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PHYSICAL REVIEW A VOLUME 6, NUMBER 1 JULY 1972

Relative Energies of the Lowest Levels of the $f^q ps^2$, $f^q ds^2$, and $f^{q+1} s^2$ Electron Configurations of the Lanthanide and Actinide Neutral Atoms*

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(Received 27 August 1971; revised manuscript received 6 March 1972)

Linearization of the differences between the lowest levels of the $f^q ps^2$, $f^q ds^2$, and $f^{q+1}s^2$ electron configurations as a function of q is demonstrated for the lanthanide and actinide series. A linear extrapolation of these differences estimates the energy of the lowest level of the $4f^{14}6p6s^2$ electron configuration of Lu to be 3.5×10^3 cm^{-1} higher than the measured value. This deviation from linearity is attributed to expected discontinuities at the $q=0$ and 14 ends of the $f^q ds^2$ series. In the actinide series the corresponding linear extrapolation predicts the lowest level of the $5f^{14}7p7s^2$ electron configuration of Lr to be $(2.3\pm3)\times10^3$ cm^{-1} above the expected $5f^{14}6d7s^2$ ground state, after correction for a corresponding 3.3×10^3 cm^{-1} deviation expected at the end of the actinide series.

Rapidly accumulating spectroscopic data for the members of the lanthanide (Ln) and actinide (An) series have yielded important new information on the relative energies of the lowest levels of the principal electron configurations. As a result there have been a number of recent efforts to correlate and predict these relative energies.[1-6] Our approach is based on the simple yet surprisingly accurate assumption that the distinctive irregular characteristic in the energy differences

$$E(f^q l s^2) - E(f^{q+1} s^2) \equiv \Delta_l E(q) \tag{1}$$

between the lowest levels of the indicated electron configurations involve only the electrostatic and spin-orbit interaction energies of the parent f^q and f^{q+1} configurations. Examples of this distinctive irregular characteristic are found here in Figs. 1–4, where the $\Delta_l E(q)$ are plotted for $l=p$ and $l=d$, for both the $4f$ (Ln) and $5f$ (An) series elements. The residual regular contributions to these energy differences derive primarily from electron attraction by the effective nuclear charge and from repulsions between the f electrons and the outer valence s^2, p, and d electrons. These we treat to a good approximation as linear in q, the number of f electrons in the parent f^q configuration, where q goes from 0 to 13 across each series.

Previously[1] we applied Jørgensen's expression[7]

$$\Delta_l E(q) = W + (E-A)\,q - \tfrac{9}{104}\,N(S)\,E^1 - M(L)\,E^3 - P(S,L,J)\,\zeta_f \tag{2}$$

(which derives from an extension of Griffith's treatment[8] of the third ionization potentials of the first transition series) in a successful correlation of $\Delta_d E(q)$ for the neutral gaseous atoms of the Ln and An series. Details of the definition of the terms in Eq. (2) and its application are given in Ref. 1. It is only important here to point out that in our application of this equation we departed in two ways from Jørgensen's original application. First, whereas Jørgensen applied it to the first $f^{q+1} \to f^q d$ band energies of various Ln(III) complexes where the number of known data points are relatively sparse and where large ligand-field contributions arise for the $f^q d$ configurations, we applied it as indicated above to the neutral Ln and An atoms where the data points are more extensive and where ligand-field contributions are nonexistent. And secondly, whereas Jørgensen approximated the Racah parameter E^1 as a constant, we provided that it be variable by taking it directly, with the Racah parameter E^3 and the spin-orbit interaction parameter ζ_f, from the published data on the $\mathrm{Ln(III)}_{aq}$ aquo-ions and on the An(III) ions in various crystals.[9,10] Because of the known isolated and shielded nature of f electrons we assumed that the above values for E^1, E^3, and ζ_f adequately represent the corresponding actual values for the neutral gaseous atoms, and that the latter are not significantly different for the $f^q ds^2$ and $f^{q+1}s^2$ configurations.

Then when the measured values of $\Delta_d E(q)$ are adjusted via subtraction of the energy of the last three terms in Eq. (2), the resulting auxiliary linear expression

$$\Delta_d E' = W + (E - A)\,q \qquad (3)$$

could be fitted to the adjusted data to within $\pm 2 \times 10^3$ cm^{-1}. Thus we correlated nine known data points of the Ln series and four known data points of the An series. Subsequent to submission of our results for publication three new measured data points were received. Two of these, $\Delta_d E(q)$ for Pa and U, were within the estimated $\pm 2 \times 10^3$ cm^{-1} error limit; however, the new $\Delta_d E(13)$ for Yb was below our predicted value by 3.8×10^3 cm^{-1}, almost twice the value of our estimated error limit.

This marginally anomalous Yb result has led us here to a general reexamination of the theoretical basis of Eq. (2), particularly with regard to its dependence upon E^1. The true dependence of $\Delta_l E(q)$ upon E^1 is obscured in Eq. (2) because the term $+\frac{9}{13}E^1$ is implicitly included in the parameter A, along with the parameter E^0 and an effective f-l-electron interaction parameter. This was originally recognized by Johnson[11] and later by Jørgensen,[12] and it can be easily verified[13] by showing that the coefficient of E^1 in the difference between the electrostatic energies of the Hund's-rule ground states of the f^q and f^{q+1} electron configurations is $-\frac{9}{104}N(S) - \frac{9}{13}q$, where the integers $N(S)$ were given previously[10] with the $M(L)$ and $P(S, L, J)$ values. The coefficients of E^3 and ζ_f in Eq. (2) were similarly checked and they were found to be accurate.

We conclude from the above that it is consistent to apply Eq. (2) as an approximation for $\Delta_l E(q)$ only if E^1 is also approximated as a constant across each series. If the E^1 values are taken, as we have done, from the literature values for various chemical complexes of the Ln(III) and An(III) ions, where they are not constant but approximately linear in q across each series, then in this more refined approximation, to be consistent, we must remove $+\frac{9}{13}E^1$ from A in the constant parameter $E - A$. Then $\Delta_l E(q)$ is properly written as

$$\Delta_l E(q) = W + (E - A')\,q - M(L)E^3 - P(S, L, J)\,\zeta_f, \qquad 0 \leqslant q < 7 \qquad (4a)$$

$$\Delta_l E(q) = W + (E - A')\,q - 9E^1 - M(L)E^3 - P(S, L, J)\,\zeta_f, \qquad 7 \leqslant q \leqslant 13 \qquad (4b)$$

where A' is introduced to distinguish the change here from the previous A.

Our first application of Eq. (4) above to $\Delta_d E(q)$ for the neutral gaseous atoms of the Ln series did not remove the Yb anomaly; moreover it produced even larger discrepancies between the observed and calculated values for the entire right-hand sides of both the Ln and An series. Now we calculated the Yb point to be much too high, taking, as before, variable E^1, E^3, and ζ_f values from the available data on the various M(III) complexes. Thus it appeared that the selection of a set of E^1, E^3, and ζ_f values is by far more critical when applying Eq. (4) than when applying Eq. (2), and this led us to consider more carefully the validity of approximating E^1, E^3, and ζ_f for the metal atoms directly from the corresponding values of the M(III) complex ions. Estimates indicated that our previous approximations for E^3 and ζ_f were adequate, because the terms involving these parameters were much too small to begin to account for the previous Yb anomaly or the even larger discrepancies we now found using Eq. (4). On the other hand, the E^1 term makes a relatively large contribution on the right-hand sides of these series, so it is here where the largest errors in $\Delta_d E(q)$ must arise due to the uncertainties in the actual values of E^1. Accordingly, we decided that if our estimated values for E^1 are adversely affecting the calculations, then it is better to approximate E^1 as a linear function[14] of q, $E^1(q) = a + bq$, and let the measured data points $\Delta_d E(q)$ determine the two constants a and b, defining an effective $E^1(q)$ for both configurations in each series.

The determination of these effective $E^1(q)$ functions for the neutral metal atoms of the Ln and An series was made in the following way: The hydrogenic ratio of 10:1 for $E^1(q)$ to $E^3(q)$ was maintained in each final determination.[15] First, there

TABLE I. The f-electron linearization function for the lanthanides $F_l(q)$ and the actinides $F_a(q)$.

q	$F_l(q)$ (10^3 cm^{-1})	$F_a(q)$ (10^3 cm^{-1})
0	−0.892	−1.420
1	−5.107	−4.298
2	−6.489	−5.106
3	0	0
4	6.806	5.564
5	5.956	5.748
6	2.596	5.227
7	47.192	31.730
8	43.382	29.646
9	43.046	30.367
10	51.482	37.661
11	60.329	45.422
12	60.796	47.192
13	57.853	46.625

are a sufficient number of measured data points $\Delta_d E(q)$ for the left half of each series to calculate a W and an $E - A'$ directly from Eq. (4a) by the method of least squares with the M(III) complex values for preliminary estimates of $E^3(q)$ and final estimates of ζ_f. Next, the linear $\Delta_d E'(q)$ function so obtained is extrapolated to the region of $q = 7$ to 13. For the right half of the series the first estimate of E^1 is then, from Eq. (4b),

$$E^1(q) = a + bq \approx \frac{\Delta_d E'(q) - \Delta_d E(q) - P(S, L, J)\,\zeta_f}{9 + \frac{1}{10}M(L)}\,, \qquad (5)$$

where $\Delta_d E(q)$ is a measured data point. Using Eq. (5), we calculated first estimates for the constants a and b from all the measured data points by the method of least squares. Finally, we obtained the best estimate for the effective $E^1(q)$ by extrapolating the first estimate above for $E^1(q)$ to the left half of the series, taking $E^3(q) = 0.1E^1(q)$, and then repeating the calculation.

As determined above, the effective $E^1(q)$ for the neutral metal Ln atoms ranges from $E^1(2) = 5.10 \times 10^3$ cm^{-1} to $E^1(12) = 5.90 \times 10^3$ cm^{-1} or $a = 4.94 \times 10^3$ cm^{-1} and $b = 0.078 \times 10^3$ cm^{-1}; this compares to the corresponding Ln(III) aquo-ion values of $E^1(2) = 4.54 \times 10^3$ cm^{-1} and $E^1(12) = 7.14 \times 10^3$ cm^{-1}. The average value of this effective $E^1(q)$ over the Ln series is about the same as over the Ln(III) aquo-ion series, but the rate of change of $E^1(q)$ across the later is three times greater than across the former.

Similarly, the effective $E^1(q)$ for the neutral metal An atoms ranges from $E^1(3) = 3.76 \times 10^3$ cm^{-1} to $E^1(12) = 4.31 \times 10^3$ cm^{-1}, or $a = 3.57 \times 10^3$ cm^{-1} and $b = 0.062 \times 10^3$ cm^{-1}; and this compares to the corresponding An(III) crystal-ion values of $E^1(3) = 3.11 \times 10^3$ cm^{-1} and $E^1(12) = 5.0 \times 10^3$ cm^{-1} (estimated).[16] It is worth noting that since we work above in an approximation which accounts for $E^1(q)$ and $E^3(q)$ as linear functions of q, to be consistent we must also account for the Racah parameter E^0, implicit in the parameter A', as a linear function of q. This in effect makes the parameter A' in Eq. (4) linear in q, and thus it implicitly introduces an additional term which is quadratic in q. Our analysis indicates, however, that to within the accuracy of the present treatment this quadratic term is insignificant.

We designate the terms other than $W + (E - A')q$ in Eq. (4) as the negative of the f-electron linearization functions $F_l(q)$ for the Ln series and $F_a(q)$ for the An series. When the numerical values of these functions, listed in Table I, are added to $\Delta_d E(q)$, they transform it into the linearized form, $\Delta_d E'(q)$, shown in Figs. 1 and 2. Furthermore, as we will show, these same numerical values apply more generally to the linearization of all $\Delta_l E(q)$ for both series.

A comparison of our present results in Fig. 1 and in Table I with those we reported earlier for the Ln $\Delta_d E(q)$ series[1] shows a generally improved correlation of data with calculations and, more

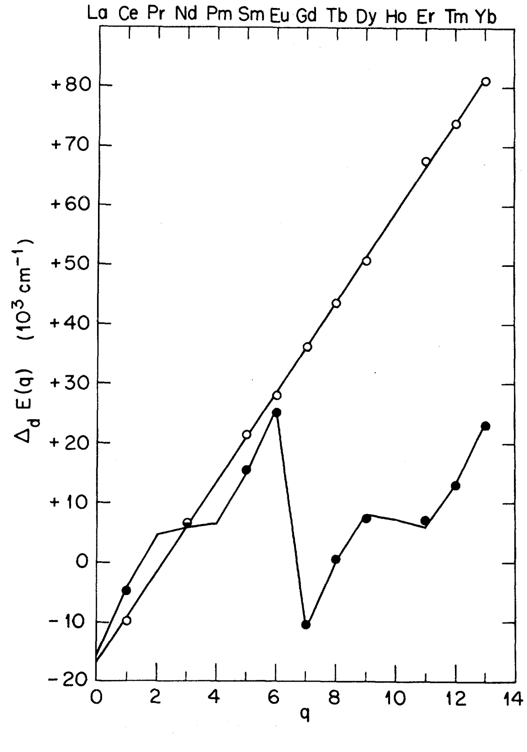

FIG. 1. Experimental (●) and calculated (solid lines) differences $\Delta_d E(q) = E(f^q ds^2) - E(f^{q+1}s^2)$ for the lanthanide neutral atoms. Also shown is the auxiliary linear function $\Delta_d E'(q)$ whose experimental points (○) are fitted by the method of least squares to a straight line. $W = -16.82 \times 10^3$ cm^{-1} and $(E - A') = 7.56 \times 10^3$ cm^{-1}.

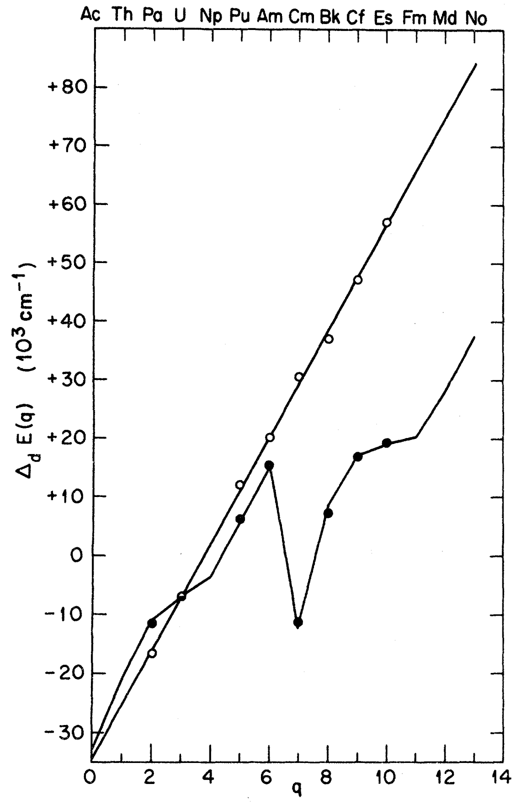

FIG. 2. Experimental (•) and calculated (solid lines) differences $\Delta_d E(q)$ for the actinide neutral atoms. $W = -34.23 \times 10^3$ cm^{-1} and $(E - A') = 9.09 \times 10^3$ cm^{-1}.

importantly, the elimination of the Yb anomaly. Similarly, a comparison of the results in Fig. 2 and in Table II with those we reported earlier[1] for the An $\Delta_d E(q)$ series shows an equally accurate correlation of data with calculations. Furthermore, now we obtain substantially lower calculated values for Md and No, and this places us in agreement with the corresponding Md and No predictions of Brewer.[2]

We have successfully extended the treatment above to many of the corresponding energy differences between electronic configurations involving f-electron promotion of the form $f^q l_1, l_2, l_3$ to $f^{q+1} l_2, l_3$ in the Ln and An gaseous atoms and ions. In all of the 15 lanthanide cases treated to date[5] we find that the $F_t(q)$ values of Table I transform the irregular differences into the linear form. In each case the slightly different value determined for the parameter $E - A'$ reflects differences in effective f-electron and valence-electron repulsions and possibly slight differences in f-electron and valence-electron shielding. Also the very different values determined for W reflect the very different valence-electron binding energies in the various systems. These fifteen cases involve a total of 86 data points, and of these, two points fail to follow the linearization to within $\pm 2 \times 10^3$ cm^{-1}, 25 points fall from 1×10^3 to 2×10^3 cm^{-1} from the straight lines, and the standard deviation of all 86 points is 0.6×10^3 cm^{-1}. Similarly, in the seven actinide cases treated to

TABLE II. Calculated and observed experimental energy differences between $E(f^q ds^2)$, $E(f^q ps^2)$, and $E(f^{q+1}s^2)$ for the lanthanide and actinide gaseous atoms.

		$\Delta_d E(q)$ (10^3 cm^{-1})		$\Delta_p E(q)$ (10^3 cm^{-1})			$\Delta_d E(q)$ (10^3 cm^{-1})		$\Delta_p E(q)$ (10^3 cm^{-1})	
q	Ln	Calc	Obs	Calc	Obs	An	Calc	Obs	Calc	Obs
0	La	−15.93	−15.197?[a]	4.48	+0.02?[b]	Ac	−32.81		−18.60	
1	Ce	−4.15	−4.76	15.41		Th	−20.84		−7.12	
2	Pr	4.80		23.44		Pa	−10.94	−11.44	2.30	1.57
3	Nd	5.87	6.76	23.60		U	−6.96	−7.02	5.80	6.44
4	Pm	6.63		23.43		Np	−3.43		8.84	
5	Sm	15.04	15.5	30.92		Pu	5.48	6.31	17.26	17.78
6	Eu	25.97	25.2	40.93		Am	15.09	15.2[c]	26.39	
7	Gd	−11.06	−10.95	2.98	2.49	Cm	−2.32	−1.21	8.48	8.05
8	Tb	0.31	0.29	13.44	13.62	Bk	8.86	7.4	19.18	
9	Dy	8.22	7.56	20.42	20.61	Cf	17.22	16.91[d]	27.06	
10	Ho	7.34		18.63		Es	19.02	19.37[d]	28.37	
11	Er	6.06	7.18	16.42	16.46	Fm	20.35		29.22	
12	Tm	13.16	13.12	22.60	20.47	Md	27.67		36.05	
13	Yb	23.67	23.19	32.19	32.06	No	37.33		45.22	

[a] This observed value has recently been suggested by Martin (Ref. 4), but it is not yet definitive, hence the question mark.

[b] This value follows from Martin's suggested observed value $\Delta_d E(0) = -15.197 \times 10^3$ cm^{-1} for La and the observed $\Delta_{pd} E(0) = 15.22 \times 10^3$ cm^{-1} value in Table III.

[c] In Ref. 1 this value is listed as $+17.858 \times 10^3$ cm^{-1} but this is inappropriate because 17.858×10^3 cm^{-1} relates to the ${}^8D_{5/2}$ level of the $5f^7 7s^2$ electron configuration of Am and this is not the lowest level. The energy of the lowest level, ${}^8H_{3/2}$, has not been measured, so we estimate it here to be 2.7×10^3 cm^{-1} below ${}^8D_{5/2}$ by reference to the analogous Eu case; cf. Ref. 1.

[d] E. F. Worden and J. G. Conway (private communication).

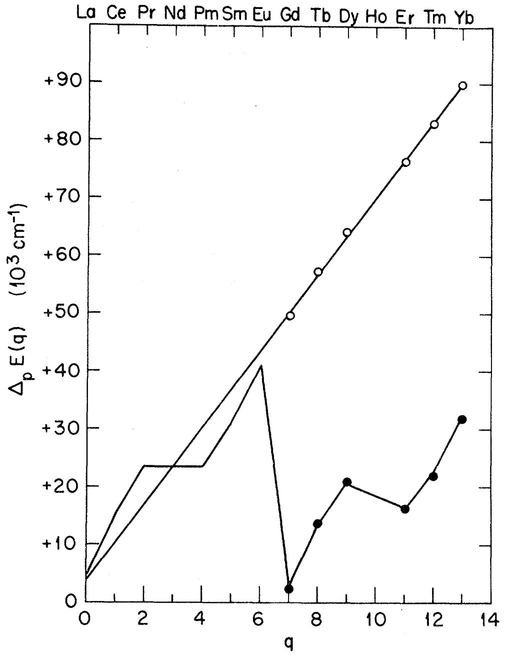

FIG. 3. Experimental (•) and calculated (solid lines) differences $\Delta_p E(q) = E(f^q p s^2) - E(f^{q+1} s^2)$ for the lanthanide neutral atoms. $W = 3.66 \times 10^3$ cm^{-1} and $(E - A') = 6.64 \times 10^3$ cm^{-1}.

date, involving over 30 data points, the numerical values of $F_a(q)$ in Table I linearize all points, with just a few rationalizable exceptions involving $q = 0$ and 1. For the purpose of the final developments in this paper, we present here in Table II and Figs. 3 and 4 some of these results for $\Delta_p E(q)$ for the Ln and An neutral atoms.

Although it is useful to apply our linearization technique in the verification and interpolation of the energy differences for the known or readily measurable lanthanide and actinide elements and ions, it is of even greater interest, in view of the recent activity in the prediction of physical and chemical properties of the superheavy elements,[12,17] to have a dependable analytic expression with which we can extrapolate the known data from the left half of the An series to describe the electronic structures of those elements and ions in the right half of this series, particularly those that are presently or permanently unavailable for spectroscopic studies. An example of such an application is shown next in our analysis of the lowest energy-level separation, $\Delta_{pd}E(q)$, between the $5f^{14}7p7s^2$ and $5f^{14}6d7s^2$ electron configurations for the An series.

Predictions recently appeared that the ground-state electron configuration of atomic Lr is not $5f^{14}6d7s^2$, as might be expected from the simple systematics of the Periodic Table, but $5f^{14}7p7s^2$. Brewer[2] smoothly extrapolated the differences between the lowest levels of the $5f^q7p7s^2$ and $5f^q6d7s^2$ electron configurations for the neutral atoms where these data are known, in the left half of the actinide series, to where they are not known in the right half. He estimated that the lowest level of the $5f^{14}7p7s^2$ configuration of Lr is the ground state and that it is below the lowest level of the $5f^{14}6d7s^2$ configuration by $(8 \pm 2) \times 10^3$ cm^{-1}. Subsequently, on the basis of the relativistic Hartree-Fock method, Mann[18] calculated this energy separation to be $(4 \pm 2) \times 10^3$ cm^{-1}, in essential agreement with Brewer's estimate.

We consider next the same data considered by Brewer, but in addition we base our extrapolation on our linearization method. We showed above that the irregular nonlinear characteristic is to a very good approximation the same for $\Delta_p E(q)$ as it is for $\Delta_d E(q)$, with one linearization function $F_l(q)$ linearizing both of these sets of lanthanide data, and another $F_a(q)$ linearizing both of the corresponding sets of actinide data. In this approximation it follows that for both series

$$\Delta_{pd}E(q) \equiv \Delta_p E(q) - \Delta_d E(q) = \Delta_p E'(q) - \Delta_d E'(q) \tag{6}$$

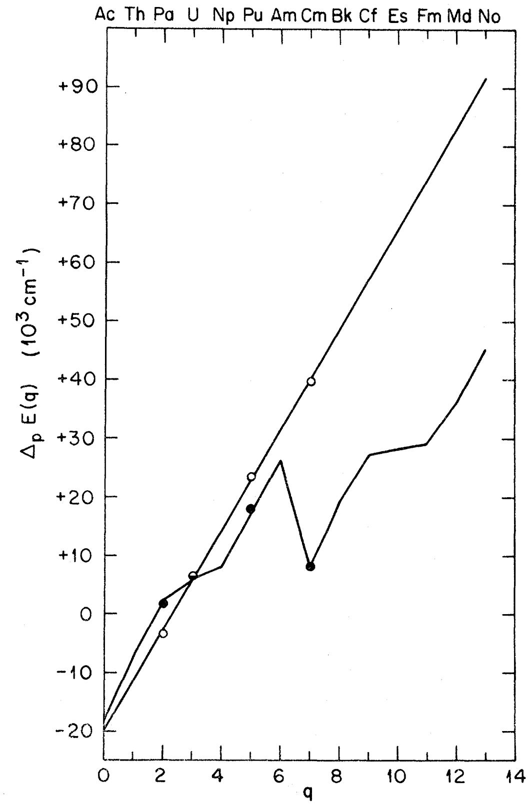

FIG. 4. Experimental (•) and calculated (solid lines) differences $\Delta_p E(q)$ for the actinide neutral atoms. $W = -20.02 \times 10^3$ cm^{-1} and $(E - A') = 8.60 \times 10^3$ cm^{-1}.

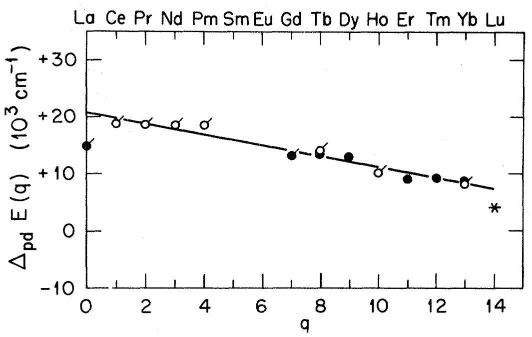

FIG. 5. The estimated linear difference $E(f^qps^2) - E(f^qds^2)$ and experimental points. The points (•) are measured differences in the neutral atom. The points (σ) are the corresponding measured differences in the singly ionized form of the element, with next lower atomic number and minus the s^2 electrons. The point (*) is the observed difference for both Lu and Yb^{+1}.

must also be linear in q with the slope and intercept predetermined by the difference between the slopes and the difference between the intercepts, respectively, of $\Delta_pE'(q)$ and $\Delta_dE'(q)$.

There are two ways to extrapolate the $\Delta_{pd}E(q)$ data according to Eq. (6). The first is to draw the straight line determined by the difference between the intercepts and the difference between the slopes of $\Delta_pE'(q)$ and $\Delta_dE'(q)$, as indicated above. We show this line for the Ln series in Fig. 5 and for the An series in Fig. 6, line a. The second way to make this extrapolation is to draw a straight line by the method of least squares directly through the $\Delta_{pd}E(q)$ measured data points of Table III and in Figs. 5 and 6. We determined the latter line for the Ln series and found that it overlaps the former line in Fig. 5.[19] Thus our argument for the linearity of $\Delta_{pd}E(q)$ is strongly supported. Similarly, we determined the latter line for the An series, as shown in Fig. 6, line b.[20] The reason for the slight difference between An lines a and b in Fig. 6 is that fewer data points are known for the An series than for the Ln series, so the slopes and intercepts for the former are somewhat less certain and the two methods of extrapolation give slightly different results. Accordingly, we draw the dashed line in Fig. 6, the average of lines a and b, as the best estimate.

Additional information listed in Table III on the measured data points $\Delta_{pd}E(q) = E(f^qp) - E(f^qd)$ for the Ln^{+1} ions[3] further supports our argument for the linearity of $\Delta_{pd}E(q)$ to within $\pm 2\times 10^3$ cm^{-1}, and it also draws attention to the somewhat larger endpoint ($q = 0$ and 14) deviations from linearity in both series. These data points are represented by the open circles in Fig. 5, where in order to maintain the proper q values Ba^{+1} is at $q = 0$, La^{+1} is at $q = 1$, etc. Coincidentally, it happens that the straight line we obtain in Fig. 5 from a least-squares fit of the six Ln points, excluding the $q = 0$ point of La and the $q = 14$ point of Lu for reasons to follow, is essentially identical to the corresponding straight line we obtain from a least-squares fit of the eight Ln^{+1} points, similarly excluding the $q = 0$ point of Ba^{+1} and the $q = 14$ point of Yb^{+1}. This shows that the effect on $\Delta_{pd}E(q)$ of the removal of two s^2 electrons from each Ln-series atom is just compensated for by the effect of the unit decrease in atomic number required here to match the q values of the Ln^{+1}-series ions to those of the Ln-series atoms. Furthermore, it is evident in Fig. 5 that this approximate equality in these $\Delta_{pd}E(q)$ values also holds at the $q = 0$ and 14 points, where significant deviations from linearity are observed. Finally, as discussed in the developments to follow, this same approximate equality in $\Delta_{pd}E(q)$ values also appears in the corresponding An and An^{+1} series in Fig. 6.

The nonlinearities at the $q = 0$ and 14 points in Fig. 5 can be accounted for, in the Jj coupling description, by that part of the f-d electron in-

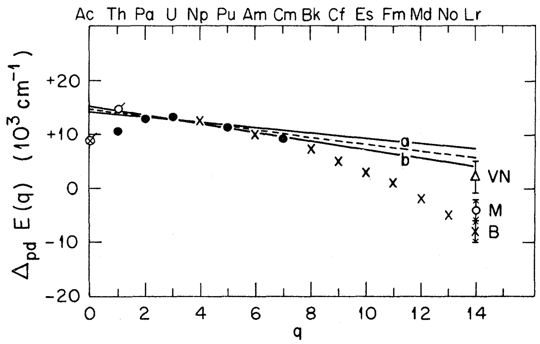

FIG. 6. Measured differences $\Delta_{pd}E(q)$ between $E(f^qps^2)$ and $E(f^qds^2)$ for the actinide neutral atoms are designated by the solid points (•). The points (σ) are the corresponding measured differences in the singly ionized form of the element, with next lower atomic number and minus the s^2 electrons. The points designated by (×) are the predicted values of Brewer which include the prediction $\Delta_{pd}E(14) = -8\times 10^3$ cm^{-1} for Lr. A second estimate, based upon relativistic Hartree-Fock calculations of Mann, (∘), also yields the negative value $\Delta_{pd}E(14) = -4\times 10^3$ cm^{-1} for Lr. The line a is the difference between the straight lines $\Delta_pE'(q)$ and $\Delta_dE'(q)$ of Figs. 4 and 2. The line b is a least-squares fit of the solid points excluding the solid point for Th (see text). The dashed line is our best linear estimate of $\Delta_{pd}E(q)$ for the An and An^{+1} series from $q = 2$ to 13; it is the average of lines a and b. The points (σ) are the corresponding measured differences in the singly ionized form of the element, with next lower atomic number and minus the s^2 electrons. The point (Δ) is our estimate of $\Delta_{pd}E(14) = (+2.3 \pm 3)\times 10^3$ cm^{-1}; it has been adjusted from the linearly extrapolated value by a predictable closed-shell discontinuity. The error bars are the authors in each case.

teraction which removes the otherwise four-fold degeneracy of the lowest $^2D_{3/2}$ state of the valence d electron. In the $q = 0$ case, the d electron is not subjected to the field of any unpaired f electrons so it experiences only the spherically symmetric fields of the core electrons and the nucleus; similarly in the $q = 14$ case, the d electron is subjected only to the fields of the spherically symmetric closed f^{14} shell, the other core electrons, and the nucleus. In all the other cases the d electron is subjected to the nonspherically symmetric field from the unpaired f electrons, and this in effect completely removes the $j = \frac{3}{2}$ degeneracy of the $^2D_{3/2}$ state. This part of the f-d—electron interaction for $q \doteq 1, 2, 3, \ldots, 13$ significantly lowers the energy of the ground state of the configuration containing the d electrons, whereas the corresponding f-p—electron interaction, which removes the degeneracy of the $^2P_{1/2}$ state of the p electron, is too small to be significant.[15] Thus for $q \doteq 1, 2, \ldots, 13$, $\Delta_{pd}E(q)$ receives a positive and approximately constant, or linear in q, contribution from this f-d interaction, whereas at $q \doteq 0, 14$ this contribution vanishes.

The effects of the above f-d interaction on $\Delta_{pd}E(q)$ are apparent for the Ln and Ln^{+1} series in Fig. 5 at $q = 0$ and 14 and, for the corresponding An and An^{+1} series, at $q = 0$ in Fig. 6. It should be noted in Fig. 6 that the points (σ) for Ra^{+1} and Ac^{+1} miss and match, respectively, the linear correlation in a similar fashion as the corresponding points in the Ln and Ln^{+1} series in Fig. 5. It should also be noted in Fig. 6 that the measured (•) point for neutral Th is anomalously low by several 10^3 cm^{-1} for reasons which probably involve unusual configuration interactions in this particular case, but which are not yet clear. Thus we excluded this Th point from the least-squares determination of line (b) in Fig. 6, and we place a question mark after this reported $\Delta_{pd}E(1)$ value for Th in Table III.

We designate $M(0)$, for example, for the mismatch at $q = 0$ between the linear correlation in Fig. 5 and the measured point, and we designate $M(14)$ for the corresponding mismatch at $q = 14$. Listed in Table IV are some of the values we determined for $M(0)$ and $M(14)$ for the various series analyzed thus far. It is apparent in Table IV that for a given series, $M(0)$ is always greater than $M(14)$ by about 2×10^3 cm^{-1}, and that for the series involving higher stages of ionization the respective M values are greater. We attribute these trends and values of M to certain of the f-d interactions discussed above, or rather to the absence of these interactions at the $q = 0$ and 14 points, and indeed, the M values in Table IV show the same trends and approximately the same values as do the known energies of the total splittings of the lowest four $^2D_{3/2}$ states of the atoms or ions in the various

TABLE III. Calculated and observed experimental energy differences $\Delta_{pd}E(q)$ between $E(f^qps^2)$ and $E(f^qds^2)$ for the lanthanide and actinide gaseous atoms.

		$\Delta_{pd}E(q)$ (10^3 cm^{-1})		$\Delta_pE(q)-\Delta_dE(q)$ (10^3 cm^{-1})		$\Delta_{pd}E(q)$ (10^3 cm^{-1})			$\Delta_{pd}E(q)$ (10^3 cm^{-1})		$\Delta_pE(q)-\Delta_dE(q)$ (10^3 cm^{-1})
q	Ln	Calc[a]	Obs	Calc	Ln^{+1}	Calc[a]	Obs	An	Calc[a]	Obs	Calc[b]
0	La	20.29	15.22	20.49	Ba^{+1}	21.08	15.39	Ac	15.27	(9.5)[c]	14.21
1	Ce	19.38		19.57	La^{+1}	20.10	18.85	Th	14.46	10.64?	13.72
2	Pr	18.48		18.64	Ce^{+1}	19.13	18.67	Pa	13.64	13.02	13.24
3	Nd	17.57		17.72	Pr^{+1}	18.16	18.78	U	12.82	13.46	12.75
4	Pm	16.66		16.80	Nd^{+1}	17.18	18.79	Np	12.01		12.27
5	Sm	15.76		15.88	Pm^{+1}	16.21		Pu	11.18	11.46	11.78
6	Eu	14.85		14.96	Sm^{+1}	15.24		Am	10.37		11.30
7	Gd	13.94	13.43	14.04	Eu^{+1}	14.26	13.85	Cm	9.56	9.26	10.81
8	Tb	13.04	13.33	13.12	Gd^{+1}	13.29	14.23	Bk	8.74		10.32
9	Dy	12.13	13.05	12.20	Tb^{+1}	12.32		Cf	7.92		9.84
10	Ho	11.22		11.28	Dy^{+1}	11.34	10.35	Es	7.10		9.35
11	Er	10.31	9.29	10.36	Ho^{+1}	10.37		Fm	6.29		8.87
12	Tm	9.41	9.35	9.44	Er^{+1}	9.39		Md	5.47		8.38
13	Yb	8.50	8.88	8.52	Tm^{+1}	8.42	8.36	No	4.65		7.90
14	Lu	7.60	4.14	7.60	Yb^{+1}	7.45	4.10	Lr	3.84	(2.3 ± 3)[d]	7.41

[a] These values are taken directly either from the solid line in Fig. 5 or solid line b in Fig. 6, as labeled. Note that they are not good estimates for $q = 0$ and 14.

[b] These values are taken directly from solid line a in Fig. 6.

[c] We accept Brewer's Ref. 2 value of $(9.5 \pm 1) \times 10^3$ cm^{-1} as the best estimate of $\Delta_{pd}E(0)$ for Ac, and we insert parentheses around this value here to indicate that it is not measured directly but is only an estimate.

[d] This is our final best value for Lr. It is the average of the adjacent calculated values 3.84×10^3 and 7.41×10^3 cm^{-1} less the $M(14) = 3.3 \times 10^3$ cm^{-1} correction from Table IV.

TABLE IV. Various variations of M.

Series	$\Delta_{pd}E(q)$	$M(0)$ (10^3 cm^{-1})	$M(14)$ (10^3 cm^{-1})
Ln^{+2}	$E(f^q p) - E(f^q d)$		5.4
Ln^{+1}	$E(f^q p) - E(f^q d)$	5.7	3.4
Ln	$E(f^q ps) - E(f^q ds)$		2.5
Ln	$E(f^q ps^2) - E(f^q ds^2)$	5.2	3.5
An^{+1}	$E(f^q p) - E(f^q d)$	5.2	(3.3)[a]
An	$E(f^q ps^2) - E(f^q ds^2)$	5.2	(3.3)[a]

[a] These values are estimates based on the reasonable assumption that the change in M from $q=0$ to 14 is approximately the same in the An and An^{+1} series as it is in the Ln and Ln^{+1} series.

series.[21–23] The latter are approximately linearly decreasing in q and they extrapolate at $q=0$ and 14 to approximately the same values as M in Table IV. The reason for the linear decrease in q is, of course, due to the respective lanthanide and actinide contractions of the f electrons relative to the d electrons with increasing Z. This being the case it is quite reasonable to approximate the $M(14)$ values for the An and An^{+1} series in Table IV as 3.3×10^3 cm^{-1}, based on the assumption that the change from $M(0)$ to $M(14)$ is approximately the same in these An and An^{+1} series as in the corresponding Ln and Ln^{+1} series.

Our final results for the $\Delta_{pd}E(q)$ energy differences for the An series are listed in Table III and displayed in Fig. 6. We obtain $(2.3\pm3)\times10^3$ cm^{-1} for $\Delta_{pd}E(14)$ for neutral atomic Lr, after making the 3.3×10^3 cm^{-1} correction here for $M(14)$, as indicated by the point Δ in Fig. 6; and incidentally, since the An^{+1} $\Delta_{pd}E(q)$ values also appear to match the respective energy differences of the An series in Fig. 6, $(2.3\pm3)\times10^3$ cm^{-1} is also our best estimate for $\Delta_{pd}E(14)$ for No^{+1}. Furthermore, we see in Fig. 6 that Brewer's estimated points (×) on the right side of the An series are consistently lower than ours, with deviations increasing with increasing Z or q. We believe that the present evidence indicates that our values are the more accurate and that this will become increasingly apparent as measured $\Delta_{pd}E(q)$ values for Bk, Cf, and Es, the only other actinides where decisive measurements can at present be made, become available.

We end this paper on three points: The first point is that in all the series we have so analyzed to date, for the atoms and the ions of the Ln and An series, no deviations from linearity have been observed which can be attributed to abrupt f-orbital expansion, toward hydrogenic f orbitals, with decreasing atomic number.[24–26] This includes, in several cases, the nonlanthanide- and nonactinide-like ions Ba^{+1} and Ra^{+1} where hydrogenic f-orbital expansion must be at least beginning, but is more likely well developed. Thus we maintain that any contributions to the energy difference arising from f-orbital expansion at the lower values of q are effectively linear in q, if they are significant, and therefore they would be accounted for in our linearization method.

The second point is that although relativistic effects are expected to be larger in the An series than in the Ln series, these contributions to the energy-level differences should be approximately linear in q, or Z, over the relatively short span of elements through these series, so that they would not contribute to any unexpected nonlinearities and are implicitly accounted for in the linear systematics of our treatment.

And our last point is that although the calculated and tentatively observed $\Delta_d E(0)$ values for La in Table II are in close agreement, from our analyses above this agreement is not expected because the end-point ($q=0$) nonlinearity should make the observed $\Delta_d E(0)$ value here near -11×10^3 cm^{-1}, or about 5×10^3 cm^{-1} more positive than the calculated value. Furthermore, the calculated value $\Delta_p E(0) = 4.48\times10^3$ cm^{-1} for La in Table II is more than 2×10^3 cm^{-1} out of agreement with the tentatively observed $\Delta_p E(0) = 0.2\times10^3$ cm^{-1} value, and end-point nonlinearities are not expected for $\Delta_p E(q)$. These results may cast some doubt on the validity of Martin's[4] suggestion that the lowest $4f6s^2$ energy level of La is at 15 197 cm^{-1}, although they do not necessarily rule it out as a possibility because unusually strong configuration interactions may prevail here in atomic La.

We thank Professor Leo Brewer, Professor David E. Henrie, and Professor Eugene Y. Wong for many helpful suggestions.

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[*] Research sponsored by the U. S. Atomic Energy Commission under contract with the Union Carbide Corp.

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PHYSICAL REVIEW A VOLUME 6, NUMBER 1 JULY 1972

Ultrasoft-X-Ray Reflection, Refraction, and Production of Photoelectrons (100–1000-eV Region)*

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(Received 14 February 1972)

The reflection, refraction, and associated production of photoelectrons by ultrasoft x rays (10–100 Å) can be important bases for the determination of material constants such as the linear x-ray absorption coefficients and the electron mean free paths. These may then be used to establish directly the photoionization cross sections and the electron-collision cross sections which account for the dominant energy-absorbing processes within solids for this energy region. Because the effective sample depths for these interactions are typically less than 100 Å, they constitute an important practical basis for surface characterization. By applying the exact theory for the reflection-refraction of a plane electromagnetic wave at an absorbing dielectric interface to the shorter-wavelength region (< 10 Å), it can be shown that the conventional approximate theory of x-ray reflection is adequate. However, the more exact theory must be applied in the region of longer x-ray wavelengths (> 50 Å). Although the derivations of the exact theory are tedious, the results can be expressed in relatively simple form as functions of two material constants α and γ, which are identifiable as the unit decrements to a complex dielectric constant, of the grazing-incidence angle, and of a parameter which is a function of this grazing angle and which becomes the angle of refraction for small angles of incidence. X-ray absorption coefficients and electron mean-free-path values have been determined from x-ray reflection and refraction and photoelectron excitation data. These values have been shown to agree reasonably well with such material constants as determined by transmission measurements through thin samples.

I. INTRODUCTION

It is well known that x rays do reflect from surfaces with high efficiency in the grazing-incidence region. The characteristic reflectance curve, which falls off to zero value with increasing angle, is the basis for an important method for determining the optical constants of the reflecting medium and its surface structure.[1,2] Also, a precise knowledge of this "total-reflection" characteristic curve is important in the design of mirror monochromators,[3] of optimized diffraction gratings, and of astronomical telescope systems for the x-ray region.

As will be described below, the refracted x-ray beam, when used to produce photoelectrons, can also be an important basis for the determination of certain constants of the medium and of its surface structure.[4]

In order to relate experimental reflection, refraction, and associated photoelectron excitation data to the optical constants, one may apply a relatively simple electromagnetic model based upon approximations permitted by the small values of the grazing-incidence angles and of complex refractive-index unit decrements which obtain for the