

Core-electron binding energies of the first thirty elements*

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(Received 23 March 1976)

A table of core-level binding energies is presented that explicitly takes into account the shifts in electronic binding energies between free atoms and the standard state, usually the metallic state. New values of core-level binding energies for Sc, Ti, V, Cr, Mn, Fe, Co, and Ni were measured by x-ray photoemission under ultrahigh-vacuum conditions. These were combined with other photoemission, optical, and x-ray data to compile binding-energy values for the first thirty elements both as free atoms and in their standard states. Comparisons are made with theoretical values.

I. INTRODUCTION

The recent discovery¹⁻³ that core-level electronic binding energies are systematically several eV lower in conducting solids than in free atoms necessitates a new tabulation of atomic energy levels. Previous tabulations⁴⁻⁶ were drawn up without regard to whether the data were taken on free atoms or solids, and serious discrepancies are found when these tabulations are compared with theoretical binding energies.

The most common type of systematic error is caused by combining optical data for valence orbitals in atoms with x-ray data for core levels in metals, then comparing the results with core-level binding energies measured directly by photoelectron spectroscopy on metals or with theoretical binding energies for free atoms. Solid-state effects^{1-3,7} render the photoelectron values systematically lower than the calculated atomic binding energies, while the values derived from x-ray and optical data are not rigorously comparable to binding energies in either atoms or metals.

In this paper we report new core-level binding energies for several of the light elements ($Z \leq 30$), particularly the 3d transition series. The data were obtained by high-resolution x-ray photoelectron spectroscopy on clean samples prepared in ultrahigh vacuum; $P \lesssim 5 \times 10^{-10}$ torr. They are combined with other available information to derive two sets of binding energies, one for free atoms and one for each element in its standard state. These empirical energies are compared in turn with calculated free-atom values and with standard-state energies estimated by approximate theoretical methods.²

Section II deals with the empirical standard-state binding energies. In Sec. III we discuss the empirical electronic binding energies of free atoms. Directly measured values are available for only a few elements. To obtain estimates of

atomic binding energies for the other elements, we have combined optical and x-ray data.

Theoretical binding energies are treated in Sec. IV. For free atoms, theoretical values are taken from the literature. These values are modified to provide estimates of electron binding energies of elements in their standard states. Finally, theory and experiment are compared in Sec. V.

II. STANDARD-STATE BINDING ENERGIES

It is convenient for our purposes to classify the first 30 elements into four groups:

- a. Group 1.* Monatomic gases (He, Ne, Ar): Only one set of binding energies is needed for these elements, because the standard states and free-atom states are identical. The compilation by Lotz⁶ and the work of Siegbahn *et al.*⁸ served as the main sources for these binding energies.
- b. Group 2.* Diatomic gases (H_2, N_2, O_2, F_2, Cl_2): Binding energies for the molecules are available, except for the core levels of Cl_2 . However, except for H_2 , the molecular orbitals are not readily identifiable with atomic orbitals on a 1:1 basis, and are omitted from Table I. They are, of course, discussed elsewhere in the literature.
- c. Group 3.* Conductors (Li, C, Na, Mg, Al, and Sc through Zn): These 15 elements have been studied in our laboratory by high-resolution x-ray photoemission using monochromatized $Al K\alpha_{1,2}$ radiation, under ultrahigh-vacuum conditions. A fresh surface of each element was prepared immediately prior to study, in most cases by *in situ* vapor deposition. Spectra of C,⁹ Li and Na,¹⁰ Mg and Al,¹¹ and Zn and Cu,² have been reported previously. Our binding energies for the other eight elements are new values.

Several conventions should be noted. The binding energies of core levels in conductors are measured relative to the Fermi energy E_F^F . To compare with atomic or molecular binding energies,

they must be augmented by the work function ϕ of each element, yielding vacuum-referenced binding energies

$$E_B^V = E_B^F + \phi. \quad (1)$$

We have listed E_B^V rather than E_B^F in Table I to facilitate comparison with atomic values. In making the work-function correction we have used the values of ϕ given in Table II.¹² We have not included any error in ϕ in the stated errors. Thus to recover the directly measured E_B^F values, Eq. (1) can be used directly, with the quoted error transferred to E_B^F .

Some of the core-level peaks in the $3d$ series are distorted by multiplet splitting and/or many-body effects. In principle it might be desirable to quote a mean value for the binding energies of these peaks. In practice this is seldom feasible, however, and we have instead quoted the position of the highest point on the peak as the binding energy. This approach provides a good fiducial point for future workers, although the actual value quoted is affected slightly by the resolution of the apparatus.

Our measurements were made with Al $K\alpha_{1,2}$ x rays (1486.6 eV). Levels with $E_B \gtrsim 1100$ eV were not readily accessible and were not measured directly. Rather, their E_B values were established with the aid of known x-ray energies.¹³ In a number of cases, x-ray energies were checked against differences in binding energy from photoemission data, and good agreement was found.

d. Group 4. The remaining elements: Be, B, Si, P, S, K, Ca. For these elements the experimental situation is less satisfactory. These elements, except for Si, have not been studied in high-vacuum conditions. The elements B and P have not, to our knowledge, been studied in their standard states by photoelectron spectroscopy in a way that would yield accurate binding energies, but rather in compounds.^{5,14} Si has been studied by several groups under ultra high-vacuum conditions; however, the charging problem in semiconductors and insulators introduces ambiguity in the reference level because the position of the true Fermi level within the bandgap is not well defined. Sulfur was studied as the elemental solid but only E_B^F values are directly available. For these four elements, we have simply taken the tabulated values of Siegbahn *et al.*, in which a 4-eV work-function correction was applied.

We did not attempt to study Be, B, K, or Ca for technical reasons. In all cases, however, values of E_B could be obtained mainly from x-ray energies.^{4,15} For the K core we obtained $E_B(2s) - E_B(2p)$ from a photoemission spectrum of KCl.

Assuming this energy difference to be maintained in the metal, we were able to establish $E_B(2s)$ for the metal. Another subtlety in these cores was the matter of whether quoted x-ray energies referred to peak values⁴ or band edges¹⁵; this was also taken into account.

III. EMPIRICAL FREE-ATOM BINDING ENERGIES

With very few exceptions, experimental values of free-atom binding energies are available only for valence shells. The conventional approach in compiling tables of atomic binding energies is to couple optical energy-level data¹⁶ with x-ray energies.⁴ We have essentially followed this procedure, but have employed certain approaches that should be specified.

First, we have attempted to estimate the binding energy of each valence electron orbital, going from the N -electron ground-state to the mean energy of the $(N-1)$ -electron excited-state configuration formed by removing an electron from the active orbital. Each ionic state in the configuration was weighted by the square of the coefficient of fractional parentage of that particular $(N-1)$ -electron LS eigenstate in the N -electron ground state. This procedure should lead to a binding energy which is, at least to first order, the weighted average over all ionic multiplets which would be observed in a photoelectron spectrum.

There is also a subtler problem which has not been considered previously. This is the matter of solid-state effects, which can shift the characteristic x-ray energies between atoms and metals. It is now well established¹⁻³ that electronic binding energies are lower in metals than in atoms. The largest contributions to the difference appear to arise through screening of the vacant orbital via extra-atomic relaxation of the metal's valence electrons, increase in the repulsive potential experienced by core electrons in metals, and (in transition metals) changes in electron configurations. These effects combine to reduce E_B^V below E_B^A for all core levels. In Sec. IV we shall make a semiempirical correction for this shift. Note, however, that the three effects also are expected to operate *differentially* to reduce the inner core-level E_B values more than those of the outer levels, because the inner levels are more effectively screened. Thus the free-atom x-ray energies should be systematically larger than those of the corresponding transitions in the metallic state. While it would be desirable to correct the experimental x-ray energies, which have been measured only in metals, upward to account for these effects, there is no satisfactory theoretical basis on which

TABLE I. Core-level electronic binding energies of the light elements (eV).^a

Element	$E_B(1s)$				$E_B(2s)$			
	A	B	C	D	A	B	C	D
¹ H	13.60 ^b	16.0 ^c	13.60 ^d	16.4 ^e				
² He	24.59 ^f	...	24.59 ^g	...				
³ Li	64.84 ^f	57.2(1) ^h	64.87 ⁱ	60.51	5.39 ^f	3.4 ^j	5.37 ^k	3.3 ^l
⁴ Be	119.3	115.6	123.33 ^m	117.6	9.32 ^f	7(1)	9.16 ⁿ	o
⁵ B	194(1)	191	199.95 ^m	193	14.05 ^f	p	12.54 ^m	o
⁶ C	p	289.3 ^j	296.5 ^q	289.1 ^r	19.39 ^f	p	17.81 ^m	o
⁷ N	p	409.93(10) ^t	410.7 ^m	411.2 ^u	25.41 ^f	p	23.86 ^m	o
⁸ O	p	543.1(2) ^t	545.0 ^m	542.2 ^v	32.31 ^f	p	31.54 ^m	o
⁹ F	p	696.71(5) ^w	696.16 ^x	695.8 ^u	40.19 ^f	p	40.02 ^m	o
¹⁰ Ne	870.37(9) ^t	...	870.4 ^{aa}	...	48.47 ^f	...	49.31 ^m	...
	$E_B(1s)$				$E_B(2s)$			
	A	B	C	D	A	B	C	D
¹¹ Na	1079.0(3) ^y	1074.0(1) ^h	1079 ^{bb,cc}	1075	70.84(10)	65.7(1) ^h	71.9 ^{bb}	68.5
¹² Mg	1310.9(10) ^z	1306.7(1) ^j	1313 ^j	1310 ^j	94.0(5)	92.25(10) ^j	97 ^j	94
¹³ Al	1567.0(8)	1562.4(5) ^j	1570 ^j	1566	125.6(8)	122.2(2) ^j	127 ^j	123 ^j
¹⁴ Si	1846	1843 ^{ee}	1850 ^{bb}	o	156 ^{ff}	153 ^{ee}	161 ^{bb}	o
¹⁵ P	2154	2153 ^{ee}	2154 ^{bb}	o	194 ^{ff}	193 ^{ee}	198 ^{bb}	o
¹⁶ S	2477	2476 ^{ee}	2482 ^{bb}	o	235 ^{ff}	233 ^{ee}	238 ^{bb}	o
¹⁷ Cl	2830	2827 ^{ee}	2834 ^{bb}	o	278 ^{ff}	274 ^{ee}	281 ^{bb}	o
¹⁸ Ar	3205.9(5) ^{bb}	...	3209 ^{bb}	...	326.3 ^{bb}	...	327 ^{bb}	...
¹⁹ K	3614.3(2)	3610.7(2)	3618 ^{bb,gg}	3615	384.3(7)	380.9(3)	386 ^{bb,hh}	383
²⁰ Ca	4042.8(20)	4041.7(4)	4052 ^{bb}	4045	442.5(20)	441(1)	450 ^{bb}	443
²¹ Sc	4494(1)	4493.0(2)	4505 ^{bb}	4497	503.2(10)	501.5(3)	511 ^{bb}	503
²² Ti	4972.2(10)	4970.1(2)	4983 ^{bb}	4974	569(1)	565.7(3)	574 ^{bb}	565
²³ V	5475(2)	5469.96(10)	5483 ^{bb}	5474	638(2)	631.5(4)	641 ^{bb}	632
²⁴ Cr	5996(2)	5995.31(15)	6005 ^{bb}	5994	703(2)	702.3(3)	707 ^{bb}	697
²⁵ Mn	6549.9(15)	6542.33(15)	6560 ^{bb}	6549	781.6(15)	773.5(16)	785 ^{bb}	774
²⁶ Fe	7124(1)	7115.94(20)	7135 ^{bb}	7123	857(2)	853(2)	863 ^{bb}	852
²⁷ Co	7725(1)	7716.4(4)	7734 ^{bb}	7721	940(1)	931.6(2)	943 ^{bb}	931
²⁸ Ni	8348(1)	8337.57(14)	8359 ^{bb}	8346	1024(2)	1015.55(50)	1028 ^{bb}	1016
²⁹ Cu	8987.6(3)	8985.2(3)	9001 ^{bb}	8997	1105.7(5)	1103.3(7)	1107 ^{bb}	1103
³⁰ Zn	9667.4(1)	9665.15(16)	...	(9664) ^{mm}	1203(1)	1200.46(25)	...	(1200) ^{mm}
	$E_B(3s)$				$E_B(3p)$			
	A	B	C	D	A	B	C	D
¹¹ Na	5.14	3.5 ^j	4.95 ^{dd}	4.0 ^l				
¹² Mg	7.65 ^f	p	6.61 ^{dd}	o				
¹³ Al	11.33 ^f	p	10.1 ^{bb}	o	5.99 ^f	p	5.4 ^{bb}	o
¹⁴ Si	15.17 ^f	p	14.1 ^{bb}	o	8.18 ^f	p	7.0 ^{bb}	o
¹⁵ P	20.17 ^f	p	18.5 ^{bb}	o	11.02 ^f	p	9.0 ^{bb}	o
¹⁶ S	21.30 ^f	p	22.8 ^{bb}	o	11.89 ^f	p	10.6 ^{bb}	o
¹⁷ Cl	25.31 ^f	p	27.9 ^{bb}	o	13.75 ^f	p	12.7 ^{bb}	o
¹⁸ Ar	29.24 ^b	...	33.3 ^{bb}	...	15.81 ^{bb,t}	...	14.7 ^{bb}	...
¹⁹ K	40.8(5)	37.1(3)	45.1 ⁱⁱ	43	24.66 ^f	20.6(1)	23.9 ^{bb}	21
²⁰ Ca	48.3(5)	47.3(6)	58 ^{bb}	52	30.1(2)	28.0(2)	36 ^{bb}	30
²¹ Sc	56.4(10)	54.64(10)	67 ^{bb}	62	33.6(10)	31.84(10)	39 ^{bb}	34
²² Ti	65(1)	62.66(20)	75 ^{bb}	69	40(1)	36.9(2)	45 ^{bb}	39
²³ V	77(1)	70.65(15)	83 ^{bb}	76	47(1)	41.54(15)	51 ^{bb}	44
²⁴ Cr	79(1)	79.7(3)	88 ^{bb}	81	49(1)	47.6(3)	53 ^{bb}	46
²⁵ Mn	94.6(9)	86.5(3)	101 ^{bb}	93	59.4(9)	51.4(2)	63 ^{bb}	55
²⁶ Fe	104(1)	96.06(20)	110 ^{bb}	101	66(1)	57.54(20)	70 ^{bb}	61
²⁷ Co	115(1)	106.41(10)	120 ^{bb}	111	73(1)	64.37(10)	76 ^{bb}	67
²⁸ Ni	125(2)	116.12(20)	129 ^{bb}	120	82(1)	71.77(14)	83 ^{bb}	74
²⁹ Cu	128.8(5)	127.15(10)	132 ^{bb}	129	83(3)	81.93(10)	85.5 ^{bb}	82.5
³⁰ Zn	145.0(1)	144.18(15)	...	(142) ^{mm}	96(3)	79.77(10)	82.9 ^{bb}	79.9
						95.61(15)	...	(93) ^{mm}
						93.00(15)		

TABLE I (Continued)

$E_B(2p)$							
A	B	C	D				
8.30 ^f	p	7.93 ^m	o				
11.26 ^f	p	11.23 ^s	o				
14.55 ^f	p	14.52 ^s	o				
16.53 ^f	p	16.40 ^s	o				
18.67 ^f	p	18.39 ^s	o				
21.66 ^b	...	21.25 ^s	...				
21.56 ^b	$E_B(2p_{1/2})$			$E_B(2p_{3/2})$			
A	B	C	D	A	B	C	D
38.38 ^f	32.9(1) ^h	36.7 ^{bb}	33	38.02 ^f	32.6(1) ^h	36.5 ^{bb}	33
55.0(5)	53.2(1) ^j	56 ^j	53	54.8(5)	52.9(1) ^j	56 ^j	53
80.7(8)	77.3(2) ^j	81 ^j	77	80.3(8)	76.9	81 ^j	77
107	104 ^{ee}	96 ^{bb}	o	106	103	95 ^{bb}	o
141	140 ^{ee}	140 ^{bb}	o	140	139 ^{ee}	138 ^{bb}	o
171	169 ^{ee}	173 ^{bb}	o	170	168 ^{ee}	172 ^{bb}	o
210	206 ^{ee}	210 ^{bb}	o	208	204 ^{ee}	208 ^{bb}	o
250.6 ^{b, bb}	...	250 ^{bb}	...	248.62(8) ^t	...	248 ^{bb}	...
303.2(4)	299.6(3)	303 ^{bb}	300	300.5(4)	296.9(3)	300 ^{bb}	297
354.7(20)	353.6(5)	361 ^{bb}	354	351.1(20)	350.0(5)	357 ^{bb}	350
408.4(10)	407.08(10)	415 ^{bb}	407	403.9(10)	402.15(10)	410 ^{bb}	402
468(1)	465.3(2)	474 ^{bb}	465	462(1)	459.2(2)	467 ^{bb}	458
532(2)	525.37(8)	534 ^{bb}	525	524(2)	517.71(8)	525 ^{bb}	516
591(2)	589.85(23)	594 ^{bb}	584	582(2)	580.54(17)	584 ^{bb}	574
662.8(10)	654.7(3)	666 ^{bb}	655	651.7(10)	643.54(15)	653 ^{bb}	642
733(1)	725.15(20)	736 ^{bb}	725	720(1)	712.05(20)	722 ^{bb}	711
810(2)	801.2(4)	810 ^{bb}	798	795(2)	786.0(4)	794 ^{bb}	782
887(1)	876.67(10)	888 ^{bb}	876	870(1)	859.42(8)	869 ^{bb}	857
960.3(4)	957.3(2)	960 ^{bb}	956	940.3(4)	937.5(2)	939 ^{bb}	935
1052.1(3)	1049.39(15)	...	(1049) ^{mm}	1029.0(3)	1026.26(15)	...	(1026) ^{mm}
$E_B(4s)$				$E_B(3d)$			
A	B	C	D	A	B	C	D
4.34 ^f	3	4.0 ^{dd}	...				
6.11 ^f	...	5.1 ^{dd}	...				
6.65 ^f	...	5.5 ^{bb}	...	8.01 ^f	4.3(1)	7.0 ^{bb}	...
7.05 ^f	...	5.8 ^{bb}	...	9.94 ^f	5.1(1)	8.3 ^{bb}	...
7.33 ^f	...	6.1 ^{bb}	...	12(1) ^{jj}	5.0(1)	9.5 ^{bb}	...
6.76 ^f	...	5.8 ^{bb}	...	8.66 ^f	6.5(1)	5.5 ^{bb}	...
7.92 ^f	...	6.6 ^{bb}	...	14.30 ^f	5.2(1)	10.7 ^{bb}	...
8.34 ^f	...	7.0 ^{bb}	...	14.7(5) ^{kk}	5.3(1)	11.7 ^{bb}	...
6.67 ^f	...	7.5 ^{bb}	...	15.8(10) ^{kk}	5.4(1)	12.7 ^{bb}	...
8.99 ^f	...	7.5 ^{bb}	...	17(1) ^{ll}	5.8(1)	13.5 ^{bb}	...
7.72 ^f	...	6.6 ^{bb}	...	10.64 ^f	7.5(1)	7.3 ^{bb}	...
9.39 ^f	17.30 ^f	14.48(10)

^aThe column headings mean: (A) free-atom experimental, (B) standard-state experimental, (C) free-atom theoretical, and (D) standard-state theoretical binding energies.

^bFrom Ref. 6.

^cThis is the vertical ionization potential. The adiabatic value is 15.45 eV. See D. H. Turner, *Molecular Photoelectron Spectroscopy* (Wiley-Interscience, New York, 1970).

^dExact solution available.

^eSee Ref. 28.

^fSee Ref. 16. When appropriate, the listed values are energies from the actual ground state to a weighted mean of ionic terms (see Sec. III).

^gFrom Ref. 20.

^hFrom Ref. 10. In those elements possessing $2p$ electrons, the splitting is from optical data.

ⁱSee Ref. 29.

^jSee Ref. 11. In those elements possessing $2p$ electrons, the splitting is from optical data.

^kSee Refs. 20 and 21.

^lUsing experimental bandwidths and work functions calculated by N. D. Lang and W. Kohn, Phys. Rev. B 3, 1215 (1971).

^mReference 18.

ⁿReference 21.

^oUnavailable.

^pNo data are available from which a reliable experimental value can be obtained, because of hybridization in the valence shell.

^qBeck and Nicolaides²³ have explicitly included correlation energy differences and compute a binding energy of 296.3 eV to the 4P ionic state. They have not considered the 2P state. For the sake of consistency, we have listed an average for the 4P and 2P from Wilson's Δ SCF calculations.¹⁸

^rFrom Ref. 27.

^sFrom Ref. 22.

^tG. Johansson, J. Hedman, A. Berndtsson, M. Klasson, and R. Nilsson, J. Elec. Spectr. and Related Phenomena 2, 295 (1973); see also Ref. 8.

^uFrom Ref. 30.

^vFrom Ref. 31.

^wT. X. Carroll, R. W. Shaw, Jr., T. D. Thomas, C. Kindle, and N. Bartlett, J. Am. Chem. Soc. 96, 1989 (1974).

^xBeck and Nicolaides find 698.0 eV to the 3P ionic state. We have listed an average over multiplets from the results of Wilson.¹⁸

^yThis value is determined from an Auger spectrum of the free atom. H. Hillig, B. Cleff, W. Mehlhorn, and W. Schmitz, Z. Phys. 268, 225 (1974).

^zThis value is determined from an Auger spectrum of the free atom. See B. Breuckmann and V. Schmidt, Z. Phys. 268, 235 (1974).

^{aa}Reference 23, in this case, the Δ SCF value is 868.6 eV. The relativistic correction is +0.8 eV, the correlation difference is +1.1 eV, and a further correction of -0.1 eV has been applied for the Lamb shift.

^{bb}From Refs. 5 and 19; the theoretical binding energies come from a relativistic Hartree-Fock-Slater calculation which includes relaxation. In some cases the relaxation energy was found by interpolating between computed values.

^{cc}Beck and Nicolaides²³ compute a transition energy of 1079.3 to the 3S multiplet; for the sake of consistency, we have listed an average over all multiplets; see footnote bb.

^{dd}E. Clementi and C. Roetti, Atomic Data and Nuclear Data Tables 14, 177 (1974). The value comes from a Δ SCF calculation.

^{ee}Not measured in standard state. Probable error $\sim \pm 2$ eV.

^{ff}Obtained from energy differences.

^{gg}Beck and Nicolaides²³ compute a binding energy of 3612.2 eV to the 3S term; see footnote bb.

^{hh}Beck and Nicolaides²³ compute an energy of 385.9 eV to the 3S component; see footnote bb.

ⁱⁱFrom Ref. 23.

^{jj}No experimental optical data exist for this case. The binding energy was extrapolated from the values for Sc and Ti.

^{kk}Not all the terms which are necessary to find the free-atom binding energy from optical data are available. Our approach was to use the known experimental terms to find E_B from standard multiplet theory³² using Mann's two-electron integrals.²⁶

^{ll}No experimental optical data exist for this case. The binding energy was obtained by comparing Mann's $3d$ orbital energy²⁶ with the experimental binding energy in Mn, Fe, and Co. This gave an empirical correction which was then applied to Ni.

^{mm}From free-atom experimental values minus the E_R^{3d} term.

to do so. We shall therefore neglect this correction, noting that the empirical core-level binding energies of free atoms may therefore be somewhat low, because they were obtained by combining optical data on the valence orbitals of free atoms with x-ray data on metals.

There are seven remaining nonmetallic elements. In three of these elements—C, N, and O—the valence shell is so thoroughly hybridized in the compounds for which data are available as to render impossible the extraction of meaningful atomic

core-level binding energies. In two elements, S and Cl, x-ray transitions have been assigned that connect the $M_I(3s)$ levels to core levels,¹³ making contact with optical data. In the remaining elements, Si and P, the " $L_{II,III}M$ " transitions were interpreted as $2p-3s$ in character. The $1s$ energies were then obtained from $K\alpha_{1,2}$ x-ray energies, and the $2s$ free-atom values were obtained from $2s-2p$ differences.⁵

Derived empirical free-atom binding energies are listed in Table I in the columns labeled A.

TABLE II. Work functions ϕ for the metallic elements, in eV. Where blank the correction is either not applicable or very small.

Element	ϕ	Element	ϕ
Li	2.4 ^a	Ti	4.3 ^b
Be	3.9 ^a	V	4.3 ^b
C	4.6 ^a	Cr	4.5 ^b
Na	2.3 ^a	Mn	4.1 ^b
Mg	3.7 ^a	Fe	4.5 ^b
Al	4.2 ^a	Co	5.0 ^b
K	2.3 ^a	Ni	5.2 ^b
Ca	3.2 ^a	Cu	4.7 ^b
Sc	3.5 ^b	Zn	4.3 ^a

^aFrom Ref. 12(b).

^bFrom Ref. 12(a).

IV. THEORETICAL BINDING ENERGIES

Free-atom theoretical binding energies are available in the literature. The values listed in column C of Table I were obtained for the most part by the "ΔSCF" (self-consistent-field) method introduced by Bagus.¹⁷ For the light elements ($Z < 10$), Wilson¹⁸ has given theoretical binding energies for transitions to a number of ionic final states. We have listed in Table I the weighted-average energies, summed over those final states that would be reached by photoemission. In the heavier elements ($Z > 10$) Siegbahn *et al.*¹⁶ and Gelius¹⁹ have calculated binding energies using an optimized relativistic Hartree-Fock-Slater model.

These ΔSCF calculations include relaxation contributions to the binding energy, but do not account for any differences in correlation energy between the two states involved in the transition. In the first and second rows of the periodic table, theoretical binding energies for the outermost electron which include the correlation-energy correction are available from the work of Frankowski and Pekeris,²⁰ Weiss,²¹ and Moser and Nesbet.²² Beck and Nicolaidis²³ have determined total energies for 1s hole states in C, F, Na, K, and Cs, while the neon 1s hole state has been treated carefully by several groups.²³⁻²⁵

Standard-state binding energies have been calculated by rigorous methods in only a few cases. These are documented in the footnotes of Table I. In many other cases the formation of bonds in solids or molecular orbitals in molecules precluded discussion of *atomic* orbital binding energies in the standard state.

For the case of core levels in metals, solid-state shifts in E_B can be large. The success of extra-atomic relaxation energy estimates^{1,2} has

led us to make estimates of core-level binding energies by correcting theoretical free-atom binding energies for solid-state effects using a model described earlier.² Specifically, we have used the relation

$$E_B(\text{solid, theo}) \cong E_B(\text{atom, theo}) - E_R^{\text{ca}} \\ \cong E_B(\text{atom, theo}) - \frac{1}{3}F^0(i, s). \quad (2)$$

Here $F^0(i, s)$ is a Coulomb integral between core level i and the screening orbital s . Numerical values of $F^0(i, s)$ were given by Mann.²⁶ We note that our earlier discussion of solid-state shifts emphasized extra-atomic relaxation, neglecting other effects that may in some cases be of equal importance.⁷ Clearly *some* estimate of the solid-state shift is needed. We note that the earlier estimates based on $\frac{1}{2}F^0(i, s)$ were about 50% high. We have therefore reduced the coefficient to $\frac{1}{3}$, and we regard this correction as a semiempirical quantity which is meant as an estimate of the entire solid-state shift rather than being associated with extra-atomic relaxation alone.

Calculated standard-state binding energies are listed in column labeled D in Table I.

V. DISCUSSION

Table I represents the first attempt to compile experimental atomic binding energies in free atoms and the standard state, while taking cognizance of the crucial differences between the two. It is also the first attempt to compare with theory with this difference in mind. Viewed in this light the result must be regarded as a substantial success.

For an empirical point of view, most core-level binding energies in the first 30 elements are now known to within errors of 0.1 eV up to 2 eV for both free atoms and the standard states. For the 1s, 2s, and 2p levels of transition-metal atoms, x-ray energy shifts from metals to atoms may increase this error to ~4 eV. Because previous binding-energy compilations did not take into account the difference between E_B values for free atoms and the standard state, they were in some cases in doubt by amounts up to the difference between the two, i.e., by up to 18 eV, in either $E_B(\text{atom})$ or $E_B(\text{metal})$.

By using ultrahigh-vacuum techniques we have removed uncertainties in previous binding-energy values of metals based on the use of oxidized samples. It should be noted, however, that our experimental E_B values for core levels of metals are in most cases remarkably close to the values given by Siegbahn *et al.*⁵ in their Appendix 2. Our data therefore strongly support the accuracy of their early work.

Before turning to a more detailed discussion of metals, we comment briefly on those elements that are nonmetallic in their standard states. Hydrogen and helium are well understood. Of the other rare gases, the argon E_B values are quite well approximated by theory, while the neon $1s$ -level results show how well a core-level binding energy can be calculated when correlation is taken into account.²³⁻²⁵ In carbon (graphite), the $1s$ -level E_B has been calculated by a "relaxation potential" theory²⁷ that has given good results for molecules. There is excellent agreement with experiment. Although semiempirical in nature, this is the nearest thing we have to a theoretical value of a core-level binding energy in a solid.

Among the diatomic molecules N_2 , O_2 , F_2 , and Cl_2 , theoretical core-level binding energies are available except for $Cl(1s)$. Agreement with experiment is very good. We have not tabulated valence-shell atomic binding energies for these molecules because the atomic levels are highly hybridized. For the same reason the atomic $1s$ binding energies of C, N, O, and F could not be estimated from x-ray data. In the nonmetals Si, S, and P, the standard-state core-level binding energies are not completely well-defined because of lack of a suitable reference level. We followed Siegbahn *et al.*⁵ in adding 4 eV—a typical work function—to the Fermi-level referenced binding energy.

Seventeen of the first 30 elements are metals. Among these there are consistent differences between atomic and metallic core-level binding energies, with the latter always smaller as expected due to extra-atomic relaxation and other solid-state effects. Furthermore, there is in general very good agreement between the "experimental" and theoretical atomic binding energies. The first case is the $Li(1s)$ level, for which the binding energy is 64.8 eV in the gas phase and 57.2 eV in the metal. The respective theoretical values are 64.9 and 60.5. In other cases the absolute values of E_B may be reproduced very well by theory [e.g., for the $Na 1s$ case, $E_B^A = 1079.1(9)$ eV, $E_B^V = 1074.0(1)$ eV, compared with theoretical values of 1079 and 1075 eV, respectively], or they may not (e.g., 4-eV error in the $K 1s$ case). Differences between E_B^V and E_B^A are always present, however; they have the expected sign and their magnitudes tend to follow quite closely the values predicted by the $\frac{1}{3}F^0$ estimate described above.

To facilitate a systematic comparison, we have made a difference plot of $2s$ binding energies for the fourth-row elements K–Zn (Fig. 1). The experimental $2s$ binding energy in the metal is taken as a reference. The "theoretical" $2s$ binding energies in the metal (open circles) lie within 2 eV

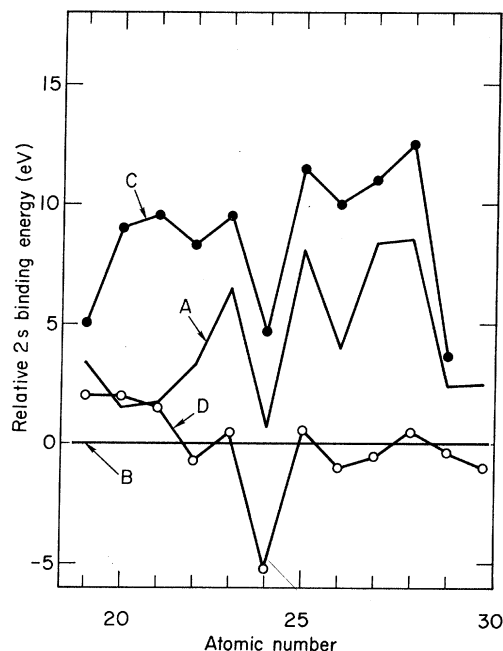


FIG. 1. Relative $2s$ electron binding energies for elements $Z = 19$ (K) through $Z = 30$ (Zn). The experimental (vacuum-referenced) binding energies in the metal (column B in Table I) are taken as reference and set at zero. Theoretical binding energies in free atoms (filled circles) and in the metals (open circles) are labeled C and D, respectively, as in Table II. Curve A gives the "experimental" free-atom binding energies derived from optical and x-ray data.

in all elements except chromium. Chromium is expected to deviate because it has the same ground-state configuration in the free atom and the metal.⁷ The theoretical and experimental free-atom binding energies lie higher in all cases. This difference is attributable to extra-atomic relaxation, initial-state screening, and configuration changes^{2,7} in the metal. An increase of the difference $E_B^A - E_B^V$ across the $3d$ transition series is clearly present, and is attributed to increasingly effective d -electron screening in the initial and final states.^{2,7} The dramatic decrease in this quantity at the filling of the d shell (between Ni and Cu) supports the interpretation that d -electron screening is responsible for the difference, but the relative contributions of the three factors dictating the amount of the screening are not accurately known.

It is also important to note in Fig. 1 that the free-atom experimental values are all lower than the free-atom theoretical binding energies. This result is presumably due to the fact that the ex-

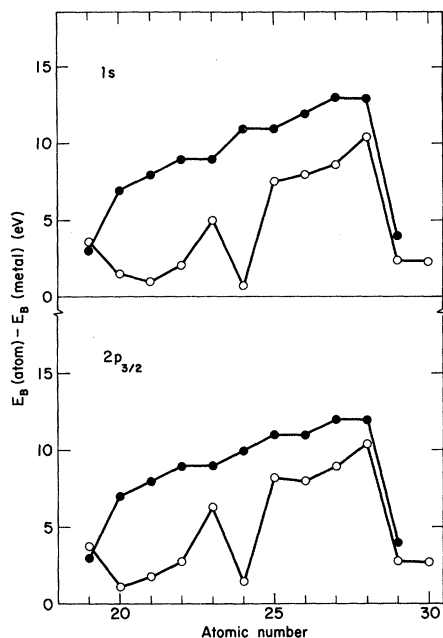


FIG. 2. Plots of the differences $E_B^A(\text{theo}) - E_B^V(\text{theo})$ (closed circles) and $E_B^A(\text{expt}) - E_B^V(\text{expt})$ (open circles) for the $1s$ (top) and $2p_{3/2}$ (bottom) levels of elements 19 (K) through 30 (Zn).

perimental values were obtained by merging free-atom optical data with solid-state x-ray data. As discussed in Sec. III, this will cause the empirical binding energies to be somewhat low.

A clearer idea of the solid-state shift can be obtained by plotting the quantities $E_B^A(\text{theo}) - E_B^V(\text{theo})$ and $E_B^A(\text{expt}) - E_B^V(\text{expt})$ as in Fig. 2. For brevity, only the $1s$ and $2p_{3/2}$ cores have been plotted; the others are similar. Again the effects mentioned above are clearly present. This phenomenon—the increase in d -wave screening across the $3d$ series, then the sharp drop at the d -shell closure—has been discussed before,²⁻⁷ but the binding-energy values used in the present work are more accurate and reliable.

In conclusion, the results presented in Table I provide very strong evidence that atomic binding energies are sufficiently well-known experimentally and understood theoretically to necessitate that a clear distinction be made between the atomic state and the metallic state in future discussions of binding energy. When this distinction is made, the size of the solid-state shift and its sensitivity to electronic structure hold forth promise of its value in elucidation of various electronic structure problems in metals.

*Work done under the auspices of the U.S. Energy Research and Development Administration.

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states, respectively. The experimental values are 64.41 and 66.15 eV (Ref. 16).

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