Correlation in the ns^2 ^1S ground states of Ca, Sr, Ba, Zn, Cd, and Hg as determined by multiconfiguration Hartree-Fock calculations and photoelectron spectroscopy

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On the basis of improved multiconfiguration Hartree-Fock calculations for the ground states of Ca, Sr, Ba, Zn, Cd, and Hg it is confirmed that recent photoelectron satellite spectra obtained by Süzer, Lee, and Shirley do require for the interpretation of the observed satellite intensities knowledge of more than just the ground-state composition. The relevant dipole matrix elements between initial and final states are also needed. It is noticed that photoelectron spectroscopy allows the observation of the relaxation of atomic orbitals on a time scale determined by the kinetic energy of the photoelectron.

Recently Süzer, Lee, and Shirley[1] have measured the photoelectron spectra of Ca, Sr, Ba, Zn, Cd, and Hg, which all have ns^2 ^1S ground states. The spectra were excited principally by the 584-Å (21.2 eV) He I line. At this photon energy the main peaks observed in the alkaline-earth atoms correspond to the removal of an ns electron which leaves the ion in the final state $(n-1)p^6 ns$ ^2S. The main peaks in the Zn, Cd, and Hg spectra correspond to the removal of an ns or an $(n-1)d$ electron, leaving the ion in the final states $(n-1)d^{10}ns$ ^2S or $(n-1)d^9 ns^2$ ^2D. However, in addition to the main peaks, several satellites were observed corresponding to different final states of the ion. Peaks corresponding to final states $(n-1)p^6 np$ ^2P and $(n-1)p^6 (n-1)d$ ^2D, for example, were observed in Ca, Sr, and Ba. (Satellites will, in the following, be identified with the corresponding final state of the ion.) This Comment is concerned with the interpretation of the satellite intensities.

Several mechanisms can contribute to the formation of the satellites. In the present case it was proposed[1] that configuration interaction in the initial state (ISCI) would provide an explanation. It can be seen that if the ground-state wave function (for the alkaline earths) is described by the expansion

$$a\,|ns^2\,{}^1S\rangle + b\,|np^2\,{}^1S\rangle + c\,|(n-1)d^2\,{}^1S\rangle\,, \qquad (1)$$

then the final states $np\,{}^2P$ and $(n-1)d\,{}^2D$ can be reached by removal of an electron associated with the second and third components of (1).

It was further suggested in Ref. 1 that the ratio of a satellite intensity to the intensity of the main peak could be compared with the square of the ratio of the relevant expansion coefficients. For example, that the ratio between the intensities of the np ^2P satellite and the main peak would correspond to the ratio b^2/a^2. Such an interpretation of the relative intensities requires, as pointed out by Süzer *et al.*,[1] that the photoionization cross section does not depend on the final state of the ion

or the photoelectron. In other words, in the above example it must be assumed that the probability for removal of a np electron from the $|np^2\,{}^1S\rangle$ component of (1) is equal to the probability for removal of a ns electron from the $|ns^2\,{}^1S\rangle$ component. Then the intensities of the np ^2P and ns ^2S peaks become proportional to the probabilities for finding np and ns electrons, respectively, in the ground state. If this assumption is correct, then experimentally determined intensity ratios would give a direct measure of the ground-state composition.

Süzer *et al.*[1] tested this interpretation by comparing the observed intensity ratios to ratios between expansion coefficients obtained in multiconfiguration Hartree-Fock (MCHF) calculations by Kim and Bagus.[2] The comparison showed that there was agreement for the np ^2P intensity ratios to within a factor of 2 but that the calculated $(n-1)d$ ^2D intensity ratios were smaller than the observed by a factor which varied from 8 (Sr) to 20 (Ba). No MCHF calculations have been published for the ground states of Zn, Cd, or Hg so that a similar comparison of results for these atoms was not possible (for the latter atoms it was possible to reach only the $np\,{}^2P$ final states with the photon energy available).

In the present work MCHF calculations have been carried out, using the code of Froese Fischer,[3] in order to provide theoretical values for a comparison with the experimental findings in Zn, Cd, and Hg. In Sr and Ba, Süzer *et al.*[1] observed satellites corresponding to the final state $4f$ ^2F of the ion. Since a $|4f^2\,{}^1S\rangle$ component was not included in the MCHF calculations of Kim and Bagus,[2] no theoretical estimate of the intensity of the $4f$ ^2F satellite could be obtained. In order to obtain such an estimate, MCHF calculations have been performed for Sr and Ba using the expansion:

$$a\,|ns^2\,{}^1S\rangle + b\,|np^2\,{}^1S\rangle + c\,|n'd^2\,{}^1S\rangle + d\,|n''f^2\,{}^1S\rangle \qquad (2)$$

with $n'=n-1$ and $n''=4$.

The main purpose of the present work was, however, to try to understand the discrepancy for the $(n-1)d$ ^2D intensity ratios for the alkaline earths. Improved MCHF calculations for Ca, Sr, and Ba have been carried out in order to test whether the difficulty in Süzer *et al.*'s interpretation of the $(n-1)d$ ^2D intensities lies with the MCHF expansion or with the assumption that knowledge of the ground-state wave function alone is sufficient to allow a prediction of the satellite intensities.

In order to improve on the ground-state wave functions for Ca, Sr, and Ba, one set of calculations was carried out using the same expansion (1) as Kim and Bagus[2] but allowing the inner $(n-1)p$ orbitals to be different for each component of the wave function. The reason is the following. Comparison of Kim and Bagus' MCHF calculation for the ground state with a HF calculation for $(n-1)d^2$ ^1S shows that the diagonal energy for the $|(n-1)d^2$ $^1S\rangle$ component in the MCHF calculation lies considerably above the HF energy. At the same time, the $(n-1)p$ orbitals are appreciably different in the two calculations. This behavior is much more pronounced for the $|(n-1)d^2$ $^1S\rangle$ than for the $|np^2$ $^1S\rangle$ component. Thus an attempt was made to see whether unconstraining the $(n-1)p$ orbitals in the MCHF calculation would allow the diagonal energy of the $|(n-1)d^2$ $^1S\rangle$ component to obtain a value closer to the HF energy,[4] which is likely to lead to an increase in the $|(n-1)d^2$ $^1S\rangle$ expansion coefficient. Froese Fischer has shown,[4,5] however, that the smaller a correlating component is the more it will deviate from the HF solution. Since the $|(n-1)d^2$ $^1S\rangle$ component is fairly small in the present case, there is consequently no certainty that it is possible to obtain a diagonal energy close to the HF one for this component. However, especially for Ba the difference in diagonal energies between $|ns^2$ $^1S\rangle$ and $|(n-1)d^2$ $^1S\rangle$ is so small that a minor change

in the diagonal energy for $|(n-1)d^2$ $^1S\rangle$ will change the ground-state composition appreciably.

Table I shows the effects of unconstraining the $(n-1)p$ orbitals for the case of Ba. Column 2 shows the wave function obtained with one common $5p$ orbital, while column 3 gives the result of keeping the same $5p$ orbital for the $|6s^2$ $^1S\rangle$ and $|6p^2$ $^1S\rangle$ components but allowing the $5p$ orbital associated with the $|5d^2$ $^1S\rangle$ component to vary freely. Column 4 shows the effect of allowing all three $5p$ orbitals to be different. It is seen that the expansion coefficients are virtually the same in all three calculations (since the diagonal energies remain essentially unchanged). Thus the equivalent results for Ca and Sr are not reported here. To allow additional inner-shell orbitals to be different is likely to have an even smaller effect on the expansion coefficients. It can therefore be concluded that this refinement of the MCHF calculations does not remove the discrepancy between the observed intensity ratios for the $(n-1)d$ ^2D satellites and the ratios between calculated expansion coefficients.

In another set of calculations for Sr and Ba the expansion (2) was used. Calculations were performed with a common inner $(n-1)p$ orbital as well as with different $(n-1)p$ orbitals for each component of the wave function. It turns out that the $|4f^2$ $^1S\rangle$ component is very small and that its inclusion in the expansion is less important than the removal of the constraint on the $(n-1)p$ orbital. Table II shows the wave functions obtained as well as the total energies and the virial coefficients.

The MCHF calculations for Zn, Cd, and Hg used the expansion (2) with $n'=n$ and $n''=4$ for Zn and Cd and $n''=5$ for Hg. Since little improvement was obtained for Ca, Sr, and Ba when the inner orbitals were unconstrained, for Zn, Cd, and Hg the inner orbitals were the same for all components of the wave function (2). Table II shows also these wave

TABLE I. Expansion coefficients and total energies as well as virial coefficients (VT) obtained in MCHF calculations for the ground state of Ba. The MCHF expansion is $a|5p^6 6s^2$ $^1S\rangle$ $+b|5p^6 6p^2$ $^1S\rangle+c|5p^6 5d^2$ $^1S\rangle$. In calculation I, the $5p$ orbital is the same for all components of the wave function. In calculation II, the $5p$ orbital is allowed to be different for the $|5d^2$ $^1S\rangle$ component, while in calculation III the $5p$ orbitals are different for all three components.

	I	II	III
a	0.952 56	0.952 43	0.952 30
b	0.287 40	0.287 27	0.288 29
c	−0.100 14	−0.101 76	−0.100 08
Total energy + 7883 (a.u.)	−0.568 274	−0.568 287	−0.568 397
V T	−1.999 999 991	−2.000 000 004	−2.000 000 002

TABLE II. MCHF expansions $a|ns^2\ {}^1S\rangle + b|np^2\ {}^1S\rangle + c|n'd^2\ {}^1S\rangle + d|n''f^2\ {}^1S\rangle$ for the ground states of Sr, Ba, Zn, Cd, and Hg. For Sr and Ba $n' = n - 1$ and $n'' = 4$, while for Zn and Cd $n' = n$ and $n'' = 4$. For Hg $n' = n$ and $n'' = 5$. Also shown are the total energies and virial coefficients (VT) obtained in the calculations. The calculations for Sr and Ba use four different $(n-1)p$ orbitals while one common $(n-1)p$ orbital is used for Zn, Cd, and Hg.

	Sr I	Ba I	Zn I	Cd I	Hg I
a	0.957 57	0.952 18	0.970 99	0.968 40	0.968 91
b	0.279 47	0.287 98	0.237 87	0.248 22	0.246 26
c	−0.070 48	−0.102 09	−0.022 45	−0.020 96	−0.019 64
d	−0.000 77	−0.003 27	0.010 11	0.012 08	0.013 44
Total energy (a.u.)	−3131.571 408	−7883.568 414	−1777.880 519	−5465.163 430	−18 409.020 65
VT	−1.999 999 957	−1.999 999 995	−1.999 999 972	−1.999 999 999	−2.000 000 001

functions.

Table III shows the observed and calculated intensity ratios for Sr, Ba, Zn, Cd, and Hg. For Sr and Ba, a comparison, except for the $4f\ {}^2F$ intensity ratios, was already carried out by Süzer et al.[1] The agreement to within a factor of 2 for the $np\ {}^2P$ intensities in Sr and Ba was estimated to be inside the experimental uncertainties as well as the uncertainties stemming from the theoretical assumptions. The experimental errors increase with decreasing photoelectron energy. The agreement for the $np\ {}^2P$ intensities in Zn, Cd, and Hg is worse than for Sr and Ba. However, the energies of the $np\ {}^2P$ photoelectrons are much smaller for the former atoms than for the latter. An estimate of the experimental errors is therefore required to decide whether the discrepancy between observed and calculated $np\,{}^2P$ intensities in Zn, Cd, and Hg is within the experimental errors. The same applies to the very large discrepancies between observed and calculated $4f\ {}^2F$ intensities

TABLE III. Comparison between experimental intensity ratios normalized to the $ns\ {}^2S$ peak and ratios between squared MCHF expansion coefficients. The observed ratios are from Süzer et al. (Ref. 1).

		$ns\ {}^2S$	$np\ {}^2P$	$n'd\ {}^2D$ [a]	$n''f\ {}^2F$ [b]
Sr	MCHF	1.00	0.085	0.0054	6.5×10^{-7}
	Observed	1.00	0.065	0.045	4×10^{-3}
Ba	MCHF	1.00	0.091	0.011	1.2×10^{-5}
	Observed	1.00	0.047	0.221	5×10^{-3}
Zn	MCHF	1.00	0.060	0.000 53	0.000 11
	Observed	1.00	0.19		
Cd	MCHF	1.00	0.066	0.000 47	0.000 16
	Observed	1.00	0.15		
Hg	MCHF	1.00	0.065	0.000 41	0.000 19
	Observed	1.00	0.32		

[a] $n' = n - 1$ for Sr and Ba; $n' = n$ otherwise.
[b] $n'' = 5$ for Hg; $n'' = 4$ otherwise.

for Sr and Ba for which the emitted photoelectrons also have fairly small energies. While it is uncertain whether there is disagreement between the observed intensity ratios for the $np\ {}^2P$ and $4f\ {}^2F$ satellites and the ratios calculated from the expansion coefficients in the ground-state wave functions, the large discrepancy for the $(n-1)d\ {}^2D$ satellites in the alkaline-earth spectra is well established [the $(n-1)d\ {}^2D$ photoelectrons have larger energies than the $np\ {}^2P$ photoelectrons], and we next consider the sources of such discrepancies.

It is reasonable to consider whether the discrepancies can be due to the neglect of relativistic effects in the present calculation. A part of the very large discrepancy for the $np\ {}^2P$ satellite in Hg could probably be ascribed to relativistic effects which are known to be important for Hg.[1,6-8] However, Süzer et al.[1] found no deviations from the theoretical LS coupling intensity ratios between spin-orbit components in Zn and Cd which indicates little influence of relativistic effects. For Ba, Grant and Rose[9] have carried out a relativistic Dirac-Fock calculation which leads to a wave function nearly identical to the nonrelativistic one. (A slight increase in the admixture of $5d^2$.) Thus the deviations for atoms other than Hg can not be caused by relativistic effects, and it seems reasonable to conclude that the nonrelativistic MCHF calculations give a reasonable description of the ground-state compositions.

Several problems are associated with attempts to predict the satellite intensity ratios from the values of the ground-state expansion coefficients obtained in MCHF calculations. One of these is inherent in the MCHF technique and caused by the fact that each component in the expansion takes into account the effect of an infinite number of terms.[5] The $|4p^2\ {}^1S\rangle$ correlation component in Ca, for example, takes into account the interaction with the terms $4p^2\ {}^1S$ and $4pnp\,{}^1S$ (for all $n>4$). Thus the coefficient b^2 should be compared to the total intensity of all $np\ {}^2P$ satellites for $n\geqslant 4$. How-

ever, the present calculation does not, in principle, contain the total $np\ {}^2P$ contribution because the $|5p^2\ {}^1S\rangle$ component of the wave function (which is not included in the present calculation) can lead to the final states $np\ {}^2P$ ($n \geq 5$). Thus in principle only a complete MCHF calculation including all terms $|np^2\ {}^1S\rangle$ ($n \geq 4$) should be compared with experiment and should be compared to the total intensity of all $np\ {}^2P$ satellites divided by the intensity of all $ns\ {}^2S$ peaks (main peak plus satellites, the latter can, however, occur for reasons other than ISCI). However, the contributions from higher terms ($n \geq 5$) is rather small and will not change the calculated $n = 4$ intensity by more than 25 to 50% at the most. As a first approximation, it therefore should be fairly safe to compare the $4p\ {}^2P$ and $4s\ {}^2S$ intensity ratio directly with b^2/a^2 if the assumption is valid that the probability for excitation is directly proportional to the expansion coefficient.

The problem of more physical interest is whether this assumption in fact is valid. The probabilities for excitation do, as noted in Ref. 1, depend not only on the expansion coefficients but also on differences in dipole matrix elements between initial and final states. A similar situation exists in optical spectroscopy where it is necessary to know not only the expansion coefficients of the initial (and in the general case also the final) state, but also the dipole matrix element connecting them in order to predict the intensities of lines arising through configuration interaction.

That the assumption is worst for the $(n-1)d\ {}^2D$ peak can be understood from the drastic change in the $(n-1)d$ orbital between the atom and the ion. In Ca I and Sr I, the $(n-1)d^2\ {}^1S$ state lies above $np^2\ {}^1S$ and probably above the first ionization limit. In Ca II and Sr II, the $(n-1)d\ {}^2D$ term is below $np\ {}^2P$ and is actually the lowest excited state. Thus, the $(n-1)d$ orbital collapses between the atom and the ion (this is true also for Ba) although the collapse is less complete than found in other cases[10,11] [a complete collapse involves that the $(n-1)p$ and $(n-1)d$ orbitals are located at approximately the same distance from the nucleus, while in the pres-

ent case the $(n-1)d$ orbital is located well outside $(n-1)p$]. However, it is clear that it is not possible in such a case to neglect the final state when calculating the transition probabilities.

A somewhat similar situation involving the collapse of a d orbital is found for the photoabsorption process in the np^6 shell of the rare gases. The dominant process is a $np \rightarrow \epsilon d$ excitation, and if the ϵd orbital is calculated in the ground-state potential, it has similarities with a collapsed bound orbital, but for the correctly coupled $np^5\ \epsilon d\ {}^1P$ final state this is not the case and use of the ground-state potential to calculate photoabsorption cross sections leads consequently to very inaccurate results.[12-14] In this case the collapse of the ϵd orbital is a result of the calculational technique and has no physical basis. However, in the present case the collapse can be said to have a certain physical reality. In the initial phase of the photoabsorption process the $(n-1)d$ electron is excited out of the $|(n-1)d^2\ {}^1S\rangle$ virtual state, and as the excited electron moves out of the atom, the orbital of the $(n-1)d$ electron left behind collapses. The time scale of the collapse will depend on the speed of the escaping electron.

The collapse can be envisaged as an extreme case of the relaxation connected with all ionization processes. The argument above shows that the use of photon energies slightly above a threshold for ionization will allow the study of relaxation phenomena on a time scale determined by the experimental conditions. The physics involved bears some relation to the post-collision effects studied recently in electron excitation when the excitation energy is close to a threshold.[15]

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