# Fine-structure intervals for the lowest $P$ terms in the Cu, Zn, Ga, and Br isoelectronic sequences for $Z \leq 92$

Lorenzo J. Curtis
*Department of Physics and Astronomy, University of Toledo, Toledo, Ohio 43606*
(Received 11 August 1986)

Theoretical and semiempirical predictions of fine-structure intervals for the lowest $P$ terms in the Cu, Zn, Ga, and Br sequences are presented for all ions with $Z \leq 92$. Through the use of screening parameter reductions of both the existing data base and the *ab initio* multiconfiguration Dirac-Fock computations reported herein, a new empirical decomposition has been discovered that permits measurements for the Cu sequence to be combined with theoretical computations to make precise predictions for the Zn, Ga, and Br sequences. These predictions are of higher precision than could be obtained solely by *ab initio* methods, and extend to much higher $Z$ than semiempirical extrapolations alone would permit. These results provide insights into the interaction of the active and core electrons, and test a method that is applicable to many other systems.

## I. INTRODUCTION

Forbidden transitions between low-lying fine-structure levels in highly ionized atoms provide a useful diagnostic tool for the analysis of high-temperature astrophysical and laboratory plasmas. $M1$ and $E2$ transitions between these levels become relatively stronger with increasing nuclear charge, and provide a source of intense radiative emission lines in an isolated and conveniently detectable wavelength region. These transitions are also useful for radiative absorption studies if the lower level is heavily populated due to its stability or metastability. Thus the $ns^2np\,^2P$ ground terms in the B, Al, and Ga sequences, the $ns^2np^5\,^2P$ ground terms in the F, Cl, and Br sequences, and the $nsnp\,^3P$ excited terms (with metastable $J=0$ levels) in the Be, Mg, and Zn sequences are important systems for consideration.

Spectroscopic identification of impurity lines requires a very accurate knowledge of the transition wavelengths. The requirements (often to within parts in $10^5$ or better) can exceed the precision attainable with available *ab initio* theoretical methods, and the use of semiempirical methods involving predictive interpolations and extrapolations of the existing data base are often necessary. Screening parametrizations[1] can yield the requisite accuracies, but they require the existence of a substantial data base within the specific isoelectronic sequence under consideration. An exposition is presented here of a new method that utilizes information in a data-rich isoelectronic sequence, together with *ab initio* calculations of a secondary quantity, to make predictions of fine structures in data-poor isoelectronic sequences.

Recently many new experimental measurements have become available and comprehensive sets of theoretical calculations have been performed for transitions in the sequences described above with $n=2$ and 3, which have been comprehensively summarized in Ref. 2. Linearized screening parametrizations have been used[3–6] to study the homologous systems with $n=4$ to moderately high stages of ionization, but there were indications that the linearization could not be extended beyond 30 stages of ionization.[7] Recent new measurements[8–15] now permit these studies of the $n=4$ sequences to be extended to a new high-charge regime, and precision observations for the Cu isoelectronic sequence are now available through 55 stages of ionization.

Studies of systematic trends in the computations and in the empirical data base have revealed an independence and separability of components of the effective screening that are associated with the closed-shell and open-shell portions of the core. A semiempirical procedure then permits experimental results for the Cu sequence to be combined with theoretical results to make reliable predictions for the Zn, Ga, and Br sequences for $Z \leq 92$. These predictions are expected to be much more accurate than *ab initio* computations, and can be extended to higher $Z$ values than standard semiempirical extrapolations.

## II. SYSTEMS SELECTED FOR STUDY

The fine-structure intervals considered herein can be designated by their nominal $LS$ designations as follows:
Cu sequence,

$$4p(^2P_{1/2}\text{-}^2P_{3/2})\ ;$$

Zn sequence,

$$4s4p(^3P_0\text{-}^3P_2)\ ;$$

Ga sequence,

$$4s^24p(^2P_{1/2}\text{-}^2P_{3/2})\ ;$$

Br sequence,

$$4s^24p^5(^2P_{3/2}\text{-}^2P_{1/2})\ .$$

For both the Ga and Br sequences the lower level corresponds to the ground state, and for the Zn sequence the lower level is metastable since its only energetically allowed decay is absolutely forbidden by the $J=0 \not\to J=0$ selection rule. Sequences such as these that contain a

 

TABLE I. Fine-structure separations for the $4p\,^2P$, $4s4p\,^3P(J=2-0)$, $4s^24p\,^2P$, and $4s^24p^5\,^2P$ terms in the Cu, Zn, Ga, and Br isoelectronic sequences, using semiempirical (SE) and Dirac-Fock (DF) methods. The SE predictions incorporate both experimental data and differential DF computations into the determination, and are expected to be more accurate than the DF calculations alone. Experimentally observed values are indicated by a source footnote in the SE column. Superscript letters denote the following. Bibliographies of source references given for a, Cu in Ref. 3; b, Zn in Ref. 4; d, Ga in Ref. 5; f, Br in Ref. 6. Recent original sources are as follows. Cu: i, Reader *et al.* in Ref. 9; j, Reader and Luther in Ref. 8; k, Seely *et al.* in Ref. 10. Zn: c, Isberg and Litzén in Ref. 11; e, Joshi and van Kleef in Ref. 12; g, Trigueiros *et al.* in Ref. 13. Ga: h, Reader *et al.* in Ref. 15.

| | | Cu sequence | | | Zn sequence | | | Ga sequence | | | Br sequence | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $Z$ | Ion | Q | SE | DF | Q | SE | DF | Q | SE | DF | Q | SE | DF |
| 29 | Cu | 0+ | 248[a] | 164 | | | | | | | | | |
| 30 | Zn | 1+ | 874[a] | 731 | 0+ | 579[b] | 500 | | | | | | |
| 31 | Ga | 2+ | 1718[a] | 1546 | 1+ | 1382[c] | 1273 | 0+ | 826[d] | 399 | | | |
| 32 | Ge | 3+ | 2788[a] | 2595 | 2+ | 2405[b] | 2280 | 1+ | 1767[d] | 1478 | | | |
| 33 | As | 4+ | 4110[a] | 3891 | 3+ | 3680[b] | 3531 | 2+ | 2940[d] | 2686 | | | |
| 34 | Se | 5+ | 5698[a] | 5455 | 4+ | 5211[e] | 5045 | 3+ | 4376[d] | 4123 | | | |
| 35 | Br | 6+ | 7580[a] | 7312 | 5+ | 7031[e] | 6846 | 4+ | 6089[d] | 5831 | 0+ | 3685[f] | 3666 |
| 36 | Kr | 7+ | 9779[a] | 9488 | 6+ | 9163[g] | 8962 | 5+ | 8108[d] | 7841 | 1+ | 5370[f] | 5368 |
| 37 | Rb | 8+ | 12 335[a] | 12 015 | 7+ | 11 591 | 11 422 | 6+ | 10 467[h] | 10 185 | 2+ | 7375[f] | 7388 |
| 38 | Sr | 9+ | 15 269[a] | 14 924 | 8+ | 14 431 | 14 257 | 7+ | 13 198[h] | 12 894 | 3+ | 9728[f] | 9758 |
| 39 | Y | 10+ | 18 622[a] | 18 249 | 9+ | 17 681 | 17 501 | 8+ | 16 322[h] | 16 003 | 4+ | 12 460[f] | 12 509 |
| 40 | Zr | 11+ | 22 425[a] | 22 024 | 10+ | 21 379 | 21 189 | 9+ | 19 884[h] | 19 546 | 5+ | 15 607[f] | 15 675 |
| 41 | Nb | 12+ | 26 720[a] | 26 288 | 11+ | 25 560 | 25 359 | 10+ | 23 928[h] | 23 560 | 6+ | 19 191[f] | 19 290 |
| 42 | Mo | 13+ | 31 547[a] | 31 079 | 12+ | 30 264 | 30 048 | 11+ | 28 467[h] | 28 083 | 7+ | 23 274[f] | 23 391 |
| 43 | Tc | 14+ | 36 953 | 36 437 | 13+ | 35 530 | 35 298 | 12+ | 33 563 | 33 156 | 8+ | 27 868 | 28 018 |
| 44 | Ru | 15+ | 42 953[i] | 42 406 | 14+ | 41 400 | 41 150 | 13+ | 39 240[h] | 38 821 | 9+ | 33 055[f] | 33 211 |
| 45 | Rh | 16+ | 49 538[i] | 49 031 | 15+ | 47 918 | 47 650 | 14+ | 45 567[h] | 45 122 | 10+ | 38 800[f] | 39 012 |
| 46 | Pd | 17+ | 56 963[i] | 56 357 | 16+ | 55 128 | 54 844 | 15+ | 52 572[h] | 52 104 | 11+ | 45 180[f] | 45 467 |
| 47 | Ag | 18+ | 65 067[i] | 64 434 | 17+ | 63 079 | 62 779 | 16+ | 60 320[h] | 59 817 | 12+ | 52 340 | 52 622 |
| 48 | Cd | 19+ | 74 012[i] | 73 313 | 18+ | 71 819 | 71 508 | 17+ | 68 855[h] | 68 311 | 13+ | 60 202 | 60 526 |
| 49 | In | 20+ | 83 774[i] | 83 045 | 19+ | 81 398 | 81 081 | 18+ | 78 161[h] | 77 636 | 14+ | 68 857 | 69 231 |
| 50 | Sn | 21+ | 94 430[i] | 93 688 | 20+ | 91 871 | 91 555 | 19+ | 88 356 | 87 850 | 15+ | 78 358 | 78 789 |
| 51 | Sb | 22+ | 106 150 | 105 297 | 21+ | 103 292 | 102 987 | 20+ | 99 492 | 99 007 | 16+ | 88 757 | 89 256 |
| 52 | Te | 23+ | 118 807 | 117 934 | 22+ | 115 719 | 115 437 | 21+ | 111 614 | 111 169 | 17+ | 100 111 | 100 690 |
| 53 | I | 24+ | 132 541 | 131 661 | 23+ | 129 211 | 128 966 | 22+ | 124 783 | 124 396 | 18+ | 112 477 | 113 151 |
| 54 | Xe | 25+ | 147 415 | 146 543 | 24+ | 143 831 | 143 640 | 23+ | 139 057 | 138 753 | 19+ | 125 915 | 126 704 |
| 55 | Cs | 26+ | 163 495 | 162 647 | 25+ | 159 642 | 159 526 | 24+ | 154 501 | 154 308 | 20+ | 140 487 | 141 412 |
| 56 | Ba | 27+ | 180 910[j] | 180 045 | 26+ | 176 711 | 176 694 | 25+ | 171 181 | 171 130 | 21+ | 156 260 | 157 345 |
| 57 | La | 28+ | 200 270[j] | 198 810 | 27+ | 195 764 | 195 219 | 26+ | 190 397 | 189 292 | 22+ | 174 049 | 174 574 |
| 58 | Ce | 29+ | 220 575 | 219 019 | 28+ | 215 751 | 215 176 | 27+ | 210 049 | 208 871 | 23+ | 192 613 | 193 173 |
| 59 | Pr | 30+ | 242 017 | 240 751 | 29+ | 236 871 | 236 644 | 28+ | 230 826 | 229 945 | 24+ | 212 271 | 213 219 |
| 60 | Nd | 31+ | 265 110[j] | 264 090 | 30+ | 259 623 | 259 707 | 29+ | 253 218 | 252 596 | 25+ | 233 488 | 234 793 |
| 61 | Pm | 32+ | 290 079 | 289 122 | 31+ | 284 234 | 284 451 | 30+ | 277 452 | 276 912 | 26+ | 256 473 | 257 979 |
| 62 | Sm | 33+ | 316 900[j] | 315 936 | 32+ | 310 681 | 310 964 | 31+ | 303 503 | 302 979 | 27+ | 281 219 | 282 864 |
| 63 | Eu | 34+ | 345 727 | 344 628 | 33+ | 339 112 | 339 342 | 32+ | 331 525 | 330 893 | 28+ | 307 864 | 309 540 |
| 64 | Gd | 35+ | 376 570[j] | 375 294 | 34+ | 369 547 | 369 681 | 33+ | 361 529 | 360 749 | 29+ | 336 423 | 338 100 |
| 65 | Tb | 36+ | 409 435 | 408 036 | 35+ | 401 984 | 402 082 | 34+ | 393 520 | 392 649 | 30+ | 366 910 | 368 644 |
| 66 | Dy | 37+ | 444 490[j] | 442 960 | 36+ | 436 599 | 436 652 | 35+ | 427 670 | 426 697 | 31+ | 399 486 | 401 275 |

TABLE I. (*Continued.*)

| | | Cu sequence | | | Zn sequence | | | Ga sequence | | | Br sequence | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $Z$ | Ion | Q | SE | DF | Q | SE | DF | Q | SE | DF | Q | SE | DF |
| 67 | Ho | 38 + | 481 925 | 480 176 | 37 + | 473 565 | 473 499 | 36 + | 464 159 | 463 003 | 32 + | 434 327 | 436 099 |
| 68 | Er | 39 + | 521 720[j] | 519 799 | 38 + | 512 880 | 512 738 | 37 + | 502 977 | 501 681 | 33 + | 471 423 | 473 228 |
| 69 | Tm | 40 + | 563 823 | 561 953 | 39 + | 554 491 | 554 494 | 38 + | 544 071 | 542 853 | 34 + | 510 733 | 512 782 |
| 70 | Yb | 41 + | 608 510[j] | 606 757 | 40 + | 598 658 | 598 884 | 39 + | 587 707 | 586 639 | 35 + | 552 507 | 554 878 |
| 71 | Lu | 42 + | 656 181 | 654 344 | 41 + | 645 798 | 646 043 | 40 + | 634 291 | 633 169 | 36 + | 597 138 | 599 645 |
| 72 | Hf | 43 + | 706 782 | 704 850 | 42 + | 695 842 | 696 103 | 41 + | 683 762 | 682 579 | 37 + | 644 567 | 647 214 |
| 73 | Ta | 44 + | 760 000[j] | 758 416 | 43 + | 748 487 | 749 209 | 42 + | 735 813 | 735 010 | 38 + | 694 518 | 697 724 |
| 74 | W | 45 + | 815 800[j] | 815 191 | 44 + | 803 701 | 805 506 | 43 + | 790 426 | 790 607 | 39 + | 746 954 | 751 318 |
| 75 | Re | 46 + | 875 502 | 875 330 | 45 + | 862 795 | 865 150 | 44 + | 848 881 | 849 526 | 40 + | 803 122 | 808 148 |
| 76 | Os | 47 + | 939 296 | 938 992 | 46 + | 925 945 | 928 300 | 45 + | 911 365 | 911 925 | 41 + | 863 194 | 868 369 |
| 77 | Ir | 48 + | 1 007 141 | 1 006 348 | 47 + | 993 127 | 995 126 | 46 + | 977 848 | 977 972 | 42 + | 927 151 | 932 146 |
| 78 | Pt | 49 + | 1 078 995 | 1 077 574 | 48 + | 1 064 284 | 1 065 805 | 47 + | 1 048 292 | 1 047 843 | 43 + | 994 952 | 999 651 |
| 79 | Au | 50 + | 1 154 812[k] | 1 152 854 | 49 + | 1 139 384 | 1 140 519 | 48 + | 1 122 650 | 1 121 721 | 44 + | 1 066 563 | 1 071 064 |
| 80 | Hg | 51 + | 1 235 101 | 1 232 379 | 50 + | 1 218 933 | 1 219 459 | 49 + | 1 201 423 | 1 199 794 | 45 + | 1 142 475 | 1 146 570 |
| 81 | Tl | 52 + | 1 319 890 | 1 316 351 | 51 + | 1 302 969 | 1 302 828 | 50 + | 1 284 648 | 1 282 264 | 46 + | 1 222 711 | 1 226 366 |
| 82 | Pb | 53 + | 1 408 405[k] | 1 404 984 | 52 + | 1 390 708 | 1 390 838 | 51 + | 1 371 570 | 1 369 342 | 47 + | 1 306 565 | 1 310 659 |
| 83 | Bi | 54 + | 1 500 481[k] | 1 498 498 | 53 + | 1 481 986 | 1 483 709 | 52 + | 1 462 002 | 1 461 248 | 48 + | 1 393 859 | 1 399 666 |
| 84 | Po | 55 + | 1 597 953 | 1 597 127 | 54 + | 1 578 650 | 1 581 675 | 53 + | 1 557 795 | 1 558 212 | 49 + | 1 486 357 | 1 493 612 |
| 85 | At | 56 + | 1 701 090 | 1 701 119 | 55 + | 1 680 945 | 1 684 984 | 54 + | 1 659 166 | 1 660 484 | 50 + | 1 584 300 | 1 592 741 |
| 86 | Rn | 57 + | 1 810 156 | 1 810 682 | 56 + | 1 789 124 | 1 793 842 | 55 + | 1 766 400 | 1 768 264 | 51 + | 1 687 945 | 1 697 254 |
| 87 | Fr | 58 + | 1 925 433 | 1 926 183 | 57 + | 1 903 508 | 1 908 618 | 56 + | 1 879 786 | 1 881 923 | 52 + | 1 797 577 | 1 807 508 |
| 88 | Ra | 59 + | 2 047 214 | 2 047 776 | 58 + | 2 024 350 | 2 029 463 | 57 + | 1 999 595 | 2 001 609 | 53 + | 1 913 470 | 1 923 655 |
| 89 | Ac | 60 + | 2 175 808 | 2 175 860 | 59 + | 2 151 985 | 2 156 778 | 58 + | 2 126 144 | 2 127 721 | 54 + | 2 035 946 | 2 046 083 |
| 90 | Th | 61 + | 2 311 538 | 2 310 693 | 60 + | 2 286 707 | 2 290 819 | 59 + | 2 259 754 | 2 260 514 | 55 + | 2 165 282 | 2 175 043 |
| 91 | Pa | 62 + | 2 454 744 | 2 452 643 | 61 + | 2 428 885 | 2 431 954 | 60 + | 2 400 747 | 2 400 353 | 56 + | 2 301 846 | 2 310 892 |
| 92 | U | 63 + | 2 605 781 | 2 601 988 | 62 + | 2 578 859 | 2 580 462 | 61 + | 2 549 505 | 2 547 513 | 57 + | 2 445 956 | 2 453 905 |

closed-shell inner core and one, two, three, or seven out-of-shell electrons are particularly well suited to semiempirical specification. Here the lowest configuration possessing nonzero fine structure contains a single spectral term, and the separations between the levels of maximum and minimum $J$ are prescribed (in the single-configuration intermediate-coupling picture) by $3\zeta/2$, where $\zeta$ is the spin-orbit energy. This is not the case for the four, five, and six out-of-shell electron configurations, and separations within and between the various spectral terms must be considered to extract $\zeta$ from the electrostatic energy contributions that also connect them.

Since each of the intervals given above corresponds to a physically interpretable quantity $\zeta$, they can usefully be compared both along and among these sequences. Moreover, the isoelectronic data base for the Cu sequence is presently the most extensive in existence, and the spin-orbit interactions that occur within its closed-shell nickel-like core differ from those in the Zn, Ga, and Br sequences only by the presence of $n=4$ electrons.

## III. EXPERIMENTAL DATA BASE

Data compilations that included detailed source references for the desired intervals in these four sequences have been published relatively recently,[3–6] and only those primary source references that have appeared subsequent to these compilations will be cited here. Primary source references not directly cited here can be found in Ref. 3 for Cu-like Ge-Mo, in Ref. 4 for Zn-like ions, in Ref. 5 for Ga-like Ga-Kr, and in Ref. 6 for Br-like ions. For the Zn sequence, not all of the source references cited in Ref. 4 are included in Table I. Here the measurements for $Z=40$–$42$ are questionable since they lie substantially off isoelectronic and isonuclear trends, and are currently the object of a reinvestigation.[14] The primary source references are extended for the Cu sequence by Refs. 8–10, for the Zn sequence by Refs. 11–13, and for the Ga sequence by Ref. 15. The observed fine-structure intervals are listed among the semiempirical predictions in the columns headed SE in Table I, and can be identified by the presence of a footnote to the primary or secondary source reference.

## IV. DIRAC-FOCK COMPUTATIONS

Single-and multiple-configuration Dirac-Fock (MCDF) computations were performed for the lowest $P$ states in the Cu, Zn, Ga, and Br isoelectronic sequences. The calculations were carried out by network using the National Magnetic Fusion Computer Center CRAY X-MP E computer, with supportive calculations using the NAS 6650 and VAX 765 computers at the University of Toledo. The code used was an improved version[16] of the program MCDF developed by Grant and co-workers.[17] Computations were made using a number of different options in the code and for various configuration inclusions, and were selected on the basis of agreement with experimental observations in the region of moderate to high $Z$. Perturbative corrections were included to account for the finite size of the nucleus and the Breit interaction, as well as vacuum polarization, electron self-energy, and other quantum electrodynamic effects. The results, selected as described below, are presented in Table I in the columns labeled DF.

Although the Cu (Ref. 18) and Zn (Ref. 19) sequences have been studied previously by MCDF methods for selected values of $Z$, these calculations were repeated here so that the results could be compared for all values of $Z$ using the same identical code. For the Cu and Zn sequences, the results quoted in Table I are single-configuration $4p$ and $4s4p$ calculations. In the case of the Ga sequence the single-configuration $4s^24p$ calculations agreed well with experiment at low $Z$, but inclusion of $4p^3$ and $4s4p^2$ seemed to improve the agreement at higher $Z$ (at the expense of lower-$Z$ agreement). Thus for the Ga sequence the results presented in Table I included these three configurations and utilized the MCDF-EAL (extended average level) option of the program.[17] The role of the inclusion of configurations of both parities for the homologous B isoelectronic sequence is discussed in Ref. 20. For the B sequence, Huang *et al.*[21] observed that an MCDF calculation of the fine structure can acquire a nonphysical gross structure residue, if inconsistent choices of configurations are used that lead to different nonrelativistic correlation energies for the two fine-structure levels. It has been asserted by Das *et al.*[20] that this problem is an artifact of the MCDF-OL (optimized level) approach, and should not affect the MCDF-EAL calculations performed here. For the Br sequence, the single-configuration $4s^24p^5$ calculations also agreed well at low $Z$, but the inclusion of the $4s4p^6$ configuration improved the agreement at higher $Z$ (again, at the expense of low-$Z$ agreement) and the two-configuration MCDF-EAL computation is reported in Table I. The role of the inclusion of configurations of both parities has been discussed for the homologous F isoelectronic sequence in Ref. 22.

## V. SCREENING PARAMETER FORMULATION

In comprehensive studies of fine-structure splittings in a wide variety of multiple-electron systems,[1] it has been found that the isoelectronic behavior of the spin-orbit energy $\zeta$ can usually be mapped into a linearly varying parameter through a data reduction using a screened hydrogenic expression. The procedure introduces no free parameters, and merely converts the fine-structure splitting into the effective central charge that would yield the same splitting in a single-electron atom. Despite its simplicity, the isoelectronic behavior of the resulting screening parameter is usually very regular and slowly varying, which permits high-precision interpolative and extrapolative predictions and manifestly reveals misclassifications. The procedure consists of converting the measured intervals $3\zeta/2$ into equivalent screening parameters through a Sommerfeld expansion of the screened Dirac energy, given for a $4p$ term by

$$3\zeta/2=R\alpha^2(Z-S)^4 \times\left[1+\sum_i C_i\alpha^{2i}(Z-S)^{2i}+\cdots\right]\Big/128\,. \quad (1)$$

Here $R$ is the reduced-mass-corrected Rydberg constant,

$\alpha$ is the fine-structure constant, $Z$ is the nuclear charge, and $S$ denotes the empirical screening parameter that Eq. (1) serves to define. To adequately describe the Dirac energy to very high $Z$, it is necessary to include a substantial number of higher-order terms in the Sommerfeld expansion (the $C_i$ coefficients are tabulated to 18th order in $\alpha Z$ in Ref. 23). It has been noted empirically that the isoelectronic regularity of $S$ is improved if detailed quantum electrodynamic corrections (functionally formulated in Ref. 24) are included in Eq. (1) (represented by the ellipsis), with the $Z$ dependences also replaced by $Z-S$.

The empirical linearization of the data is accomplished by plotting the screening parameter $S$ versus the reciprocal screened charge $1/(Z-S)$. If a few ions near the neutral end of the sequence (where mixing with excited core configurations becomes significant) are excluded, this plot is usually very nearly linear for over 20 stages of ionization.[1,3–6] In such cases, the system can be precisely described by the two parameters $a$ and $b$, obtained by their weighted least-squares adjustment to the reduced data in the fitting equation

$$S=a+b/(Z-S)\ . \tag{2}$$

As will be shown below, this linearity seems to break down abruptly at about 30 stages of ionization. Classical models have been considered[7] that suggest a relativistic restructuring of the inner core occurs in the vicinity $Z=60$, which could explain this behavior. As a test of the conjecture that the break in slope is a result of effects within the inner core, we have tested a model in which the screening parameters for the various charge states of a given atom are decomposed into two parts, corresponding to the closed- and open-shell portions of the core:

$$S=S_0+\Delta S\ . \tag{3}$$

For the sequences considered here, $S_0$ is associated with the closed nickel-like core and is assumed to be the same for all four sequences, and $\Delta S$ is associated with the passive $n=4$ electrons, is zero for the Cu sequence, and differs among the Zn, Ga, and Br sequences.

## VI. RESULTS

The isoelectronic behavior of both the data base and the Dirac-Fock calculations is displayed through a reduction to $S$, plotted versus $1/(Z-S)$, in Fig. 1. Circles indicate the measured data, solid lines denote the calculations, and dashed lines trace the charge states of Br ($Z=35$) and Nd ($Z=60$) through the various sequences. Several trends can be noted. There is a definite tendency for the Dirac-Fock calculations to overestimate the screening (underestimate the splitting) for the Cu, Zn, and Ga sequences, and this tendency decreases with increasing $Z$. For the Br sequence (which is an inverted structure arising from hole rather than electron states), the Dirac-Fock calculations underestimate the screening, and this also decreases with increasing $Z$. In the region between $Z=35$ and $Z=60$ the experimental points form nearly straight lines on this plot, although the Dirac-Fock calculations contain small curvatures. For $Z>60$, the theoretical values for $S$ drop sharply for all four sequences, as do the experimental values for the Cu sequence.

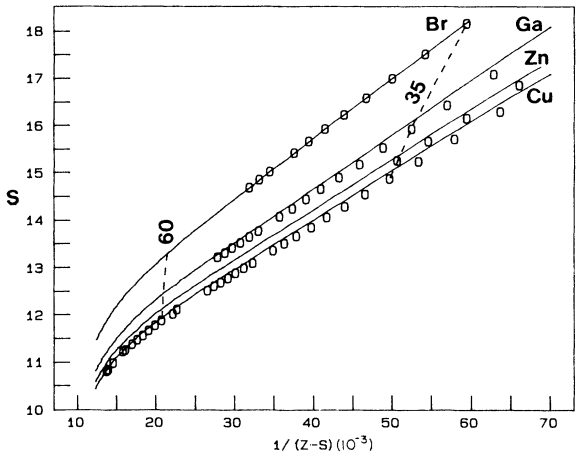


FIG. 1. Fine-structure separations for the Cu, Zn, Ga, and Br sequences, reduced to a screening parameter plot of $S$ vs $1/(Z-S)$ using Eq. (1). The circles denote experimental measurements, the solid lines trace the Dirac-Fock calculations, and the dashed lines connect the ions of Br ($Z=35$) and of Nd ($Z=60$) across the sequences.

Although data extending to and beyond $Z=60$ exist only for the Cu sequence, the theoretical calculations for all four sequences are very similar in shape (although displaced from each other) in the region $Z>60$. If the downturn in $S$ beyond $Z=60$ has its origin deep within the inner core, then the Cu sequence, which has only inner-core screening, should specify this behavior for all four sequences considered here. To test this, the screening parameter $S_0$ for the Cu sequence was subtracted from the corresponding quantity $S$ for each of the other three

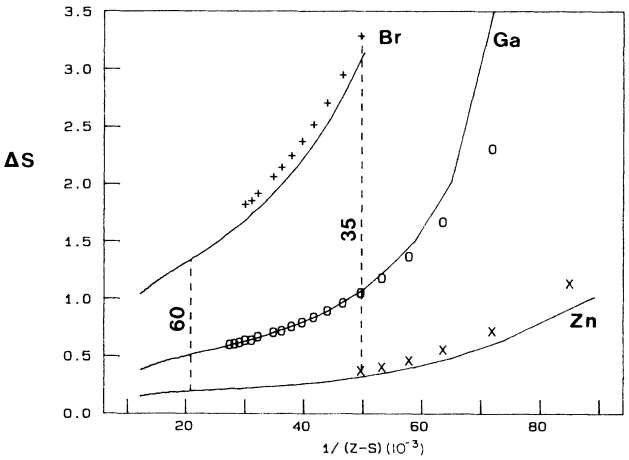


FIG. 2. Subtracted element-by-element differences between the screening parameter in either the Zn, Ga, or Br sequence and the corresponding quantity in the Cu sequence. The experimental values are denoted by ×, Zn sequence; ○, Ga sequence; and +, Br sequence. The solid lines trace the Dirac-Fock calculations, and the dashed lines connect ions of Br ($Z=35$) and Nd ($Z=60$) across the sequences.

sequences to form $\Delta S$ in Eq. (3), using both the experimental and the theoretical values. The results are presented in Fig. 2, plotted versus the reciprocal screened charge for the Cu sequence. Although these plots are not linear, there are useful features. The drop off beyond $Z=60$ is no longer present, indicating that no part of it arises from the screening by $n=4$ electrons, and suggesting that a reliable extrapolation can be made to $Z=92$. Further, the experimental and theoretical $\Delta S$ curves are very similar in shape, and can be brought into almost exact agreement if the Dirac-Fock differences are multiplied by the empirical factors 1.25 for the Zn sequence, 1.03 for the Ga sequence, and 1.08 for the Br sequence.

The semiempirical interpolations and extrapolations presented in the columns labeled SE in Table I were obtained by exploitation of features displayed in Figs. 1 and 2. For $Z \leq 56$, the linearity of the plot in Fig. 1 was utilized, and a linear fit to Eq. (2) was used to interpolate and extrapolate. For $57 \leq Z \leq 92$, two types of corrections were necessary. First, $S_0$ as obtained from the Cu data was interpolated using a quadratic polynomial in the quantity $1/(Z-S_0)$, and extrapolated similarly from $Z=83$ to $Z=92$ using the theoretical value at $Z=92$. The predicted values for $\Delta S$ were computed from the theoretical differences, corrected by the factors 1.25, 1.03, and 1.08 as described above, and added to the values for $S_0$. The values of $S$ so obtained were used in Eq. (1) to compute the appropriate fine structures for each sequence. Except for cases where experimental values exist, these semiempirical values are reported in Table I in the columns labeled SE.

## VII. CONCLUSIONS

The methods presented here permit reliable extrapolations of fine-structure splittings in the Zn, Ga, and Br isoelectronic sequences through more than 40 stages of ionization. The accuracy of these predictions is subject to experimental verification, but the trends in Figs. 1 and 2 suggest that this may approach the precision of the available measurements in the Cu sequence. The method should be applicable to extrapolative predictions in other similar sets of isoelectronic sequences, and the separability of the closed- and open-shell screening effects revealed here suggests possible improvements in the *ab initio* formulation.

## ACKNOWLEDGMENTS

I am grateful to David Ellis, Jan Olof Ekberg, Roger Haar, and Joseph Reader for valuable discussions. The work was supported by the U. S. Department of Energy, Division of Chemical Sciences, under Contract No. DE-AS05-80ER10676.

[1]B. Edlen, *Spektroskopie I,* Vol. XXVII of *Handbuch der Physik,* edited by S. Flügge (Springer, Berlin, 1964), pp. 80–220.
[2]V. Kaufman and J. Sugar, J. Phys. Chem. Ref. Data **15**, 321 (1986).
[3]L. J. Curtis, J. Phys. B **14**, 631 (1981); Phys. Lett. **64A**, 43 (1977).
[4]L. J. Curtis, J. Opt. Soc. Am. B **2**, 407 (1985).
[5]L. J. Curtis, J. Reader, S. Goldsmith, B. Denne, and E. Hinnov, Phys. Rev. A **29**, 2248 (1984).
[6]L. J. Curtis and P. S. Ramanujam, Phys. Scr. **27**, 417 (1983).
[7]L. J. Curtis and R. R. Silbar, J. Phys. B **17**, 4087 (1984).
[8]J. Reader and G. Luther, Phys. Scr. **24**, 732 (1981).
[9]J. Reader, N. Acquista, and D. Cooper, J. Opt. Soc. Am. **73**, 1765 (1983).
[10]J. F. Seely, J. O. Ekberg, C. M. Brown, U. Feldman, W. E. Behring, J. Reader, and M. C. Richardson, Phys. Rev. Lett. **57**, 2924 (1986).
[11]B. Isberg and U. Litzén, Phys. Scr. **31**, 533 (1985).
[12]Y. N. Joshi and Th. A. M. van Kleef, Phys. Scr. **34**, 135 (1986).
[13]A. Trigueiros, S.-G. Pettersson, and J. G. Reyna Almandos, Phys. Scr. **34**, 164 (1986).
[14]J. Reader and U. Litzén (private communication).
[15]J. Reader, N. Acquista, and S. Goldsmith, J. Opt. Soc. Am. B **3**, 874 (1986).
[16]I. P. Grant (private communication).
[17]I. P. Grant, B. J. McKenzie, P. H. Norrington, D. F. Mayers, and N. C. Pyper, Comput. Phys. Commun. **21**, 207 (1980).
[18]K.-T. Cheng and Y.-K. Kim, At. Data Nucl. Data Tables **22**, 547 (1978).
[19]K.-N. Huang (private communication).
[20]B. P. Das, J. Hata, and I. P. Grant, J. Phys. B **17**, L1 (1984).
[21]K.-N. Huang, Y. K. Kim, K. T. Cheng, and J. P. Desclaux, Phys. Rev. Lett. **48**, 1245 (1982).
[22]J. Hata, I. P. Grant, and B. P. Das, J. Phys. B **16**, L189 (1983).
[23]L. J. Curtis, J. Phys. B **10**, L641 (1977).
[24]L. J. Curtis, J. Phys. B **18**, L651 (1985); **19**, 1699(E) (1986).