One-Electron Energies of Atoms, Molecules, and Solids*

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In the method of the self-consistent field, the one-electron energies of the occupied orbitals agree closely with ionization energies of the corresponding atom or molecular system. To compare such calculations with experiment, we need a table of ionization energies of the atoms. Such a table is set up in the present paper. For the outer electrons, we use optical data, finding the energy of each configuration as the weighted mean of all the states in that configuration. For the inner electrons, we use x-ray data, and for this purpose present a revised table of x-ray term values. The two sets of values should not agree, for the zero of energy in optical spectra is that for an electron removed an infinite distance from the isolated atom, while in x-ray terms all energies are referred to the Fermi energy in the crystal. For the alkali metals, measurements of both types can be intercompared, and it is shown that for Li the Fermi level lies about 0.8 rydberg, below the zero of energy for the atom, for Na and K about 0.5, and for Rb about 0.4 rydberg. Using this information, appropriate corrections are applied for the other atoms, and a table of ionization energies of the atoms is constructed. The values in this table are compared with experimental information from soft x-ray spectra, and theoretical calculations of energy levels in atoms, molecules, and solids.

IN the method of the self-consistent field, it is known that the energy levels of the one-electron problems of motion of the various electrons in the self-consistent fields agree well with the corresponding ionization energies of the system. The theorem of Koopmans[1] tells us why this should be so. The purpose of the present paper is to set up a reliable table of experimental ionization energies of the isolated atoms, to use in making comparisons with self-consistent field calculations. We discuss the relation of this table to experimental values of energy levels in molecules and solids, and to theoretical values as computed by self-consistent fields. The reason why such a comparison is timely is that we are very recently beginning to get reliable calculations for molecules, made by the MO SCF (molecular orbital self-consistent field) method, and calculations for solids, made by the energy-band method.

For the outer electrons of the atom, we require the data of optical spectroscopy, which are admirable summarized in the tables prepared by the National Bureau of Standards,[2] which at present extend through Nb, with atomic number 41. We do not wish, however, merely to use the atomic ionization potentials, for these refer to the energy required to remove an electron from the lowest energy level of the atom, leaving the ion in its lowest energy level. This lowest energy level, in an atom with a complex spectrum, may be considerably below the properly weighted center of gravity of the configuration of the atom concerned. In making a self-consistent field calculation, however, the multiplet structure is not ordinarily taken into account in the first stage of the calculation, but only later, by solving a secular problem which accounts for the spreading

apart of the various levels of the multiplet. This secular problem will leave the average value of the energy levels invariant, on account of the invariance of the trace of a matrix. Consequently the average value of all the experimental terms in a spectrum coming from a given configuration, suitably weighted according to their *a priori* probability, will give a more reliable estimate of the energy of that configuration than will the lowest energy level of the configuration. We can expect that the difference of these weighted mean energies of the atom and ion will be more reliable experimental quantities with which to compare one-electron energies than will the ordinary ionization potentials.

Consequently, we have computed such weighted mean energies of the ground-state configuration of each of the atoms up to Nb, and similar weighted means of the configurations of the singly ionized ions resulting from the neutral atom by removing one of its electrons. The differences between these energies of the atom and ion give ionization energies which may be expected to agree approximately with the one-electron energies in the self-consistent field calculations for the atoms. These values are tabulated in the upper part of Table I. There are some cases, particularly in the iron group, where some of the energy levels of complicated configurations have not been observed. In most such cases, there are other similar spectra of neighboring atoms where such missing terms have been located. By intercomparison, we have estimated the missing terms, which in no case are very important ones. On account of the necessity of making these estimates, some of the ionization energies in the iron group are likely to be in error by several units in the second decimal place.

For the inner electrons, one must use x-ray data. The writer has not been able to find a reliable tabulation of x-ray term values, containing the results of recent measurements, particularly of soft x-ray levels. Consequently, we have prepared such a table, given in Table II. The sources of information are described in

TABLE I. One-electron energies of free atoms (rydbergs).[a]

		1s	2s	2p	3s	3p	3d	4s	4p	4d	5s
H	1	1.00									
He	2	1.81									
Li	3	4.77	0.40								
Be	4	8.9	0.69								
B	5	14.5	1.03	0.42							
C	6	21.6	1.43	0.79							
N	7	30.0	1.88	0.95							
O	8	39.9	2.38	1.17							
F	9	51.2	2.95	1.37							
Ne	10	64.0	3.56	1.59							
Na	11	79.4	5.2	2.80	0.38						
Mg	12	96.5	7.0	4.1	0.56						
Al	13	115.3	9.0	5.8	0.83	0.44					
Si	14	135.9	11.5	7.8	1.10	0.57					
P	15	158.3	14.1	10.1	1.35	0.72					
S	16	182.4	17.0	12.5	1.54	0.86					
Cl	17	208.4	20.3	15.3	1.86	1.01					
A	18	236.2	24.2	18.5	2.15	1.16					
K	19	266.2	28.2	22.2	3.0	1.81		0.32			
Ca	20	297.9	32.8	26.1	3.7	2.4		0.45			
Sc	21	331.1	37.3	30.0	4.2	2.6	0.59	0.55			
Ti	22	366.1	42.0	34.0	4.8	2.9	0.68	0.52			
V	23	402.9	46.9	38.3	5.3	3.2	0.74	0.55			
Cr	24	441.6	51.9	43.0	6.0	3.6	0.75	0.57			
Mn	25	482.0	57.7	47.8	6.6	4.0	0.57	0.50			
Fe	26	524.3	63.0	52.8	7.3	4.4	0.64	0.53			
Co	27	568.3	69.0	58.2	8.0	4.9	0.66	0.53			
Ni	28	614.1	75.3	63.7	8.7	5.4	0.73	0.55			
Cu	29	662.0	81.3	69.6	9.6	6.1	0.79	0.57			
Zn	30	712.0	88.7	76.2	10.5	7.0	1.28	0.69			
Ga	31	764.0	96.4	83.0	11.8	7.9	1.6	0.93	0.44		
Ge	32	818.2	104.6	90.5	13.5	9.4	2.4	1.15	0.55		
As	33	874.5	113.0	98.5	15.4	10.8	3.4	1.30	0.68		
Se	34	932.6	122.1	106.8	17.3	12.2	4.5	1.54	0.80		
Br	35	993.0	131.7	115.6	19.9	13.8	5.6	1.80	0.93		
Kr	36	1055.5	142.0	124.7	22.1	15.9	7.1	2.00	1.03		
Rb	37	1120.1	152.7	134.5	24.3	18.3	8.7	2.7	1.56		0.31
Sr	38	1186.7	163.7	144.6	26.8	20.5	10.4	3.3	2.0		0.42
Y	39	1255.3	175.1	155.0	29.4	22.7	12.0	3.7	2.3	0.48	0.64
Zr	40	1325.9	186.7	165.5	32.0	24.8	13.6	4.1	2.3	0.61	0.54
Nb	41	1398.9	199.3	176.9	35.1	27.6	15.8	5.0	3.1		0.58

[a] Entries above the line are determined from optical data, those below the line from x-ray data. The entries for Li 1s, Na 2p, K 3p, and Rb 4p are determined from both sorts of data. To bring about agreement, as explained in the text, the x-ray levels of Be to C are increased numerically by 0.7 ry with respect to those in Table II, those of the elements from N to F are increased by 0.6, for elements from Na to Zn by 0.5, and those from Ga on by 0.4 ry. The K level of Ne is not modified, since it was determined by an optical transition of the free atom. For A, on the other hand, the K level was determined by absorption of the free atom, and the absorption edge presumably included the broadened transitions to the bound levels 4p, 5p, etc., as well as to the continuum, so that this case corresponds more nearly to that of a solid than of a free atom. The x-ray levels from Table II were used to form properly weighted mean energies for the different j values of the same configuration, before being incorporated in Table I.

In the iron group, there is a discontinuity in our treatment of the optical levels, between Cr and Mn, indicated by a line in the table. At the beginning of the group, the ground-state configuration (as judged by the weighted mean of the term values) is that with two 4s electrons, while at the end of the group it is that with one 4s electron. For the elements up through Cr that with two 4s electrons is definitely lower, for Mn they are very nearly the same, and for the elements from Fe on the lowest configuration is that with one 4s electron. We have assumed as the ground state configuration that with two 4s electrons up through Cr, and that with one 4s from Mn on.

Though energy values for the optical states are listed to two decimal places, there are a number of places in the transition groups where levels had to be estimated from neighboring spectra, and the second decimal place may be uncertain by several units.

the notes to that table. It will be noticed that, in contrast to the existing tables of x-ray term values, we have distinguished sharply between the inner levels, where the separation into such levels as L_1, L_2, L_3 is appropriate, and the outer levels, which as we now know from the theory of solids are broadened into valence or conduction bands. For these outer bands, we have indicated the range of energy in which they are located, as determined by Skinner and other observers of soft x-rays. The writer cannot claim to be an expert on x-rays, or to have been able to make a critical review of the data, but nevertheless he believes that Table II is considerably more reliable than other available tables.

We now notice that the x-ray data are not strictly

TABLE II. X-ray term values (rydbergs).[a]

		K 1s $j=1/2$	L_1 2s 1/2	L_2 2p 1/2	L_3 2p 3/2	M_1 3s 1/2	M_2 3p 1/2	M_3 3p 3/2	M_4 3d 3/2	M_5 3d 5/2	N_1 4s 1/2	$N_{2,3}$ 4p 1/2, 3/2
Li	3	4.0		0–0.3								
Be	4	8.2		0–1.0								
B	5	13.8		0–2.2								
C	6	20.9		0–2.3								
N	7	29.4										
O	8	39.3										
F	9	50.6										
Ne	10	64.0	L_1	L_2	L_3							
Na	11	78.9	4.7	2.3	2.3	0–0.2						
Mg	12	96.0	6.5	3.6	3.6	0–0.5						
Al	13	114.8	8.5	5.3	5.3	0–0.9						
Si	14	135.4	11.0	7.4	7.3	0–1.2						
P	15	157.8	13.6	9.7	9.6	0–2.9						
S	16	181.9	16.5	12.1	12.0	0–3.3						
Cl	17	207.9	19.8	14.9	14.8							
A	18	235.7	(23.7)	18.1	19.7	M_1	M_2	M_3				
K	19	265.7	27.7	21.9	21.6	2.5	1.3	1.3	0–0.1			
Ca	20	297.4	32.3	25.8	25.5	3.2	1.9	1.9	0–0.2			
Sc	21	(330.6)	(36.8)	(29.7)	(29.4)	(3.7)	(2.1)	(2.1)				
Ti	22	365.6	41.5	33.9	33.4	4.3	2.4	2.4	0–0.4			
V	23	402.4	46.4	38.2	37.7	4.8	2.7	2.7	0–0.6			
Cr	24	441.1	51.4	43.0	42.3	5.5	3.1	3.1	0–0.5			
Mn	25	481.5	57.2	47.9	47.1	6.1	3.5	3.5	0–0.4			
Fe	26	523.8	62.5	53.1	52.1	6.8	3.9	3.9	0–0.4			
Co	27	567.8	(68.5)	58.5	57.4	7.5	4.4	4.4	0–0.5			
Ni	28	613.6	74.8	64.1	62.9	8.2	4.9	4.9	0–0.4			
Cu	29	661.5	80.8	70.2	68.7	9.1	5.6	5.6	0–0.5			
Zn	30	711.5	88.2	76.9	75.2	10.0	6.5	6.5	0–0.8			
Ga	31	763.6	(96.0)	84.0	82.1	11.4	7.5	7.5	1.2	1.2		
Ge	32	817.8	(104.2)	91.8	89.5	13.1	9.0	9.0	2.0	2.0		
As	33	874.1	112.6	100.1	97.5	15.0	10.4	10.4	3.0	3.0		
Se	34	932.2	(121.7)	108.6	105.6	16.9	11.8	11.8	4.1	4.1		
Br	35	992.6	(131.3)	117.8	114.3	19.5	13.6	13.2	5.3	5.1		
Kr	36	1055.1	(141.6)	127.2	123.4	(21.7)	(16.0)	(15.4)	(6.8)	(6.7)		
Rb	37	1119.7	152.3	137.4	133.0	23.9	18.4	17.7	8.4	8.3	2.3	1.2
Sr	38	1186.3	163.3	147.9	143.0	26.4	20.7	19.9	10.1	9.9	2.9	1.6
Y	39	1254.9	174.7	158.7	153.2	29.0	23.0	22.1	11.7	11.6	3.3	1.9
Zr	40	1325.5	186.3	169.8	163.6	31.6	25.1	24.2	13.3	13.1	3.7	1.9
Nb	41	1398.5	198.9	181.7	174.7	34.7	28.1	26.9	15.5	15.3	4.6	2.7

a Most of the data for this table are taken from Landolt-Bornstein's tables (Verlag Julius Springer, Berlin, 1950), eighth edition, Vol. 1, 1. Teil, pp 226–227. That tabulation, unfortunately, was far from up to date at the time of its publication, and therefore the data given there have been corrected in the light of information not included. For Li, Be, B, and C, and the band widths of these elements and those from Na through S, we have used the results of H. W. B. Skinner, Trans. Roy. Soc. (London) A239, 95 (1940). For the band widths of K and Ca, we have used R. H. Kingston, Phys. Rev. 84, 944 (1951), and for the band widths of the elements from Ti to Zn we have used H. W. B. Skinner, Phil. Mag. 45, 1070 (1954). Results on the elements K to Cu are taken from V. H. Sanner, dissertation, Uppsala, 1941 (unpublished), quoted by H. Niehrs, Ergeb. exakt. Naturwiss. 23, 359 (1950). That very useful review article contains the best and most up-to-date survey of the soft x-ray levels which the writer has seen, including many references, and the results quoted by Niehrs have been considered in setting up Table II. The K levels of Zn, Ga, and Ge are taken from W. W. Beeman and H. Friedman, Phys. Rev. 56, 392 (1939), and the other levels of these elements have been corrected, using results quoted in Landolt-Bornstein and in M. Siegbahn, Spektroskopie der Röntgenstrahlen (Verlag Julius Springer, Berlin, 1931), second edition, which of course is the authority for work done up to its time of publication. Values given in parentheses are estimated by interpolation. In the case of Sc, in which results are quoted in the tables, we have diminished the tabulated values by 0.6 ry, thereby bringing the values into smooth relationship with the neighboring elements. It seems likely that there is an error in the determination of the K absorption limit for this element, which would account for this discrepancy. A similar discrepancy of 2.0 ry in the levels of Ga exists in all published tables, but the new determination of its K absorption limit by Beeman and Friedman, mentioned above, has removed this discrepancy, so that in Table II the values for Ga fall smoothly in line with neighboring elements.

comparable with the optical data, and cannot immediately be incorporated into Table I. First, of course, we must make a properly weighted average of the two states in a doublet, as L_2 and L_3. But quite aside from this, the values are not comparable because the energies are referred to different zeros of energy. This will be clear from Fig. 1, which illustrates the case of sodium.

In Fig. 1, we have illustrated, as accurately as possible, the potential energy felt by an electron in the sodium atom, as determined in a self-consistent field way (in this case, we have used the well-known potential of Prokofjew,[3] which was set up empirically so that the one-electron energies in it would agree as closely as
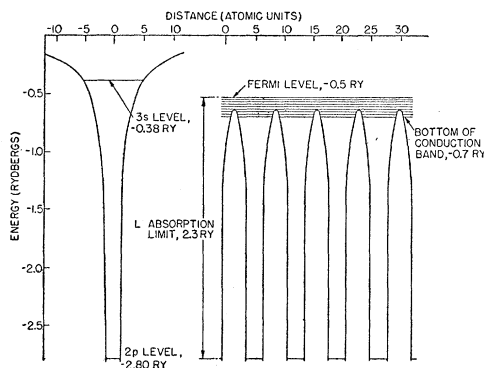
[3] W. Prokofjew, Z. Physik 58, 255 (1929).

FIG. 1. Energy values in sodium atom and sodium crystal. At left, potential energy of electron in sodium atom, as function of distance from nucleus, going to zero energy at infinite distance, and showing the 3s level at -0.38 ry and the 2p at -2.80 ry. At right, potential energy in sodium crystal, along a line in 111 direction passing through nearest neighbor atoms. This is drawn so that the potential energy near the nucleus, and the x-ray levels, agree with those of the isolated atom. The conduction band extends downward from the Fermi level, at -0.5 ry, to about -0.7 ry. The L absorption limit is observed when an electron is raised from the 2p level to the Fermi level, corresponding to 2.3 ry.

possible with observed term values), and the corresponding potential energy in the sodium crystal, at points along a line in the 111 direction, passing through the centers of nearest-neighbor atoms. For the atom, we have shown the 2p and 3s energy levels, and for the crystal the conduction band and the 2p level. In this case, and in the other alkali metals, we fortunately know all the required energies. The 2p level in the atom is at -2.80 rydbergs, the 3s at -0.38 ry. In the metal, the 2p term value is given as 2.3 ry, and the breadth of the conduction band is about 0.2 ry. Now the x-ray energy levels are set by the absorption limits: the zero of energy is set at the lowest energy level to which an electron can be ejected from an inner level. That is, all x-ray terms are measured from the Fermi level as a zero. If we now adjust the additive constant in the energy for the metal so that the x-ray levels will coincide (that is, so that the potential energy at a point well inside the atom is identical in metal and isolated atom), it is clear that in this case the Fermi level must lie about 0.5 ry below the energy of the atom at infinite distance. Similar arguments show that the depression of the Fermi level for Li is about 0.8 ry, for K about 0.5, and for Rb about 0.4. These are the only elements for which this comparison can be made.

It is clear, then, that in order to find the ionization energies of isolated atoms, using the x-ray term values as a starting point, we must increase the numerical value of each of the x-ray terms by an amount equal to the depression of the Fermi level. Since we do not know this for any elements but the alkali metals, we have done the best we could, and have simply used a smooth interpolation between these elements to deduce an amount by which we should increase the term values. Thus, we have increased the term values of the ele-

ments from Be to C by 0.7 ry, those from N to F by 0.6, those from Na to Zn by 0.5, and those from Ga to Nb by 0.4. The only exception is Ne, in which the original measurements[4] represented a K_α emission line of the gaseous atom, so that this value should require no further correction. The energies entered in Table I, for the inner electrons of the atom, are derived from the empirical x-ray term values of Table II by the procedure which we have just described.

In Fig. 2, we show graphically the energy values of Table I. We also show, by black rectangles, the breadths of the outer bands for the various elements, in the cases where they have been measured. Our adjustment of the x-ray levels to take account of the depression of the Fermi level has, of course, determined the height of the top of these black rectangles, which represents the Fermi level. The accuracy of modern determinations of x-ray term values is well shown by the comparative smoothness of the curves. If one uses an older table of x-ray term values, rather than the corrected values of Table II, the curves are much less smooth. Also, if one uses optical ionization potentials rather than the energy differences of weighted mean values for the various configurations, as we have done, the upper parts of the curve are much less smooth.

Before going on to discuss the relation of these energy values to the problem of molecules and solids, let us take up one objection which some persons may well make. For instance, Skinner,[5] in 1932, discussing Li by means of a figure very much like our Fig. 1, on the basis of much less experimental knowledge than we now have, concluded that he could not form a consistent picture of what was going on along the lines we are following in this paper, and therefore sought other interpretations of the situation. He noted that a Li atom which has lost a K electron, as in the initial state of the transition in which a conduction electron falls back into a vacancy in the K shell, is really much like an atom whose atomic number is one unit greater, or a Be atom, as far as its outer structure is concerned. He considered that such a Be atom, introduced into the Li lattice, would have a potential well so much deeper than the ordinary Li atom that it would create a low-lying discrete level, below the bottom of the conduction band, and he thought he was seeing evidence of the existence of such a level. He felt that the simple one-electron picture was quite inadequate to explain what was going on. Various other workers in the field of soft x-ray spectroscopy have made similar remarks at one time or another, and it seems desirable to examine them critically, and see whether they invalidate the simple one-electron picture.

The first part of this discussion can well be a consideration of Koopmans' theorem; the experimenters in the field are not usually aware of its assumptions or its implications. Koopmans considered a Hartree-Fock

[4] J. M. Backovsky, Compt. rend. **202**, 1671 (1936).
[5] H. W. B. Skinner, Proc. Roy. Soc. (London) **A135**, 84 (1932).

solution for an atom (though his results hold equally well for a molecule or solid). From the Hartree-Fock method one can immediately compute the energy of the atom, in its ground state. One can then set up a wave function for the ion, built up out of the same orbitals which are used for the ground state of the atom, but merely omitting the orbital of the electron which has been removed. One can calculate the expectation value of the energy for this wave function, and subtract from it the energy of the ground state of the atom. Koopmans showed that this difference is precisely equal to the one-electron energy parameter for the electron which has been removed.

Now it is obvious to anyone that the wave function for the ionized state, determined in this way, will be less accurate than for the ground state. The wave function for the ground state is determined by varying the one-electron orbitals to minimize its energy, and we have used the same orbitals for the ion, rather than varying them over again to minimize the energy of the ion. The ion really should have more concentrated orbitals, pulled in by the greater nuclear charge. If we correct for this, by solving separately for the ion, or by using second-order perturbation calculations, we shall find that the energy of the ion will be depressed, and the apparent ionization energy will decrease, since the energy of the ground state will not be affected. In other words, we expect to find that the Hartree-Fock one-electron energy parameters give too large values for the x-ray term values. This expectation proves to be generally correct, when we compare atomic calculations with the observations.

The error in the energy arising from this incorrect wave function, however, on account of the perturbation theory, will be a small quantity of the second order, if the error in the wave function is small of the first order. The incorrect wave function, being too extended in space, will have too high a potential energy. On the other hand, since it corresponds to a disturbance of too great effective wavelength, it will have too small a kinetic energy. To the first approximation, these effects will cancel, leaving only a second-order correction to the energy, which may be expected to be small.

We may furthermore expect this type of error in the results of Hartree-Fock calculations to be roughly the same in atom and crystal, so that it should not affect the validity of the type of comparison between the two which we have made. This should be true, at least, if there is not a gross change in the character of the wave function in going from an atom to an ion. If Skinner's hypothesis were true, however, and there were a new discrete level which appeared in the solid, below the level of the continuum, this would be such a decided change in wave function that we might well doubt the applicability of Koopmans' theorem. Let us examine this question, and see if we expect such a level to appear.

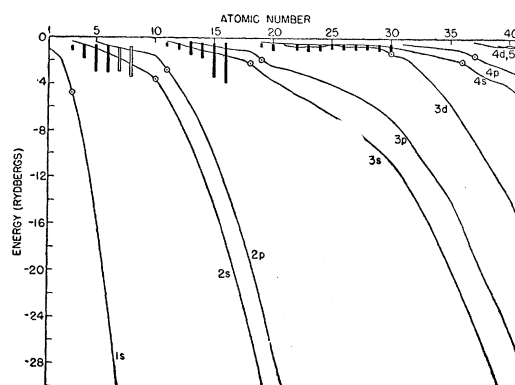We know a good deal more about the nature of impurity levels in solids at present than we did a few

FIG. 2. One-electron energies of atoms, molecules, and solids. The full lines represent the energy values for the atoms, from Table II. The black rectangles represent the filled bands of electrons in the solids. The open rectangles, for the elements oxygen and nitrogen, represent the energy range in which one-electron energies have been calculated for various molecules involving these elements, by the MO SCF method. For carbon, similar calculations on molecules, and on the crystal, give energy levels lying within the range shown by the black rectangle. The circles on each full line indicate the point where the optical and x-ray data join.

years ago, and can now answer this question with considerable assurance. The writer and Koster[6] have shown that when an atom whose atomic number is greater than that of the atoms of the crystal replaces an atom of a metallic crystal, there are two quite different possible things which may happen. If the atomic number is enough greater, it is quite true that a new level will appear below the continuum. If the difference is smaller, however, no new level will appear. The wave functions will be modified, so that the wave functions corresponding to the lower energy levels in the band will become somewhat more concentrated toward the impurity atom, those corresponding to the higher (and generally unoccupied) energy levels will tend to avoid the impurity atom, but unless the difference in atomic number exceeds a critical amount, there will be no discrete level, and no major modification of the wave functions. It seems most likely that a difference of a single unit in atomic number is not enough to result in a discrete level. In a metal, the conduction electrons will tend to shield the crystal from the added Coulomb field resulting from the impurity atom, so that the perturbation produced by this atom is not nearly as great as one would suppose at first sight, and this is why the critical perturbation is not exceeded.

The situation in an insulator or semiconductor of course will be different. There, an impurity atom whose atomic number is one unit greater than the atoms of the lattice (or an atom which has lost an inner electron) will be an ordinary donor atom, and will produce a discrete level, hydrogenic in type and extending rather far out in space, below the conduction band, and another one below the valence band. As far as the valence

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[6] G. F. Koster and J. C. Slater, Phys. Rev. **96**, 1208 (1954).

band is concerned, we do not ordinarily consider this discrete level, for the charge which it contains will just balance the compensating decrease in charge density in the other wave functions of the valence band. When the inner electron of the atom is removed, the electrons of the valence band will instantly and automatically rearrange themselves, in such a way as just to fill the revised valence band, including the discrete level, with very small change of charge density. There will in addition be a level appearing just below the conduction band. This will be the familiar donor level, which in principle could be filled with an electron, which would tend to produce electrical neutrality of the atom which has lost its inner electron, but which in practice would not acquire that electron in the short time concerned in the x-ray experiment, or would lose it again immediately on account of thermal excitation. In other words, the net result is a very small change in the charge density in the valence band, as a result of the ionization of the inner electron.

In either of these cases, then, we seem to have the necessary conditions for the application of Koopmans' theorem: the outer electrons will not suffer any large change in wave function when the inner electron is removed. The writer believes, therefore, that a one-electron picture can describe consistently the relations between the levels of the isolated atom and of the crystal of the corresponding element, without the need of introducing any additional discrete levels to complicate the picture. We can expect a self-consistent field calculation, with exchange, to give energy levels for the atom, and the crystal or molecule, which are comparable with each other, though they may be somewhat inaccurate as compared with the experimental values of Table I. To see that the inaccuracies are not very great, however, we may quote the calculated values for the argon atom,[7] almost the only neutral atom for which complete calculations with exchange have been made, and therefore for which we can make direct comparison with the values of Table I. The calculated $1s$ level is 237.2, compared with 236.2 of Table I; for $2s$, 24.6 compared with 24.2; for $2p$, 19.1 compared with 18.5; for $3s$, 2.56 compared with 2.15; and for $3p$, 1.18 compared with 1.16. As we expect, the numbers are all somewhat large, but the agreement in general is remarkable.

Now let us go on to discuss various other aspects of one-electron energies. In calculations of energy bands of solids, very often the potential energy used for the solid has not been comparable with that for the isolated atom, so that a direct comparison is not possible. However, in the calculation of Na by Wigner and Seitz and by the writer,[8] the potential in the solid was taken

to be the Prokofjew potential, as it is in the atom, and the depression of the energy band on going from the atom to the solid is in agreement with that shown in Fig. 1, to an accuracy of about 1 ev. In the calculation of Manning and Krutter on Ca,[9] it is indicated how one can adjust the potential used in the crystal to agree with the atom, and they find a band extending from about -0.60 to -0.95 ry, indicating a depression of the Fermi level of about the expected amount, and about the expected width. Herman's calculation[10] on diamond uses a potential which appears as if it might be comparable with the atomic potential. His band, stretching from about -0.9 to -2.4 ry, is roughly in agreement with what we should expect. It is to be emphasized that in future work on energy bands, it would be highly desirable to adjust the potential energy so that its value near the nucleus agrees with that in the isolated atom, so that one can make the sort of comparison of the absolute value of energy levels with the atomic ones which we are discussing here, as well as comparing band widths.

Several molecules have recently been discussed by the molecular orbital method, and their one-electron energies determined. Thus, Mulligan,[11] in his calculation of CO_2, finds L levels running from -11.5 ev to -44.9 ev, or from -0.8 ry to -3.3 ry. The lower levels are largely composed of oxygen wave functions. Similarly for CO, Sahni[12] has levels from -1.0 to -3.2 ry, and Ellison and Shull,[13] in their work on H_2O, find levels from -0.9 to -2.7 ry. These calculations suggest that we are likely to find levels down to about -3.3 ry in molecules containing oxygen, and in Fig. 2 we have shown a rectangle enclosing these energy values. For N_2, Scherr[14] in unpublished calculations finds levels from -1.1 ry to -2.9 ry; we show this energy range as well in Fig. 2. For CH_4, Nesbet[15] in other unpublished work finds the levels to lie between -1.1 ry and -2.0 ry, well within the range shown by the black rectangle in Fig. 2 for carbon. We get the impression, in other words, that the spread of one-electron energy levels in simple molecules will be substantially the same as in solids. This is, of course, what we should expect. It is well known that the splitting of energy levels in a solid is comparable in magnitude with that in a molecule; the only difference is that, as the molecule becomes larger and approaches a solid, more and more energy levels become crowded into the same energy range, and finally become a continuous band.

It seems, then, that the one-electron energies which one can find from ionization energies of atoms and

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[7] D. R. Hartree and W. Hartree, Proc. Roy. Soc. (London) A166, 450 (1938).

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[9] M. F. Manning and H. M. Krutter, Phys. Rev. 51, 761 (1937).
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[11] J. F. Mulligan, J. Chem. Phys. 19, 347 (1951).
[12] R. C. Sahni, Trans. Faraday Soc. 49, 1246 (1953).
[13] F. O. Ellison and H. Shull, J. Chem. Phys. 21, 1420 (1953).
[14] C. W. Sherr, thesis, University of Chicago (unpublished). *Note added in proof.*—See also J. Chem. Phys. 23, 569 (1955).
[15] R. K. Nesbet, thesis, Cambridge University (unpublished).

crystals, and which one can calculate using the self-consistent field method for atoms, molecules, and solids, show a good consistency with each other. Such comparison as we have made here, between the one-electron energies of the atoms and of the other systems, could well be made in the course of future calculations of molecular wave functions or energy bands. In particular, it is interesting to observe the great increase in the width of the bands as we go through the first two periods, adding more electrons and reducing interatomic distances. A particularly interesting thing will be to find just how the $3d$ level drops below the valence band, in the elements to the neighborhood of Ge. Interesting deductions regarding molecular binding are of course suggested by the drop of the average value of the one-electron energy in a band, below the atomic levels, but we shall not try to go further into the implications of the results in the present paper.

Differential Cross-Section Measurements for Large-Angle Collisions of Helium, Neon, and Argon Ions with Argon Atoms at Energies to 100 kev*

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The differential cross section for the scattering of positive charge from collisions of noble gas ions with the target gas argon has been measured. The ion beam is passed through a chamber containing the target gas at a pressure of a few microns of mercury, which is low enough to insure that single collisions will predominate. The particles scattered out of the beam are collected and the total positive charge is measured. The collector incorporates collimating holes to select only those particles at a chosen scattering angle with a resolution of about two degrees. The apparatus allows the angle to be varied continuously up to thirty-eight degrees. Data are presented for collisions of singly ionized helium, neon, and argon ions with argon atoms at 25, 50, and 100 kev. The cross sections observed differ from those expected from the Rutherford scattering law and these differences are interpreted in terms of electron screening, ionization, and charge exchange.

1. INTRODUCTION

THE large-angle collisions studied here are those in which ions of helium, neon, and argon with an energy from 25 000 to 100 000 electron volts collide with stationary argon atoms. These collisions can be expected to follow the Rutherford scattering law in the limit of sufficiently high energies, but at the lower energies there will be a modification due to the screening effect of the electrons.

In this energy range the vast majority of the collisions will be small-angle and, in fact, these small-angle collisions account for nearly all of the total cross section. There have been numerous studies of the total cross sections for elastic scattering, charge exchange, and ionization in this energy range.[1-3]

Although the few large-angle collisions which do occur account for a nearly negligible portion of the total cross section, they are interesting, for these are collisions in which the atoms come very close together.

Their study gives information regarding the potential energy function between two atoms at very close distances on an atomic (not nuclear) scale. Under some conditions in these experiments, the actual distance of closest approach is less than the radius of the innermost classical electron orbits of either of the colliding atoms. This means that the electron configuration during the collision will be complicated.

In this energy range, the relative velocity of the ion and atom in the collision is of the same order of magnitude as the classical orbital velocity of the atomic electrons. This is the condition under which ionization and charge exchange cross sections are thought to be a maximum.[1]

The scattered particle current into a given solid-angle segment depends on the forces between the atoms during the collision, but the scattered positive charge measured in the experiments described here depends, in addition, on the extent to which the scattered particle was ionized or neutralized during the collision. Specifically, we are measuring in these experiments the differential cross section for scattering of positive charge.

Heydenburg, Hafstad, and Tuve[4] have performed differential cross section measurements for collisions of protons with protons at 600 to 900 kev. Their apparatus is similar in some respects to that to be described here.

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[1] H. S. W. Massey and E. H. S. Burhop, *Electronic and Ionic Impact Phenomena* (Oxford University Press, London, 1952). Chapter VIII contains an excellent discussion and bibliography of this field.

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