $E_k = E_i + \hbar\omega$). The term $\rho(E_k)$ is the density of final states with energy $E_k$.

## B. The Classical Radiation Field and the Photoelectron 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

$$\mathcal{H} = \mathcal{H}_0 + \left(\frac{-i\hbar e}{2mc} \underset{\sim}{\nabla}\cdot\underset{\sim}{A} - \frac{i\hbar e}{mc} \underset{\sim}{A}\cdot\underset{\sim}{\nabla} + \frac{e^2}{2mc^2} |A|^2\right) - e\phi \quad . \tag{16}$$

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 $\mathcal{H}_0$ represents the Hamiltonian describing the particles in the absence of the field, and the vector $-i\hbar\underset{\sim}{\nabla}$ is a sum of momentum operators for the individual particles

$$\underset{\sim}{\nabla} = \sum_i (\underset{\sim}{\nabla}_i) \quad . \tag{17}$$

The radiation field itself is described by the vector potential $\underset{\sim}{A}$ and a scalar potential $\phi$. These are related to the electric and magnetic

field strengths, $\underset{\sim}{E}$ and $\underset{\sim}{H}$, by

$$\underset{\sim}{E} = -\frac{1}{c}\frac{\partial}{\partial t}\underset{\sim}{A} - \underset{\sim}{\nabla}\phi$$
$$\underset{\sim}{H} = \underset{\sim}{\nabla}\times\underset{\sim}{A} \quad . \tag{18}$$

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

$$\underset{\sim}{\nabla}\cdot\underset{\sim}{A} = 0 \quad ,$$
$$\phi = 0 \quad . \tag{19}$$

Since we have assumed that the field is weak, we furthermore neglect the term in $|A|^2$, and finally obtain:

$$\mathcal{H} = \mathcal{H}_0 - \frac{i\hbar e}{mc}\underset{\sim}{A}\cdot\underset{\sim}{\nabla} \tag{20}$$

or

$$V(t) = \frac{-i\hbar e}{mc}\underset{\sim}{A}\cdot\underset{\sim}{\nabla} \quad . \tag{21}$$

Now the vector potential for radiation propagating in the form of a plane wave of wave vector $\underset{\sim}{q}$ and frequency $\omega$ can be written

$$\underset{\sim}{A} = \underset{\sim}{u}A_0\left(e^{-i\underset{\sim}{q}\cdot\underset{\sim}{r}}e^{i\omega t} + e^{i\underset{\sim}{q}\cdot\underset{\sim}{r}}e^{-i\omega t}\right) \tag{22}$$

where $\underset{\sim}{u}$ 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 related to the square of the amplitude:

$$I = \frac{\omega^2}{2\pi c}A_0^2 \quad . \tag{23}$$

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

$$P_{k\leftarrow i} = \frac{4\pi^2 \hbar e^2 I}{m^2 c\omega^2} \rho(E_k) \left| \underset{\sim}{u} \cdot \langle \Psi_k | e^{i\underset{\sim}{q}\cdot \underset{\sim}{r}} \underset{\sim}{\nabla} | \Psi_i \rangle \right|^2 \quad . \tag{24}$$

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 result.

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

$$\frac{d\sigma_{k\leftarrow i}}{d\Omega} = \frac{\pi \hbar^2 e}{m^2 c\omega} \rho(E_k) \left| \underset{\sim}{u} \cdot \langle \Psi_k | e^{i\underset{\sim}{q}\cdot \underset{\sim}{r}} \underset{\sim}{\nabla} | \Psi_i \rangle \right|^2 \quad , \tag{25}$$

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 photoionization 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

$$e^{i\underset{\sim}{q}\cdot\underset{\sim}{r}} = 1 + i\underset{\sim}{q}\cdot\underset{\sim}{r} + 1/2(i\underset{\sim}{q}\cdot\underset{\sim}{r})^2 + \ldots \tag{26}$$

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 wave vector of the photoelectron.[3]

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., NY); Merzbacher, Quantum Mechanics (John Wiley & Sons, Inc., NY).

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

$$\langle \Psi_k | \underset{\sim}{\nabla} | \Psi_i \rangle = \frac{-m(E_k - E_i)}{\hbar^2} \langle \Psi_k | \underset{\sim}{r} | \Psi_i \rangle \quad .$$

## III. THE WAVEFUNCTIONS

Let us now consider the eigenstates of the electrostatic Hamiltonian in the absence of perturbation. In systems containing two or more electrons, exact solutions of the Schrodinger equation 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 wavefunctions which we seek are eigenstates of the non-relativistic electrostatic Hamiltonian for an N-electron system in the field of a nucleus of charge Z,

$$\mathcal{H}_0 = \sum_{i=1}^{N} \left[-1/2\ \nabla_i^2 - \frac{Z}{r_i}\right] + \sum_{i}^{N} \sum_{j>i}^{N} \frac{1}{r_{ij}} \quad . \tag{27}$$

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.[1]

Nearly all work on this problem involves the use of the Variation Principle. This approach employs an approximate form for the N-electron wavefunction that contains adjustable parameters which are then varied to minimize the expectation value of the Hamiltonian. As long as certain conditions are met,[2] the energy found in this way must be an upper bound to the actual energy, and the optimized parameters define the best approximation to the true wavefunction available within the confines of that particular model. If several models are compared,

and the calculations are ab initio in the sense that no empirical or semi-empirical "fiddling around" is done in the variation, then the model which yields the lowest energy must, therefore, yield a more accurate wavefunction. However, it is not necessarily the case that the expectation values of operators other than the Hamiltonian converge to their exact values in the same manner that the energy does. Chapter VII contains an example of a situation where a relatively large improvement in the energy has a negligible effect on satellite intensities computed from the wavefunction, whereas an additional small decrease in the energy leads to a great improvement in the intensities.

## A. One-Electron Models

The one-electron approximation lies at the heart of our qualitative understanding of electronic structure and is nearly always the starting point for further refinements in the theory. The basic assumption is 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.,

$$\Psi_0(1,2, \ldots N) = \phi_1(1)\ \phi_2(2)\ \ldots\ \phi_N(N) \quad . \tag{28}$$

The spin orbital $\phi_1(1)$ 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 $\beta(1)$.

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,

$$\chi_1(1) = \mathbb{R}_{N\ell}(r_1)\ Y_{\ell m}(\theta_1,\phi_1) \quad . \tag{29}$$

The quantum numbers n, $\ell$ and m are the same as those in the hydrogen problem and so we speak of the orbitals as being s, p, or d-like, etc. The radial function $\mathbb{R}_{n\ell}(r)$ 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. When (or if) convergence is achieved, the 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 wavefunctions. The simplest wavefunction for a closed shell atom which preserves the product form of Hartree but satsifies the antisymmetry requirement is given by Eq. (30):

$$\Psi_0(1,2,\ .\ .\ .\ N) = A(N)\{\phi_1(1)\ \phi_2(2)\ .\ .\ .\ \phi_N(N) \tag{30}$$

$A(N)$ 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:

$$\Psi_0(N) = \frac{1}{(N!)^{1/2}} \begin{vmatrix} \phi_1(1) & \phi_2(1) & \cdots & \phi_N(1) \\ \phi_1(2) & \phi_2(2) & \cdots & \phi_N(2) \\ \vdots & & & \\ \phi_1(N) & \phi_2(N) & \cdots & \phi_N(N) \end{vmatrix} \quad . \tag{31}$$

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

$$F\phi_i(1) = \sum_j^{N/2} \varepsilon_{ij}\phi_j(1) \tag{32a}$$

The $\varepsilon_{ij}$ are Lagrangian multipliers which preserve orthogonality amongst the orbitals; the sum runs over all N/2 spatial orbitals $\phi_j$. The Fock operator is given by

$$F = h + \sum_j 2J_j - K_j \tag{32b}$$

with the one-electron and Coulomb operators defined by

$$h = -1/2\ \nabla_1^2 - z/r_1 \tag{32c}$$

$$J_j(1) = \int \phi_j^*(1)\ \frac{1}{r_{12}}\ \phi_j(1)\ d\tau_1 \tag{32d}$$

The exchange term is represented by an integral operator; i.e.,

$$K_j(1)\ \phi_i(1) = \left\{ \int \phi_j^*(2)\ \frac{1}{r_{12}}\ \phi_i(2)\ d\tau_2 \right\} \phi_j(1) \qquad (32e)$$

The reason we have written out the Fock equations explicitly is to point out the presence of the Lagrangian multipliers, $\varepsilon_{ij}$. 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 <u>not uniquely determined</u>, the 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[4] 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 <u>canonical</u> set which result from that particular unitary transformation which diagonalizes the Lagrangian multiplier matrix . It is fortunate that Koopmans' Theorem 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-electron wavefunction to a final state characterized by another many-electron wavefunction. The canonical Hartree-Fock orbitals are "special" for describing this process because they happen to lump most

of the "many-electron" effects into one orbital. This is discussed further in Section C.

Although we have been discussing the Fock equations for an atomic system, upon the assumption of the Born-Oppenheimer approximation[5] 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,

$$\phi_i = \sum_k C_{ik}\eta_k \quad .$$

The functions $\{\eta\}$ 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.[6] 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.[7]

## 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.[8] 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 short range instantaneous repulsion between electrons. The CI concepts introduced below will be used in the discussion of the cross section in Chapter 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 Eqs. (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 complete set of Slater determinants. Thus the exact wavefunction can be written

$$\Psi_0(N) = \sum_k C_k \, k \quad , \tag{33}$$

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, although the Hartree-Fock

electron density for a closed shell species can be shown to be unaltered by CI in the first order of perturbation theory,[9,10] changes in the charge density brought about by higher orders are often very important in the computation of dipole moments, the electrostatic field at the nucleus, etc.[7]

The exact form and convergence properties of the CI wavefunction are dependent of 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 Sinanoglu[11] 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 the reduces the energy. In the $^1S$ ground state of the neon atom, e.g., this correlation energy has been estimated[12] 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 possess the correct symmetry for the state in question. Even at this level, the concept of the one electron in a particular orbital must often be abandoned. The asymmetry of the Coulomb field means that it is no longer 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.

As an example, the $2s^2 \rightarrow 2p^2$ excitation is very important for correlating the ground state of Be. Qualitatively, this type of configuration interaction is in essence simply relaxing certain restrictions which are placed on the one-electron functions in the traditional Hartree-Fock method; e.g., forcing the spatial orbital to accommodate both an $\alpha$ and $\beta$ spin electron, requiring the orbitals to have a specific angular momentum, etc. It is not surprising, then, that many extensions of Hartree-Fock theory which relax these restrictions and yet retain a "one-electron" like approach are fairly abundant.[7]

A particularly useful categorization of correlation contributions to the wavefunction has been given by McKoy and Sinanoglu.[13] These authors begin by partitioning the one-electron orbital space into two distinct regions. The first is termed the "Hartree-Fock sea". It consists of the orbitals which are occupied in the Hartree-Fock configuration and those which are nearly degenerate with the Hartree-Fock set. For example, in Be the sea (also sometimes called the internal set) consists of the 1s, 2s, and 2p orbitals. In a molecule the internal set is usually defined as all those molecular orbitals which originate from "internal" atomic orbitals. That is, the internal set in a first row diatomic would consist of the six sigma and two pi orbitals which are formed from the 1s, 2s, and 2p functions on the constituent atoms.

The second region (the external set) contains all those orbitals not included in the Hartree-Fock sea which are necessary to form a complete space of one-electron functions. Correlation is then divided into three categories:

(a) Internal correlation--a rearrangement within the Hartree-Fock sea. Two electrons make a "transition" from orbitals occupied in the Hartree-Fock configuration to virtual orbitals within the sea. This type of correlation is usually the most important CI effect in the sense of large mixing coefficients. The $2s^2 \rightarrow 2p^2$ excitation in beryllium is an example.

(b) Semi-internal--one electron is excited within the sea while another goes into the external space. Certain distributions of this type are responsible for the orbital polarization necessary in open shell systems to correct for the assumptions of a central field. In terms of mixing coefficients, this effect is generally smaller than internal correlation.

(c) External--two electrons are excited into the external space. These excitations can have important consequences on the energy, but usually lead to small mixing coefficients. The ground state of the neon atom is a case where this is the only correlation mechanism possible.

In introducing these topics, we have defined the categories in terms of two-electron excitations relative to the Hartree-Fock configuration. In the most general form, one speaks only of distribution of electrons. If the system contains N electrons, the internal contribution corresponds to distributing N electrons in the internal space in all possible ways (consistent with the Pauli principle, the symmetry of the state, etc). The semi-internal configurations come from all distributions of the type $(N - 1)_{int}(1)_{ext}$, and external correlation effects are embodied in the distributions $(N - 2)_{int}(2)_{ext}$.

The importance of this classification is that the first two contributions (a and b) are the structure dependent correlation terms; they are a function of the orbital structure of the state in question, its symmetry, etc. The external contribution, however, is more nearly a description of the "instantaneous" repulsion of a pair of electrons. McKoy and Sinanoglu term it a dynamical effect. It is the portion of the correlation energy which can be described in terms of 1/2(N)(N - 1) "pair" correlation energies which are roughly transferable among states of differing N and symmetry.

## C. Koopmans' Theorem

The result which Tjallings Koopmans obtained for the ionization potential of an electron is certainly well known. It would seem to this writer that he is probably the most referenced economist in the chemistry and physics literature.[14] It is less widely understood exactly what it is that Koopmans was trying to show. This subject is treated briefly in this section.

Earlier, we mentioned that because the Hartree-Fock determinant is invariant under a unitary transformation of its orbitals, it is not immediately obvious which set of orbitals is the most "physically" meaningful. Let us assume that one set of orbitals, denoted by $\{\phi\}$, has been found, and then address ourselves to the problem of ionization by construction all the primary ionic configurations which can be formed from the set $\{\phi\}$. If we have N electrons in the initial state, we will have N/2 spatial orbitals $(\phi_1 \ldots \phi_{N/2})$ and N/2 primary ionic configurations:

$$\Psi^{-i}(N-1) = \frac{1}{[(N-1)!]^{1/2}} |\phi_1\bar{\phi}_1 \cdots \phi_i , \phi_{i+1}\bar{\phi}_{i+1} \cdots \bar{\phi}_{N/2}| , \quad (34)$$

in each of which we have "ionized" an electron from the spin-orbital $\bar{\phi}_i$. The bar above the orbital denotes a beta spin function.

The binding energies will be given by

$$E_B^i = E_{GS}(N) - \langle \Psi^{-i}(N-1)|\mathcal{H}|\Psi^{-i}(N-1)\rangle \quad (35)$$

where $E_{GS}(N)$ is the total Hartree-Fock energy of the ground state. These ionization potentials will depend on our original choice of orbitals through the last term, and the best wavefunction for the lowest ionic state of a given symmetry can be found by minimizing the last term. When we <u>restrict</u> the space available for the variation to just the set of occupied ground state orbitals, we can write the optimal orbitals $\{\phi'\}$ in terms of the ground state orbitals:

$$\underset{\sim}{\phi}' = \underset{\sim}{U}\underset{\sim}{\phi} \quad (36)$$

Koopmans showed that the transformation $\underset{\sim}{U}$ which minimized the ionic state energy was the one which diagonalizes the Lagrangian multiplier matrix in Eq. (32) and results in the canonical orbitals. The familiar result is that the binding energy for orbital i is given in this representation as $-\varepsilon_{ii}$. Newton[15] has emphasized that this variational approach provides an upper bound to the energy of the lowest ionic state of a given symmetry only.

There is another feature of the canonical orbitals which makes them particularly useful for describing ionization. If we form the Hamiltonian matrix of the primary ionic configurations in terms of an arbitrary orbital set, it will in general not be diagonal

$$\langle \Psi^{-i} | \mathcal{H} | \Psi^{-j} \rangle = - \left\{ \langle \phi_j | h | \phi_i \rangle + \sum_{\ell}^{N/2} \langle \phi_j | 2J_\ell - K_\ell | \phi_i \rangle \right\} . \quad (37)$$

This follows from the Slater-Condon rules for determinantal wavefunctions which differ by a single orbital replacement. Note that the term on the right is simply an off-diagonal element of the N electron Fock matrix. Thus we find (multiply Eq. (32a) on the left by $\phi_j^*$ and integrate over all space)

$$F_{ji} \equiv \langle \phi_j | F | \phi_i \rangle = \varepsilon_{ij} = - \langle \Psi^{-i} | \mathcal{H} | \Psi^{-j} \rangle \quad (38)$$

This important relationship means that by choosing the orbital set which diagonalizes the Lagrangian multiplier matrix, we have also effectively diagonalized the CI matrix of all the primary ionic configurations.[16] Thus, canonical Hartree-Fock orbitals are "special" for describing ionization because they anticipate a "zeroth-order" orbital relaxation in the final state.

To illustrate this point, consider the transition from the ground state of the mulecule carbon monoxide ($^1\Sigma^+$) to its first ionic state possessing $^2\Sigma^+$ character. This transition can be described fairly accurately in terms of the ionization of an electron from the canonical orbital 5σ. This "molecular orbital" closely resembles a "long pair" on the carbon atom, but it has an appreciable amplitude on both atomic centers. 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 electron pairs.[17] A description of the same transition in terms of these localized orbitals could be obtained by diagonalizing the primary ionic configuration matrix. The

energy of the lowest $^2\Sigma^+$ state would be the same as that predicted by the 5σ cannonical orbital energy; the eigenvector corresponding to the state would be a superposition of primary ionic states, and we would be forced to talk about ionization of "part of an electron" from the carbon "lone pair", another fraction of an electron from a carbon-oxygen "bonding" orbital, etc. In this representation the transition must be referred to as a many-electron 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. This 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.

### D. McDonald's Theorem and "ΔSCF" Calculations

The first step in moving beyond Koopmans' description of a primary ionic state is usually what is termed a "ΔSCF" calculation. Philosophically, it is identical to Koopmans' approach of minimizing the energy of the ionic state. The new twist is that, as opposed to limited variation (just in the space of the occupied ground state orbitals), one uses the entire orbital space (occupied + virtual); in other words, a separate Hartree-Fock calculation is done for the ion and the binding energy is obtained as the difference in the total energies of the two states involved.

In a purely formal vein, this increased variational flexibility must result in a decrease in the binding energy (a relaxation energy) compared to Koopmans' result. More importantly, the relaxation energy has a very physical interpretation. It reflects an additional

rearrangement of the electrons in the system to shield the positive hole left by the ionization event. This response is a function of the molecular environment, and relaxation can have important consequences in phenomena such as the chemical shift and multiplet splitting.[18-20] As we will see in a later chapter, it is also responsible for one of the mechanisms which populate the satellite states observed in PES. Furthermore, the relaxation associated with core orbital ionization can be shown to be very similar to the orbital rearrangement which occurs in one of the most fundamental acid-base reactions: proton attachment. This relationship, when combined with the effects of changes in the initial state environment, means that shifts in core-level binding energies in a series of molecules can be related to the shifts in their proton affinities; a connection which provides insight into both core-level shifts and chemical reactivity.[21-23] Thus orbital relaxation plays an important role in PES as well as in other situations.

In carrying out the ΔSCF calculations proposed above, a problem arises which has its origins in McDonald's Theorem.[2] It can be summarized as follows: the N roots of the secular equation which results from applying the variation principle to a model function of N parameters necessarily yield upper bounds to only the N lowest exact solutions.

McDonald's Theorem is often used to argue that SCF and CI calculations on highly excited hole states of atoms and molecules are not necessarily upper bounds. For instance, the 1s hole state in neon lies well above all the excited states of $^2S$ symmetry based on the 2s hole state (including the continuum of "shakeoff" states). In

order to guarantee a rigorous upper bound to the energy of this state we would have to include at least as many configurations as there are lower states (an obvious technical difficulty since this number is infinite), or, alternatively, constrain the 1s hole state wavefunction to be orthogonal to the exact wavefunctions of all the lower states (another non-trivial problem). In spite of these difficulties, it is possible to do Hartree-Fock and configuration interaction calculations on these states that converge to a reasonable energy, and which (when compared to experiment) appear to provide upper bounds.[24,25] Bagus[24] has pointed out that this implies we have extremely closely satisfied the criterion of orthogonality to all lower states, a result which adds even more support to the shell model of electronic structure.

This author has never experienced any convergence or "variational collapse" problems in calculations on hole states in atoms. This is also the case for core levels in molecules, but not so for the valence molecular orbitals. The valence hole states of carbon monoxide serve as an explicit example of these problems. CO has the ground state SCF occupancy

$$1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma^2 1\pi^4 ({}^1\Sigma^+)$$

Although there are no problems in obtaining an SCF solution for the 5σ hole state (the lowest ionic state of ${}^2\Sigma^+$ symmetry), the 4σ hole state gradually collapses into the 5σ hole state during the course of the SCF iterations, as shown in Fig. 1.

These SCF results were obtained by an "annihilation of singles" procedure[26] utilizing a root-shifting technique suggested by Grein and

Chang.[27] While this root-shifting trick slows down the collapse, it does not prevent it. It is interesting to note that the 4σ hole state initially drops very quickly from the Koopmans' Theorem value, appears to level off a bit, and then collapses into the 5σ hole state. At first sight, one might expect a plateau to be a rather good approximation to the relaxed ionic state, and with a larger shift one can damp the collapse even more. It would be hazardous to conclude, however, that this plateau represents an upper bound and one would have to treat the solution with skepticism. In fact, a comparison of the binding energy predicted by the plateau (16.5 eV) vs the experimental result (19.8 eV) is not encouraging, since most ΔSCF calculations employing a basis set of similar quality reproduce valence level binding energies to within ±1.5 eV.

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0 0 0 0 4 5 0 6 3 2 3



FIGURE CAPTION

Fig. 1. An example of variational collapse is provided by plotting the energy of the carbon monoxide $4\sigma^{-1}$ SCF wavefunction vs the number of natural orbital iterations.[28] The energy quickly drops from the Koopmans' Theorem result (iteration 0), appears to be converging, and then collapses into the solution for the $5\sigma$ hole state (the lowest ionic state). The plateau does not appear to provide a reasonable approximation to the $4\sigma$ hole state (see text).

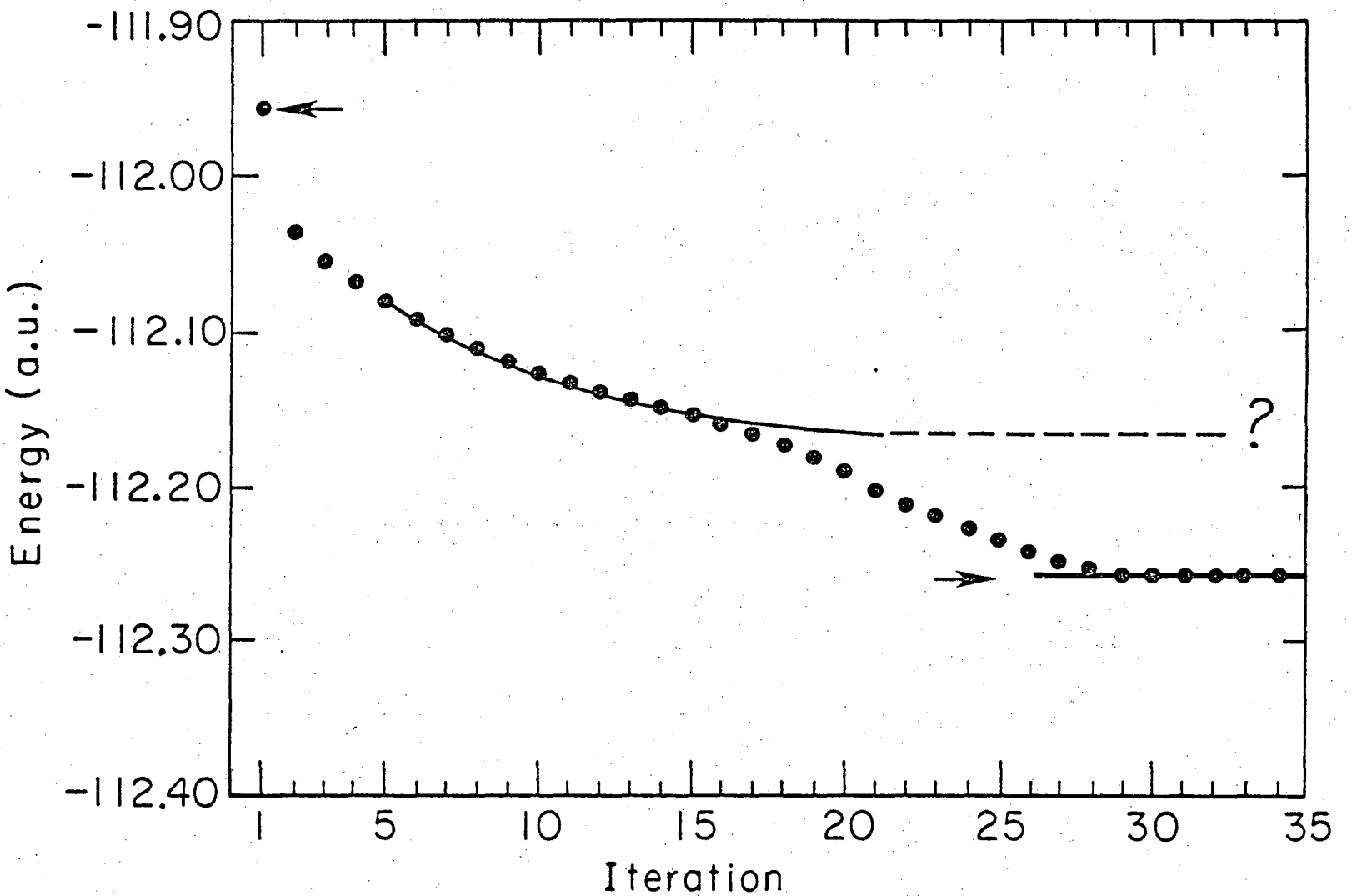


Fig. 1.

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## IV. THE FINAL STATE IN PHOTOIONIZATION

In Chapter 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 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 continuum function for the outgoing photoelectron must be chosen such that the N-electron final state satisfies the dipole selection rules. Thus ionization of the 1s electron in neon is 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 s or d waves coupled to a $^2P$ ionic core, again yielding a $^1P$ total final state. In a situation such as this, a completely general treatment should allow the s and d channels to mix. This could be termed a continuum state configuration interaction (CSCI) between the two $^1P$ final states. With an appropriate choice of continuum functions, however, this intra-channel coupling can be eliminated;[1] as a general

rule of thumb the $\ell \rightarrow \ell + 1$ channel dominates the photoionization cross section well above threshold ($\gtrsim$100 eV).

## B. Satellite States

Toward higher binding energy from each of these primary peaks there are generally satellites which reflect 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 20-80% as intense as the primary peak. The first satellites observed and assigned in X-ray photoelectron spectroscopy could be described as one-electron excitations accompanying ionization. These excitations followed "one-electron" monopole selection rules, e.g., ionization of the neon 1s 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 ionic 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 calculations described in Chapter VI have shown that the most intense satellites in the F 1s spectrum of hydrogen fluoride involve strong mixing of both $3\sigma \rightarrow 5\sigma$ (roughly F $2p_\sigma \rightarrow$ F 3s) and $1\pi \rightarrow 2\pi$ (F $2p_\rho \rightarrow$ F $3p_\pi$) excitations. Any attempt to describe this state as being reached by a <u>single</u> 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.

More recently, however, it has become increasingly apparent that the criterion for observation of this type of satellite is not that it follows one electron monopole selection rules, but rather that its dominant configuration has the possibility to mix with, and thereby gain intensity from, the primary hole state. For example, in the XPS spectrum of the argon atom there is a broad feature ~10 eV from the 3s primary hole state. This peak has an intensity of ~20% that of the 3s peak. Spears et al.[2] have suggested that most of the intensity in this region is due to the final ionic state ($3s^2 3p^4 3d; {}^2S$). Although this configuration differs by two orbitals from the primary ionic state ($3s^1 3p^6; {}^2S$), it mixes strongly and "steals intensity" from the

latter. Spears et al. termed this a "CI" satellite, but noted that in a more general sense the conventional "monopole" satellites also fell into this classification.

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 $Ne^+$ ($1s^1 2s^2 2p^5 3s$). This path is termed "conjugate shapeup" 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. The distinction in this case is complicated again when the many-electron nature of the wave-function is considered. The same ionic state could be imagined to be reached through ionization of the 2p electron accompanied by the monopole excitation $1s \rightarrow 3s$. The important factor is that the final ionic state has $^2P$ symmetry and cannot mix with the primary ionic state. A peak corresponding to this state has been observed by Gelius[3] and has an intensity of 0.06% relative to the 1s hole state.

The more common conjugate shakeup situation occurs when ionization and excitation occur in the same shell. For example, the final state $1s^2 2s^2 2p^4 3s(\varepsilon p)$, reached in the one-electron model through the transitions $2p \rightarrow \varepsilon p$, $2p \rightarrow 3s$, cannot be reached via the usual monopole selection rules. The ionic state also has the wrong parity to mix with 2p hole state. Wuillemier and Krause[4] have estimated that an upper limit for the intensity of this process relative to the normal case (final electron configuration $1s^2 2s^2 2p^4 3p$) 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, mercury, and lead.[5] The ground state of Hg, e.g., is described by the Hartree-Fock determinant

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

The 6s level primary ionic state

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

is observed as well as the conjugate state

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

The latter is roughly 1% as intense as the primary peak (at the He(I) photon energy). In a one-electron model, the conjugate excitation $6s \rightarrow 6p$ is invoked to explain the presence of this final state. Berkowitz et al.,[5] however, have shown that a great deal of the transition moment to this state is caused by admixture of the "nearly degenerate" configuration

$$[\text{core}]\ 6p^2\ (^1S)$$

into the <u>ground state</u> wavefunction. Thus the inclusion of correlation into the ground state of Hg is a very important mechanism of contributing to the observed satellite structure.

To summarize this qualitative overview of satellites we again point out that the ionic states observed fall into two classes: those which have the proper symmetry to mix with a nearby primary ionic state and those which do not. It will be shown in the next section that, in the absence of many-electron effects, there would be no satellites at all <u>observed</u> in photoelectron spectroscopy. For this reason the satellites are also referred to as "correlation peaks".

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## 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

$$\Psi_i(N) = \frac{1}{(N!)^{1/2}} |\phi_1(1)\ \phi_2(2)\ .\ .\ .\ \phi_N(N)| \tag{39}$$

and

$$\Psi_f(N) = \frac{1}{(N!)^{1/2}} |\chi(1)\ \phi_2'(2)\ .\ .\ .\ \phi_N'(N)| \quad . \tag{40}$$

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, $\chi(1)$, with the orbital $\phi_1$; i.e., if the set $\{\phi_2', \phi_3', \ .\ .\ .\}$ closely resembles $\{\phi_2, \phi_3, \ .\ .\ .\}$ 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[1]

$$T_{f\leftarrow i} = \langle \Psi_f(N) \left| \sum_{k=1}^{N} \underset{\sim}{\nabla}_k \right| \Psi_i(N) \rangle = \langle \chi | \underset{\sim}{\nabla}_1 | \phi_1 \rangle \langle \Psi_f(N-1,\chi,1) | \Psi_i(N-1,\phi_1,1) \rangle$$

$$+ \sum_{j=2}^{N} (-1)^{1+j} \langle \chi | \nabla_1 | \phi_j \rangle \langle \Psi_f(N-1,\chi,1) | \Psi_i(N-1,\phi_j,1) \rangle \quad .$$

$$+ \sum_{j=1}^{N} (-1)^{1+j} \langle \chi | \phi_j \rangle \langle \Psi_f(N-1,\chi,1) \left| \sum_{k=2}^{N} \underset{\sim}{\nabla}_k \right| \Psi_i(N-1,\phi_j,1) \rangle \quad . \qquad (41)$$

The notation $\Psi_f(N-1,\chi,1)$ refers to an N - 1 electron Slater determinant which is formed from the N-electron determinant by deleting the column containing the orbital $\chi$ and the row denoting electron 1; i.e.,

$$\Psi_f(N-1,\chi,1) = \frac{1}{[(N-1)!]^{1/2}} \begin{vmatrix} \phi_2'(2)\phi_3'(2) & \cdots & \phi_N'(2) \\ \phi_2'(3)\phi_3'(3) & \cdots & \phi_N'(3) \\ \vdots & & \\ \phi_2'(N)\phi_3'(N) & \cdots & \phi_N'(N) \end{vmatrix} \quad . \qquad (42)$$

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 $\chi$ has either $\alpha$ or $\beta$ spin (depending on the nature of $\phi_1$), certain terms in the sums over j in Eq. (41) vanish by spin orthogonality. For the present, however, we will retain the full expression, but simplify its appearance with the following definitions:

$$S^{1j} \equiv \langle \Psi_f(N-1,\chi,1)\ \Psi_i(N-1,\phi_j,1)\rangle$$

$$P^{1j} \equiv \langle \Psi_f(N-1),\chi,1)\left|\sum_{k=2}^{N} \underset{\sim}{\nabla}_k\right|\Psi_i(N-1,\phi_j,1)\rangle \quad .$$

Equation (41) is then given by

$$T_{f\leftarrow i} = \langle\chi|\nabla_1|\phi_1\rangle\ S^{11} + \sum_{j=2}^{N}(-1)^{1+j}\langle\chi|\nabla_1|\phi_j\rangle\ S^{1j} + \sum_{j=1}^{N}(-1)^{1+j}\langle\chi|\phi_j\rangle\ P^{1j} \quad . \tag{43}$$

The first term of Eq. (43) 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 $\langle\chi|\nabla_1|\phi_1\rangle$ can be non-zero only if $\chi$ 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 0.9 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., $\phi_2 = \phi_2'$, $\phi_2 = \phi_3'$, etc--all the sums in Eq. (43) would vanish, $S^{11}$ would be unity, and we would be left with the <u>active electron approximation</u>.

$$T_{f\leftarrow i} = \langle\chi|\nabla_1|\phi_1\rangle \quad . \tag{44}$$

In addition, if we consider an excited state "based" on the primary peak ($\phi_1$), the overlap integral $S^{11}$ vanishes and the satellites are therefore forbidden. Relaxation thus introduces a multiplicative

factor which reduces the contribution of the one-electron moment in the primary peak and distributes it among the various excited states.

The first sum over j in Eq. (43) stems 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. (43) arises from the action of the remaining momentum operators, $\nabla_2$ through $\nabla_N$. 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.[2]

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. (43)

$$\langle \chi_p | \nabla | 1s \rangle \, S^{1,1s}$$

will dominate. The normal shakeup mechanism is involved in the nonvanishing term

$$\langle \chi_p | \nabla | 2s \rangle \, S^{1,2s} \quad .$$

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

$$\langle \chi_p | 2p \rangle \; P^{1,2p}$$

involves ionization of the 2p electron, accompanied (roughly speaking) by the excitation 1s → 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

$$R_2 = \frac{\langle \chi_p | \nabla | 2s \rangle \; S^{1,2s}}{\langle \chi_p | \nabla | 1s \rangle \; S^{1,1s}} \tag{45}$$

If $R_2$ is substantial compared to unity, retention of the second term is warranted. Now

$$\frac{S^{1,2s}}{S^{1,1s}} << 1 \quad ;$$

in fact a rough estimate for this term based on Bagus' results[3] is $10^{-3}$. Furthermore $\langle \chi_p | \nabla | 2s \rangle / \langle \chi_p | \nabla | 1s \rangle$ 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

$$R_3 = \frac{\langle \chi_p | 2p \rangle \; P^{1,2p}}{\langle \chi_p | \nabla | 1s \rangle \; S^{1,1s}} \quad . \tag{46}$$

To estimate the factor $\langle \chi_p | 2p \rangle / \langle \chi_p | \nabla | 1s \rangle$ we note that if we choose a plane wave for $\chi_p$, i.e., $\chi_p \propto e^{i\underset{\sim}{k}\cdot\underset{\sim}{r}}$, then $\langle \chi_p | \nabla | 2p \rangle = ik \langle \chi_p | 2p \rangle$, and

$$\frac{|\langle \chi_p | 2p \rangle|^2}{|\langle \chi_p | \nabla | 1s \rangle|^2} = \frac{1}{k^2} \frac{|\langle \chi_p | \nabla | 2p \rangle|^2}{|\langle \chi_p | \nabla | 1s \rangle|^2} \quad . \tag{47}$$

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 <u>X-ray emission</u> transition moment--in the approximation in which relaxed orbitals are used for the initial (1s hole) state and the neutron 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 at XPS energies. Recently Williams[4] has analyzed the various terms for the specific case of Ne 1s ionization. In this work a Hartree-Fock continuum function was generated in the field of a fully relaxed core. It is found that the ratio $R_2$ was less than 10% from threshold to 2000 eV photon energy. $R_3$, however, was as

large as 0.65 a few eV above threshold. It quickly becomes small at higher photon energies and 100 eV above threshold is only ~10%. An interesting result of this work is that although the third term is large in the region about threshold, the first term is smaller than the analogous result using Koopmans' Theorem; the net effect is that the relaxed core and frozen orbital results are very similar near threshold and begin to deviate from one another only when the third term has become small.

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 over-estimation has been noted by Wuilemier and Krause[5] 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 wave-function which explicitly includes configuration interaction.[6]

## B. Configuration Interaction

Thus far we have used a single determinantal description for both the initial and final states, but accounted for relaxation within a ΔSCF model. From the discussion in Chapter III, it should be apparent that orbital relaxation could also be treated by using the ground state canonical orbitals in a CI expansion which includes configurations other than the primary ionic states. The configurations which would be necessary for describing the orbital polarization are the single excitations with respect to each primary state.[7] Including double replacements will give even better descriptions of the ionic states; the exact eigenstates ultimately being given by a full CI within the complete one-electron basis. The effect of these interactions will be to distribute the original primary ionic configurations over a number of roots of the Hamiltonian matrix, thereby providing one mechanism for populating satellites (final ionic state configuration interaction; FISCI). Thus, in the absence of initial state correlation, the satellite intensities are given by the projection of the Koopmans' Theorem hole state onto the exact ionic state wavefunctions.

In the discussion which follows a completely general orbital basis will be used. This is done because it is usually a necessity in actual practice. Although the equations which determine the satellite intensities become rather cumbersome in the general case, they are still essentially saying that the satellite intensity is governed by the projection of the frozen-orbital state (or a multi-determinantal variant of it) onto the exact wavefunctions. For detailed discussions of the theory of satellite intensities the reader is referred to the

papers of Åberg,[8] Martin and Shirley,[9] Manson,[10] and Basch.[11]

Suppose that the initial state is described by a multiconfiguration wavefunction $\Psi_0(N)$

$$\Psi_0(N) = \sum_m D_{0m}\Phi_m(N) \quad , \tag{48}$$

where $D_{0m}$ is the coefficient of the configuration $\Phi_m$ 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,

$$\Psi_{f'}(N) = \sum_n D_{f'n}\Phi'_n(N) \quad , \tag{49}$$

where the primes on the configurations denote that they have been formed from a set of orbitals appropriate for the final state. Note that the configurations are functions of all N electrons and we should, therefore, in principle allow for the possibility of mixing among the various channels in the continuum (CSCI),[10] a phenomenon which can have marked effects on absolute cross sections. In addition, $\{\Phi'(N)\}$ should also include any "bound states" which may be imbedded in the continuum. Mixing of this sort leads to autoionization and greatly enhances the photoionization cross section. Autoionization also has a very dramatic effect on the satellite intensities in Ba

excited by He I radiation.[12] In the case of XPS satellites, however, these effects have thus far not been crucial to an understanding of the structure of the spectrum and we, therefore, specialize to the case where each configuration contains the same one electron function $\chi_{f'}$, and perform the CI on the ion alone. Thus

$$\Psi_{f'}(N) = \chi_{f'}(1) \sum_n C_{f'n}\Phi_n'(N - 1) \quad . \tag{50}$$

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. (48) and (50) into the expression for the transition moment (Eq. (41)) yields

$$T_{f'0} = \sum_{m,n} C^*_{f'n} D_{0m} \langle \chi_{f'} | \nabla | \phi_1 \rangle \, S^{11}_{nm} + \ldots \tag{51}$$

We have again assumed that the final state predominantly involves ionization from orbital $\phi_1$. $S_{nm}$ is the (N - 1) electron overlap integral between configurations n and m and the dots represent the other terms obtained. These additional terms have been examined for the F 1s satellites in HF and been found to be negligible (see Chapter VI). In view of the previous discussion they should be small for core-level ionization in general (well above threshold) and will be neglected.

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

$$\frac{T_{00}}{T_{f'0}} \approx \frac{\langle \chi_0 | \nabla | \phi_1 \rangle}{\langle \chi_{f'} | \nabla | \phi_1 \rangle} \frac{\sum_{m,n} C^*_{0n} D_{0m} S^{11}_{nm}}{\sum_{m,n} C^*_{f'n} D_{0m} S^{11}_{nm}} \quad . \tag{52}$$

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",

$$\frac{I_{00}}{I_{f'0}} \approx \frac{\left| \sum_{m,n} C^*_{0n} D_{0m} S^{11}_{nm} \right|^2}{\left| \sum_{m,n} C^*_{f'n} D_{0m} S^{11}_{nm} \right|^2} \quad . \tag{53}$$

This expression, which arises from a straightforward application of first-order time dependent perturbation theory, is identical in form to a multi-determinantal extension of Åberg's application of the sudden approximation to satellite intensities.[8]

To illustrate these CI effects, we have drawn a state diagram for neon in Fig. 1. On the left is the Hartree-Fock level for the ground state and one of its excited configurations; above these are the primary ionic state and a first approximation to the "shakeup" state. For simplicity, we have suppressed the exchange interaction in the ionic states; i.e., there are actually two $^2S$ states which result from the configuration $1s2s^2 2p^5 3p$. 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 coefficients to the configurations in each eigenstate. These have magnitudes

$$a_0 \, , \, a_0' \, , \, b_0' \sim 1$$

$$a_1 \, , \, a_1' \, , \, b_1' \sim 0.1$$

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 A, 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 B might also contribute an amount of the same order of magnitude since, although the product of coefficients is

small, the determinantal overlap is large. Path B is the predominant contribution to the argon satellite ($3s^2 3p^4 3d$) mentioned earlier. Table 1 shows the results of calculations performed on the argon ion. As is evident from a study of the table, the 3s hole state has a very large admixture of $3s^2 3p^4 3d$, a "nearly degenerate" configuration.[13] By simple orthogonality arguments, this leads to a large contribution of the primary ionic configuration in the satellite, and hence a large relative intensity via path B. The simple rule which follows from these arguments is that the dominant configurations of the most intense satellites observed in a PES spectrum should be those which mix strongly with the primary hole state, i.e., those configurations which originate from an internal correlation mechanism. It is also important to realize that the ionization event produces a hole in the Hartree-Fock sea; distributions which were not allowed in the ground state may now become possible.

The two contributions mentioned thus far arise from FISCI. For similar reasons, the analog of path C is also important for the satellites and it arises through an initial state CI mechanism. The contribution from path D is obviously smaller than the others. An example of the importance of initial-state configuration interaction (ISCI) is found in the case of the Ne 1s satellites. In Table II I have compared the satellite intensities computed using a common final state wavefunction with the Hartree-Fock and a correlated initial state. This will be discussed further in Chapter VII, but it can be seen that the introduction of path D nearly doubles the predicted satellite intensities and brings them into very good agreement with experiment.

ISCI also provides a means of populating states which cannot mix with the primary ionic state. For instance, beryllium is described by the Hartree-Fock configuration $1s^2 2s^2$. The satellite $1s^2 2p(^2P)$ cannot mix with the primary hole state $1s^2 2s(^2S)$. There is, however, an admixture of $1s^2 2p^2$ in the ground state of Be, i.e.,

$$\Psi_{Be} = C_1 |1s^2 2s^2| + C_2 |1s^2 2p^2| + \ldots \tag{54}$$

The latter determinant can give rise to a transition moment of the form

$$C_2 \langle 2p' | 2p \rangle \langle {}^{\varepsilon s}_{\varepsilon d} | r | 2p \rangle$$

The relative intensity of the satellite is then

$$\frac{I_{2p}}{I_{2s}} \cong \frac{C_2^2}{C_1^2} \frac{\langle 2p' | 2p \rangle^2}{\langle 2s' | 2s \rangle^2} \frac{\left| T_{\substack{\varepsilon s \\ \varepsilon d}} \leftarrow 2p \right|^2}{|T_{\varepsilon p \leftarrow 2s}|^2} \tag{55}$$

The two overlap integrals are presumably very nearly equal. If the same can be said for the one electron moments T, the experimental results could be used to determine the relative amplitudes of the mixing coefficients, a very exciting possibility. More work is needed to determine if this will actually be the case.[14]

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.[15] 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 (strong internal

correlation possibilities, 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.

### C. Sum Rules on Energy and Intensity

At the beginning of the last section, FISCI was qualitatively introduced by expanding the actual eigenstates of the ion in terms of the Koopmans' primary ionic states and additional excitations derived from them. Two interesting sum rules arise when we invert this idea and expand the frozen orbital ionic state in terms of the actual eigenstates. The first relates the difference in energy between the Koopmans' state and the exact primary hole state to the intensity and energy of the satellites, and the second is concerned with the relationship between photoionization cross sections computed with frozen orbitals and exact eigenstates.

Both sum rules begin with the observation that the eigenstates of the ionic Hamiltonian form a complete set, and we can obviously write the expansion

$$\Psi_{K\Gamma}^{-i} = \sum_{j=0}^{\infty} \langle \Psi_j | \Psi_{K\Gamma}^{-i} \rangle \, | \Psi_j \rangle \equiv \sum_{j=0}^{\infty} C_{ij} | \Psi_j \rangle \quad . \tag{56}$$

The sum over j includes <u>all</u> ionic states; it converts to an integral over any continua.

If we take the expectation of the Hamiltonian for this state, we find

$$\langle \Psi_{KT}^{-i} | \mathcal{H} | \Psi_{KT}^{-i} \rangle = \sum_{k,j} c_{ik}^{*} c_{ij} \langle \Psi_k | \mathcal{H} | \Psi_j \rangle \tag{57}$$

or

$$E_{KT} = \sum_{j=0}^{\infty} c_{ij}^2 E_j \tag{58}$$

The coefficient $c_{i0}$ denotes the projection of the Koopmans' state onto the exact primary hole state and $c_{ij}^2/c_{i0}^2$ is thus the relative intensity of the satellite j ($I_j/I_0$--assuming constant transition moment, etc from Section B). This can be arranged into the normalized form (recalling that $\sum_{j=0}^{\infty} c_{ij}^2 = 1$)

$$E_{KT} = \frac{\sum_{j=0}^{\infty} (I_j/I_0)\ E_j}{\sum_{j=0}^{\infty} (I_j/I_0)} \tag{59}$$

We see that the Koopmans' Theorem ionic state energy is the intensity weighted centroid of the PES spectrum. Another interesting form is obtained by subtracting $E_0$ from both sides,

$$E_{KT} - E_0 = \frac{\sum_{j=1}^{\infty} (I_j/I_o)(E_j - E_0)}{\sum_{j=0}^{\infty} (I_j/I_o)} \tag{60}$$

or

$$E_R = \frac{\sum_{j=1}^{\infty} (I_j/I_0)\, \Delta_j}{\sum_{j=0}^{\infty} (I_j/I_0)} \tag{61}$$

The quantity $E_R$ is the energy difference between Koopmans' approximation and the actual final state energy. It should be very nearly equal to the ΔSCF relaxation energy, even though it contains some additional correlation energy.

This relationship was first pointed out by Lundqvist[16] and Manne and Åberg.[17] Since all the quantities on the right hand side of Eq. (61) are experimentally determinable, in principle this provides a means for experimentally finding the relaxation energy. In practice this is usually not possible because the intensity distribution over the double ionization ("shakeoff") continuum is not easily extracted from the spectrum.

From Eq. (61) 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.

There is another sum rule which follows directly from the expansion of Eq. (56) and the discussion in the earlier part of this chapter. In our notation, this can be written

$$\sigma_{KT}^{-i} = \sum_{j=0}^{\infty} \sigma_j \tag{62}$$

This says that the cross section for ionization to the frozen orbital state $\left(\psi_{KT}^{-i}\right)$ is actually the sum of the cross sections to the actual hole state and the satellites based on it. This was initially pointed out and discussed by Fadley.[18] He stressed that because of this, orbital ionization cross sections computed using frozen orbitals are not directly comparable to experimental cross sections observed in PES, but are more appropriate for experimental situations where no discrimination on the basis of ionic state energy is made.

## D. Good Things to Know and Tell

It is unfortunately the case that the accurate determination of these ionic state wavefunctions is an extremely difficult task. Only recently have reliable calculations of satellite spectra begun to appear in the literature, and much of this work is still in preprint form.[19] Difficulties encountered in ionic state calculations which do not generally arise in more standard calculations on the ground states of atoms and molecules are that (a) the ionic states actually

lie in a continuum and appropriate precautions should be taken (see footnote 13); (b) one desires to treat several states (the specific ones being generally unknown beforehand) at an equally good (or poor) level of sophistication; and (c) the satellites usually contain several open shells and are not always dominated by a single reference configuration.

Because of these problems, there are no really "standard" models which have evolved to treat the problem, and the experimentalist attempting to evaluate the quality of a calculation must be rather well versed in the various approximations and techniques of ab initio calculations. In fact, most of my time on these problems was spent learning exactly "what you can get away with". It seems appropriate, therefore, to enumerate a few of the computational details which should be present (or at least examined) in a good calculation to ensure semi-quantitative results.

(1) The basis set should be at least of double zeta plus polarization quality. For instance, we found that the order of the first two ionic states of $N_2$ $(5\sigma^{-1},1\pi^{-1})$ reverses when one simply adds a single d (polarization) function to each atomic center. If one is attempting to describe satellites which are Rydberg-like, additional diffuse functions are obviously necessary. It is also important to realize that the "valence" excited states of some neutral molecules are also partially Rydberg-like in character.[20] This will presumably also be the case for valence-like satellites as well.

(2) It is desirable to treat both the primary state and the satellites at the same level of accuracy in the CI calculation. The union of all single excitations with respect to all reference states

can remedy the problem encountered in choosing an occupied orbital basis which will describe both the primary state and the satellites. The neglect of this is a criticism which can be leveled at the first work on this problem that I did, the HF calculations reported in the next chapter. If possible, the internal correlation effects in each reference state should also be included in the configuration list, since they can have important consequences on the mixing coefficients. This, unfortunately, can lead to a very large Hamiltonian matrix. A somewhat more restrictive model, but one which should be reasonably good and within reach, is similar to Schaefer's "first order" configuration list.

In this approach, one first generates all single and double replacements in the internal space. These configurations should be the ones which mix most strongly with the primary ionic state and are therefore the prime a priori candidates for the most intense satellites. Considerations of near degeneracy and simple perturbation theory should allow one to choose a subset ot these as reference states. In the same manner that these were selected by referring to the primary state, the internal excitations expected to be most important for each satellite are then included. The union of all single replacements into the full space with respect to all reference states then completes the list and accounts for the orbital polarization needed. The net effect of this is to include the major internal correlation and orbital polarization contributions for both the primary state and the satellites. In defining the virtual orbitals which compose part of the internal space, natural orbital analyses and/or multi-configuration

SCF calculations may be helpful.

(3) There is always the possibility of an interaction with the continuum. This problem can be treated in certain approaches,[21] but it is difficult to do so in standard bound state CI approaches.

(4) The importance of initial state correlation has already been pointed out. In terms of the model for the final ionic state wavefunction presented in (2), the ground state wavefunction should include at least the internal correlation contributions.

(5) In valence shell ionization, primary ionic states of the same symmetry are close in energy, and there may be substantial mixing among them, as well as with the satellite configurations. In these situations, the overlap model for treating intensity may be inadequate. The intensity should be given by the projection onto each primary Koopmans' state weighted by the appropriate one-electron transition moment.

These considerations should be taken into account in any calculation which aspires to semi-quantitative results. For more qualitative purposes, such as simply assigning the satellites to a specific configuration(s), less sophisticated approaches may be adequate.[22]

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Table I. Configuration interaction wavefunctions for $Ar^+(^2S)$.*

| Root | $E_{CALC}$ | $E^{**}_{EXP}$ | $I^{\dagger}_{CALC}$ | $I^{\dagger\dagger}_{EXP}$ | Configurations | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | $3s^1 3p^6$ | $3s^3 3p^4 4s$ | $3s^2 3p^4 3d$ | $3s^2 3p^4 4d$ | $3s^2 3p^4 5s$ |
| 1 | -525.8845 a.u. (0.0) | 0.0 eV | 100% (0.63) | 100% | 0.794 | 0.028 | 0.464 | -0.186 | -0.008 |
| 2 | 8.8 eV | 7.3 eV | 2.5% | 4±2 | 0.126 | 0.864 | -0.350 | -0.095 | -0.019 |
| 3 | 10.4 eV | 9.3 eV | 14.4% | 17±2 | 0.301 | -0.385 | -0.699 | -0.395 | -0.029 |
| 4 | 13.0 eV | 12.0 eV | 15.1% | 6±3 | 0.309 | -0.078 | -0.265 | +0.830 | -0.117 |
| 5 | 14.8 eV | --- | 0.6% | --- | -0.061 | 0.004 | 0.058 | -0.087 | -0.940 |

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†These values all pertain to the Hartree-Fock initial state. The square of the overlap in the 3s hole state is given parenthetically, all others are percentages relative to it.

††D. P. Spears, H. J. Fischbeck, and T. A. Carlson, Phys. Rev. A 9, 1603 (1974). These values are an average of the $AlK_\alpha$ and $MgK_\alpha$ results.

Table II. Neon 1s correlation-state energies and intensities.[a]

| State | $\Delta E$(theo)[b] | $\Delta E$[c](exp) | $I^{d}_{HF}$(theo) | $I^{e}_{ISCI}$(theo) | $I^{f}$(exp) |
|---|---|---|---|---|---|
| (1s hole-state) | 0.0(-96.694 a.u.) | 0.0 | 100(0.824) | 100(0.774) | 100 |
| 2p→3p | 36.4 | 37.35(2) | 1.26 | 2.47 | 3.15(10) |
| 2p→3p | 39.9 | 40.76(3) | 1.68 | 2.60 | 3.13(10) |
| 2p→4p | 41.9 | 42.34(2) | 0.85 | 1.48 | 2.02(10) |
| 2p→5p | 43.0 | 44.08(5) | 0.24 | 0.43 | 0.42(06) |
| 2p→6p | 45.2 | 45.10(7) | 0.05 | 0.09 | ~0.15 |
| 2p→4p | 46.0 | 46.44(5) | 0.46 | 0.70 | 0.96(11) |
| 2p→5p | 47.4 | 48.47(7) | 0.07 | 0.11 | 0.17(05) |
| 2p→6p | 49.5 | --- | 0.04 | 0.06 | --- |

[a]From R. L. Martin and D. A. Shirley, Phys. Rev. A, 13, 1475 (1976).

[b]Absolute energy of the 1s hole state in Hartree atomic units given parenthetically; all others in eV relative to it.

[c]Relative energies (from Ref. 3, Chapter IV), in eV.

[d]Hartree-Fock initial state wavefunction; the parenthetical number is the square of the actual overlap in the 1s-hole state. The relative peak intensities are given as percentages of this value.

[e]Correlated initial state wavefunction; this included double excitations into the Rydberg orbitals for the ground state; i.e., configurations of the form $1s^2 2s^2 2p^4 np^2$, etc.

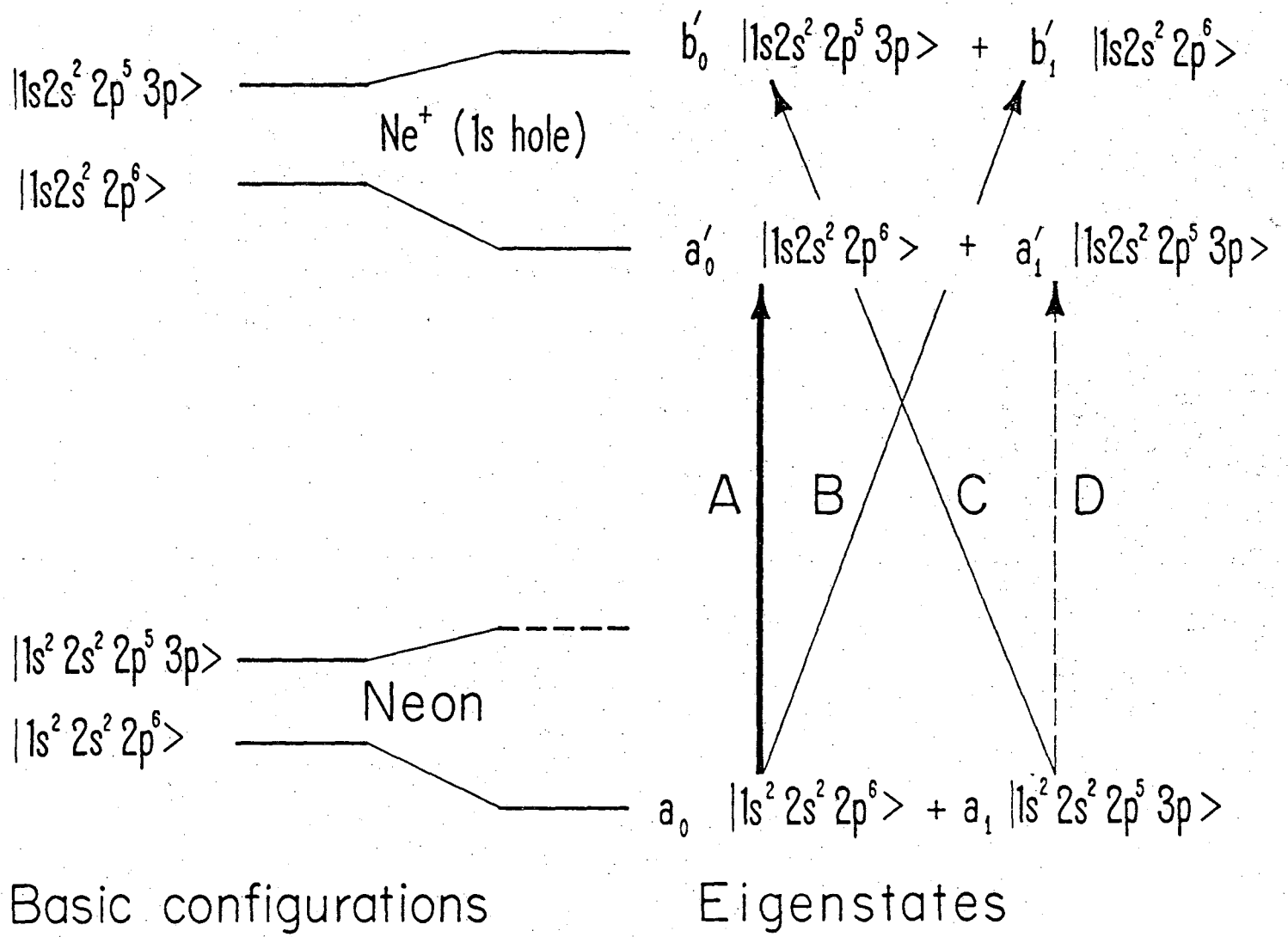
[f]From Ref. 3, Chapter IV. We have estimated a value for the (2p→6p) state from Gelius' figure.



0 0 0 0 4 5 0 9 3 4 0

FIGURE CAPTIONS

Fig. 1. Simple model to illustrate the effect of initial-state configuration interaction on correlation-peak intensities in Ne 1s photoemission (not to scale). With 1s exchange suppressed, the $Ne^+$ (1s hole) configuration manifold would closely resemble the ground state manifold (left). Introducing configuration interaction, this 1:1 correspondence would also obtain for the eigenstates (right), and $a_0 \sim a_0'$, $a_1 \sim a_0'$, etc. The main peak arises primarily from path A. Paths B and C arise because the two configurations "look for themselves" in the correlation state. They are of roughly equal strength, but the dashed path (D) is weak.




XBL759-4146

Fig. 1.

# VI. HYDROGEN FLUORIDE SATELLITE STRUCTURE

## A. Introduction

Photoemission spectra of atomic core levels in atoms and molecules yield for each core level j a main peak at an electron kinetic energy

$$K = \hbar\omega - E_B^{(0)} \quad . \tag{63}$$

Here $\hbar\omega$ is the photon energy and $E_B^{(0)}$ is the binding energy of core level j. This main peak corresponds to a special atomic or molecular ion final state. In a single-determinant description, this state would be formed from the ground state by removing an electron from orbital j and allowing the wavefunctions of the passive electrons to relax adiabatically (i.e., without changing their quantum numbers).

If $\hbar\omega$ is substantially larger than $E_B^{(0)}$, additional weak satellite peaks may also be observed at higher binding energies $E_B^{n'}$. Qualitatively, one usually describes these states as arising from at lease a two-electron excitation from the ground state (ionization accompanied by "shakeup"). A quantitative theoretical treatment of the transition cross section to such states, however, shows that one-electron descriptions may be misleading. The cross section for such a transition owes much of its strength to many-body effects. In particular, configuration interaction (CI) in both the initial and final state is required; hence, the latter are more accurately described as "correlation states", and the satellite peaks as "correlation peaks".

The theoretical formalism for calculating correlation-state spectra was described in the preceding paper[1] (hereafter called I). We report in the present paper a complete study of the fluorine 1s correlation-state

spectra in gaseous HF. To our knowledge this is the first case in which several of the theoretical nuances developed in I have been applied. It is also the first case showing quantitative agreement between experiment and theory.

Experimental procedures and results are given in Section B. Section C describes both the means of obtaining the necessary wave-functions and the method used to compute intensities. Conclusions are drawn in Section D.

## B. Experimental

The gaseous sample was obtained by a evaporation of 99.9% + pure liquid HF, purchased from Matheson Gas Products, Inc. At 26°C the association constants of HF are:[2]

$$2\ HF \rightleftharpoons (HF)_2 \quad \log\ \beta_2 = -3.80 \quad ,$$

$$6\ HF \rightleftharpoons (HF)_6 \quad \log\ \beta_6 = -13.94 \quad ,$$

with pressures expressed in torr. Thus oligomerization is unimportant at the pressures of <1 torr used in this work.

The photoelectron spectra were obtained using $AlK\alpha_{1,2}$ X-rays (1486.6 eV) on the 50 cm radius Berkeley iron-free magnetic spectrometer.[3] Spectral data points were taken at ~0.4 eV energy increments, at pressures of ~50 and ~350 microns (Fig. 1). The analyzer chamber was maintained at a pressure of approximately $10^{-5}$ torr. The high pressure spectrum was used to determine which of the satellites of the F 1s main line were caused by inelastic electron collisions since the relative intensities of these peaks should increase with pressure. If the low pressure spectrum (Fig. 1b) is subtracted from the high pressure

spectrum (Fig. 1a), with appropriate weighting to equalize the main F 1s peaks, the result is an inelastic electron loss spectrum.

The low pressure spectrum was fitted (Fig. 2) using a non-linear least squares program which automatically took into account the (weak) $AlK\alpha_3$ and $K\alpha_4$ components as well as the slight change of the energy window caused by the magnetic spectrometer (which produces spectra linear in momentum). The main peak, corresponding to the F 1s hole state, was fitted best by a sum of three Lorentzian functions and these were used as the fundamental form for the "correlation" peaks.

No attempt was made to locate satellites with intensity 0.1% or less of the main peak. It was necessary to fix the area ratios and separations of states 7 and 10 relative to their large neighbors (5 and 9 respectively). Theoretical area ratios and separations, described below, were used for these two cases.

Because of the large number of unknowns, the energy positions and full widths at half-maximum (FWHM) of a few peaks were initially fixed, and the fitting program was constrained to vary only the parameters for those remaining. These newly found optimum parameters were then frozen and the rest of the set (those originally fixed) varied. This successive approximation technique was continued until a self-consistent set of parameters was found. The quality of the fit was judged from the statistical $\chi^2$ and visual examination of the plot (Fig. 2).

The results in Table I indicate that the theoretical intensities are in excellent agreement with experiment. Theoretical energies, relative to the main line, are 2.1 to 3.5 eV higher than experiment.[4]

For the weaker satellites which are relatively near the double ionization ("shakeoff") limit, this excellent agreement is obtained only with a deconvoluted peak which has a very large FWHM. We regard such close agreement with experiment in this region as largely fortuitous. As the shakeoff limit is approached, one would expect to begin to observed Rydberg series. Our spectrometer cannot resolve these and our calculations should become progressively less reliable as the limit is approached. Thus both the experimental and theoretical intensities in this region may have rather large error bars. These problems in no way affect the major conclusions of our work.

## C. Theoretical

The correlation-peak spectrum was calculated using the theoretical formalism described in I.[5] Two major levels of sophistication were used for the wavefunctions necessary in this work. First, configuration interaction among the ionic final states was considered, with the ground state represented by a single Slater determinant. In the next step, CI in the ground state was also included. For each of these cases the relative intensities of the correlation peaks were computed in the overlap approximation.

It was shown in I that, except for terms to be discussed in Appendix I (which are small for core-level satellites), the dipole and sudden approximations give identical results in the overlap approximation. Results are displayed in Table I for final state CI (Method A) and for initial state CI (Method B). In addition an estimate of the variation in the energy-dependent term was obtained assuming the photoelectron continuum function to be represented by a plane wave. This causes the relative intensities calculated from the dipole

approximation and the energy dependent form of the sudden approximation (i.e., before the $k\to\infty$ limit is taken) to be very slightly different.. The variation in the energy-dependent factor, Q(E), is shown in Table II. The product of this factor and the overlap term gives the final set of relative intensities shown in Table II.

The means of calculating the various wavefunctions are discussed in Section C-1 followed by a description of the one-electron basis set in Section C-2. Section C-3 deals with the overlap and energy-dependent portions of the cross section.

1. The Wavefunctions

A set of SCF orbitals was found for the ground state occupancy

$$1\sigma^2 2\sigma^2 3\sigma^2 1\pi^4 (^1\Sigma^+) \quad ,$$

by using an iterative natural orbital "annihilation of singles" technique.[6,7] The energy obtained with this technique is identical to that which would follow from a standard Hartree-Fock-Roothaan calculation. The orbitals, however, are natural orbitals instead of the standard canonical set which diagonalize the Fock matrix. They were transformed into the canonical set by the appropriate unitary transformation.

Using the canonical orbitals found in this way as trial vectors, a further "annihilation of singles" calculation was carried out on the ion $HF^+$ at the internuclear separation of the neutral molecule. This yielded a wavefunction for the single configuration $1\sigma^1 2\sigma^2 3\sigma^2 1\pi^4 (^2\Sigma^+)$, which will be termed the "reference state". It corresponds to the F 1s hole state, and represents the wavefunction which would be found by applying the Hartree-Fock-Roothaan equations to this open shell single determinant.

To obtain appropriate wavefunctions for the excited states in the vicinity of the reference state, a configuration expansion was employed. All single excitations with respect to the reference state which possessed $^2\Sigma^+$ symmetry were included. For our basis set of 14σ and 6π molecular orbitals, this results in 66 configurations. These can be represented.

$$2\sigma^2 3\sigma^2 m\sigma 1\pi^4 \qquad (1\sigma \rightarrow m\sigma)$$
$$1\sigma^1 2\sigma 3\sigma^2 m\sigma 1\pi^4 \qquad (2\sigma \rightarrow m\sigma)$$
$$1\sigma^1 2\sigma^2 3\sigma m\sigma 1\pi^4 \qquad (3\sigma \rightarrow m\sigma)$$
$$1\sigma^1 2\sigma^2 3\sigma^2 1\pi^3 n\pi \qquad (1\pi \rightarrow n\pi) \quad .$$

For the last three types there are three electrons outside closed shells; thus <u>two</u> $^2\Sigma^+$ configurations exist for each single excitation. Both of these configurations were included in the expansion.[8]

With the one-electron basis set defined by the orbitals for the F 1s reference state, the Hamiltonian matrix within this configuration space was formed and diagonalized. We assume that the resulting roots and eigenvectors are reasonably good approximations to those excited $^2\Sigma^+$ states of $HF^+$ that lie in the energy region near the reference state.[9]

Initially we hoped that by limiting the expansion to single excitations, each excited state could be rather straightforwardly interpreted in terms of a one-electron transition from the reference state. We found, however, that when the virtual canonical orbitals of the reference state were used in the one-electron basis, several excitations mixed strongly in the eigenvectors of interest. In other words, the unoccupied eigenvectors from the hole-state calculation

are not very good approximations to the excited-state orbitals. For this reason, the virtual canonical orbitals were transformed into a set appropriate for describing the motion of an electron in the field of an N-2 electron core. The orbitals found in this way reflect more closely the potential experienced by the "excited" electron. This transformation has been used in similar problems previously,[10] and we will not discuss it here. This new starting set gave, in most cases, excited states which could be well described in terms of one-electron excitations from the reference state determinant.

The description of the ionic states was concluded by performing a final SCF calculation on the ion $HF^{2+}$ in the configuration

$$1\sigma^1 2\sigma^2 3\sigma^2 1\pi^3 (^3\Pi) \quad .$$

The energy of this state relative to the reference state is interpreted as the threshold of "shakeoff" phenomena.

A brief discussion of the rationale involved in the computation of the initial state CI wavefunction seems in order. After the work on ionic HF, we knew the general nature of the correlation states which could be described by our basis set; in particular, we knew the predominant virtual molecular orbital involved in describing a given correlation state. This dictated the choice of the configuration expansion for the ground state. The virtual orbitals important in describing the correlation states correspond reasonably well to the first four virtual $\sigma$ orbitals and first three virtual $\pi$ orbitals in the ground state calculation (see Table III). The excited configurations in the initial state involving these orbitals should then be the ones possessing a large overlap integral with the correlation states. Our

approach was, therefore, to reduce the ground state virtual space to include only these orbitals. All single and double excitations from the valence orbitals ($3\sigma,1\pi$) into this reduced set (generating a total of 105 configurations) were included.[11] This reduction was necessary due to the size limitations of our computer programs and the expense involved in computing the transition moments involving non-orthogonal orbitals.

2. The Basis Set for Hydrogen Fluoride

The basis set finally chosen consisted of normalized Slater-type orbitals (STO's). It is set out in Table III. The requirements that the basis set must satisfy are twofold. First, it was found that a double-zeta description of the valence orbitals is necessary to account correctly for the effects of electronic relaxation in the F 1s hole state. Furthermore, the proper Rydberg-type orbitals must be included in the basis set in order to obtain a reliable description of the excited states. We approached this problem by augmenting the double zeta basis set of Huzinaga and Arnau[12] for the fluorine atom with a 3d polarization function ($\xi$ = 2.500) and two H 1s functions (exponents 1.000 and 1.500). To this set we systematically added Rydberg-type orbitals on the fluorine atom. A total of eight calculations were performed in this way. The final set consisted of fourteen sigma- and six pi-type functions.

In the first few calculations, Rydberg orbitals on fluorine were chosen on the basis of Slater's rules. One might expect, in the united-atom limit, that the orbitals of the $He^+$ ion ($n \geqslant 3$) would be appropriate for the Rydberg states based on the F 1s hole state. We

found, however, that the exponents estimated in this way were too diffuse.[13] The final set contains orbitals with exponents slightly larger than those suggested by Slater's rules.

Not all of the excited states that can be calculated for a given basis set will have physical significance. Our final basis gave stable energies and transition moments, with respect to addition of further orbitals and slight modifications of the exponents of existing orbitals, for those excited states which we felt were physically reasonable. It does not represent an optimized set of orbitals; rather it is one which is sufficiently flexible to meet our particular needs. The philosophy of our approach was to employ a large enough basis set in the $HF^+$ CI calculation to reproduce the lowest 10 "shakeup" states reliably both in energy and in orbital composition (hence in peak intensity). These are the states that appear clearly in the experimental spectrum before the "shakeoff" ionization limit.

An indication of the completness of the basis set for at least two of the states of interest here is afforded by comparison with previous work. The final set chosen gives an SCF energy of -100.0553 a.u.[14] for the $^1\Sigma^+$ ground state of HF. The near Hartree-Fock result of Cade and Huo[15] is -100.0703 a.u. The same basis yields an energy of -74.5670 a.u. for the F 1s hole state, to be compared with Schwartz's result of -74.5365 a.u.[16] The calculated F 1s binding energy is 693.5 eV, which is slightly higher than the value of 693.3 eV reported by Schwartz. Our $^3\Pi$ shakeoff limit falls at -73.2872 a.u., or 34.8 eV above the primary hole state.

The compositions of the molecular orbitals which are most important for describing "shakeup" phenomena in HF are given for the ground state and the ionic states in Table IIIA and Table IIIB respectively.

3. Intensity Calculations

The intensity of each final-state peak relative to that of the main peak was first calculated in the overlap approximation (Eq. (23b) or Eq. (26b) from Section III-A). If only final-state CI was considered (Method A), the relation

$$\frac{I(n')}{I(0)} = \frac{\left|\sum_n C^*_{n'n} S^{11}_n\right|^2}{\left|\sum_n C^*_{0n} S^{11}_n\right|^2} \tag{64}$$

is appropriate. The extension of the theory to include configuration interaction in the initial-state (Method B) leads to

$$\frac{I(n')}{I(0)} = \frac{\left|\sum_{n,m} C^*_{n'n} C_{0m} S^{11}_{nm}\right|^2}{\left|\sum_{n,m} C^*_{0n} D_{0m} S^{11}_{nm}\right|^2} \quad . \tag{65}$$

Here $C_{n'n}$ and $D_{0m}$ are the coefficients of the configurations (n and m) in the eigenvectors of the final and initial states, respectively. For HF these would have the form

$$\begin{aligned} |\Psi_f^{(n')}\rangle = {} & C_{n'0}|1\sigma 2\sigma^2 3\sigma^2 1\pi^4 (^2\Sigma^+)\rangle \\ & + C_{n'1}|1\sigma 2\sigma^2 3\sigma 4\sigma 1\pi^4 (A^2\Sigma^+)\rangle \\ & + C_{n'2}|1\sigma 2\sigma^2 3\sigma 4\sigma 1\pi^4 (B^2\Sigma^+)\rangle + \ldots \end{aligned}$$

$$|\Psi_i^{(0)}\rangle = D_{00}|1\sigma^2 2\sigma^2 3\sigma^2 1\pi^4(^1\Sigma^+)\rangle + D_{01}|1\sigma^2 2\sigma^2 3\sigma 4\sigma 1\pi^4(^1\Sigma^+)\rangle + \ldots$$

where, for the final state $|\Psi_f^{(n')}\rangle$, the two linearly independent doublet spin functions which can be constructed from the orbital occupancy are denoted by A and B.

The overlap functions $S_{nm}^{11}$ were discussed in Section III-A. Here they actually refer to a sum of determinantal overlap integrals, the nature of the sum being determined by the expansion coefficients of the Slater determinants in the configuration. For HF the superscripts "11" refer to the deletion of the row containing electron 1 and the column containing the basis function $1\sigma\beta$ from the ground state determinant(s).

Analysis of the energy dependent factor in the cross section, Q(E), requires specification of the photoelectron continuum function $|\chi\rangle$. For the purposes of estimation, we chose the plane wave approximation

$$\chi = (2\pi)^{-3/2} e^{i\underset{\sim}{k}\cdot\underset{\sim}{r}} \quad .$$

For a given photon energy, this term in the dipole cross section is

$$Q(E)_{DIPOLE} = \rho(E)\,|\langle\phi_{1\sigma}|\underset{\sim}{\nabla}|\chi\rangle|^2 \propto k^2\rho(E)\,|\langle\phi_{1\sigma}|\chi\rangle|^2 \qquad (66)$$

where k is the wavevector of the photoelectron, $\rho(E)$ is the density of final continuum states (proportional to k), and $\langle\phi_{1\sigma}|\chi\rangle$ is the overlap of the $1\sigma$ orbital (a linear combination of STO's) with the plane wave $|\chi\rangle$.

The sudden approximation gives

$$Q(E)_{SUDDEN} = \rho(E)\,|\langle\phi_{1\sigma}|\chi\rangle|^2 \quad . \tag{67}$$

Both of these expressions are slowly varying for the slight changes in k across the manifold of the HF correlation states. They are displayed in Table II.

## D. Conclusions

The conclusions drawn below refer specifically to the F 1s correlation-state peaks in the high-energy XPS spectrum of HF. We believe that most of them are more generally true for comparable spectra, but the exact extent to which they apply can be ascertained better following theoretical analysis of additional cases.

First and perhaps of most importance, the excellent agreement between experiment and Method B (Table I) provides strong evidence that the overlap approximation embodied in Eq. (3) is adequate to describe such a high-energy core-level correlation-state spectrum.

The corollary conclusion is that initial-state CI must be included, since Method A (Table I) gives poor intensity predictions. This is entirely expected in view of the discussion in I, but it has not been recognized in previous work on core level satellite spectra. Examination of Table II and, of course, the results of the overlap approximation, imply that the energy-dependent factor in the cross section can safely be neglected at these energies. At lower photon energies, however, these terms might be expected to become more important. It is difficult to say at what point they would no longer be negligible, and, perhaps more importantly, at what point the plane

wave approximation itself becomes poor. Our results, in fact, do not imply that the plane wave approximation is good even at these energies. They simply suggest that the energy dependence--whatever its form-- is slowly varying. The usefulness of the plane wave approximation is an important question at the present time since several theoretical models for predicting the intensities of molecular orbital photoemission spectra use either it or a closely related type of continuum function. Further work on this point is in progress in our laboratory.

The primary components of the dipole cross section--Q(E) and the overlap integral $S_n^{11}$--have already been discussed. There are additional terms in the cross section, however, and in the Appendix we report the results of calculations which evaluate the leading corrections for a few of the states of HF studied here. They are all found to be negligible at the photon energies used in our experiment.

It is interesting to interpret the correlation peak intensities in terms of "shakeup" excitation into virtual orbitals. An examination of Table IV shows that the first two correlation states (1 and 2) can be described fairly well as arising from the $3\sigma \rightarrow 4\sigma$ transition. These two final states are describable as molecular valence states, the remainder of the spectrum corresponding primarily to Rydberg-like states. Only state 2 of this pair is predicted to have an observable intensity, and it is indeed the first state observed in the experimental spectrum. It seems reasonable to assert that the relatively low intensity of this transition is attributable to the charge transfer nature of the excitation. The $3\sigma$ orbital is the bonding combination of the F(2p) and (1s) orbitals and is largely localized on the fluorine atom,

while the $4\sigma$ is the antibonding combination and is primarily hydrogen-like. Since the orbitals have their large components in different regions of space, one would expect a small overlap. This interpretation seems plausible, but there are also more subtle effects that contribute substantially to the cross section. These are the small admixture of the $1\pi \rightarrow 2\pi$ excitation into state 2, the even smaller admixture of the reference state, and the effect of configuration interaction in the initial state. This last point is very important and can be seen quite clearly in Table I. The inclusion of initial state CI (Method B) nearly doubles the predicted intensity of state 2 relative to the primary hole state.[17]

The most intense peak in the spectrum, state 5, corresponds to the $1\pi \rightarrow 2\pi$, or $F(2p_\pi) \rightarrow F(3p_\pi)$ excitation. Its counterpart, state 3, is also relatively intense. The next most intense peak in the spectrum is state 9, the $F(2p_\pi) \rightarrow F(4p_\pi)$ excitation. These results, of course, would be expected on the basis of a simple one-electron overlap model.

Satellites with smaller intensities are less predictable. State 7 is primarily attributable to the $3\sigma \rightarrow 5\sigma$ excitation. It would be tempting to say that since the $5\sigma$ orbital is F(3s)-like, there should be very little overlap with the $3\sigma$ orbital in the ground state (which is mainly $F(2p_\sigma)$-like), and this causes the small intensity of state 7. These arguments, however, are probably oversimplified since there is a fairly large component of $3\sigma \rightarrow 6\sigma$ ($F2p_\sigma \rightarrow F3p_\sigma$) in the wavefunction. Configuration mixing makes it nearly impossible to give rough <u>a priori</u> estimates of intensities. For example, the $3\sigma \rightarrow 6\sigma$ excitation is

important in state 8, and it might therefore be expected to be rather intense. It is not. The $F(2p_\sigma) \rightarrow F(4s)$ excitation, state 10, on the other hand, has a much larger intensity. The reasons for these differences in overlap are complex, and are tied into the specific nature of configuration mixing in these excitated states. Since the configurations enter into the wavefunction with a phase, they can either add intensity to the predominant configuration, or cancel what intensity the dominant configuration might supply. These problems are expected to be more severe in molecules than atoms since there is generally a much denser excited-state manifold in the molecular species.

Finally, we note that the HF molecule is isoelectronic with the neon atom. One might, therefore, expect to see some similarities in their satellite spectra. In Figs. 3a and 3b we have drawn a bar spectrum of the most intense satellites in Ne[18] and HF. Above each bar we have assigned an orbital which serves to roughly identify the final state.

The most intense satellites in the Ne 1s spectrum are derived from $2p \rightarrow np$ excitations. If one images the two nuclei in HF being adiabatically compressed into a united atom, the $3\sigma$ and $1\pi$ orbitals of the molecule correlate with Ne 2p while $4\sigma$ and $2\pi$ correlate with the Neon 3p orbital. Since the major intensity in neon comes from the $2p \rightarrow 3p$ excitation, it is not surprising that the most intense peaks in HF arise from the $3\sigma \rightarrow 4\sigma$ and $1\pi \rightarrow 2\pi$ excitations. The $(1\pi \rightarrow 4\pi)$ state in HF is also relatively intense and correlates with the $2p \rightarrow 4p$ excitation in the united atom.

Another qualitatively interesting comparison is to consider the "equivalent cores" analog of the F 1s hole state in HF, i.e., the species $(NeH)^+$. The charge distribution in this system is presumably intermediate in character between the two extremes Ne - $H^+$ and $Ne^+$ - H, with the latter being the more chemically reasonable. The correlation states of HF should thus be similar to the excited states of $Ne^+$, inasmuch as the hydrogen nucleus is adequately shielded by its electron. The states of $Ne^+$ derived from 2p → 3p excitations[19] are shown diagramatically in Fig. 3c. They have been given intensities based on the total degeneracy of each state. This simple picture seems to work quite well, as can be seen by comparing Fig. 3c to Fig. 3b. Although no detailed correlation between specific states can be drawn, this model reproduces the observed shift in HF vs Ne toward smaller satellite separation from the primary state.

In summary, the correlation-peak spectrum of HF can be calculated quite satisfactorily in the overlap approximation. The intensities of the correlation peaks are very dependent upon the effects of configuration interaction in both the initial and final states. At present, quantitative predictions of such spectra based on simple one-electron models seem doomed to failure. Even qualitative estimates and assignments are very difficult considering the importance of configuration interaction in the final state. The effect of CI in the initial state is to increase the intensities of the shakeup states at the expense of the primary hole state. For HF, the shakeup states are all roughly twice as intense once initial state CI is included.

## E. Appendix

In the preceding paper (I), a formalism for the photoemission cross section was presented in which the usual assumption of "frozen orbitals" was not made. This introduced a number of additional terms (Eq. (17)) not present in the usual expression for the cross section. In this appendix we report numerical results for some of these corrections for many of the states involved in HF. These values were calculated early in our work, simply to satisfy us that they were indeed negligible. The absolute numbers, therefore, come from a basis set that differs slightly from the final one. However, a comparison of the relative importance of the corrections should be meaningful.

The overlap contributions ($\sum_n C_{n'n} S_n^{1j} \equiv \Delta_{n'}^{1j}$) are shown in Table V. The term ($j = 1\sigma\beta$) obviously dominates all other j. Furthermore, since $\langle\chi|\underset{\sim}{p}|j\rangle \ll \langle\chi|\underset{\sim}{p}|1\sigma\rangle$ at X-ray energies, the entire second term in Eq. (17) can safely be disregarded. The conjugate factors ($\sum_n C_{n'n}[\prod_\ell \phi'_{\ell n}|\sum_{k=2} p_k|\Psi_i(N-1,\phi_j,1)] \equiv \Gamma_{n'}^{1j}$) are larger and somewhat less predictable. We estimate their importance as follows.

In the plane wave approximation for $\chi$, the term $j = 1\sigma$ will affect the cross section as

$$\sigma_{n'} \propto |\underset{\sim}{u} \cdot \langle \underset{\sim}{k}\Delta_{n'}^{11} + \underset{\sim}{\Gamma}_{n'}^{11}\rangle|^2 \quad . \tag{68}$$

Since $\underset{\sim}{k}$ and $\underset{\sim}{\Gamma}$ are vectors, the "conjugate" correction will be angularly dependent. In the gas phase, one might average this expression over all possible orientations of the molecules with respect to $\underset{\sim}{u}$, and for unpolarized X-rays, average over all polarizations. This leaves

an expression which is dependent on the angle between the photoelectron exit slit and the photon propagation direction. This angle in our instrument is $\pi/2$.

After preforming these averages, one finds that the cross section is proportional to

$$\sigma_{n'} \propto \left(\Delta_{n'}^{11}\right)^2 + \frac{2}{3k^2}\left(\Gamma_{n'}^{11}\right)^2 \quad . \tag{69}$$

Although $\Gamma_{n'}^{11}$ can sometimes be comparable to $\Delta_{n'}^{11}$ (see Table V), the factor $1/k^2$ effectively quenches this contribution well above threshold. The other terms ($\Gamma_{n'}^{1j}, j \neq 1\sigma$) are also negligible since they enter the expression multiplied by a smaller overlap integral $\langle\chi|j\rangle$.

We conclude that well above threshold only the first terms of Eq. (I.8) should be necessary for the calculation of photoionization cross sections for core levels. As threshold is approached, the conjugate mechanism may become more important due to the presence of the $1/k^2$ multiplicative factor.

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9. This approach does not necessarily imply that our description of the excited states is better than a single configuration wavefunction. The optimum spin-orbitals to construct such a configuration, however, are very difficult to obtain, and this configuration expansion is simply a relatively easy approach to generating the necessary excited state wavefunctions. The important thing this model allows for is the mixing of the various $^2\Sigma^+$ final states which can be reached in terms of both $\sigma \rightarrow \sigma$ and $\pi \rightarrow \pi$ excitations.

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Table I. Correlation Peak Intensities in the Overlap Approximation

| State[a] | I (theo)[b] Method A | I (theo)[b] Method B | I(expt)[c] | FWHM (eV) | E(theo)[d] (eV) | E(expt)[d] (eV) |
|---|---|---|---|---|---|---|
| 0 | (1.000) | (1.000) | (1.000) | 1.4 | (693.5) | 694.0(5) |
| 1 | 0.000 | 0.001 | – | – | 23.89 | |
| 2 | 0.012 | 0.020 | 0.019(3) | 2.1(3) | 25.90 | 22.4(2) |
| 3 | 0.015 | 0.030 | 0.030(4) | 2.3(3) | 29.57 | 26.50(9) |
| 4 | 0.000 | 0.000 | – | – | 30,89 | – |
| 5 | 0.036 | 0.062 | 0.057(5) | 3.7(3) | 32.35 | 29.90(7) |
| 6 | 0.000 | 0.001 | – | – | 32.72 | – |
| 7 | 0.007 | 0.012 | 0.010 | 4.7(3) | 33.31 | 30.87 |
| 8 | 0.000 | 0.000 | – | – | 33.74 | – |
| 9 | 0.028 | 0.041 | 0.038(5) | 7.1(9) | 34.84 | 32.7(3) |
| 10 | 0.005 | 0.007 | 0.007 | 7.9(9) | 35.43 | 33.3 |
| 11 | 0.000 | 0.000 | – | – | 35.72 | – |

a) In order of increasing energy. "Reference state" is numbered 0, as in Fig. 1 and text.

b) All intensities normalized to peak 0. Absolute values of the overlap integral in state 0 are 0.78115 (Method A), 0.71970 (Method B).

c) Error in last place given parenthetically.

d) First entry is the absolute binding energy of the reference state; the others are incremental energies relative to this.



0 0 0 0 4 5 0 6 3 5 2

Table II. Energy Dependence of Correlation Peak Cross Sections

| State[a] | Q(E)[b] (dipole) | Q(E)[b] (sudden) | I(theo)[c] (dipole) | I(theo)[c] (sudden) |
|---|---|---|---|---|
| 0 | 1.0 | 1.0 | 1.0 | 1.0 |
| 1 | 0.980 | 1.011 | 0.001 | 0.001 |
| 2 | 0.979 | 1.012 | 0.020 | 0.020 |
| 3 | 0.976 | 1.012 | 0.029 | 0.030 |
| 4 | 0.975 | 1.014 | 0.000 | 0.000 |
| 5 | 0.973 | 1.015 | 0.060 | 0.063 |
| 6 | 0.973 | 1.015 | 0.001 | 0.001 |
| 7 | 0.973 | 1.015 | 0.012 | 0.012 |
| 8 | 0.972 | 1.016 | 0.000 | 0.000 |
| 9 | 0.972 | 1.016 | 0.040 | 0.041 |
| 10 | 0.971 | 1.017 | 0.007 | 0.007 |
| 11 | 0.971 | 1.017 | 0.000 | 0.000 |

a) In order of increasing energy; state 0 is the "reference state".

b) Normalized to state 0.

c) Computed as the product of the energy dependent term, Q(E), and the overlap term for our best wavefunctions (Method B in Table I).

Table III. Basis Set of Slater Functions and Selected One-Electron Orbitals used in the CI Wavefunctions

A. HF Ground State

| | Slater Function[a] | | Molecular Orbitals | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Type | ζ | 1σ | 2σ | 3σ | 4σ | 5σ | 6σ | 7σ | 1π | 2π | 3π | 4π |
| 1. | F(1s) | 7.716 | -0.6768 | 0.2873 | 0.0665 | -0.0729 | 0.1185 | 0.0143 | -0.0384 | | | | |
| 2. | F(1s') | 10.514 | -0.3313 | -0.0154 | -0.0031 | -0.0054 | -0.0250 | 0.0088 | 0.0039 | | | | |
| 3. | F(2s) | 1.933 | -0.0034 | -0.4249 | -0.1301 | 0.4412 | 0.1233 | -0.2966 | 0.1057 | | | | |
| 4. | F(2s') | 3.120 | 0.0021 | -0.6228 | -0.1699 | 0.2847 | -0.2811 | -0.1380 | 0.1436 | | | | |
| 5. | F(2p) | 1.847 | 0.0005 | -0.0885 | 0.6050 | 0.4963 | 0.2023 | -0.0010 | 0.0957 | -0.7149 | -0.2956 | -0.0323 | 0.1401 |
| 6. | F(2p') | 4.175 | -0.0012 | -0.0266 | 0.2852 | 0.3050 | 0.1327 | 0.0056 | 0.0509 | -0.3386 | -0.2534 | -0.0143 | 0.0958 |
| 7. | F(3d) | 2.500 | 0.0001 | -0.0216 | 0.0453 | -0.0232 | -0.0300 | 0.0878 | 0.0201 | -0.0263 | 0.0116 | -0.0552 | -0.0003 |
| 8. | F(3s) | 1.000 | -0.0001 | -0.0417 | -0.0024 | -0.2278 | 1.1467 | -0.6601 | -0.0954 | | | | |
| 9. | F(3p) | 1.000 | -0.0009 | -0.0193 | 0.0238 | 0.0163 | -0.2236 | -1.1454 | -0.0880 | -0.0600 | 1.0928 | 0.1275 | -0.7086 |
| 10. | F(3d') | 0.800 | -0.0002 | -0.0080 | 0.0134 | 0.0244 | -0.1275 | 0.1289 | 0.6961 | -0.0157 | 0.1735 | -0.9572 | 0.1114 |
| 11. | F(4s) | 0.600 | -0.0001 | 0.0051 | 0.0036 | -0.0292 | -0.0576 | -0.1121 | 0.7936 | | | | |
| 12. | F(4p) | 0.600 | 0.0002 | -0.0016 | 0.0015 | 0.0245 | 0.0023 | -0.2400 | 0.3504 | 0.0089 | -0.0814 | 0.1208 | 1.2224 |
| 13. | H(1s) | 1.000 | 0.0028 | 0.1841 | -0.0297 | -1.7194 | -0.5649 | 1.5561 | -0.7593 | | | | |
| 14. | H(1s') | 1.500 | -0.0018 | -0.2311 | 0.3042 | 0.3169 | 0.0954 | -0.3849 | 0.3402 | | | | |

B. $HF^+$, F(1s) Hole State

| | Slater Function | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Type | ζ | 1σ | 2σ | 3σ | 4σ | 5σ | 6σ | 7σ | 1π | 2π | 3π | 4π |
| 1. | F(1s) | 7.716 | -0.5892 | 0.3055 | 0.0909 | -0.0403 | 0.0588 | -0.0087 | 0.0258 | | | | |
| 2. | F(1s') | 10.514 | -0.4178 | 0.0035 | -0.0038 | -0.0125 | -0.0177 | -0.0119 | -0.0024 | | | | |
| 3. | F(2s) | 1.933 | -0.0305 | -0.2378 | -0.0022 | 0.5674 | 0.1979 | 0.3954 | -0.0922 | | | | |
| 4. | F(2s') | 3.120 | 0.0071 | -0.8100 | -0.2620 | 0.1700 | -0.0562 | 0.1087 | -0.0539 | | | | |
| 5. | F(2p) | 1.847 | -0.0005 | -0.1273 | 0.5742 | 0.4799 | 0.2672 | 0.0312 | -0.0984 | 0.6168 | 0.2489 | 0.0288 | 0.2153 |
| 6. | F(2p') | 4.175 | 0.0005 | -0.0714 | 0.4383 | 0.1111 | 0.0615 | 0.0153 | -0.0147 | 0.4970 | 0.0996 | 0.0046 | 0.0638 |
| 7. | F(3d) | 2.500 | -0.0008 | -0.0252 | 0.0474 | 0.0057 | -0.0168 | -0.0349 | -0.0062 | 0.0282 | -0.0067 | 0.0159 | -0.0035 |
| 8. | F(3s) | 1.000 | -0.0023 | -0.0435 | 0.0635 | 0.0661 | 1.3143 | 0.4695 | 0.4924 | | | | |
| 9. | F(3p) | 1.000 | -0.0065 | -0.0111 | -0.0084 | 0.0563 | 0.1808 | 1.0704 | 0.3730 | -0.0571 | -0.9613 | -0.1002 | -0.9615 |
| 10. | F(3d') | 0.800 | -0.0022 | -0.0073 | 0.0192 | -0.0409 | -0.1653 | 0.1510 | -0.5887 | 0.0051 | -0.2936 | 0.9282 | 0.2020 |
| 11. | F(4s) | 0.600 | -0.0007 | 0.0062 | -0.0079 | -0.0189 | 0.0819 | 0.1583 | -0.9247 | | | | |
| 12. | F(4p) | 0.600 | 0.0011 | -0.0046 | 0.0145 | -0.0146 | -0.0501 | 0.4501 | -0.1900 | 0.0201 | -0.1271 | -0.2970 | 1.1986 |
| 13. | H(1s) | 1.000 | 0.0238 | 0.1929 | -0.2628 | -1.7866 | -1.3668 | -1.7129 | 0.1798 | | | | |
| 14. | H(1s') | 1.500 | -0.0134 | -0.2196 | 0.3289 | 0.3656 | 0.3365 | 0.4841 | -0.1434 | | | | |

a) Here $\psi \propto r^{n-1} e^{-\zeta r}$, where n is the principal quantum number.

Table IV. Important Configurations for Describing the Correlation States

| Configuration* | | State 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1. $1\sigma^1 2\sigma^2 3\sigma^2 1\pi^4$ | (a) | 0.9957 | 0.0317 | 0.0170 | 0.0224 | -0.0269 | 0.0118 | -0.0014 | -0.0164 | -0.0052 | -0.0013 | 0.0027 | 0.0084 |
| 2. $1\sigma^1 2\sigma^2 3\sigma^1 4\sigma^1 1\pi^4$ | (b) | -0.0075 | 0.6215 | -0.7227 | 0.1656 | -0.0181 | -0.1269 | 0.0319 | 0.0395 | 0.0487 | -0.1340 | 0.0191 | 0.0123 |
| | (c) | 0.0229 | -0.7494 | -0.5950 | 0.1153 | -0.0865 | -0.0707 | 0.0371 | -0.0597 | 0.0264 | -0.0362 | 0.0182 | -0.0162 |
| 3. $1\sigma^1 2\sigma^2 3\sigma^1 5\sigma^1 1\pi^4$ | (b) | -0.0055 | -0.0095 | 0.1233 | -0.2445 | -0.7273 | -0.2901 | 0.1297 | 0.2317 | 0.3651 | -0.2458 | 0.0770 | 0.0405 |
| | (c) | 0.0161 | -0.0759 | -0.0342 | -0.0440 | 0.2883 | 0.2912 | -0.1350 | 0.7881 | 0.0640 | -0.1951 | 0.1067 | 0.0930 |
| 4. $1\sigma^1 2\sigma^2 3\sigma^1 6\sigma^1 1\pi^4$ | (b) | 0.0011 | -0.0065 | 0.0188 | 0.0402 | 0.2482 | 0.1689 | -0.1184 | -0.3500 | 0.8056 | 0.0648 | 0.1219 | 0.0517 |
| | (c) | -0.0029 | -0.0209 | -0.0121 | 0.0204 | -0.0820 | -0.0801 | 0.0208 | -0.1628 | -0.3110 | 0.1045 | -0.0068 | 0.0300 |
| 5. $1\sigma^1 2\sigma^2 3\sigma^1 7\sigma^1 1\pi^4$ | (b) | 0.0007 | -0.0172 | 0.0319 | 0.0204 | 0.0508 | 0.0037 | -0.0280 | -0.0394 | 0.0729 | -0.3003 | -0.9030 | 0.1157 |
| | (c) | -0.0021 | 0.0276 | 0.0307 | -0.0042 | -0.0092 | -0.0150 | 0.0014 | -0.0257 | 0.0516 | 0.0688 | 0.2043 | -0.0270 |
| 6. $1\sigma^1 2\sigma^2 3\sigma^2 1\pi^3 2\pi^1$ | (d) | -0.0148 | -0.0469 | 0.2702 | 0.8815 | 0.0001 | -0.2825 | 0.0561 | 0.1141 | 0.0410 | -0.1243 | 0.0666 | -0.0032 |
| | (e) | 0.0242 | -0.0478 | 0.0567 | -0.3138 | 0.5126 | -0.7284 | 0.1145 | -0.0098 | -0.0096 | -0.2211 | 0.1032 | 0.0081 |
| 7. $1\sigma^1 2\sigma^2 3\sigma^2 1\pi^3 3\pi^1$ | (d) | -0.0010 | -0.0026 | -0.0134 | -0.0057 | -0.1160 | -0.2392 | -0.9600 | -0.0082 | -0.0430 | 0.0159 | 0.0003 | -0.0418 |
| | (e) | 0.0017 | 0.0099 | -0.0010 | -0.0092 | 0.0163 | 0.0098 | 0.0308 | 0.0767 | 0.0833 | -0.0283 | -0.1048 | -0.9794 |
| 8. $1\sigma^1 2\sigma^2 3\sigma^2 1\pi^3 4\pi^1$ | (d) | -0.0092 | -0.0165 | 0.0660 | -0.0393 | -0.0167 | 0.3076 | -0.0726 | -0.3383 | -0.2199 | -0.7779 | 0.2492 | -0.0520 |
| | (e) | 0.0151 | -0.0164 | 0.0203 | -0.0806 | 0.0851 | -0.0030 | 0.0056 | 0.0115 | 0.0180 | 0.1319 | -0.1118 | -0.0341 |

*The configurations have the following specific forms.

a. $1.0\ (1\sigma\alpha\ 2\sigma\alpha\ 2\sigma\beta\ 3\sigma\alpha\ 3\sigma\beta\ 1\pi_+\alpha\ 1\pi_+\beta\ 1\pi_-\alpha\ 1\pi_-\beta)$

b. $0.7990\ (1\sigma\alpha\ m\sigma\alpha\ n\sigma\beta) - 0.5453\ (1\sigma\alpha\ m\sigma\beta\ n\sigma\alpha)$
$-0.2537\ (1\sigma\beta\ m\sigma\alpha\ n\sigma\alpha)$

c. $-0.1683\ (1\sigma\alpha\ m\sigma\alpha\ n\sigma\beta) - 0.6078\ (1\sigma\alpha\ m\sigma\beta\ n\sigma\alpha) + 0.7761\ (1\sigma\beta\ m\sigma\alpha\ n\sigma\alpha)$

d. $0.5773\ (1\sigma\alpha\ 1\pi_-\alpha\ m\pi_-\beta) - 0.2845\ (1\sigma\alpha\ 1\pi_-\beta\ m\pi_-\alpha)$
$+0.5773\ (1\sigma\alpha\ 1\pi_+\alpha\ m\pi_+\beta) - 0.2845\ (1\sigma\alpha\ 1\pi_+\beta\ m\pi_+\alpha)$
$-0.2929\ (1\sigma\beta\ 1\pi_-\alpha\ m\pi_+\alpha) - 0.2929\ (1\sigma\beta\ 1\pi_+\alpha\ m\pi_-\alpha)$

e. $0.0049\ (1\sigma\alpha 1\pi_-\alpha\ m\pi_-\beta) - 0.5024\ (1\sigma\alpha\ 1\pi_-\beta\ m\pi_-\alpha)$
$+0.0049\ (1\sigma\alpha\ 1\bar{\pi}_+\alpha\ m\bar{\pi}_+\beta) - 0.5024\ (1\sigma\alpha\ 1\bar{\pi}_+\beta\ m\bar{\pi}_+\alpha)$
$+0.4975\ (1\sigma\beta\ 1\pi_-\alpha\ m\pi_+\alpha) + 0.4975\ (1\sigma\beta\ 1\pi_+\alpha\ m\pi_+\alpha)$

Table V. Comparison of Overlap and Conjugate Terms in Photoemission Cross Sections for HF[a,b]

| n' | j = 1σ β | | j = 2σ β | | j = 3σ β | | j = 1π[c] |
|---|---|---|---|---|---|---|---|
| | $\Delta^{1j}_{n'}$ | $\Gamma^{1j}_{n'}$ | $\Delta^{1j}_{n'}$ | $\Gamma^{1j}_{n'}$ | $\Delta^{1j}_{n'}$ | $\Gamma^{1j}_{n'}$ | $\Gamma^{1j}_{n'}$ |
| 0 | 0.885 | 0.091 | -0.006 | -0.138 | -0.001 | - | -1.84 |
| 1 | -0.014 | 0.192 | 0.001 | - | -0.006 | - | - |
| 2 | 0.104 | -0.454 | 0.000 | - | 0.001 | - | - |
| 3 | -0.111 | 0.190 | 0.001 | - | -0.003 | - | - |
| 4 | -0.002 | 0.075 | -0.000 | - | -0.002 | - | - |
| 5 | -0.178 | 0.082 | 0.000 | 0.085 | 0.001 | -0.019 | 0.700 |
| 6 | 0.007 | 0.335 | -0.000 | - | 0.000 | - | - |
| 7 | 0.083 | 0.178 | -0.000 | - | 0.000 | - | - |
| 8 | -0.051 | 0.273 | 0.000 | - | -0.002 | - | - |
| 9 | -0.018 | -0.258 | 0.000 | - | -0.000 | - | - |
| 10 | -0.034 | -0.034 | 0.000 | - | -0.003 | - | - |

a. See Appendix I for definitions of $\Delta^{1j}_{n'}$ and $\Gamma^{1j}_{n'}$. The units for $\Gamma^{1j}_{n'}$ are reciprocal bohrs.

b. The dashes represent calculations which were not performed.

c. Note that $\Delta^{1j}_{n'}$ for j = 1π vanishes in all states by symmetry.

FIGURE CAPTIONS

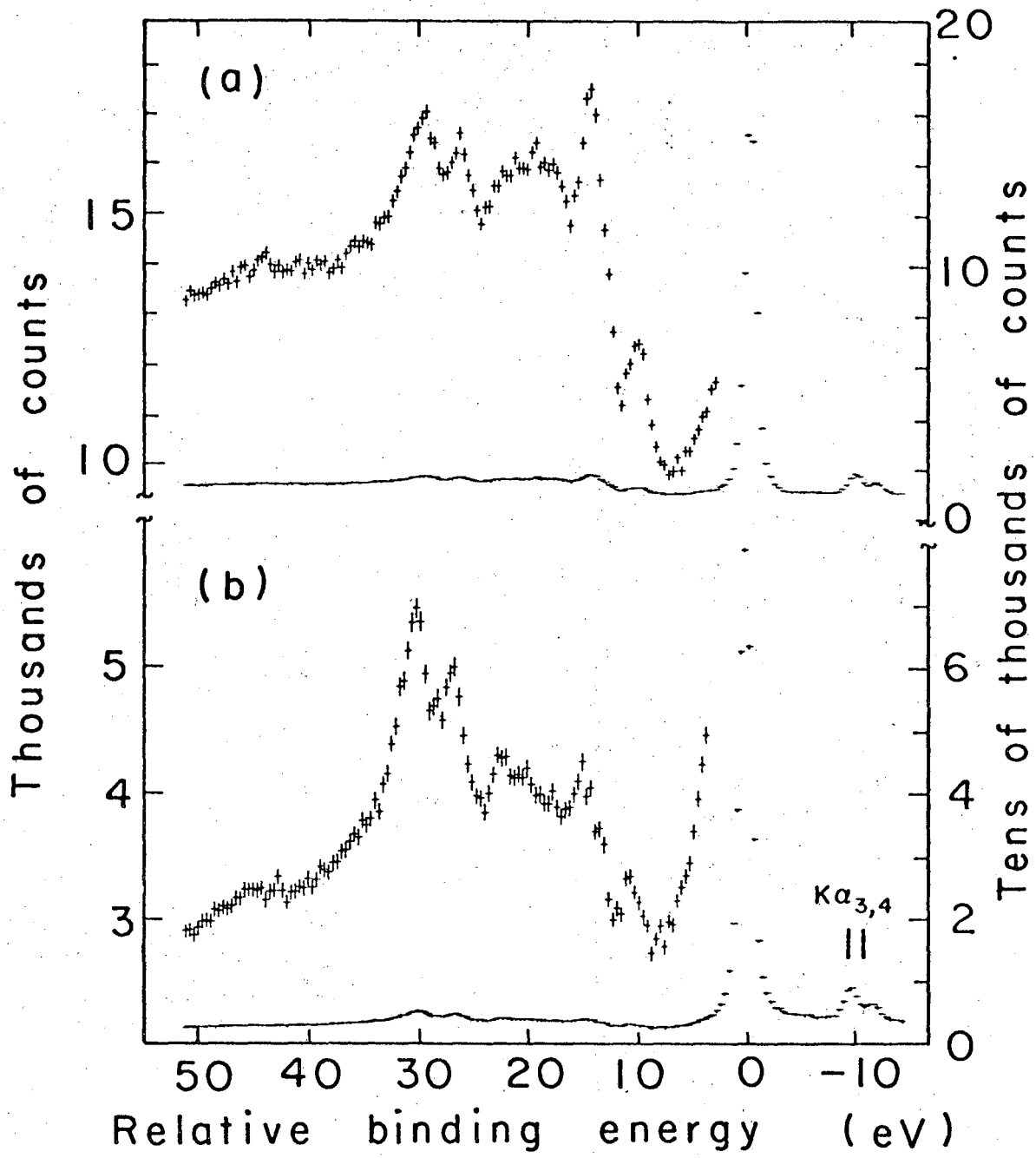
Fig. 1. (a) High pressure and (b) low-pressure photoelectron spectra of the F 1s region in HF using $AlK\alpha_{1,2}$ X-rays. The scale for the correlation and inelastic loss peaks is expanded 20 times that for the main peak.

Fig. 2. Correlation peaks for HF F 1s relative to the main line along with the computer fit (see Table I and text). The crosses represent actual data points; the circles represent data connected for the inelastic energy loss peak at about 20 eV.

Fig. 3. (a) The most intense satellites of the Ne 1s hole state. The correlation of these states with the HF satellites is shown by the dotted lines. (b) The most intense states of the HF satellite spectrum. The abscissa is the separation from the primary state and the ordinate is the intensity relative to the primary state. Above each bar an orbital designation is provided which roughly identifies the final state (see text). (c) The excited states derived from the configuration $1s^2 2s^2 2p^2 3p$ of the $Ne^+$ ion. They have been given intensities based on the total degeneracy of each state.

0 0 0 0 4 5 0 6 3 5 5






XBL 752-166

Fig. 1.

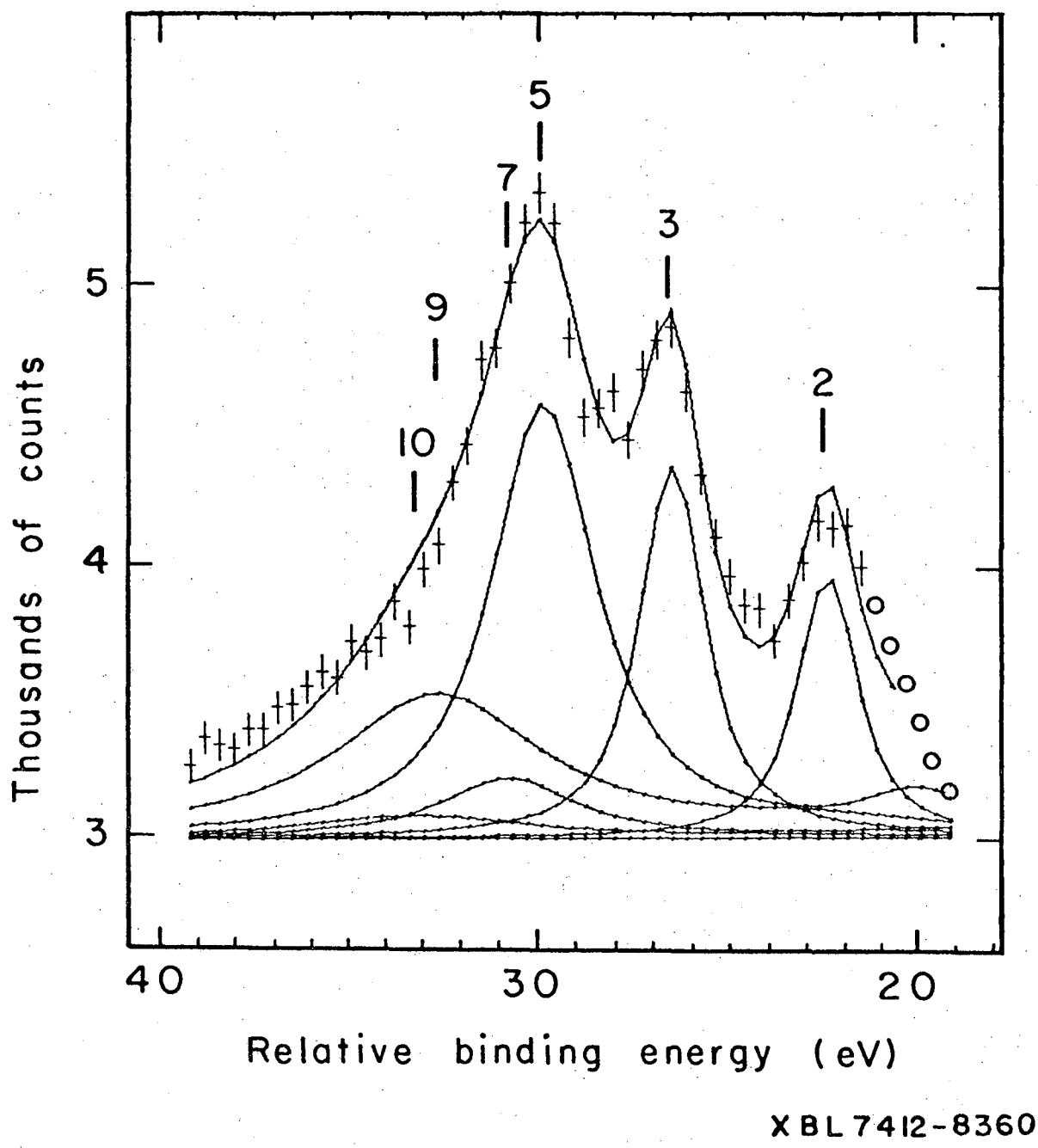
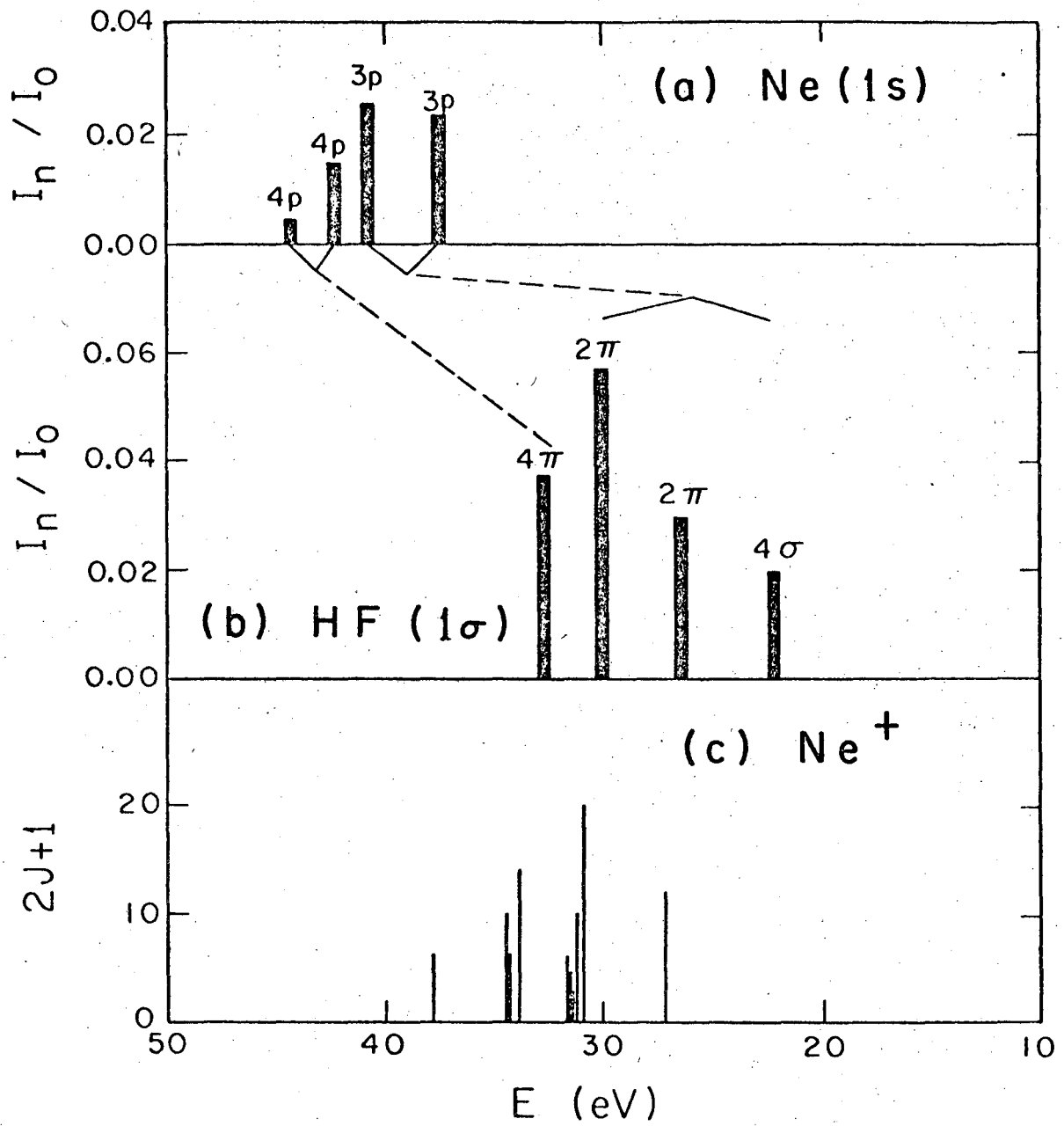

5
7
3
9
2
10
5
4
3
Thousands of counts
40
30
20
Relative binding energy (eV)
XBL 7412-8360

Fig. 2.

0 0 0 0 4 5 0 6 3 5 6






XBL752-2269

Fig. 3.

# VII. Ne (1s) SATELLITE STRUCTURE

## A. Introduction

When monochromatic radiation excites photoelectrons from a given atomic species, a series of strong peaks usually appears in the kinetic energy spectrum of the outgoing electrons. Each of the peaks corresponds to a final ionic state in which a single electron has been ejected from the 1s, 2s, $2p_{1/2}$, $2p_{3/2}$, etc, level. The initial atomic state energy $E_i$ and the final ionic state energy $E_f$ are related to the photoelectron's kinetic energy K by

$$E_i + h\nu = E_f + K \quad . \tag{70}$$

Associated with each strong peak there are also usually several weaker satellite peaks. These arise through excitation of higher-energy final states of the ion. The satellite states usually have the same symmetry as the "main" peak and, in common with it, they have an electron missing from the same subshell of the atomic core. The terms "shakeup states", "configuration-interaction states", and "correlation states" have been applied to these satellites.

The neon 1s orbital provides the most suitable test case for studying correlation satellites theoretically. Krause et al.[1] first found 1s correlation states in $Ne^+$, at relatively low resolution. Carlson et al.[2] and Siegbahn et al.[3] subsequently reported better-resolved spectra. Recently, Gelius[4] reported a high-resolution spectrum in which a total of 13 correlation peaks were identified. Nine of these peaks were assigned to one-electron excitation to states of $^2S$ symmetry--the same symmetry as the main 1s state. The energies and intensities were accurately determined: the experimental situation is,

therefore, quite satisfactory.

From a theoretical standpoint the Ne 1s correlation-state energies are well understood, having been calculated by Bagus and Gelius[5] using a multi-configuration Hartree-Fock (MCHF) method. The energies are not necessarily related to the photoemission process, however, and interpretation of correlation-peak spectra in terms of energies alone neglects most of the unique information that these spectra contain. To extract this information and make a definitive interpretation, we must construct a theory that accounts for the satellite intensities. The only theoretical intensities heretofore available were given by Krause et al.[6] They used an MCHF approach to estimate the intensities of the first two satellites. Good agreement with experiment was obtained, but it was probably fortuitous, as we shall show below. The MCHF approach is not readily extended to spectra containing several satellites, and a better model is required. The object of this paper is to present such a model.

In Section VII-B the theory of correlation-state spectra is briefly discussed. Basis sets and Hartree-Fock results are dealt with in Section VII-C. In Section VII-D we describe attempts to predict correlation-state intensities with both the MCHF model and an orthogonalized modification. Configuration-interaction techniques are introduced and applied to the final-state manifold in Section VII-E, and in Section VII-F this approach is extended to the initial state.

## B. Theory

In the photoelectric effect a photon excites an N-electron system from its ground state $\Psi_0$ into an excited state which we may write symbolically as the product of a state vector $\Psi_j(N - 1)$ describing the residual N - 1 electron ionic system and a continuum function $\chi_j(\vec{\gamma}_N \vec{k}_N)$ for the outgoing electron,

$$\Psi_i(N) \sim \Psi_j(N - 1)\ \chi_j(\vec{\gamma}_N \vec{k}_N) \quad .$$

This is actually an oversimplified form. Several approximations were made for computational simplicity. We have neglected coupling of channels in the continuum, a point recently discussed in connection with satellite spectra by Manson.[7] Far from threshold this effect should be small,[8] and it is not included in this work. In view of the agreement with experiment obtained in the calculations discussed below, we conclude that coupling of continuum channels is not crucial to an understanding of the satellite intensities in the Ne 1s region excited by $AlK_\alpha$ X-rays (photoelectron kinetic energy of ~600 eV). From a computational standpoint, this approximation allows one to determine an ionic state of any desired accuracy, and then to generate a single continuum function in this ionic potential for an appropriately antisymmetrized N-electron L·S eigenstate.

We also have neglected contributions to the dipole matrix element which arise explicitly from the antisymmetric nature of the initial state and from any energy dependence over the satellite-states' energy range in the one-electron photoelectron cross section.[9] We studied the effects of these simplifications on a similar correlation-state calculation on hydrogen fluoride,[10] and found them to be small.

With these approximations the calculation of relative intensities $I_j$ of the correlation states reduces to evaluation of an expression identical to the sudden-approximation result of Åberg,[11]

$$I_j \propto |\langle\Psi_i(N'1s)|\Psi_j(N-1)|^2 \quad ; \tag{71}$$

where $\Psi_i(N'1s)$ denotes the N - 1 electron function formed from the neon ground-state wavefunction by removing the $N^{th}$ electron and a 1s orbital (i.e., by striking the appropriate row and column from each determinant describing the ground state). Thus our task is to find appropriate descriptions of $\Psi_i(N)$ and $\Psi_j(N-1)$ for all j of interest.

Before describing in detail the basis sets that were employed, let us make some general observations about the correlation states. The ground state of neon is of course mainly $1s^2 2s^2 2p^6$ (but see Section VI). The main peak in the Nels photoemission spectrum is $1s2s^2 2p^6$, $^2S$. As Krause et al. have shown,[1] other $^2S$ states can be formed, for example, by promoting an electron to an np orbital and recoupling with the hole to $^1S$ or $^3S$, then recoupling to 1s to form $^2S$, viz,

$$\phi_1(np) = 2s^2 2p^5 np(^3S)\ 1s\ (^2S)$$

$$\phi_2(np) = 2s^2 2p^5 np(^1S)\ 1s\ (^2S)$$

and similarly for ns. These two single "configuration state functions" represent the simplest treatment of the final ionic state. If we were to compute intensities at this stage, employing a single-determinantal initial state and using Koopmans' approximation for the final state orbitals, both states would have an identically zero overlap with the initial state. If, on the other hand, we performed separate

Hartree-Fock calculations for both of these final states, the orbitals for the final states would no longer be orthogonal to those of the initial state and orbital relaxation would provide a mechanism for populating $\phi_2(np)$. In this coupling scheme, however, even with relaxation $\phi_1(np)$ is still orthogonal to the initial state by virtue of the valence electron spin coupling. Because two satellites corresponding to the configuration $1s2s^2 2p^5 3p$ are experimentally observed, Krause et al. pointed out[1] that at the very least eigenstates must be formed from $\phi_1$ and $\phi_2$:

$$\begin{aligned} \Psi_{np}(\text{lower}) &= a\phi_1(np) + (1 - a^2)^{1/2}\, \phi_2(np) \\ \Psi_{np}(\text{upper}) &= b\phi_1(np) + (1 - b^2)^{1/2}\, \phi_2(np) \end{aligned} \tag{72}$$

Of course the true eigenstates cannot be written so simply; they are linear combinations of all the basis states. Nevertheless, the dominant terms in the expansion of $\Psi_{np}$ (upper or lower) tend to be $\phi_1(np)$ and $\phi_2(np)$; we shall, therefore retain the notation $\Psi_{np}$ (upper) and $\Psi_{np}$ (lower) for the eigenstates.

A comment on the "shakeup" terminology is in order. It is convenient to enumerate configurations that admix with the main configuration, $Ne^+(1s^1 2s^2 2p^6)$, by "promoting" one electron at a time and recoupling to a $^2S$ term. This "promotion" is a computational convience that has meaning only in the context of a preselected basis set. In particular, it has nothing to do with the ionization process. The early literature on the subject[1,2] used terms such as "monopole excitation", "monopole transition" and "two-electron excitation" in describing the occurrence of correlation states. More recently,

correlation-state peaks in transition-metal complexes have been attributed to "ligand-to-metal charge transfer". These terms had heuristic value during the development of the subject, but they can be misleading if interpreted literally. We note that there is no monopole transition and no shakeup transition. The correlation peaks arise in exactly the same way as do the main peaks.[12] It is also not rigorously correct to describe the correlation states as resulting from two-electron excitation. Because of the potentially misleading nature of the terms "shakeup" and "monopole transition", we prefer the term "correlation states".

## C. Basis Sets and Hartree-Fock Results

The SCF calculations were all done with Roothaan's analytic expansion,[13] using the Slater-type orbitals (STO's)

$$\phi_{n\ell m} = [(2\xi)^{2n+1}/(2n)!]^{1/2}\, r^{n-1} e^{-\xi r} Y_{\ell m}(\theta,\phi) \tag{73}$$

The final basis set chosen for our SCF calculations is given in Table I. It was formed by augmenting the set of five s-like and four p-like STO's optimized by Bagus[14] for the Ne ground state with a set of seven Rydberg orbitals. The exponents in the Rydberg STO's were chosen by matching $\langle r\rangle_n$ to the results found by Bagus and Gelius[5] in a numerical MCHF calculation on the Ne (1s hole) states, using

$$\langle r\rangle_n = \frac{2n+1}{2\xi_n}$$

and

$$\langle r^2\rangle_n = \frac{(n+1)(2n+1)}{2\xi_n^2}$$

Two values of $\xi_n$ were obtained from each of these two relations, corresponding to the upper and lower np states. The agreement among the four $\xi_n$ values for each n was excellent. The values quoted in Table I are averages. The exponent $\xi_6 = 0.30$ lies slightly above an estimate made by extrapolation of $\xi_n$ vs n. Slater's rules[15] give exponents of 1.02, 0.54, 0.50, and 0.48 for n = 3, 4, 5, and 6, respectively. Because $\xi_n$ is l-independent for STO's, we took $\xi_{ns} = \xi_{np}$ for all n.

Table II gives the Hartree-Fock energy results obtained with this basis set for the Ne ground state, the $Ne^+$ 1s hole state, and the two 2p shake-off limits; i.e., the lowest $^1P$ and $^3P$ states of $Ne^{++}(1s2s^2 2p^5)$, which mark the onset of new continuum manifolds. The total energy of the Ne 1s hole state is quite close to the value of -96.62571 a.u. reported by Bagus, confirming that the augmented initial-state basis set is sufficiently flexible to describe both states. The results in Table II give

$$E_B(1s) = 868.6 \text{ eV}$$

$$^3P \text{ Shakeoff Limit} = 45.15 \text{ eV}$$

$$^1P \text{ Shakeoff Limit} = 49.46 \text{ eV}$$

In the Ne 1s photoelectron spectrum the most intense satellites are members of the Rydberg series approaching these two double ionization limits. We, therefore, elected to focus our calculations on the states derived from $2p \rightarrow np$.

The adequacy of this minimal Rydberg basis was tested by comparing the energies of the correlation states as calculated with this set

(by employing a configuration interaction (CI) expansion to be described later) with energies obtained using a set in which the 3s and 3p orbitals were "split" into two STO basis functions. The correlation state energies were all identical within 0.1 eV. We, therefore, believe that the minimum Rydberg basis is adequate for describing the correlation states.

D. Multiconfiguration Hartree-Fock Results

All previous thebretical treatments of the Ne 1s correlation-state spectrum were based on the MCHF model, which allows simultaneous optimization of both the orbitals and coefficients of a configuration interaction expansion. In this section we report the Ne 1s satellite intensities calculated with the MCHF wavefunctions of Bagus and Gelius. Specifically, each state was separately optimized for the two term expansion of Eq. (3). As Bagus and Gelius have shown,[3,4] the energies of the Ne 1s satellites can be computed quite satisfactorily by this method. The intensities, however, are another matter. The MCHF wavefunctions are orthogonal neither to each other nor to the main 1s hole state. Thus the MCHF correlation-state intensities, which are calculated from overlap integrals, cannot be taken very seriously. We have also recalculated the intensities after Schmidt-orthogonalizing the MCHF wavefunctions. After having thus exhausted the immediate possibilities of this method, we turn in Section VII-E to a configuration-interaction model for treating the correlation states.

The results are presented in Table III. As pointed out previously,[3,4] the correlation-state energies agree well with experiment, essentially falling into place if a constant shift of 1.7 eV is applied relative

to the main 1s state. A straightforward computation of the correlation-state intensities (i.e., overlap with the ground state) yields the values given in Column 4 of Table III. While the agreement with experiment (Column 6) of some of the peaks is fairly good, the 3p peak intensities are far too large. This discrepency is eliminated by successive Schmidt orthogonalization of each final state to those below it in energy (Table III, Column 5). This procedure removes the conceptual error or nonorthogonality but replaces it by another, because the order of Schmidt orthogonalization is both important and arbitrary. Carlson et al.,[2,6] employing an identical procedure, computed intensities for the $2p^5 3p$ (lower) and $2p^5 3p$ (upper) states of 2.3% and 2.9% respectively. These are in marked disagreement with the intensities we have found using either our first approach or the orthogonalized modification. We assume that the source of the disagreement lies in the fact that they did not compute the complete overlap integral with the ground state, but rather approximated it as the one-electron orbital overlap integral $\langle 2p(\text{initial state}) | 3p(\text{final state}) \rangle$. As it is not clear how the MCHF method can be improved, we leave it at this point.

### E. Final-State Configuration Interaction

A configuration-interaction calculation was carried out on the Ne 1s correlation states using the program described by Schaefer.[16] The one-electron functions used in the CI were generated by Schmidt-orthogonalizing single Slater-type orbitals to the Hartree-Fock orbitals for an appropriate core (by "core", we mean the 1s, 2s, and 2p atomic orbitals). The STO's used to define the functions were the

Rydberg orbitals in the original basis, two 2s and two 2p orbitals from the original basis (2s', 2s'', 2p'', 2p'''), a 1s orbital with $\xi = 12.0$, and a 3d STO with $\xi = 3.5$. The reason for including the Rydberg orbitals is obvious, and the remainder of the functions are chosen so as to be able to describe orbital reorganization and electron-electron correlation in the n = 2 shell. This scheme generates a basis set of 8s, 7p and 1d function.

The choice of an appropriate core presents a problem. The simplest configuration expansion one can imagine which will generate the correlation states as excited roots of the Hamiltonian is simply all single excitations with respect to $1s^1 2s^2 2p^6$. For the initially occupied orbitals, one might choose either the SCF orbitals in the main $Ne^+$ 1s hole state or those in the $^3P$ (or $^1P$) state of $Ne^{2+}(1s2s^2 2p^5)$. The former would be expected to favor the main hole state energetically, while the latter would favor the satellites; i.e., the optimum 1s, 2s, and 2p orbitals in the configuration $1s^1 2s^2 2p^5 np$ should be nearer to those of the 2p shakeoff limit than the main hole state. We note first that the $^3P$ and $^1P$ occupied SCF orbitals are very similar and give nearly identical correlation state spacings and intensities when we use them in the CI described above. To illustrate the difference that is entailed by choosing the $Ne^+$ 1s hole state vs the $Ne^{2+}$ $^3P$ state orbitals, we found

$$E[3p(\text{upper}) - E(\text{main peak})] = 42.45 \text{ eV } (Ne^+ \text{ orbitals})$$
$$40.73 \text{ eV } (Ne^{2+}\ {}^3P \text{ orbitals})$$

with intensities of 2.9% and 1.5% of the main peak, respectively. To eliminate this orbital dependence we considered several orbital distribution schemes for the Ne 1s final-state wavefunctions. We adopted one that is designed to treat the main 1s hole state and six np correlation states (n = 3,4,5) equally. This distribution is the union of single excitations with respect to the reference configurations.

$$1s^1 2s^2 2p^6$$
$$1s^1 2s^2 2p^5 3p$$
$$1s^1 2s^2 2p^5 4p$$

and

$$1s^1 2s^2 2p^5 5p$$

with the constraint that the 1s occupation is always one. This should allow the 2s and 2p orbitals to readjust to whatever form is appropriate for the state in question. Our goal in this single excitation scheme, therefore, is to treat the satellites <u>and</u> the main state <u>at least</u> at the Hartree-Fock level, independent of the orbital basis.[17]

The excitations that this approach involved fall schematically into certain categories, as illustrated below:

| orbital | 1s | 2s,2p | Virtuals |
|---|---|---|---|
| occ. no. | 1 | 8 | 0 |
| | 1 | 7 | 1 |

from $1s^1 2s^2 2p^6$, and

| orbital | 1s | 2s,2p | 3p | Virtuals |
|---|---|---|---|---|
| occ. no. | 1 | 7 | 1 | 0 |
| | 1 | 6 | 2 | 0 |
| | 1 | 6 | 1 | 1 |
| | 1 | 7 | 0 | 1 |

from $1s^1 2s^2 2p^6 3p$, etc. Using this approach we calculated the final-state energies and peak intensities using both the $Ne^+$ 1s hole state and the $Ne^{2+}(1s2s^2 2p^5)$ $^3P$ state occupied orbitals. The results showed much better internal agreement. The worst discrepancy in energy relative to the main peak was 0.9 eV, and the largest discrepancy in intensity was 0.3% (again for 3p(upper)). Most of the differences were much smaller.

Energies and intensities are set out in Table IV, Columns 3-5. We shall refer to this result as Calculation 1. The energies of the correlation states relative to the main peak show an improvement relative to the MCHF results in Table III: an average shift of 0.83 eV vs 1.72 for the six states in that table. The absolute energies of all the states were lower than the energies of the corresponding MCHF states found by Bagus and Gelius; we, therefore, feel we have satisfied our goal of treating all the final states at least at the Hartree-Fock level.

The intensities in Table IV, Column 5 are systematically lower than experiment by about a factor of two. We considered improving the correlation-state wave functions further, but decided against doing so. The wave functions described above already involve 226

configuration state functions. The next logical improvement would be to include the union of all double excitations, which would greatly increase the number of configuration state functions. Rather than spending any further effort focusing on the final states, we decided to study the effect of electron-electron correlation in the initial state.

## F. Initial-State Configuration Interaction

Early treatments of correlation satellites considered valence excitations in the final states but treated the initial state as a single configuration. This asymmetric approach was justified in the context of identifying peaks and calculating their energies. For predicting intensities, however, such a model would not only be quantitatively unsatisfactory (as the above calculations have shown), but it would actually be conceptually wrong, because it systematically excludes about half the effect, as we show below.

Recently initial-state configuration interaction (ISCI) has emerged as an important factor in photoelectron spectroscopy. Valence-band spectra of atomic Cd,[18] Hg,[19] and Pb[20] show satellite peaks arising from configurations introduced into the ground state by ISCI. In molecular HF, the F(1s) correlation-state spectrum is strongly affected by ISCI.[10] The "spontaneous interconfiguration fluctuation" of recent interest in mixed-valence rare-earth compounds[21] is of course simply another name for ISCI. With these developments in mind we were naturally led to consider ISCI in neon, even though it is nominally a closed-shell atom.

Let us first examine the type of correction ISCI would be expected to provide. If we could suppress the exchange interaction between the Ne 1s electron and the valence electrons in the $Ne^+$ 1s hole states, the two $1s2s^2 2p^5 np\ ^2S$ states would be replaced by $(2p^5 np)\ ^1S$ and $^3S$ states. The former would be very similar to the $1s^2 2s^2 2p^5 np,\ ^1S$ excited state in atomic neon (the $^3S$ state also has an analog in atomic neon, but it is not admixed into the ground state). Similar 1:1 correspondence would obtain between the other configurations in the Ne and $Ne^+$ (1s hole) manifolds with the 1s exchange splitting removed. The energy spacings of the configurations would be slightly greater in the ion, but otherwise the two manifolds of configurations would be very similar, as depicted in Fig. 1 (left side).

Now let us introduce configuration interaction in both manifolds while continuing to suppress exchange involving the 1s electron in the ionic manifold. Correlated eigenstates are generated as shown in Fig. 1 (right side). We describe these eigenstates by coefficients as shown, and note these have magnitudes

$$a_0\ ,\ a_0'\ ,\ b_0'\ \ldots \sim 1$$
$$a_1\ ,\ a_1'\ ,\ b_1'\ \ldots \sim 0.1$$

Now if we consider 1s photoemission in neon, there are four contributions to the intensity-determining overlap integrals. Path A (Fig. 1) is the largest term, of effective intensity

$$I_A \sim |a_0 a_0'|^2 \sim 1 \quad ,$$

where, for the sake of this example, we take the overlap integrals to be 1 or 0. It connects the main configuration in the ground state and the lowest hole state. Path B connects the ground state with the correlation states. If the ground state were not correlated (i.e., $a_n = 0$ for $n > 0$), then B would be the only mechanism for reaching correlation states, and the intensities of those peaks would be

$$I_B \sim |a_0 b_1'|^2 \sim 0.01 \quad .$$

At this point it is instructive to see how the two major sources of satellite intensity cited previously in the literature are related to this model. In most calculations of satellite intensities, different one-electron functions are used to describe the ground state and the ionic states. In this circumstance, the "relaxation" will cause the two orbital sets to be non-orthogonal and we would not be able to make the assumption that the overlap integrals are either zero or unity. It is always possible, however (at least in principle), to perform a CI calculation on the ionic states using the ground-state orbitals. If this set were complete and we performed a full CI, we would obtain the exact wavefunctions for the ionic states, and the effective intensity would be determined (in our example) by the coefficient $b_1'$. The magnitude of this coefficient would be determined by both "orbital reorganization"--roughly speaking, the single excitations relative to the predominant configuration of the satellite, and "correlation"--double and higher excitations. The former situation has led to what is termed "shakeup" and the latter to "configuration interaction" states; the two groups of excitations are closely coupled,

of course, and viewed in this broader picture the approximations we have made thus far are perfectly adequate to describe qualitatively both types of states. Initial-state configuration interaction provides a new avenue for populating final states; it introduces Path C. It is obvious that it could have the same magnitude as Path B, and since it is added to the other contributions before squaring the matrix element, its neglect can lead to intensity estimates which are either too high or too low. It also provides a mechanism for populating satellites which do not have the correct symmetry to mix with the main hole state (although this is not obvious in our example). The satellites arising in this case have been termed "ISCI" states.[18]

In the neon ground-state CI calculations the one-electron functions were chosen in exactly the same way as in the previous calculations, except that the STO's were orthogonalized to the ground state HF orbitals. This virtual space was initially partitioned into a "Rydberg space" (RS) and a "correlating space" (CS). The RS (three s-type and four p-type orbitals) consisted of those orbitals formed from orthogonalizing the Rydberg STO's, while the remainder defines the CS (three s-type, two p-type, and one d-orbital). We made this separation because it is well known that the optimum virtual orbitals for computing the correlation energy have large amplitudes in the region of the valence electrons, and, therefore, Rydberg orbitals are not usually important in correlation energy computations.

The configurations in our next calculation included single excitations into both the CS and RS, plus double excitations into the CS. We refer to this as calculation 2, and it included the

following distributions

| (1s) | (2s,2p) | $(1s',2s',2s'',2p',2p'',3d)_{CS}$ | $(3s,4s,5s,3p,4p,5p,6p)_{RS}$ |
|---|---|---|---|
| 2 | 8 | 0 | 0 |
| 2 | 7 | 1 | 0 |
| 2 | 7 | 0 | 1 |
| 2 | 6 | 2 | 0 |

The resulting total energy was lowered by 0.21 a.u. from the Hartree-Fock value, thus picking up 55% of the Ne($^1$S) L-shell correlation energy (0.33 a.u.) reported by Nesbet.[22] The Ne 1s correlation-peak intensities are not improved, however; in fact they are slightly poorer (Table IV, Column 6). We infer that improvement of the total energy is by itself no criterion for the value of the wavefunction in describing correlation-state phenomena. Consideration of the simple model given earlier shows that correlation-state intensities will be greatly affected only if similar configurations are admixed into the ground state; i.e., Path C must be brought into play. In Calculation 3, therefore, we transferred the 3s and 3p orbitals from the RS to CS, thereby including double excitations of the form $1s^2 2s^2 2p^4 3p^2$, $1s^2 2p^6 3s^2$, etc, in addition to those in Calculation 2.

The results were dramatic. As Table IV, Column 7 shows, the intensities of the 3p(upper) and 3p(lower) peaks were more than doubled to near the experimental values. The 4p, etc, intensities were not significantly improved, however. Encouraged by the success of calculation 3 for 3p intensities, we moved the 4s and 4p orbitals over into the correlating space in Calculation 4. This eventually doubled the 4p(lower) and 4p(upper) intensities, bringing them up toward the

experimental values, while reducing the 3p values only slightly. In the next step--Calculation 5--in which the 5s, 5p, and 6p orbitals were brought over into the correlating space (Column 9, Table IV) the 5p and 6p intensities were likewise increased to approach the experimental value (Table IV, Column 10). These results are illustrated in Fig. 2. It seems safe to conclude on the basis of these calculations that the correct theoretical intensities of a given correlation state can be calculated if that state is adequately represented in the configurations that describe the initial state (via Path C), but that only about 1/2 the experimental intensity is predicted otherwise (Path B).

This result confirms the expectations of our simple model. Calculations 1-5 clearly show that total energy alone is no criterion of adequacy of the wavefunctions in predicting correlation-state phenomena. Calculation 2 included 55% of the total L-shell correlation energy (82% of the correlation energy which can be recovered by double excitations in our basis), but gave no improvement on intensities relative to Calculation 1. Calculation 5, which gave much better intensities, improved the computed L-shell correlation energy to only 67% of the total value. Figure 3 illustrates this point.

In summary, this prototype calculation on neon has shown for the first time that quantitative correlation-state intensities are accessible within the framework of the sudden approximation. Agreement with experiment was achieved only by taking into account configuration interaction in the initial state. Clearly the correlation-state intensities are very sensitive to the details of electron correlations

in the ground state. We conclude that core-level satellite spectra possess the potential of yielding unique information about ground-state electron correlation.

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TABLE I. Basis set of STOs for the neon SCF calculations[a]

| nℓ | ξ | nℓ | ξ |
|---|---|---|---|
| 1s | 15.439 | 2p | 10.542 |
| 1s' | 8.806 | 2p' | 4.956 |
| 2s | 3.764 | 2p'' | 2.793 |
| 2s' | 2.301 | 2p''' | 1.623 |
| 3s' | 10.995 | 3p | 0.90 |
| 3s | 0.90 | 4p | 0.55 |
| 4s | 0.55 | 5p | 0.39 |
| 5s | 0.39 | 6p | 0.30 |

a) The functional form is given in Eq. 2. Rydberg orbitals appear below dashed lines.

TABLE II. Hartree-Fock energy results from the basis set in Table 1.

| Species | State | Energy (au) | Virial Coefficient | Orbital Energies (au) $-\varepsilon(1s)$ | $-\varepsilon(2s)$ | $-\varepsilon(2p)$ |
|---|---|---|---|---|---|---|
| Ne | $1s^2 2s^2 2p^6 (^1S)$ | -128.54708 | 2.00000 | 32.77 | 1.93 | 0.85 |
| Ne+ | $1s2s^2 2p^6 (^2S)$ | - 96. 62402 | 2.00009 | 37.17 | 2.85 | 1.82 |
| $Ne^{2+}$ | $1s2s^2 2p^5 (^3P)$ | - 94.96461 | 1.99980 | 38.30 | 3.69 | 2.76 |
| $Ne^{2+}$ | $1s2s^2 2p^5 (^1P)$ | - 94.80628 | 1.99979 | 38.18 | 3.71 | 2.75 |

TABLE III. The MCHF results for $Ne^+$ 1s correlation states.

| State | Energy (eV above main peak) Ref. 3,5 | Expt(Ref.4) | Intensity (relative to 100 for main peak) MCHF | Orthogonalized MCHF | Expt.(Ref.4) |
|---|---|---|---|---|---|
| 3p (lower) | 35.59 | 37.35 (2) | 9.25 | 3.35 | 3.15 (8) |
| 3p (upper) | 39.46 | 40.76 (3) | 5.45 | 1.97 | 3.13 (10) |
| 4p (lower) | 40.50 | 42.34 (2) | 2.31 | 0.74 | 2.02 (10) |
| 4p (upper) | 44.62 | 46.44 (5) | 0.89 | 0.36 | 0.90 (11) |
| 5p (lower) | 42.38 | 44.08 (5) | 0.95 | 0.29 | 0.42 (6) |
| 5p (upper) | 46.60 | 48.47 (7) | 0.31 | 0.13 | 0.17 (5) |



0 0 0 0 4 5 0 6 3 6 8

TABLE IV. Neon 1s correlation-state energies and intensities, from configuration-interaction calculations.

| Root[a] | Excitation | -E(au) | ΔE(eV) | $I_1$[b,c] | $I_2$ | $I_3$ | $I_4$ | $I_5$ | I[d](expt) |
|---|---|---|---|---|---|---|---|---|---|
| | | | | (0.824) | (0.809) | (0.782) | (0.777) | (0.774) | --- |
| 1 | (1s hole-state) | 96.69406 | 0.0 | 100 | 100 | 100 | 100 | 100 | 100 |
| 2 | 2p → 3p | 95.35753 | 36.4 | 1.26 | 0.79 | 2.58 | 2.51 | 2.47 | 3.15(10) |
| 3 | 2p → 3p | 95.22639 | 39.9 | 1.68 | 1.27 | 3.02 | 2.71 | 2.60 | 3.13(10) |
| 4 | 2p → 4p | 95.15613 | 41.9 | 0.85 | 0.54 | 0.66 | 1.53 | 1.48 | 2.02(10) |
| 5 | 2p → 5p | 95.11399 | 43.0 | 0.24 | 0.14 | 0.15 | 0.12 | 0.43 | 0.42(06) |
| 6 | 2p → 6p | 95.03181 | 45.2 | 0.05 | 0.02 | 0.02 | 0.01 | 0.09 | ~0.15[e] |
| 7 | 2p → 4p | 95.00479 | 46.0 | 0.46 | 0.32 | 0.24 | 0.57 | 0.70 | 0.96(11) |
| 8 | 2p → 5p | 94.95227 | 47.4 | 0.07 | 0.05 | 0.05 | 0.02 | 0.11 | 0.17(5) |
| 9 | 2p → 6p | 94.87348 | 49.5 | 0.04 | 0.03 | 0.02 | 0.02 | 0.06 | --- |

a) A characteristic of this type of CI calculation is that some roots are nonsensical: the calculation tries to simulate states that are not adequately spanned by our basis set. These begin to occur after the ninth root and have been omitted. The excitation assignments were made by examining the eigenvectors.

b) Subscripts refer to calculations as numbered in text. The same final-state functions were used throughout. "1" refers to Hartree-Fock initial state; "2" included double excitation to the basic correlating space. In 3,4 and 5 the (3s,3p),(4s,4p), and (5s,5p,6p) orbitals, respectively, were cumulatively transferred to the correlating space.

c) Parenthetical number is actual overlap in the 1s hole state. The relative peak intensities are given as percentages of this value

d) Ref. 4

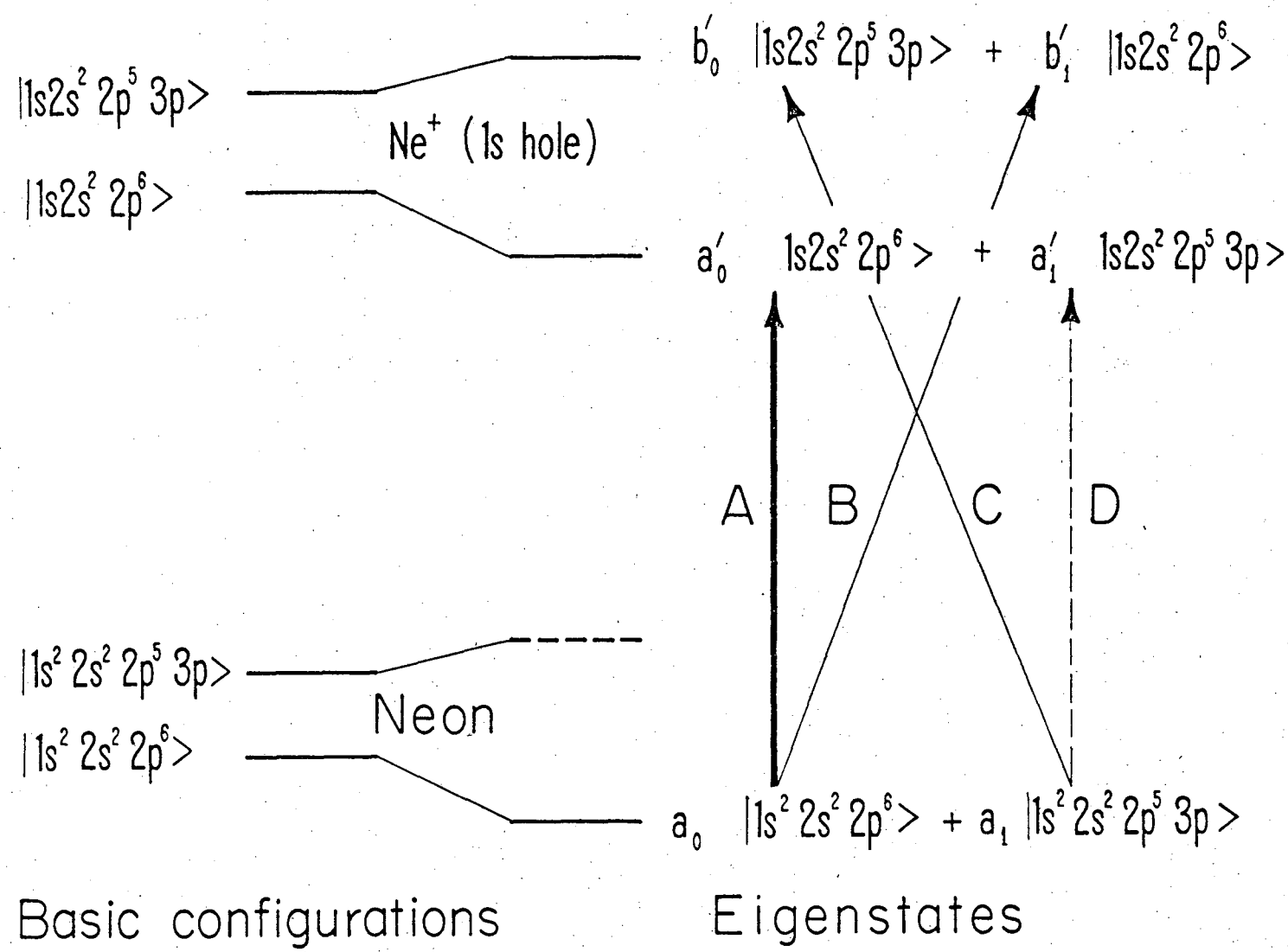
e) Our estimate, from Gelius' figure, Ref. 4

FIGURE CAPTIONS

Fig. 1. Simple model to illustrate the effect of initial-state configuration interaction on correlation-peak intensities in Ne 1s photoemission (not to scale). With 1s exchange suppressed, the $Ne^+$ (1s hole) configuration manifold would closely resemble the ground state manifold (left). Introducing configuration interaction, this 1:1 correspondence would also obtain for the eigenstates (right), and $a_0 \sim a_0'$, $a_1 \sim a_1'$, etc. The main peak arises primarily from path A. Paths B and C arise because the two configurations "look for themselves" in the correlation state. They are of roughly equal strength, but the dashed path (D) is weak.

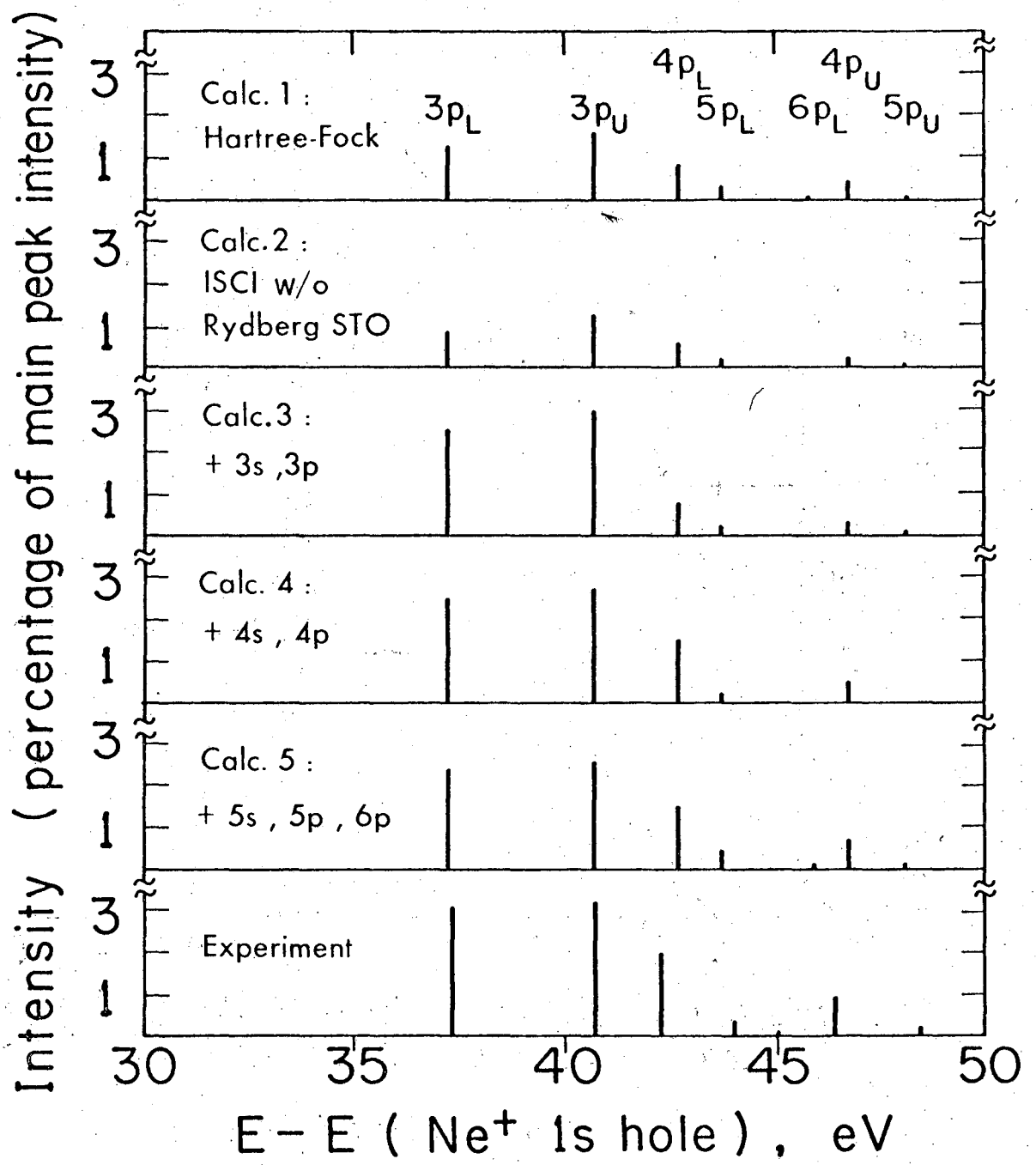
Fig. 2. Bar diagram of the 2p → np peak intensities for eight correlation states of $Ne^+$ (1s hole). As in text, Calculation 1 is Hartree-Fock in the initial state. Calculation 2 includes correlation, but with no double-electron excitation into the Rydberg orbitals. Calculations 3, 4 and 5 include double excitation into the (3s,3p), (3s,ep,4s,4p), and (3s,3p,4s,4p,5s,5p,6p) orbitals respectively. The calculated energies have been shifted upward by 0.8 eV to facilitate comparison with experiment.

Fig. 3. Percentages of experimental correlation-state peak intensities based on sum of np(upper) + np(lower), and total L-shell correlation energies, obtained from various initial-state calculations described in text. The basic CI calculation picks up much of the correlation energy, but the peak intensities are brought into reasonable agreement with experiment only as each state is successively moved into the correlating space.



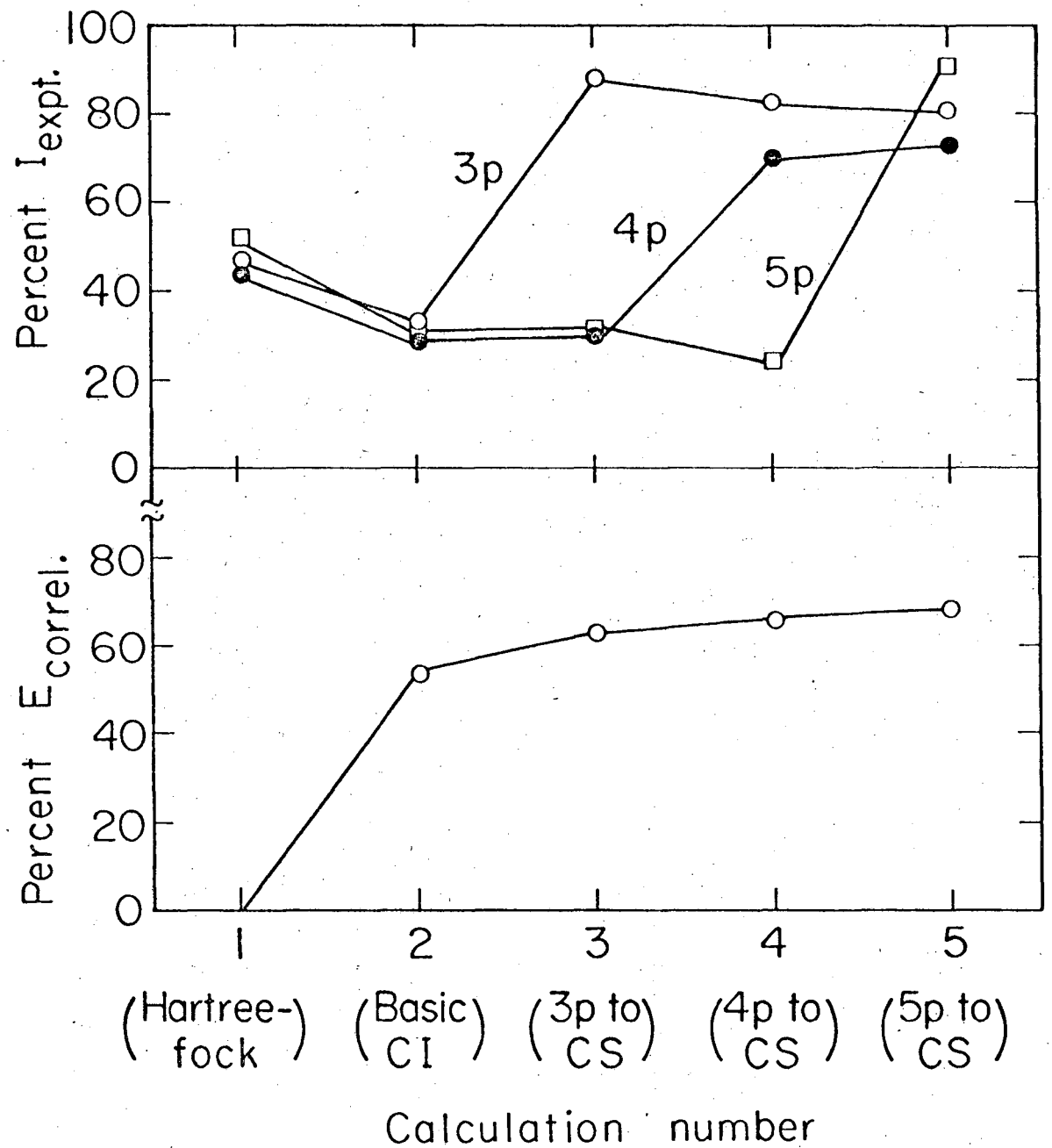

XBL759-4146

Fig. 1.




XBL759-4144

Fig. 2.




XBL759-4145

Fig. 3.

0 0 0 0 4 5 0 6 3 7 0



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0 0 0 0 4 5 0 0 3 7 1

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