Calculations of photoionization of the 4*d* subshells of Ba and Ba^{2+}

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Photoionization cross sections for the $4d^{10}$ subshells of Ba and Ba^{2+} have been calculated in the Hartree-Fock approximation with and without inclusion of relaxation effects. Use has also been made of the geometric mean between length and velocity results. The present calculations are compared with previous calculations and with results of experiments.

During the past decade there has been considerable interest, both theoretical[1-11] and experimental,[12,13] in the photoabsorption by 4*d* electrons in barium. Recent experimental results on barium by Hecht and Lindau[14] and by Franck and Schnatterly,[15] and on Ba, Ba^+, and Ba^{2+} by Lucatorto *et al.*[16] indicate continued interest in this problem.

In early papers[1,2] Wendin used the random-phase approximation with exchange (RPAE) and approximate inclusion of relaxation and relativistic effects to predict a collective resonance in the 4*d*-photoionization cross section of barium. A subsequent calculation by Fliflet *et al.*[3] calculated Hartree-Fock length and velocity cross sections and included the lowest-order term in many-body perturbation theory. This term accounts for correlations in the initial state and brought the length and velocity results into fairly close agreement. The calculations of Fliflet *et al.*[3] are in fairly reasonable agreement with the experimental results by Connerade and Mansfield[12] and by Rabe, Radler, and Wolff.[13] Fliflet *et al.*[3] also presented results of an RPAE calculation which was in poor agreement with experiment[12,13] and also disagreed with the approximate RPAE calculation by Wendin.[1,2] However, the RPAE calculation without approximations by Wendin[6] is in reasonable agreement with that by Fliflet *et al.*[3]

It was subsequently found[17] that if all the second-order RPAE diagrams were included in a many-body perturbation treatment, the cross section tended to peak too sharply. However, inclusion of relaxation effects tends to cancel the effect of the higher-order RPAE diagrams. The effects of relaxation are included by calculating all excited states in the relaxed field of the ion rather than in the field determined by using orbitals of the neutral atom with one electron removed. A study of the competing effects of higher-order RPAE diagrams and relaxation was presented for the $4d^{10}$ subshell of cadmium by Carter and Kelly.[18] Use was also made of the proposal by Hansen[19] that the geometric mean of length or velocity is less sensitive to ground-state correlations than either length or velocity separately. When there is a subshell with strong absorption such as $4d^{10}$, the length and velocity results tend to bracket experiment, with length larger than velocity. Inclusion of ground-state correlations tends to bring length and velocity into close agreement and rather close to what is obtained by taking the geometric mean. When a subshell has a small cross section and is strongly affected by correlations with neighboring subshells, it is then necessary to calculate the correlations explicitly rather than simply taking the geometric mean of length and velocity.

Hecht and Lindau[14] compare their recent experimental results for 4*d* absorption in barium with various calculations and state that *only the most sophisticated of these calculations have been able to adequately describe previously measured absorption spectra.*[12,13]

The purpose of this paper is to present Hartree-Fock results using the geometric mean of length and velocity calculated both with relaxation and without relaxation. Our results are shown in Fig. 1 and compared with the experimental results of Hecht and Lindau[14] and with RPAE results. The relaxed Hartree-Fock results calculated with length and velocity operators are also listed in Table I along with the geometric mean and the experimental values of Hecht and Lindau.[14] The curve labeled RPAE was calculated by Fliflet *et al.*[3] including correlations only in the $4d^{10}$ subshell. The small kink in the curve about 100 eV is due to a statistical separation into spin-orbit components. The ionization energy was taken as the experimental value (99.28 eV) given by Connerade and Mans-

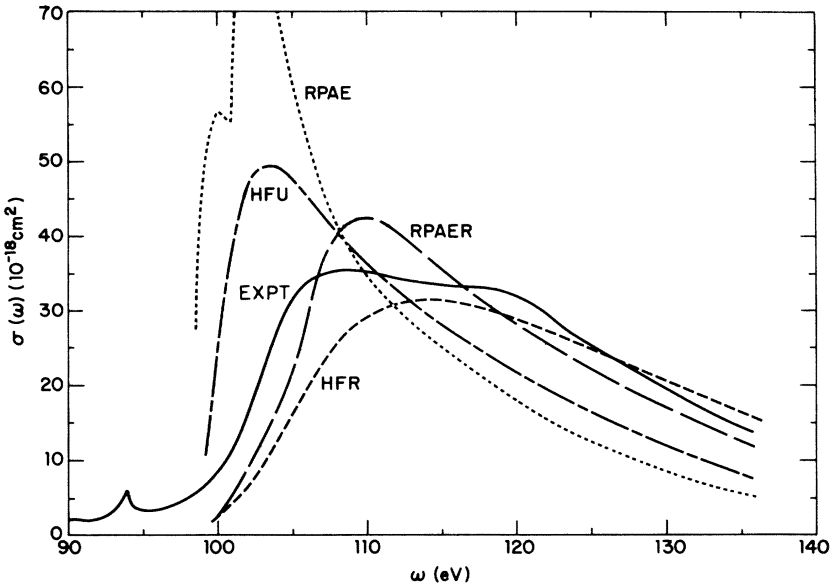

FIG. 1. Photoionization cross section for the $4d^{10}$ subshell of Ba. Expt, experiment by Hecht and Lindau, Ref. 14. ····· RPAE, random-phase approximation with exchange by Fliflet *et al.*, Ref. 3. —— —— —— RPAER, random-phase approximation with relaxed states by Amusia *et al.*, Ref. 8. —— — —— HFU, Hartree-Fock geometric mean calculation with unrelaxed states, present work. - - - HFR, Hartree-Fock geometric mean calculation with relaxed states, present work.

TABLE I. Relaxed Hartree-Fock $4d^{10}$ subshell cross sections (10^{-18} cm^2).

Energy (eV)	HFL[a]	HFV[b]	HFG[c]	Expt[d]
99.42	1.99	1.72	1.84	7.0
100.51	3.64	2.78	3.16	9.2
102.68	10.02	6.85	8.26	19.9
104.18	16.34	10.87	13.30	29.0
105.95	24.39	15.95	19.70	34.0
107.99	32.21	20.83	25.87	35.4
110.30	37.58	24.05	30.04	35.0
112.89	39.72	25.18	31.60	33.8
118.87	37.48	23.19	29.46	32.7
122.27	34.67	21.12	27.03	28.7
125.95	31.21	18.67	24.11	24.0
129.89	27.26	15.96	20.83	19.4
134.11	22.97	13.12	17.34	14.5
143.36	14.47	7.77	10.58	
153.70	7.76	3.85	5.43	
165.13	3.60	1.62	2.38	
177.65	1.47	0.63	0.91	

[a]Hartree-Fock length relaxed.
[b]Hartree-Fock velocity relaxed.
[c]Hartree-Fock geometric mean of length and velocity relaxed. Geometric mean of *kp* and *kf* cross sections taken seriously.
[d]Experimental results from Hecht and Lindau, Ref. 14.

field.[12] Early RPAE results by Amusia[5] differed from those by Fliflet *et al.*,[3] but a later RPAE calculation by Amusia, Ivanov, and Chernysheva[8] is in close agreement with those by Fliflet *et al.*[3] and by Wendin.[6] Amusia *et al.* have also carried out an RPAE calculation using excited states calculated in the relaxed field of the Ba^+ ion $4d^9 5s^2 5p^6 6s^2$. This cross section labeled RPAER (random-phase approximation with relaxation) is shown in Fig. 1. It is readily seen that the RPAE calculations for Ba are extremely sensitive to relaxation effects.

The Hartree-Fock calculations were carried out with $4d^9 kf\,^1P$ and $4d^9 kp\,^1P$ excited states. The contributions of the *kp* final states to the total cross section are very small (approximately 1×10^{-18} cm^2 at maximum) compared to the *kf* contributions, and only unrelaxed *kp* states were used. In Fig. 1 the curve labeled HFU (HFR) is the geometric mean of Hartree-Fock length and velocity results using unrelaxed (relaxed) states. It can be seen that there is a very large effect due to relaxation for them as well as for the RPAE curves. The HFU and HFR results near threshold are too large and too small, respectively; and the HFR curve peaks at a higher energy than the HFU curve. At higher energies the HFR results become

larger than the HFU results. These same qualitative features were found in the cadmium calculations[18] but are more pronounced in the case of barium. These Hartree-Fock results differ qualitatively from those by Combet-Farnoux[4] shown in Fig. 1 of the paper by Hecht and Lindau.[14] Combet-Farnoux did not do a direct Hartree-Fock calculation, however, but included the exchange terms by carrying out an interchannel interaction calculation.[4]

Zangwill and Soven[11] have calculated the $4d$ cross section using a time-dependent density-functional technique. The structure of their calculations is identical (except for numerical techniques) with the RPAE except that the Hartree-Fock energies and orbitals used in the RPAE are replaced by local density approximation (LDA) orbitals.[20] The LDA orbitals used by Zangwill and Soven are calculated in a field which is asymptotically neutral (of V^N type) rather than coulombic (of V^{N-1} type) as would be expected physically. Their $4d$-subshell cross section is in good agreement with experiment; however, they report[20] that in other cases in which agreement with experiment is good, it is worsened by approximately 50% when the orbitals are calculated in a potential with a Coulomb tail. Their calculations also do not account for relaxation effects which are seen to be very significant both in the RPAE and Hartree-Fock calculations.

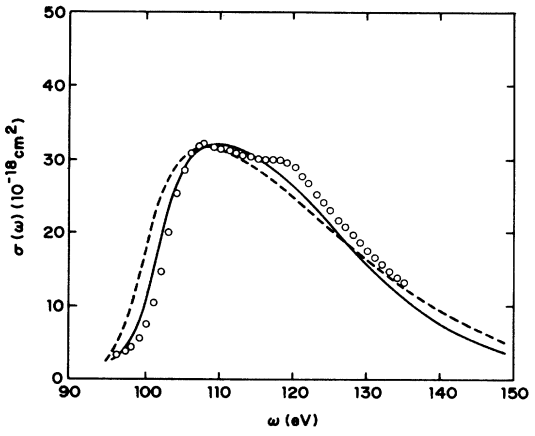

FIG. 2. Photoionization cross section of the $4d^{10}$ subshell of Ba. ——, calculation by Zangwill and Soven, Ref. 21. ---, Hartree-Fock calculation with relaxed states and threshold at 93.8 eV from Ref. 11. ○ experimental results by Hecht and Lindau, Ref. 14, normalized to peak of calculated curve by Zangwill and Soven.

Hecht and Lindau report that their data have been normalized to the peak of the RPAER calculation. However, the curve by Hecht and Landau peaks near 35.5×10^{-18} cm^2 whereas the RPAER calculation of reference peaks near 43×10^{-18} cm^2. However, the data by Hecht and Lindau are in good agreement with the total absorption measurements by Rabe, Radler, and Wolff. The curve by Rabe *et al.*, which represents total absorption rather than just the $4d$ subshell, peaks at approximately 39×10^{-18} cm^2 near 106 eV and is in close agreement with that by Hecht and Lindau beyond 110 eV. In addition, the curve by Hecht and Lindau also is in good agreement with the very recent total absorption data by Lucatorto *et al.*[16]

In Fig. 2 the results of Zangwill and Soven are shown for the $4d^{10}$ subshell.[21] The data of Hecht and Lindau have been normalized to the peak of the Zangwill-Soven cross section and are shown as open circles. The dashed curve is our relaxed Hartree-Fock calculation calculated using the local density approximation threshold (93.8 eV) obtained by Zangwill and Soven.[11,21]

The calculations for neutral barium are very sensitive to the field in which the outgoing electron's wave function is calculated. It is then of interest to examine the $4d$ cross sections for ionized barium for comparison. Lucatorto *et al.*[16] have recently measured the $4d$ absorption spectra of Ba, Ba^+, and Ba^{2+}. The spectra of Ba and Ba^+ are similar, with most of the absorption in the continuum. For Ba^{2+}, however, there is much absorption in discrete lines and the photoionization cross section is reduced compared to Ba and Ba^+. We have carried out Hartree-Fock calculations (both relaxed and unrelaxed) for the $4d^{10}$-photoionization cross section of Ba^{2+} $4d^{10}5s^25p^6$. Our results, taking the geometric mean between length and velocity, are shown in Fig. 3. Our calculations only included the $4d\rightarrow\epsilon f$ transitions; the $4d\rightarrow\epsilon p$ transitions are expected to be negligible as for Ba. The experimental points in Fig. 3 are from the recent measurements by Lucatorto *et al.*[16] and have an estimated uncertainty of 25%. By comparing Figs. 1 and 3, it is clear that there is less continuum oscillator strength for Ba^{2+} than for Ba; and for Ba^{2+}, unlike Ba and Ba^+, Lucatorto *et al.*[16] see much oscillator strength in discrete autoionizing lines lying below the $4d^9\,^2D_{5/2,3/2}$ limits. In Fig. 3 both the relaxed (HFR) and the unrelaxed (HFU) cross sections show a monotonic decrease with increasing photon energy which is consistent with the experimental results. Contrary to the case of

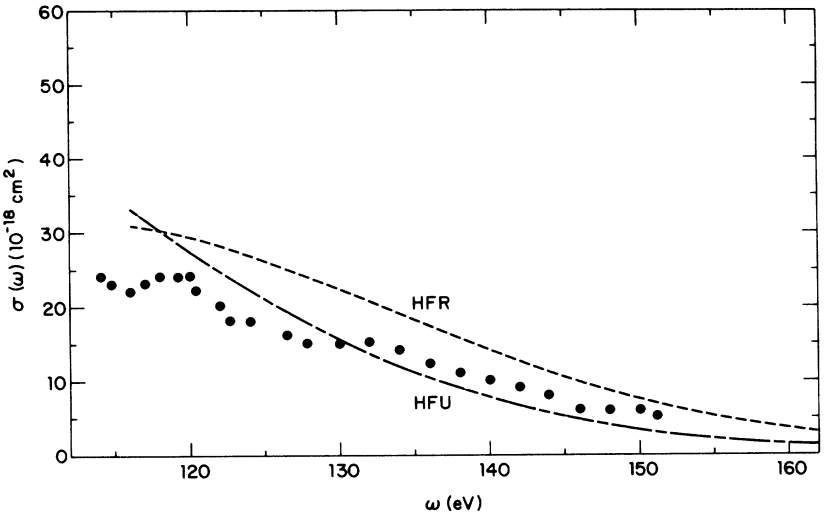

FIG. 3. Photoionization cross section for the $4d^{10}$ subshell of Ba^{2+}, $4d \rightarrow \epsilon f \ldots$, experimental points by Lucatorto *et al.*, Ref. 16. — — — HFR, Hartree-Fock geometric mean calculation with relaxed states, present work. —— — —— HFU, Hartree-Fock geometric mean calculation with unrelaxed states, present work.

neutral barium, however, the HFU results appear to be in better agreement with experiment, although the quoted experimental accuracy is only 25%.

In summary, this work demonstrates that Hartree-Fock calculations can give reasonable photoionization results for a complicated system such as the $4d^{10}$ subshell of barium. Further, relaxation effects can in cases such as neutral barium be very important in cross section calculations. In addition, the utility of the geometric mean between length and velocity has been demonstrated.

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