PHYSICAL REVIEW A VOLUME 13, NUMBER 4 APRIL 1976

Theory of the neon 1s correlation-peak intensities*

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(Received 11 December 1975)

The correlation-state spectrum accompanying 1s photoemission in atomic neon was calculated by several methods, using the sudden approximation and focusing on states that are approximately described by single-electron excitation of the form $2p \rightarrow np$. All the calculations gave satisfactory energy values, but the predicted intensities differed widely. Multiconfiguration Hartree-Fock (MCHF) orbitals and orthogonalized MCHF orbitals gave intensities in poor agreement with experiment. A final-state configuration-interaction calculation gave accurate energies for seven $2p \rightarrow np$ correlation states, but when combined with a single-determinant initial state, yielded intensities low by about a factor of 2. Initial-state configuration interaction (ISCI), including double-electron excitation of the form $2p^6 \rightarrow 2p^4np^2$, etc., brought the intensities of the $2p^5\ np$-type states into agreement with experiment. It was thus shown that ISCI is of equal importance to final-state CI in determining correlation-peak intensities. Correlation-state (or "shakeup") spectra therefore contain unique information about electron correlation in the ground state.

I. 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

$$E_i + h\nu = E_f + K. \qquad (1)$$

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 "shake-up 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 multiconfiguration 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 Sec. II the theory of correlation-state spectra is briefly discussed. Basis sets and Hartree-Fock results are dealt with in Sec. III. In Sec. IV 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 Sec. V, and in Sec. VI this approach is extended to the initial state.

II. THEORY

In the photoelectric effect a photon excites an N-electron system from its ground state ψ_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,

$$\psi_i(N) \sim \psi_j(N-1)\,\chi_j(\vec{\gamma}_N\vec{k}_N)\,.$$

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 Al K_α 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 $\vec{L}\cdot\vec{S}$ 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]

$$I_j \propto |\langle \psi_i(N'1s)\,|\,\psi_j(N-1)\rangle|^2\,, \tag{2}$$

where $\psi_i(N'1s)$ denotes the $(N-1)$-electron function formed from the neon ground-state wave function by removing the Nth 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 Sec. VI). The main peak in the Ne $1s$ photoemission spectrum is $1s2s^22p^6$, ${}^2S$. 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's 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 $1s\ 2s^2 2p^5 3p$ are experimentally observed, Krause *et al.* pointed out[1] that, at the very least, eigenstates must be formed from ϕ_1 and ϕ_2:

$$\begin{aligned}\psi_{np}(\text{lower}) &= a\phi_1(np) + (1-a^2)^{1/2}\phi_2(np)\,,\\ \psi_{np}(\text{upper}) &= b\phi_1(np) + (1-b^2)^{1/2}\phi_2(np)\,.\end{aligned} \tag{3}$$

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 ψ_{np} (upper or lower) tend to be $\phi_1(np)$ and $\phi_2(np)$; we shall therefore retain the notation ψ_{np} (upper) and ψ_{np} (lower) for the eigenstates.

A comment on the "shake-up" 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 convenience 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 shake-up 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 "shake-up" and "monopole transition," we prefer the term "correlation states."

III. BASIC SETS AND HARTREE-FOCK RESULTS

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

$$\phi_{nlm} = [(2\xi)^{2n+1}/(2n)!]^{1/2} r^{n-1} e^{-\xi r} Y_{lm}(\theta, \phi) . \quad (4)$$

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 $\langle r\rangle_n$ and $\langle r^2\rangle_n$ to the results found by Bagus and Gelius[5] in a numerical MCHF calculation on the Ne (1s hole) states, using

$$\langle r\rangle_n = (2n+1)/2\xi_n$$

and

$$\langle r^2\rangle_n = (n+1)(2n+1)/2\xi_n^2 .$$

Two values of ξ_n were obtained from each of these two relations, corresponding to the upper and lower np states. The agreement among the four ξ_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 ξ_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 ξ_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 shakeoff limits, i.e., the lowest ^1P and ^3P states of Ne^{++} ($1s2s^22p^5$), 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

$E_B(1s) = 868.6$ eV,

^3P shakeoff limit = 45.15 eV,

^1P shakeoff limit = 49.46 eV.

TABLE I. Basis set of STO's 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. (4). Rydberg orbitals appear below dashed lines.

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.

IV. MULTICONFIGURATION HARTREE-FOCK RESULTS

All previous theoretical 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 wave functions 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 wave functions 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 wave functions. After having thus exhausted the immediate possibilities of this method, we turn in Sec. V 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 in-

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

Species	State	Energy (a.u.)	Virial coefficient	Orbital energies (a.u.) $-\epsilon(1s)$	$-\epsilon(2s)$	$-\epsilon(2p)$
Ne	$1s^2 2s^2 2p^6 (^1S)$	−128.547 08	2.000 00	32.77	1.93	0.85
Ne^+	$1s 2s^2 2p^6 (^2S)$	−96.624 02	2.000 09	37.17	2.85	1.82
Ne^{2+}	$1s 2s^2 2p^5 (^3P)$	−94.964 61	1.999 80	38.30	3.69	2.76
Ne^{2+}	$1s 2s^2 2p^5 (^1P)$	−94.806 28	1.999 79	38.18	3.71	2.75

tensities (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 of 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.

V. 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 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+} ($1s 2s^2 2p^5$). 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 $2p$ shake-off 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 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,

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

State	Energy (eV above main peak) Refs. 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)

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

Root[a]	Excitation	$-E$ (a.u.)	ΔE (eV)	I_1[b,c]	I_2	I_3	I_4	I_5	I (expt.)[d]
				(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	$2p \rightarrow 3p$	95.35753	36.4	1.26	0.79	2.58	2.51	2.47	3.15(10)
3	$2p \rightarrow 3p$	95.22639	39.9	1.68	1.27	3.02	2.71	2.60	3.13(10)
4	$2p \rightarrow 4p$	95.15613	41.9	0.85	0.54	0.66	1.53	1.48	2.02(10)
5	$2p \rightarrow 5p$	95.11399	43.0	0.24	0.14	0.15	0.12	0.43	0.42(06)
6	$2p \rightarrow 6p$	95.03181	45.2	0.05	0.02	0.02	0.01	0.09	~0.15[e]
7	$2p \rightarrow 4p$	95.00479	46.0	0.46	0.32	0.24	0.57	0.70	0.96(11)
8	$2p \rightarrow 5p$	94.95227	47.4	0.07	0.05	0.05	0.02	0.11	0.17(5)
9	$2p \rightarrow 6p$	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] Reference 4.

[e] Our estimate, from Gelius's figure, Ref. 4.

respectively. To eliminate this orbital dependence we considered several orbital distribution schemes for the Ne 1s final-state wave functions. 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

$$1s^1 2s^2 2p^6,\quad 1s^1 2s^2 2p^5 3p,\quad 1s^1 2s^2 2p^5 4p,\quad 1s^1 2s^2 2p^5 5p,$$

with the constraint that the 1s occupation is always 1. 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 *and* the main state *at least* 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 vs 1.72 eV for the six states in Table III. 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 2. 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 correlation in the initial state.

VI. 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 $1s2s^22p^5np$ ^2S states would be replaced by $(2p^5np)$ ^1S and ^3S states. The former would be very similar to the $1s^22s^22p^5np$, ^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

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

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

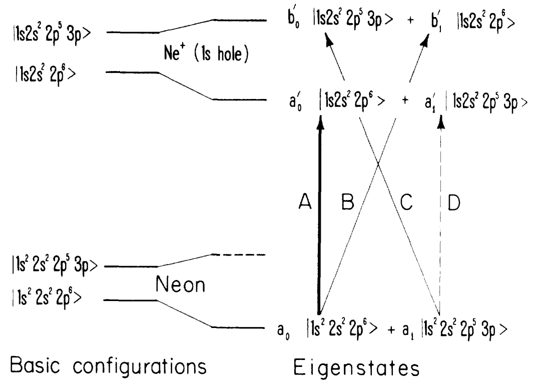

FIG. 1. Simple model to illustrate the effect of initial-state configuration interaction on correlation-peak intensities in Ne 1s photoemission (not to scale). With 1s exchange suppressed, the Ne$^+$ (1s hole) configuration manifold would closely resemble the ground-state manifold (left). Introducing 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.

$$I_{\mathrm{A}} \sim |a_0 a_0'|^2 \sim 1\,,$$

where, for the sake of this example, we take the overlap integrals to be 1 or zero. 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

$$I_{\mathrm{B}} \sim |a_0 b_1'|^2 \sim 0.01\,.$$

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 nonorthogonal, 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 wave functions 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:

$(1s)$	$(2s, 2p)$	$(1s', 2s', 2s'', 2p', 2p'', 3d)_{\text{CS}}$	$(3s, 4s, 5s, 3p, 4p, 5p, 6p)_{\text{RS}}$
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 (^1S) 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 wave function 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 we therefore 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 (Table IV, column 9) 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 one-half 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

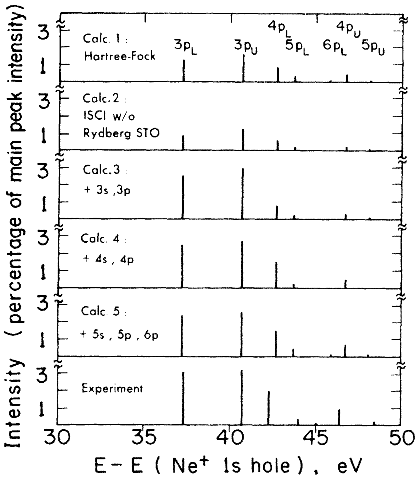

FIG. 2. Bar diagram of the $2p \rightarrow np$ peak intensities for eight correlation states of Ne^+ (1s hole). As in text, calculation 1 is Hartree-Fock in the initial state. Calculation 2 includes correlation, but with no double-electron excitation into the Rydberg orbitals. Calculations 3, 4, and 5 include double excitation into the ($3s, 3p$), ($3s, 3p, 4s, 4p$), 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.

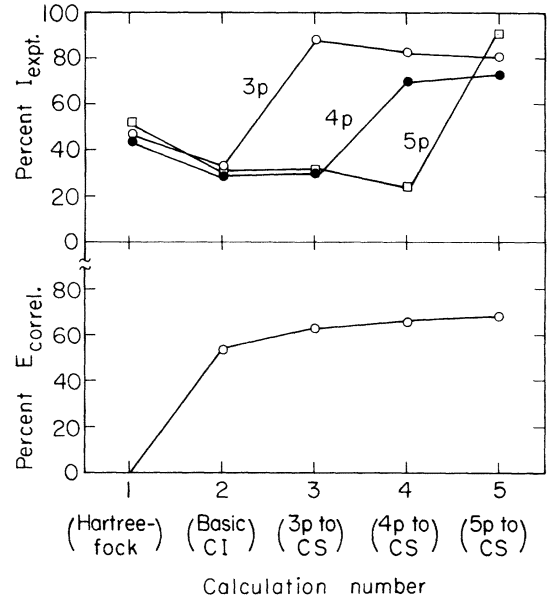

FIG. 3. Percentages of experimental correlation-state peak intensities based on sum of np (upper) $+np$ (lower), and total L-shell correlation energies, obtained from various initial-state calculations described in text. The basic CI calculation picks up much of the correlation energy, but the peak intensities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

of the wave functions 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.

ACKNOWLEDGMENTS

We would like to thank Dr. P. S. Bagus for making his MCHF wave functions available to us and Professor H. F. Schaefer for providing us with his atomic CI program.

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*Work performed under the auspices of the Energy Research and Development Administration.

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