IONIZATION ENERGY AS A FUNCTION OF NUCLEAR CHARGE

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ABSTRACT.—Three new quadratic formulas relating ionization potential and atomic number are investigated. It is found that the new formulas are in no way superior to previously used quadratic forms. The judgments are made not only by the usual appeal to experiment but by new applications of statistical methods to chemical research. The new techniques suggest a new function which may be superior to all present functions for the prediction of electron affinities. Finally, this investigation presents and demonstrates the operation of a new philosophy which chemists in the age of computers should adopt.

By the use of perturbation theory in a quantum mechanical framework, Bethe and Salpeter (1957) derived an expression for the ionization energy, I, of an atom or ion. It is

$$I = \sum_{n=-2}^{n=\infty} a_n \left(\frac{1}{Z} \right)^n \qquad (1)$$

where Z is the nuclear charge of the ion or atom, n is the order of the perturbation, and the a_n are numbers derivable from quantum mechanical integrals. The term $(1/Z)$ functions as a natural perturbation parameter.

Glockler (1934) suggested an empirical relationship between I and Z many years before the development of perturbation theory as a useful chemical tool. His functional form is simply a truncated version of Equation (1) in which only the first three terms are used. Glockler evaluated the constants a_n with the aid of experimental data for eighteen isoelectronic series. The difference in method of obtaining the constants a_n reflects, of course, the difference in an empirical approach and a theoretical approach.

In the intervening years many workers tried, either empirically or semi-empirically, to predict ionization energy as a function of nuclear charge in an isoelectronic series. Most of the resulting equations were either truncated forms of Equation (1) or truncated forms of Equation (1) with an altered independent variable. The principal alteration was to use an effective nuclear charge, Z_{eff};

$$Z_{eff} = Z - s \qquad (2)$$

where s is a parameter to be adjusted. The total energy, E, of an atom or ion may be given by an expansion of the same form as that for I. In the case of E, the parameter s represents screening, i. e., a partial shielding of the nuclear charge by the other electrons in the atom. A *raison d'etre* for trying to obtain a correct relationship between ionization energy and nuclear charge is that the relationship can be used to predict electron affinities which are not easily measurable.

The purpose of the present paper is threefold in nature. Since many empirical formulas have been suggested, but their functional form has been restricted, there is a possibility that some peculiar functional form might be superior to the form more commonly accepted. Thus, this paper compares empirical formulas of widely diverse functional forms which relate ionization energy to nuclear charge. Second, this paper investigates the use of statistical tools to test the "goodness" of such formulas. For an applied mathematician, e. g., a chemist, it has often been sufficient to say a formula is "good" if it reproduces experimental data within experimental error. However, it is conceivable that statistical tools may provide more rigorous criteria. Finally, the paper suggests a philosophy in the use of "canned" computer programs. The use of computers are pervading chemistry to a greater and greater degree. As more and more chemists use this new tool, it is apparent that the chemist must make more use of programs which are available for general distribution (e. g., cf. SHARE (1966)) rather than spending precious research man-hours doing routine programing. Optimal use of such programs demands that the user utilize such programs to the fullest.

EXPERIMENTAL DESIGN

A single format, truncation after the quadratic term, was used throughout the project. The purpose of the constraint was to control a condition in the same sense as an experimenter controls temperature in order to limit the effects which may be observed in a single experiment.

Before proceeding further, an important ambiguity in notation must be mentioned. The independent variable is usually conceived of as being that experimental variable to which a value may be freely assigned (usually from a measurement) whereas the dependent variable is that variable whose value is fixed when the values of all independent variables have been assigned. For example, in Equation (1), Z is the independent variable and I is the dependent variable. Alternatively, a transformation could be made such that (1/Z) is the independent variable and I is the dependent variable. On the other hand, in statistical methods, each of the terms containing a function of the independent variable just described is itself called an independent variable. For example, in Equation (1), Z^2, Z, Z^0, Z^{-1}, etc. would each be an independent variable while I is the dependent variable. Thus, the distinction between independence and dependence is the same for both the experimentalist and the statistician, but the statistician considers each term a variable. Such a procedure is not unreasonable when one considers that the coefficient of each term is an unknown whose value is being sought.

Five different independent variables (in the experimental sense) were selected for this investigation. They are defined in the following equations.

$$I = a_1 + a_2 Z + a_3 Z^2 \qquad (3)$$

$$I = a_1 + a_2 (Z^{-1}) + a_3 (Z^{-1})^2 \qquad (4)$$

$$I = a_1 + a_2 (\ln Z) + a_3 (\ln Z)^2 \qquad (5)$$

$$I = a_1 + a_2 (e^{Z}) + a_3 (e^{Z})^2 \qquad (6)$$

$$I = a_1 + a_2 (Z_{eff}) + a_3 (Z_{eff})^2 \qquad (7)$$

where a_1, a_2, and a_3 are constants to be fitted by a statistical procedure. These constants will differ numerically according to the equation in which they are being used.

Equation (3) is simply the first three terms of Equation (1). If these terms dominate the series, then one would expect the coefficients to be very similar to those obtained by Scherr, et al. Further, Equation (3) is the same equation used by Glockler in his empirical fitting procedure. Except for small differences resulting from refinement of experimental data, one would expect that the coefficients from the present research would agree with those obtained by Glockler. Thus, Equation (3) is expected to form a point of reference from which conclusions may be drawn.

Equations (4) through (6) represent test equations which bear no similarity to the known behavior of ionization energies. If present theories are correct, whatever tests are made should indicate that these equations are much poorer than Equation (3). Mention should be made of the fact that Equation (4) is another truncated variant of Equation (1); i. e., a variant using terms 3, 4, and 5 of that infinite series. This fact alone should indicate the futility of using Equation (4) since it is known (Eyring, et al., 1944) that the ionization energy of the hydrogen atom is given by the leading term, alone, of Equation (1).

Equation (7) is a refined form of Equation (3) which takes into account the screening defined in Equation (2). In this investigation, the screening values of Slater (1930) are used. If screening is correctly introduced by this procedure, then one would expect to obtain the best possible results within the framework of this investigation.

All values of ionization energy (in e. v.) and nuclear charge (in a. u.) which were used in this work were those given by Moore (1949). Five different isoelectronic series were selected for the study, *viz.*, Li I, C I, F I, Cl I, and Na I. The series were selected in such a manner that one could study trends within families (alkali metals and halogens) of the periodic table as well as within rows (second and third) of the periodic table.

Each isoelectronic series does not contain the same number of observations; C I and F I have ten members in the series, Li I and Cl I have twelve members, and Na I has nineteen members. Since certain statistical quantities depend on the number of observations, the experiment would have been more clearly delineated if the same number of observations had been used in each set. On the other hand, it seemed more desirable to obtain those empirical equations which would best describe all available experimental data. Otherwise the investigation would, perforce, include a detailed study of the source of each experimental datum in order to determine which of the data should be eliminated. In most cases the incrementation in Z is one unit of charge. However, there are exceptions; e. g., in the Li I series, the value of Ne VIII is not available.

The canned program which was selected was one which contained a least squares fitting procedure using the Choleski method (Purcell, 1965 and was designed for use with the IBM 7040 computer. The program was available from a library of programs maintained by the Data Processing and Computing Center of The Southern Illinois University and was used as part of a closed-shop operation. The authors had to supply only data cards which specified the experimental variables and parameter cards which specified certain information defining Equations (3) through (7). The set of five isoelectronic series was run once for each type of equation. In addition to the usual fitted coefficients, this very flexible program supplied many other pieces of information. In accordance with one of the objectives of this investigation, an attempt was made to use each and every piece of information which was given in the output.

The initial use of parameter cards was tested with data from the H I isoelectronic series (eight observations) applied to Equation (3). Although not part of the designed experiment, the results from this test run are included for completeness.

RESULTS

Each of the coefficients for Equations (3) through (7) which were obtained for each of the isoelectronic series are tabulated in TABLE 1. TABLE 1 also lists some results from other workers to be used for comparison purposes.

One of the important questions which continually plague workers attempting to obtain a good empirical equation for I as a function of Z is the accuracy of ionization energies. In general, the results are more accurately known for atoms with a small number of electrons. Further, the members of an isoelectronic series with the smaller net charges usually have been measured more accurately than the members with the larger net charges. Those two generalities are reflected in the comparison of the current results to those obtained by Glock-

TABLE 1.—The Empirical Coefficients as Determined by a Least Squares Procedure.

	Isoelectronic Series	a_1 (e.v.)	$-a_2$ (e.v./a.u. charge)	a_3 (e.v./(a.u. charge)^2)
Equation (3)........	H I	0.12972641	0.12723064	13.624758
	Li I	8.0037403	11.138675	3.4242794
	C I	45.443210	26.397603	3.4488094
	F I	105.35315	40.366608	3.3936465
	Na I	96.291934	25.519966	1.5630960
	Cl I	221.30235	38.436418	1.5379277
Equation (3)......... Glockler (1934)	H I	0.0	0.0	13.54
	Li I	8.25	11.25	3.43
	C I	51.87	28.23	3.58
	F I	155.4	48.95	3.75
	Na I	127.9	30.41	1.75
	Cl I	372.3	55.14	2.0
Equation (3)......... Converted from results of Scherr, et al. (1962)	Li I	6.83564799	10.82361748	3.40104189
	C I	38.36499862	25.34099010	3.40115236
	F I	97.68274169	40.06441025	3.40120967
Equation (4).........	Li I	981.71967	8330.6768	16615.070
	C I	1303.1854	17685.773	60264.041
	F I	2350.1607	46251.092	229567.27
	Na I	1982.5491	51543.017	333953.38
	Cl I	2194.7406	75076.033	648087.50
Equation (5).........	Li I	696.26691	983.58003	346.26477
	C I	1883.7636	2012.2824	542.63488
	F I	5099.8576	4561.9070	1026.0776
	Na I	5447.0626	4323.0479	860.38890
	Cl I	8184.6853	5898.4383	1064.1948
Equation (6).........	Li I	122.17326	—5.6297618(—4)[a]	—1.2738849(—10)
	C I	90.069235	—3.5037666(—4)	—7.6305203(—11)
	F I	117.43045	—1.4471459(—5)	—2.7544501(—14)
Equation (7).........	Li I	—1.0359764	—0.50392628	3.4242762
	C I	—1.0671940	7.4295491	3.4488344
	F I	0.96321105	14.574671	3.3936363
	Na I	—7.2371806	—1.9904304	1.563100
	Cl I	—14.9236308	4.9109156	1.5379840
Equation (7)......... Converted from results of Scherr, et al. (1962)	Li I	—1.77593973	0.0	3.40104189
	C I	—8.85690549	0.0	3.40115236
	F I	—20.30358715	0.0	3.40120967

[a] The values of a_2 and a_3 obtained for Equation (6) are the entry values multipled by a factor of ten raised to the power in parentheses.

ler who had poorer and far fewer data with which to work. For example, agreement between coefficients for the Li I series varies between 0.3% and 2.5% while agreement between coefficients for the Cl I series varies between 31% and 68%. Nevertheless, this comparison helps establish the correctness of the current procedures.

Scherr, et al. (1962) have developed a semi-empirical technique for determining the coefficients of Equation (1) and the coefficients of an equation of the form of Equation (1) but with Z_{eff} as the independent variable. The coefficients of the first three terms in their equations are based upon perturbation theory and may be considered as "experimental" results. Therefore, although their functional forms differ from those tested in this investigation, these coefficients are given for comparison in TABLE 1. The values of a_3 given by Scherr, et al. were made by *a priori* choices rather than by mathematical procedures such as in the present investigation. Therefore, their a_3 values reproduce exactly the values from perturbation theory. Further, their method of selecting s yields values different from the values used in this investigation.

It is not possible to quote complete results direct from perturbation theory. Even Bethe and Salpeter use a semi-empirical technique to obtain the higher order coefficients including a_6. The difference in the work of these authors and that of Scherr, et al. lies in their choice of wave functions for optimizing the higher order coefficients. Since Scherr, et al. have been more complete in their treatment, their results are used for comparison purposes.

A comparison to results from perturbation theory is simple. Perturbation theory assumes the infinite series given by Equation (1). The coefficients for each member of the series are evaluated without regard to the higher members. The series is truncated when a given worker finds that computational effort is too great to continue the problem. On the other hand, in the present empirical fitting procedure, the least squares method provides the best possible coefficients for the assumed truncated version. That is, contributions from cubic, quartic, and higher terms are redistributed among the linear and quadratic terms which have been used. If the terms of Equation (1) become less important with increasing n, then the results of the present empirical method with the functional form predicted by perturbation theory, might reasonably be expected to provide coefficients of the same order of magnitude (power of ten) as the coefficients obtained from perturbation theory. Similar comments apply to truncated versions of the equations given by Scherr, et al.

TABLE 1 shows that even a truncated version of Equation (1) does give coefficients quite similar to the "experimental" coefficients. Although Equation (3) is written in the usual mathematical form, the Z^2 term is the leading term of the series. The coefficient of this leading term would be the hydrogen-like energy ($-\frac{1}{2}n^2$ a. u.) if there were no interaction between the electrons of the atom or ion. For the three rows of the periodic table involved in the sample series of this investigation, the coefficient values are 13.624758 e. v., 3.406189 e. v., and 1.513862 e. v. The results of perturbation theory do not yield a constant value for each series in a given row of the periodic table because the theory takes into account mass differences. Nevertheless, TABLE 1 shows that the present empirical method very nearly predicts the correct value of the coefficient of the dominating term in Equation (1). This comparison to theory verifies the conclusion that current data is more accurate than those used by Glockler. Further comparisons as to the "goodness" of Equations (3) through (7) cannot be made through a simple examination of the coefficients because of the differences in functional form of the theoretical equation and the empirical equations.

TABLE 1 shows that the value of a_3 is essentially the same for Equations (3) and (7). This equality is explained if Z from Equation (2) is substituted into Equation (3). The result, in terms of the coefficients of Equation (3), is

$$I = (a_1 + a_2 s + a_3 s^2) + (a_2 + 2a_3 s)Z_{eff} + a_3 Z_{eff}^2 \qquad (8)$$

But Equation (8) is nothing more than Equation (7) with the constants, except a_3, redefined. This substitution proves that no matter what value of s is selected, the coefficient of Z^2 in Equation (7) will be the same as that in Equation (3). The slight differences shown in Table 1 are due to rounding-off processes during the computer runs. The same comments apply to the two corresponding "experimental" equations of Scherr, et al.

In TABLE 1, no values are presented for the Na I and Cl I series with Equation (6). This is due to the fact that the computer gave an underflow error during the processing of Equation (6). That is, somewhere during the calculations, a number became smaller than that which can be accommodated by the IBM 7040. Conceivably the data could have been manipulated to bypass this error. However, since one of the objectives of this research was to work within the framework of the canned program, no attempt was made to rectify the error. The fact that errors such as this do occur emphasizes that the future researcher in chemistry will not simply be a technician but that he must learn something about the tool with which he is working. That is, the greater the degree of proficiency which the researcher attains, the more versatile will be the research program that results. Nevertheless, there is, as this project shows, a great deal which can be learned from minimum versatility.

Finally, one may establish correlations to the periodic table. The constancy of a_3 in a periodic row and the decrease in a_3 from Equations (3) and (7) as Z increases in a periodic group has already been discussed. The values of a_1 and a_2 from Equation (3), the values of a_1, a_2, and a_3 from Equations (4) and (5), and the value of a_3 from Equation (7) increase with increasing Z both in a group and in a row. In every case except a_1 from Equation (5) the increase is not monotonic in Z; e. g., there is a decrease in the value of the coefficient as Z is increased from 9 to 11. All of these changes reflect the changes in the values of Z which are input for the various isoelectronic series. That is, as larger Z values are used, the above mentioned coefficients in the various equations must compensate for the fact that the loading coefficient, a_0, is decreasing within every periodic group. The fact that the increase is not monotonic reflects the well-known changes in the input values of I with increasing Z.

The fact that a_2 from Equation (7) fits the general pattern of change with Z is fortuitous. Examination of Equation (8) shows that the coefficients, a_1 and a_2, of Equation (7) are highly dependent upon the selected value of s. No general comment can be made about a_2 and a_3 as a function of Z without knowledge of the functional dependence of s on Z. The variation in a_1 precisely illustrates this point.

The variation of I values with Z is completely dominated by the independent variable, e^Z, in Equation (6). The rapidly increasing nature of this variable dictates that a_1, a_2, and a_3 from Equation (6) must be extremely small with the degree of smallness increasing rapidly as the value of Z increases. Such behavior is indeed observed in TABLE 1.

One page of the output lists the input values of the dependent variable, the values of the dependent variable predicted by the empirical equation which is derived in the run, and the differences in the two values. Although the magnitude of these differences would be an indication of "goodness", a percentage quantity was defined, viz.,

$$D \equiv \frac{(\text{Deviation})_{\text{rms}}}{\bar{I}} \times 100 \tag{9}$$

where D is the percent deviation, $\bar{I}$ is the mean value of the dependent variable, and

$$(\text{Deviation})_{\text{rms}} = \left[\frac{\sum_{i=1}^{i=n} d_i^2}{n} \right]^{1/2}$$

where n is the number of observations and d_i is the i^{th} difference between the input value and the corresponding predicted value of the independent variable. The values of D for each isoelectronic series with each empirical equation are tabulated in TABLE 2.

In the present investigation, the order of magnitude of the deviations would be sufficient. However, the definition of D [Equation (9)] is provided for those experiments where the range of the dependent variable differs by more than a magnitude. An alternate definition of D, based upon the mean value of the absolute deviation, could have been used. The present definition though yields a truer picture of the "goodness" of an equation. For example, if one observation is very inaccurate, the root-mean-square deviation will be much greater than the average deviation. The average absolute deviation was calculated for each series with each equation and the trends herein reported do not change.

An examination of TABLE 2 shows that the results for Equations (3) and (7) are the same. The equality is to be expected according to the discussion associated with Equation (8). These equations prove to be much better than Equation (5) which in turn is better than Equations (4) and (6). The term "much better" corresponds to a ratio in D values of two orders or more of magnitude while the term "better" corresponds to a ratio of one order of magnitude.

TABLE 2.—Statistical Tests of the Empirical Coefficients.

	Isoelectronic Series	Percent Average Deviation	Correlation Coefficient		Sum of Deviations Squared	Total Proporation of Variance	Trivariate Correlation Coefficient Squared	Estimated Variance of I
			r_{Il}	r_{IQ}				
Equation (3)	H I	0.009199	0.9761	1.0000	0.1	0.99999992	1.0000	0.01094
	Li I	0.01602	0.9779	0.9993	0.0	0.99999995	1.0000	0.00260
	C I	0.01850	0.9825	0.9977	0.05	0.99999981	1.0000	0.00474
	F I	0.1905	0.9793	0.9965	1.8	0.99999482	1.0000	0.25725
	Na I	0.08307	0.9794	0.9967	1.0	0.99999876	1.0000	0.06250
	Cl I	0.2933	0.9885	0.9965	2.51	0.99998202	1.0000	0.27691
Equation (3) Calculated from Glockler (1934)	H I	0.6633	0.9811	1.0000	5.3956	0.99985014	1.0000	2.69780
	Li I	0.09562	0.9828	0.9985	1.41015	0.99982190	0.9998	0.47005
	C I	2.218	0.9946	0.9986	0.03631	1.00000000	1.0000	0.0
	F I	3.200	1.0000	1.0000	—0.00045	1.00000000	1.0000	0.0
	Na I	8.005	0.9902	0.9961	18.7156	0.99379777	0.9961	6.23845
	Cl I	13.61	0.9975	0.9990	6.3027	1.00000000	0.9940	0.0
Equation (3) Calculated from Scherr, et al. (1962)	Li I	0.3216	0.9779	0.9993	0.0	0.99999995	1.0000	0.00260
	C I	0.9472	0.9825	0.9977	0.05	0.99999981	1.0000	0.00474
	F I	1.188	0.9793	0.9965	1.8	0.99999482	1.0000	0.25725
Equation (4)	Li I	25.70	—0.8039	—0.6805	42878.2	0.91205409	0.9550	4764.2391
	C I	10.93	—0.9042	—0.8469	3743.13	0.97932645	0.9896	534.73074
	F I	11.18	—0.9042	—0.8536	6309.40	0.98183328	0.9909	901.34262
	Na I	12.62	—0.8954	—0.8343	20494.8	0.97481099	0.9873	1280.9238
	Cl I	3.773	—0.9583	—0.9367	406.79	0.99706418	0.9985	45.19683
Equation (5)	Li I	9.653	0.9132	0.9526	6048.9	0.98759336	0.9938	672.09722
	C I	4.169	0.9510	0.9669	561.72	0.99695286	0.9985	78.81585
	F I	4.148	0.9476	0.9613	903.49	0.99739861	0.9987	129.06864
	Na I	6.165	0.9454	0.9590	3072.00	0.99622431	0.9981	192.00293
	Cl I	1.366	0.9758	0.9804	127.50	0.99907994	0.9995	14.16450

	Isoelectronic Series	Percent Average Deviation	Correlation Coefficient		Sum of Deviations Squared	Total Proportion of Variance	Trivariate Correlation Coefficient Squared	Estimated Variance of I
			r_{Il}	r_{IQ}				
Equation (6)…………….	Li I	39.70	0.7668	0.6351	102292.3	0.79019171	0.8889	11365.813
	C I	29.80	0.8123	0.6852	27805.9	0.84642571	0.9200	3972.2692
	F I	29.38	0.7950	0.7709	43545.86	0.87461790	0.9352	6220.8364
Equation (7)…………….	Li I	0.01602	0.9779	1.0000	0.0	0.99999999	1.0000	0.0
	C I	0.01850	0.9825	0.9997	0.02	0.99999996	1.0000	0.00112
	F I	0.1905	0.9793	0.9992	1.76	0.99999495	1.0000	0.25112
	Na I	0.08307	0.9794	0.9999	0.90	0.99999887	1.0000	0.05762
	Cl I	0.2933	0.9885	0.9998	2.42	0.99998258	1.0000	0.26801
Equation (7)……………. Calculated from Scherr, et al. (1962)	Li I	0.3213	0.9771	1.0001	0.0	1.00000000	1.0000	0.0
	C I	0.9578	0.9825	1.0000	2.291	0.99998431	1.0000	0.32786
	F I	1.174	0.9809	1.0000	0.0	1.00000000	1.0000	0.0
Equation (1)……………. Calculated (with n = 2) from Scherr, et al. (1962)	Li I	0.2930	0.9779	………	………	………	………	………
	C I	0.3090	0.9825	………	………	………	………	………
	F I	0.4586	0.9793	………	………	………	………	………

Within the framework of a given equation, an ordering can also be established. For example, with Equations (3) and (7), the I values of the Li series are predicted "much better" than the I values of the Cl series; with Equation (4), the converse is true. (In this context, comparison is defined by powers of two rather than ten.) To understand this phenomenon, one must consider that deviations will occur because of three factors: (1) Accuracy of experimental data, (2) Functional relationship between the variables, and (3) Range of variables. Although there is a difference in the accuracy of ionization energies for various isoelectronic series, the differences are not so great as to cause the reversal of "goodness" of prediction for the Cl and Li sequences. The second factor is ruled out since in a given comparison only one functional relationship is being considered. Consequently the variation in order is due to the ranges of the variables which were used in determining the coefficients of the empirical equations. For example, for the Li series the mean value of Z is 8.9 while the corresponding value for the Cl series is 22.5; the mean value of Z^{-1} for the Li series is 0.14 while the corresponding value for the Cl series is 0.046. Inclusion of the square terms in each equation does not alter the argument since these powers behave in the same manner as the first powers. The mean value of the square of the deviations, d^2, obtained with a least squares procedure, is a function of the variances of Z and I [σ_Z^2 and σ_I^2], the covariance of Z and I [σ_{ZI}], and the mean value of Z $[\overline{Z}]$ (cf. Lindgren, 1960, for the definitions of statistical terms). The output yields the mean of each variable (in the statistical sense) and the standard deviation (square root of the variance) of each variable, as well as the sums (in Z'Z matrix form) from which these quantities are derived. In a curve fitting procedure, these quantities *per se* are not useful as criteria for "goodness" but they may be used in calculating other quantities which are useful.

One such useful quantity is the correlation coefficient, r_{ps}. The program output presents (in matrix form) the correlation coefficient for each pair of variables (in a statistical sense), p and q. TABLE 2 tabulates the correlation coefficients between the ionization energy, I, and the linear variable, *l*, of each empirical equation, r_{Il}, and between I and the quadratic variable, Q, of each equation, r_{IQ}. The absolute value of the correlation coefficient itself is not sufficient to make judgments, because the question of significance of a particular coefficient is also relevant. However, significance depends on the number of observations, but, since this factor is constant within a given isoelectronic series, some valid comparisons can be made without specifying the significance of the coefficient. The magnitude of the coefficients is very large compared to the usual values which are obtained in typical statistical problems, but the magnitudes obtained in this study are typical of those obtained in other chemical studies (cf. Foley, et al., 1964).

The quadratic term correlates better in Equations (3), (5), and (7); the linear term is better in Equations (4) and (6). The quadratic term is expected to be the dominating term in Equation (3) since it is the leading term of Equation (1). Similarly, since Equation (4) contains terms three, four, and five of Equation (1), the linear term of Equation (4), which corresponds to term four of Equation (1), is expected to be the dominating term of Equation (4). One might expect that the best correlation in Equation (4) would be to the constant term since it corresponds to term three in Equation (1), but that supposition cannot be verified by the present technique since the method of calculation leads to an undefined r_{ps}. The coefficients of the linear terms of Equations (3) and (7) are identical since Z_{eff} differs from Z by only a constant. On the other hand, a much higher degree of correlation is obtained for the quadratic term. The improvement indicates that I is more properly a function of Z_{eff} than of Z.

A cursory comparison of the magnitudes of r_{ps} for each empirical equation leads to the same ordering which was obtained with the average root-mean-square deviation except for the improvement of Equation (7) over Equation (3). Again, the ordering within the framework of a specified equation type is of little consequence because of the differences in variable ranges.

The correlation coefficient can be used to select the proper variables (in the statistical sense) with which to form an empirical equation. For example, the common method of improving Equation (3) is to add the next two terms of Equation (1). The present results indicate that a better choice would be to add the two variables given by Equation (5). That is,

$$I = a_1 + a_2Z + a_3Z^2 + a_4(\ln Z) + a_5(\ln Z)^2 \qquad (10)$$

would be a better choice for a five-parameter empirical equation than the choice based upon perturbation theory. Equation (10) could be further improved with the addition of a sixth parameter by substituting Z_{eff} for Z. The average root-mean-square deviations obtained after such a substitution would not be the same as those obtained before substitution since Equation (10) contains terms which are not linear in Z.

A speculation can be made that Equation (10) would correspond to the functional form which a universal (in the sense of fitting all isoelectronic sequences) function relating ionization energy to atomic number would take. Although inverse powers of Z correctly follow from perturbation theory, the present investigation indicates that perhaps the usual perturbation theory does not apply to all isoelectronic sequences. Certainly other phenomena are known in which atoms of low and high Z behave in a different manner; e. g., the reversal of order of the 3d and 4s energy levels with increasing Z (Herzberg, 1944).

Scherr, et al. also used Moore's tables as the source of their experimental ionization energies. Since the calculation of correlation coefficients depends only on the input values of the variables (in an experimental sense), identical values are obtained with Equation (3) as shown in TABLE 1. On the other hand, since their value of Z_{eff} differs and since the quadratic term in Equation (7) correlates in a different manner than the quadratic term in Equation (3), values of these correlation coefficients were calculated and entered in TABLE 2. The results show that there is perfect correlation between I and the Z_{eff}^2 term of Scherr, et al. The result is not surprising since their parameter was chosen to optimize Equation (7) through quadratic terms and since there is no linear term over which to spread the fit. Within rounding errors, correlation to the linear term is identical to that obtained with Z. In these calculations a slight rounding error leads to the improbable value of 1.0001. No entries are given for the quadratic term of the "experimental" equation since there is no *a priori* way of determining the correct independent variable (in the experimental sense).

The input data of Glockler was obtained from tables by Bacher and Goudsmit (1932) and from extrapolation of their data. (Modern data may result from experimental extrapolation but the resulting inadequacies are better disguised.) Correlation coefficients were calculated from the tabular data but no extrapolated values were used. The perfect correlation for F I results from the fact that only two values of I were available. The results show less correlation to the quadratic term and more correlation to the linear term than in the present investigation. If one assumes that the quadratic term should, as indicated by perturbation theory, dominate the equation, then the only possible conclusion is inaccuracy in the older data.

The essence of the Choleski method is to convert a problem of fitting the independent variable to a function of the dependent variables (in the statistical sense) to one of fitting the independent variable to a function of orthonormal polynomials (Rushton, 1951). The Choleski resolution derives, from the Z′Z matrix, a matrix T′. The output of the canned program yields the elements of T′. The output also yields the inverse of the T′ matrix. The elements of the i^{th} row vector of the inverse matrix are the coefficients of the i^{th} linear combination of the independent variables (in the statistical sense) which is the i^{th} orthonormal polynomial.

The orthogonalization procedure is a Gram-Schmidt process (Courant and Hilbert, 1953). Therefore, the explicit form of the orthonormal polynomials depends upon the order in which the independent variables (in the statistical sense) are used. This, in turn, means that the elements of the matrix and its inverse which is derived in the Choleski resolution are dependent upon the ordering of the independent variables.

The next quantities which are presented in the output are: the coefficients of the representation of the dependent variable as a function of the derived orthonormal polynomials, l_i; the square of each of these coefficients, l_i^2; the cumulative sum of the square of these coefficients, Σl_i^2; and the proportion of the variance due to each of the independent variables in the order they occur. It is clear that the coefficients which give the best fit depend upon the form of the orthonormal polynomials and, consequently, upon the order in which the original independent variables are used. This in turn implies that any statistical information in this particular output which depends upon the components of the resolution is of little value. On the other hand, cumulative or total information based upon the use of all independent variables (in the statistical sense) should be invariant with respect to the order in which the independent variables were used.

For example, it can be shown that

$$Y'Y = L'L + E'E \qquad (11)$$

where Y is the matrix of the dependent variable, I, L is the matrix of the l_i coefficients, E is the matrix of the errors between the fitted equation and the observables, and ′ indicates the transpose of the matrix. Each of the matrix products in Equation (11) is a 1 x 1 matrix; i. e., each product is simply the respective sum of squares. The product E′E is the quantity $\sum_{i=1}^{i=n} d_i^2$, the sum of the deviations squared, used to calculate the quantity D of Equation (9). It would appear that the sum of the deviations squared can be obtained directly from the output by subtracting the cumulative l_I^2 value of the last independent variable (in the statistical sense) from the $\sum_{i=1}^{i=n} y_i^2$ value. These differences are given in TABLE 2.

Direct calculation verifies that the difference values tabulated for Equations (4), (5), and (6) are indeed the sum of the deviations squared. However, the values tabulated for Equations (3) and (7) are, generally, not equal to the sum of the deviations squared which are obtained by direct calculation. The error is not due to any error in Equation (11) but rather to loss of significant figures. Since output of this canned program yields all sums to eight significant figures, one can be certain that the last figure is unreliable due to rounding errors. As has been shown, and will be shown further, it is possible that calculation errors cause uncertainty in the pentultimate significant figure. It is this lack of sufficient, reliable significant figures which causes the difficulties in obtaining the sum of the deviations for Equations (3) and (7). For example, the direct calculation of the sum of the deviations squared for the Li I sequence with Equation (3) gives 0.0164, but the eight significant figures of the output are sufficient only to obtain the tenths digit. The value tabulated in TABLE 2 is 0.0 which is correct to the tenths digit.

Since the l_i are coefficients of an expansion in orthonormal polynomials, each l_i^2 is the contribution of the i^th^ degree of freedom (in the order which the independent, statistical variables are taken) to the residual I² sum of the preceding i-1 contributions. Further, each l_i^2 depends upon the correlation coefficients. For example, the contribution of the second independent variable, l_I^2, is given by

$$l_I^2 = Nr_{1I}^2\sigma_I^2 \qquad (12)$$

Clearly, the value of l_I^2 in the output would have been greater if the quadratic term had been given second since $r_{IQ} > r_{II}$. If one term of the expansion dominates the expansion, and if that term is listed first, its contribution will be most of the I² sum. This is the same type of information which was obtained from the r_{pq} Values. Indeed, in this investigation, the I² sum was more evenly dispersed among the degrees of freedom when Glockler's data were used than when Moore's data were used.

Since most of the different isoelectronic series had a different number of observables, the d² sum is more difficult to use than, say, the quantity D. However, the d² sum values lead to the same conclusions (when such values are significant) as have previously been obtained. The values listed under Scherr, et al. with Z as the independent variable (in the experimental sense) are the same as those in the present investigation since the input data are the same. No results are listed for the "experimental" equation since no *a priori* knowledge of the independent variable (in the experimental sense) exists.

As indicated, the output shows the contribution to the variance of each degree of freedom which is represented by each of the independent variables (in the statistical sense). This distribution is accomplished by converting each l_i^2 to an estimate of a sample variance for that term. The individual contributions, being order dependent are of little use in judging "goodness". Consequently, the individual contributions were summed over all independent variables (in the statistical sense). These values are given in TABLE 2. The values show that Equations (3) and (7) almost recover the total variance. Equation (7) is slightly better, thus reflecting the increased correlation between Z_{eff}^2 and I as compared to Z^2 and I. This particular test puts Equation (5) in a very favorable position and Equation (6) in an extremely bad position. Although the numerical difference between the total proportion for Equation (5) and Equation (6) is small, there is a definite indication of the former being the better equation.

The values listed under Glockler are misleading. The number of points in each of these isoelectronic series is few. With such a small number, e. g., two for F I, the total variance is more easily fitted by equations with few independent variables (in the statistical sense). On the other hand, the nearly perfect values listed under Scherr, et al. with Z_{eff} as the independent variable (in the experimental sense) truly reflect the "goodness" of their Z_{eff} values as compared to the Z_{eff} values used in this investigation. The reader should note that although Glockler and Scherr, et al. use fitting equations whose coefficient of the linear term is zero, this does not eliminate contributions to the I^2 sum or to the total variance by the linear term. These contributions depend only on the values of the Z'Z matrix and the Z'I matrix, i. e., on values which are derived from the input variable values. In preparing comparisons to the present work, the contributions of the linear term are always included. By reversing the order of the independent variables (in the statistical sense) one could calculate what contribution to the total variance is actually lost by Glockler and by Scherr, et al. in omitting the linear term. From the previous discussion, the omission, by Glockler, of the linear term in the H I sequence is more significant than the omissions by Scherr, et al. Thus, with the Z_{eff} of Scherr, et al. one obtains an equation which is essentially linear in the quadratic term.

The next quantity which is calculated by the canned program is the multiple correlation coefficient (Baten, 1938). This quantity is similar to the correlation coefficient which was previously discussed except that the multiple correlation coefficient correlates the dependent variable to two or more of the independent variables (in the statistical sense). In the present investigation, there are only two independent variables (aside from the weighting factor) which means that only a trivariate correlation coefficient, $R_{I.ZQ}$, is needed to represent the correlation between the dependent variable and all of the independent variables. The square of this quantity, $R_{I.ZQ}^2$, is tabulated in TABLE 2. The output of the Choleski program actually lists the square of the multiple correlation coefficient as each independent variable is added. Therefore, the first value which is tabulated is simply r_{IZ}^2 which can be obtained by squaring the value of r_{IZ}. If the independent variables had been in some order other than that specified by Equations (3) through (7), the first value given in the output would have been the square of a different bivariate correlation coefficient.

An analysis of $R_{I.ZQ}^2$ yields the same information on "goodness" which has been obtained before. The ordering of equations is the same as with all other criteria, but this particular criterion is another one which does emphasize the "poorness" of Equation (6). On the other hand, this criterion is not as sensitive as others in ordering the various isoelectronic sequences using one particular equation. This failure is due not only to the fact that the output of the canned program yields $R_{I.ZQ}^2$ to only four decimal places but that other, different methods of calculation from the output indicate that reliance can only be placed upon the first five decimal places. For example, a direct calculation using the values of the bivariate correlation coefficients given in the output yields, for Li I with Equation (3), $R_{I.ZQ}^2 = 0.99999052$. It can be shown that the trivariate correlation coefficient is also equal to the sum of the proportions of variance given in Column 6 of TABLE 2. Thus, for Li I with Equation (3), $R_{I.ZQ}^2 = 0.99999995$. These two methods of calculation show that reliance can only be placed upon the first five decimal places. This conclusion is sufficient to show that one cannot use $R_{I.ZQ}^2$ from this output to sort the various isoelectronic sequences according to "goodness" for each of the equations which were tested.

The values of $R_{I.ZQ}^2$ for the work of Glockler and Scherr, et al. are also quite close to unity. In fact, the values for Scherr, et al. show perfect multiple correlation. Once again, though, the values obtained with Glockler's data indicate some experimental error in the data. These very high values of $R_{I,ZQ}^2$ continue to indicate that one must be able to obtain these multiple correlation coefficients to a higher degree of accuracy or must rely on an alternate criterion.

To continually encounter statistics which are so close to the limiting values of the statistics causes one to pause to consider a method of obtaining statistics away from their limiting values. Perhaps one might be reminded of the techniques used by Scatchard (1949) to find the functional behavior of the nonideal properties of solution by first subtracting the theoretical ideal behavior from the experimental observable. Then, since Z^2 appears to be the variable which contributes the most in each of the statistical studies, one might define a new dependent variable, $I - aZ^2$. Then the revised equation could then be tested by the techniques which have been outlined. One would expect to find that quantities such as $R_{I,ZQ}^2$ and total proportion of variance would not be so close to their limiting values. However, the values might still be quite high compared to values obtained in other statistical studies, e. g., some psychological studies or perhaps I.Q. as a function of height. This conclusion is indicated by the many bivariate correlation coefficients obtained in this study which have exceeded 0.9.

The real problem in creating a new dependent variable, $I - aZ^2$, is the choice of the coefficient a. That is, placing the Z^2 term with the dependent variable assumes that one knows precisely its contribution. Therefore, the redefined problem would no longer be susceptible to a solution wherein all contributions of Z would be obtained under a least squares criterion. Such comments have already been made concerning the results of Scherr, et al. and the H I results of Glockler. That is, only Column 2 of TABLE 2 can be used to judge "goodness" of a fitted equation which is not obtained under a least squares criterion. The experimenter's dilemma is clear; either create an equation for which many statistical tests are not sufficiently sensitive or create an equation with *a priori* knowledge inserted by the experimenter.

The final column of TABLE 2 tabulates a statistical quantity which is sensitive enough to distinguish between equations containing high degrees of correlation. This quantity, called the estimated variance of I or, symbolically, s^2 (also called the sample standard error of estimate or sample standard error of prediction), is an unbiased χ^2-estimate of σ^2, the variance of I about the regression curve (Pearson and Hartley, 1956). The canned program obtains an s^2 value after each variable (in the statistical sense) is added. Like many of the preceding quantities, the stepwise s^2 values are dependent upon the order in which the independent variables (in the statistical sense) are taken. Since the last value provides an estimate of the variance of I after all independent variables are added, it is not order dependent. Thus, it is this final value that is tabulated in TABLE 2.

The estimated variance of I is related to the population standard error of prediction (also called the population standard error of estimate), σ_e^2, by

$$s^2 = \frac{N}{N - K} \sigma_e^2 \qquad (13)$$

where N is the number of observations and K is the number of independent variables (in the statistical sense) including the statistical weight. The quantity σ_e^2 is precisely the square of the quantity $(\text{Deviation})_{\text{rms}}$ which is used in Equation (9) (Baten, 1938). That is, σ_e^2 is simply the mean value of the square of the deviations.

The s^2 values give approximately the same information as the Percent Average Deviation; e. g., the ordering of the various equations is precisely the same. But, there are some individual variations concerning the ordering of isoelectronic sequences within the framework of single test equations. For example, the H I series best fits Equation (3) if one uses the criterion of Percent Average Deviation but is only the third best fit if s^2 is used as a criterion. The differences occur because the dependent observables of some test series have a very large magnitude compared to the corresponding values of other test series. The Percent Average Deviation reflects this information while s^2 does not. For this reason alone the authors prefer Percent Average Deviation as a criterion. On the other hand, it is readily apparent that either criterion satisfactorily orders the test equations, thus one might argue that differences within the framework of a single equation are not significant enough to warrant their use in judging "goodness".

Since several different statistics have been considered, the question arises as to the significance of the various statistics. Perhaps significance can best be explained by the following example. Suppose that values of r_{IQ} other than the predicted value occur in 1% of a sample of a given population; i. e., the predicted value occurs in 99% of the measurements. Now suppose that values of r_{IQ} other than the predicted value occur in 5% of the measured sample. In the language of statistics, the r_{IQ} values occurring 99% (99th percentile) of the time or at the 1% level are more significant than the r_{IQ} values at the 5% level.

The canned program calculates, after the addition of each independent variable (in the statistical sense excluding the weighting variable), an F-ratio (Pearson and Hartley, 1956) from which one can evaluate the significance of the bivariate and multivariate correlation coefficients. In this investigation, the value of the bivariate correlation coefficient, r_{II}, and the squared value of the multivariate correlation coefficient, $R_{I,IQ}^2$, are listed in TABLE 2. The F-ratios corresponding to each of these correlation coefficients, $F_{I,I}$ and $F_{I,IQ}$, respectively, are given in TABLE 3. The output format of the program is such that any value greater than 9.99999 x 10^5 is considered as infinity. For purposes of comparison these values have been calculated directly and are given in TABLE 3 in square brackets. The output F values were compared to F values listed in tables given by Dixon and Massey (1957). The greatest level of significance indicated by their tables is at the 0.05% level. The percent levels are also given in TABLE 3. The results show that all multivariate correlation coefficients obtained in this study are highly significant.

Formally the F-ratio tests a null hypothesis. In this particular case, the F-ratio tests whether the dependent variable is uncorrelated to the independent variables, i. e., R = O (Anderson, 1958). If the calculated F-value exceeds the F-value tabulated for an upper α% level, then the null hypothesis is rejected at that α% level. The implication then follows that the higher the α% level at which the null hypothesis is rejected the more highly correlated are the variables. An alternate approach would be to test directly the hypothesis that variables are correlated but that test would involve a much more complex probability distribution containing a confluent hypergeometric function for which comparison tables are not readily available.

Although the calculation of the F-ratio essentially involves the evaluation of the quantity (R^2/1-R^2), the calculation is equivalent to finding the ratio of the sum of squares due to the independent variables (excluding the weight) to the residual sum of squares. Consequently, an alternate statement of the null hypothesis is that there is no significant difference between the two sums. Rejection of the null hypothesis in this form indicates that there is a significant difference between the value of the dependent variable as predicted by the regression curve and the value as predicted by its own mean value. The importance of testing the significance of R is made clear from statistical theory which shows that it is the only quantity which is invariant with respect to changes of location of the variables, to changes in scale of the dependent variable, and to non-singular transformations of the independent variables (Anderson, 1958).

Usually the F-ratio is used only to determine levels of significance, but with care it may be used to judge "goodness" (Hoppesch, et al., 1961). Caution must be used here to assure that only those F-ratios which have the same degrees of freedom are compared. For example, in comparing Percent Average Deviation, it was possible to obtain an average value for all series with each single equation and compare the averages. With the F-ratio, it is only possible to compare the F-value of each isoelectronic series with each equation. If this is done (with either $F_{I,I}$ or $F_{I,IQ}$), the same ordering of equations is obtained as with the other criteria. The incorporation of the degrees of freedom into the judging criterion removes the uncertainty which was mentioned in the discussion of r_{II} and r_{IQ}. The problem still remains as to what F-value is so large as to be called infinity. Obviously beyond a certain upper limit, there is no meaning in comparing two F-ratios.

In a like manner, within the framework of a single equation, one can compare various isoelectronic series if they have the same degrees of freedom. In the present study, Li I and Cl I form a pair and C I and F I form a pair since the two members of each pair have the same

TABLE 3.—Significance of Statistical Tests.

	Isoelectronic Series	$F_{I,I}$	Significance of $F_{I,I}$	$F_{I,IQ}$	Significance of $F_{I,IQ}$	$-t_{I,I}$	Significance of $-t_{I,I}$	$t_{I,IQ}$	Significance of $t_{I,IQ}$
Equation (3)............	H I	121.2748	0.05	[3.02356(7)][a]	0.05	1.7103	14.79	1688.5907	0.0
	Li I	218.7341	0.05	[9.36099(7)]	0.05	507.0516	0.0	2860.9490	0.0
	C I	222.6369	0.05	[1.90857(7)]	0.05	416.3854	0.0	1150.6629	0.0
	F I	186.9062	0.05	6.25913(5)	0.05	97.3206	0.0	235.3851	0.0
	Na I	400.2941	0.05	[6.50911(6)]	0.05	295.0537	0.0	728.2373	0.0
	Cl I	428.5264	0.05	2.50298(5)	0.05	59.1653	0.0	106.7753	0.0
Equation (3)............ Calculated from Glockler (1934)	H I	76.9852	0.05	1.27076(4)	0.05	0.0		30.8445	0.11
	Li I	113.1967	0.05	1.34593(4)	0.05	67.7397	0.0	1404.6690	0.0
	C I	92.2085	0.05	Infinity	0.05				
	F I	Infinity	0.05	Infinity	0.05				
	Na I	201.7400	0.05	389.5768	0.05	2.7509	7.08	4.2795	2.35
	Cl I	100.8302	0.05	Infinity	0.05				
Equation (3)............ Calculated from Scherr, et al. (1962)	Li I	218.7341	0.05	[9.36099(7)]	0.05	29.1125	0.0	167.8966	0.0
	C I	222.6369	0.05	[1.90857(7)]	0.05	13.7416	0.0	39.0110	0.0
	F I	186.9062	0.05	6.25913(5)	0.05	15.3668	0.0	37.5310	0.0
Equation (4)............	Li I	18.2634	0.5	46.6678	0.05	6.7786	0.01	5.2161	0.06
	C I	35.8607	0.05	165.7985	0.05	9.4196	0.0	7.3999	0.01
	F I	35.8476	0.05	189.1600	0.05	9.8782	0.0	7.9562	0.01
	Na I	68.7305	0.05	309.5989	0.05	13.3060	0.0	10.4860	0.0
	Cl I	112.5415	0.05	1528.2841	0.05	19.1455	0.0	15.5295	0.0
Equation (5)............	Li I	50.2332	0.05	358.2090	0.05	7.6248	0.0	10.5563	0.0
	C I	75.6960	0.05	1145.1186	0.05	11.9331	0.0	14.5801	0.0
	F I	70.3922	0.05	1341.9332	0.05	14.0415	0.0	16.3586	0.0
	Na I	142.9093	0.05	2110.8244	0.05	18.0117	0.0	20.8448	0.0
	Cl I	198.6601	0.05	4886.4205	0.05	19.2445	0.0	21.4427	0.0

	Isoelectronic Series	$F_{I,l}$	Significance of $F_{I,l}$	$F_{I,lq}$	Significance of $F_{I,lq}$	-$t_{I,l}$	Significance of -$t_{I,l}$	$t_{I,lq}$	Significance of $t_{I,lq}$
Equation (6)............	Li I	14.2734	0.5	16.9482	0.1	—4.0733	0.28	—2.9449	1.64
	C I	15.5222	0.5	19.2903	0.5	—4.1449	0.43	—2.9158	2.25
	F I	13.7435	1	24.4147	0.1	—3.9561	0.55	—3.6798	0.79
Equation (7)............	Li I	218.7343	0.05	Infinity	0.05	[—33.2671]	0.0	[3394.5174]	0.0
	C I	222.6364	0.05	[1.06436(8)]	0.05	325.3820	0.0	2372.1596	0.0
	F I	186.9071	0.05	6.92861(5)]	0.05	48.1645	0.0	238.2444	0.0
	Na I	400.2962	0.05	[7.06073(6)]	0.05	—42.1294	0.0	758.4664	0.0
	Cl I	428.5375	0.05	2.58659(5)]	0.05	14.8099	0.0	108.5332	0.0
Equation (7)............ Calculated from Sherr, et al. (1962)	Li I	210.7743	0.05	Infinity	0.05	0.0	....	168.0106	0.0
	C I	222.5879	0.05	[2.76120(5)]	0.05	0.0	....	85.9613	0.0
	F I	203.7729	0.05	Infinity	0.05	0.0	....	37.9329	0.0
Equation (1)............ Calculated (with n = 2) from Scherr, et al. (1962)	Li I	218.7341	0.05	....	....	....	....	....	....
	C I	222.6369	0.05	....	....	....	....	....	....
	F I	186.9062	0.05	....	....	....	....	....	....

[a] The values of $F_{I,lq}$ are the entry values multiplied by a factor of ten raised to the power in parentheses.

number of observations as well as the same number of independent variables (in the statistical sense). Comparison of the F-values of each member of a pair within the framework of each equation leads to the same general conclusions which have been obtained previously. In one instance though a comparison of nearly equal values of $F_{I,IQ}$ led to a reversal of the ordering obtained with r_{IQ}. However, the criteria are not strictly comparable since one quantity deals with a bivariate relationship while the other deals with a trivariate relationship. This small discrepancy emphasizes the danger in trying to make all comparisons absolute That is, a comparison of two numbers such as 1145 and 1342 may mean no more than the two quantities have equal "goodness".

The values of infinity of $F_{I,I}$ and $F_{I,IQ}$ shown under Glockler in Table 3 result from the limited number of experimental points which were used to make the calculation. For example, only three points were available for F I and Cl I. These three points exactly defined a quadratic curve and, hence, led to an $R_{I,IQ}$ value of 1.000 which, in turn, yields a value of infinity for $F_{I,IQ}$. If the extrapolated values of Glockler had been available it is likely that a large but not infinite value would have been obtained. On the other hand, the values of infinity shown under Scherr, et al. in Table 3 result from round off errors, i. e., to within the number of significant figures which were used, the error sum of squares was zero.

This Choleski program also calculates values which allow one to assay the significance of the coefficients of the independent variables (in the statistical sense and excluding the weight variable) which have been obtained in the study. The statistical test which is used is the two-tailed t-test (Pearson and Hartley, 1956). The Student's t-value for a_2, $t_{I,I}$, and the Student's t-value for a_3, $t_{I,IQ}$, are given in Table 3. During this test, the program calculates the percent level of significance of the Student's t-value to two decimal places which eliminates the need of any table look-up. These levels of significance in percent are also given in Table 3. Corresponding values for the equation of Glockler and for the equations of Scherr, et al. were calculated with the available data. No entries are posted for the Glockler sequences for which the number of data points equals the number of unknown coefficients. Then the fitted coefficients would each have t-values of infinity since they could contain no error. However, this type of high significance is not comparable to the other values of the table. Also, no values of significance are given for the linear term of the H I series as calculated by Glockler or to the linear term in each of the equations in effective nuclear charge which were obtained by Scherr, et al. In these cases, the coefficient was assumed to be zero and, in the calculation procedure, a zero coefficient would lead to a zero t-value which would indicate no significance at all. Once again this type of significance is not comparable to the other values given in Table 3. For the Li I series with Equation (7), the round off within the program yielded a t-value of zero. Therefore, for comparison purposes, this value was calculated directly and entered in Table 3 in brackets. The entries in Table 3 indicate a high level of significance for each coefficient except a_2 of the H I series using Equation (3). This one exception is explained by the fact that the fitted value is close to zero which indicates a high probability of fluctuation about the zero value predicted by Quantum Theory for hydrogen-like species.

As with the F-ratio, the t-test may be used to judge "goodness" if one compares only those quantities with equal degrees of freedom. In general the conclusions are the same as the conclusions from the comparisons made with the F-ratio. One distinct difference though occurs with the t-test values for the linear term of Equation (7) with each isoelectronic series. These values are not similar to the values obtained with Equation (3) although one would have guessed that the same reliability would have been obtained in the two cases since the transformation to Z_{eff} is linear. The only apparent explanation seems to be that the linear combination leading to the linear term of Equation (7) leads to an a_2 value which is smaller than the corresponding coefficient of Equation (3). Since the coefficient appears in the numerator of the t-test calculation, the t-value is also smaller unless the error sum of squares is also smaller, but the results on Percent Average Deviation show that the error sum of squares is not smaller. Again, as with the F-ratio, the improvement in the reliability of the quadratic term with the use of Z_{eff} is minimal for F I, Na I, and Cl I. This

TABLE 4.—Electron Affinities (in e. v.)

Ion	Equation (3)	Equation (3) Glockler (1934)	Equation (3) Scherr, et al. (1962)	Equation (4)	Equation (5)	Equation (6)	Equation (7)	Equation (7) Scherr, et al. (1962)	Complete Scherr, et al. (1962)	Experimental
He⁻	—0.5765	—0.53	—1.2074	970.1488	180.8613	122.1774	—0.5766	—1.2076	—0.02	>0[a]
B⁻	—0.3245	0.22	—3.3111	176.5924	50.6975	90.1212	—0.3240	—3.3310	—0.36	>0[a]
O⁻	—0.3861	3.80	—5.1551	155.7628	50.4771	117.4414	—0.3866	—5.1572	1.30	1.465[a]
Ne⁻	—2.5978	—1.2	....	167.7812	54.5689	....	—2.5978	....	....	....
S⁻	0.0291	2.06	....	34.0803	11.4657	....	0.0309	....	....	2.07[b]

[a] From data of L.M. Branscomb as given by Scherr, et al. (1962)
[b] Branscomb and Smith (1956)

fact implies that the Slater s values are not very good choices for obtaining Z_{eff}. However, the s choice of Scherr, et al. leads to no greater improvement in comparing the quadratic term of Equations (3) and (7) for F I. Therefore the difficulty may be in the input experimental data rather than the choice of s. An examination of the t-values also does not show Equation (5) to be much better than Equations (4) and (6) as has been true with some of the other criteria.

The t-distribution may be used to establish confidence limits on the coefficients of the independent variables (in the statistical sense) (Dixon and Massey, 1957). The method compels each experimenter to judge at what statistical level he wishes to establish the confidence limits. This element of variability plus the fact that the goals of this investigation were concerned only with "goodness" of the various equations and not the details of the equations dictate the omission of any tabulation of confidence limits. However, for the purpose of illustration, a direct calculation shows that at the 1% level the errors in a_2 and a_3 for Li I with Equation (3) are 0.039 and 0.00074, respectively.

The output provides the researcher with one check on the errors which occur during the processing of the data. This is done by listing the maximum absolute difference between the original Z'Z matrix and the Z'Z matrix which is obtained upon inverting the derived $(Z'Z)^{-1}$ matrix. In this investigation, the numerical checks verify the conclusions which have been drawn with reference to the size and range of the variables which have been used.

Finally, there is one other method of testing "goodness" which must, if possible, be used by the applied mathematician. That criterion is the comparison to experiment. The substitution of a Z value one less than that of the neutral atom for which the isoelectronic series is named yields the electron affinity of the atomic specie represented by that Z value. The results are tabulated in TABLE 4. For comparison the values obtained with the equations of Glockler, the values obtained with the truncated versions of the equations of Scherr, et al., the values obtained with the final equations of Scherr, et al., and the available experimental values are also given in TABLE 4.

The hazards of this extrapolation procedure are discussed by Scherr, et al. and their references. As a result of these hazards, comparisons made to results from other workers may shed as much light on the value of the present equations as the direct comparison to experiment.

The electron affinities calculated from Equations (3) and (7) are essentially the same. These values are uniformly too low when compared to the experimental values; and, in fact, the stability of He^-, B^-, and O^- is incorrectly predicted. However, the same is true for the values from the truncated equations of Scherr, et al. The present results though are closer to experiment than these truncated results of Scherr, et al. The explanation of these differences is simply that Scherr, et al. depend upon the extra terms in their final function to correct this discrepancy whereas the least squares method attempts to accomplish the correction by the method of fitting. The fact that the results of Equations (3) and (7) do not agree as well with experiment as the final results of Scherr, et al. indicates that Equations (3) and (7) have insufficient independent variables (in the statistical sense).

Equations (4), (5), and (6) yield electron affinities which deviate widely from the experimental values. The large discrepancies emphasize the magnitude which the statistical quantities must assume in order to have meaning for the chemist. For example, the value of $R_{t,(0)}$, 0.998, which was obtained with Equation (5) for Na I is not close enough to unity to indicate that the equation will yield good electron affinities. That is, the techniques which have been discussed are not to be dismissed as useless, but they must be viewed in terms of a defined frame of reference. The comparison to experiment establishes that frame of reference. In fact, for Ne^- where no experimental data is available, the statistical criteria are the only criteria available. Further, the statistical criteria yield information concerning the individual degrees of freedom (the independent statistical variables) which are not obtainable in the comparison to experiment.

The percent deviations of the predicted electron affinities are greater, with each equation, than the Percent Average Deviations which are given in TABLE 2. This can be explained by an examination of the individual deviations of each isoelectronic series with each equation. First, considered as a function of Z, none of the deviations within each isoelectronic series are completely random, although those of Equations (3) and (7) approach randomness. Second, the deviations for the predicted values of the first member, Z_1, and the last member Z_l, of each isoelectronic series are very large compared to the mean deviation. Combining these two facts, one concluded that an extrapolation to Z_l+1 or Z_1-1 will lead to a predicted value whose deviation from the expected true value is greater than any of the other deviations of the predicted values of the series members from their true values. This conclusion suggests the possibility that lack of sufficient and/or good data is responsible for the inability of a least squares procedure to provide a quadratic fit which can adequately reproduce experiment.

For the convenience of the reader, a sample of the output is given in the Appendix. Each step of the sample has an accompanying explanation. The sample is for the Li I isoelectronic sequence using Equation (3).

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Appendix—Sample of Computer Output with Authors' Explanation.

Output	Explanation
Y = A + B*X + C*X**2 LITHIUM ISOELECTRONIC SERIES DEPENDENT VARIABLE IS VARIABLE 1	$I = a_1 + a_2Z + a_3Z^2$
NUMBER OF OBSERVATIONS IS 12	
SUMS OF VARIABLES 0.27907639E 04 0.12000000E 02 0.10700000E 03 0.11350000E 04	ΣI N ΣZ ΣZ^2
XY-VECTOR 0.11365816E 07 0.27907639E 04 0.34068531E 05 0.43621537E 06	ΣI^2 ΣI ΣIZ ΣIZ^2
XX MATRIX, LOWER TRIANGLE	Z′Z Matrix
WEIGHTING VARIABLE IS NUMBERED VARIABLE 2	Weighting variable is the constant
INDEPENDENT VARIABLE (ROW) IS 2 0.12000000E 02	Weight $= a_1$ $N = (Z'Z)_{11}$
INDEPENDENT VARIABLE (ROW) IS 3 0.10700000E 03 0.11350000E 04	Z $\Sigma Z = (Z'Z)_{21}$ $\Sigma Z^2 = (Z'Z)_{22}$
INDEPENDENT VARIABLE (ROW) IS 4 0.11350000E 04 0.13391000E 05 0.16829500E 06	Z^2 $\Sigma Z^2 = (Z'Z)_{31}$ $\Sigma Z^3 = (Z'Z)_{32}$ $\Sigma Z^4 = (Z'Z)_{33}$
MEANS OF ALL VARIABLES 0.23256366E 03 0.10000000E 01 0.89166665E 01 0.94583332E 02	$\bar{I}$ $\bar{N}$ $\bar{Z}$ $\bar{Z^2}$
STANDARD DEVIATIONS OF ALL VARIABLES 0.20156706E 03 −0.00000000E−38 0.38828326E 01 0.71264131E 02	σ_I σN σ_Z σ_{Z^2}
CORRELATION MATRIX DEPENDENT VARIABLE IS LOWEST NUMBERED VARIABLE	[N.B. W = Weighting Variable]

Output	Explanation
ROW 1 1.0000	r_{11}
ROW 2 9.9999 9.9999	r_{IW} r_{WW}
ROW 3 0.9779 9.9999 1.0000	r_{1I} r_{WI} r_{II}
ROW 4 0.9993 9.9999 0.9850 1.0000	r_{1Q} r_{WQ} r_{IQ} r_{QQ}
T-TRANSPOSE MATRIX, LOWER TRIANGLE	
ROW 2 0.34641016E 01	T'_{11}
ROW 3 0.30888239E 02 0.13450527E 02	T'_{21} T'_{22}
ROW 4 0.32764627E 03 0.24315653E 03 0.42635886E 02	T'_{31} T'_{32} T'_{33}
T-TRANSPOSE INVERSE MATRIX, LOWER TRIANGLE	
ROW 2 0.28867513E 00	$(T')^{-1}_{11}$
ROW 3 -0.66292318E 00 0.74346527E-01	$(T')^{-1}_{21}$ $(T')^{-1}_{22}$
ROW 4 0.15623170E 01 -0.42400534E 00 0.23454420E-01	$(T')^{-1}_{31}$ $(T')^{-1}_{32}$ $(T')^{-1}_{33}$

Output | **Explanation**

```
L VECTOR
                                              SUM OF                PROP
VAR        L-COEF            L-SQUARE       L-SQUARE            VAR ADDED
 2    0.80562413E 03    0.64903025E 06    0.64903025E 06    0.00000000E-38
 3    0.68281487E 03    0.46623616E 06    0.11152664E 07    0.95628111E 00
 4    0.14599719E 03    0.21315180E 05    0.11365816E 07    0.43718840E-01
```

W l_0 l_0^2 l_0^2 —
Z l_1 l_1^2 $l_0^2+l_1^2$ A/T
Z² l_2 l_2^2 $l_0^2+l_1^2+l_2^2$ B/T

[N.B. $A=(\Sigma I^2-l_0^2)/N-1$
$B=(\Sigma I^2-l_0^2-l_1^2)/N-2$
$C=(\Sigma I^2-l_0^2-l_1^2-l_2^2)/N-3$
$T=A+B+C$]

```
VAR          R-SQ     EST VAR OF Y          F-RATIO     DF
 3         0.9563    0.21315203E 04        218.7341    1/ 10

 4         1.0000    0.26041666E-02        ********    2/  9
```

Z B/T B l_{12}/B V—2/ N—V+1
Z² $\frac{B+C}{T}$ C $\frac{l_1^2+l_2^2}{C(V-1)}$ V—1/ N—V

[N.B. V = Number of Variables]

```
VECTOR OF B-COEFFICIENTS
VAR       B-COEF
 2    0.80037403E 01
 3   -0.11138675E 02
 4    0.34242794E 01
```

W a_1
Z a_2
Z² a_3

```
T-TESTS ON B-COEFFICIENTS
VAR   STUDENTS T   STANDARD ERROR    DF     SIG°
 3     -507.0516    0.21967538E-01    9    0.0000
 4     2860.9490    0.11969033E-02    9    0.0000
```

Z a_1/D_2 D_2 N-V *
Z² a_2/D_3 D_3 N-V *
[N.B. * Equivalent to percentile from t-tables
$D_2=[(Z'Z)^{-1}_{22}C]^{\frac{1}{2}}$
$D_3=[(Z'Z)^{-1}_{33}C]^{\frac{1}{2}}$]

```
XX-INVERSE MATRIX, LOWER TRIANGLE
ROW 2
     0.29636349E 01

ROW 3
    -0.71171679E 00      0.18530794E 00

ROW 4
     0.36643239E-01     -0.99447993E-02      0.55010981E-03

MAXIMUM ABSOLUTE DIFFERENCE BETWEEN ORIGINAL XX MATRIX AND
  DOUBLY INVERTED MATRIX IS 0.10351563E 00

PREDICTED VALUES AND RESIDUALS
    OBSERVATION            ACTUAL           PREDICTED         DIFFERENCE
              1       0.53900000E 01     0.54062311E 01    -0.16231179E-01
              2       0.18206000E 02     0.18237513E 02    -0.31512499E-01
              3       0.37920000E 02     0.37917352E 02     0.26473999E-02
              4       0.64476000E 02     0.64445752E 02     0.30247688E-01
              5       0.97862999E 02     0.97822708E 02     0.40290833E-01
              6       0.13808000E 03     0.13804823E 03     0.31772614E-01
              7       0.18513900E 03     0.18512230E 03     0.16698837E-01
              8       0.29978000E 03     0.29981612E 03    -0.36128998E-01
              9       0.36736000E 03     0.36743588E 03    -0.75881958E-01
             10       0.44190000E 03     0.44190419E 03    -0.41923523E-02
             11       0.52319999E 03     0.52322106E 03    -0.21064758E-01
             12       0.61144999E 03     0.61138649E 03     0.63507080E-01
```

$$\begin{array}{lll}
(Z'Z)^{-1}_{11} & & \\
(Z'Z)^{-1}_{21} & (Z'Z)^{-1}_{22} & \\
(Z'Z)^{-1}_{31} & (Z'Z)^{-1}_{32} & (Z'Z)^{-1}_{33}
\end{array}$$

1	I_1	I_1(Pred)	I_1-I_1(Pred)
2	I_2	I_2(Pred)	I_2-I_2(Pred)
3	I_3	I_3(Pred)	I_3-I_3(Pred)
4	I_4	I_4(Pred)	I_4-I_4(Pred)
5	I_5	I_5(Pred)	I_5-I_5(Pred)
6	I_6	I_6(Pred)	I_6-I_6(Pred)
7	I_7	I_7(Pred)	I_7-I_7(Pred)
8	I_8	I_8(Pred)	I_8-I_8(Pred)
9	I_9	I_9(Pred)	I_9-I_9(Pred)
10	I_{10}	I_{10}(Pred)	I_{10}-I_{10}(Pred)
11	I_{11}	I_{11}(Pred)	I_{11}-I_{11}(Pred)
12	I_{12}	I_{12}(Pred)	I_{12}-I_{12}(Pred)

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