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Z expansions of the total electronic energy for isoelectronic atoms: A method for determining $\bar{V}_{en}$ and $\bar{V}_{ee}$ from experimental total electronic energies

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The Z dependence of the total electronic energy for an atomic isoelectronic series, was investigated in several different ways, first by the consideration of a Taylor-series expansion of $\bar{V}_{en}$, the average electron-nuclear attractive potential energy, used in conjunction with the virial and Hellmann-Feynman theorems and, secondly, a Taylor-series expansion of $\bar{V}_{ee}$, the average electron-electron repulsive potential energy, used in conjunction with the same two theorems. A direct Taylor-series expansion of the total energy E was also studied. Convergence of these expansions was inferred from the rate of convergence of least-squares fits of tabulated values of the total electronic energies as a function of the increasing number of terms in the expansion. Theoretical nonrelativistic Hartree-Fock energies, accurate theoretical nonrelativistic energies, and experimental total energies, the latter approximately corrected for relativistic and quantum electrodynamic effects, were used in the fits. These expansions were compared with $1/Z$ expansion results. All Taylor-series variants studied showed comparable or superior convergence properties to the $1/Z$ expansion. The choice of a $\bar{V}_{en}$ or a $\bar{V}_{ee}$ expansion forces certain behavior on the total electronic energy E as a function of Z. From a least-squares rate-of-convergence criterion and other considerations it appears that the Taylor-series expansion of $\bar{V}_{en}$ offers slightly better results. It is pointed out that by the use of the virial and Hellmann-Feynman theorems it is possible to obtain accurate estimates of $\bar{V}_{ee}$ and $\bar{V}_{en}$ from a knowledge of total electronic energies of isoelectronic series alone. The technique is applied to accurate values for the He isoelectronic series and experimental data corrected for relativistic and radiative contributions for the He through Ne isoelectronic series in order to determine the effect of electron correlation on the quantities $\bar{V}_{en}$ and $\bar{V}_{ee}$. Comparisons are made with available experimental and theoretical results in the case of Ne. The Z expansions for the energy were also used to fit individual ionization potentials across an isoelectronic series. These fits were used to predict electron affinities and improved values for certain ionization potentials.

I. INTRODUCTION

Accurate analytical expressions for the total electronic energy E in atoms as a function of the atomic number Z in an isolectronic sequence have long been of interest in predicting ionization potentials[1] and electron affinities.[2] The main method for obtaining expressions for the Z dependence of E has been the use of perturbation theory to obtain the so-called $1/Z$ expansion.[3] There have been reports, however, of convergence problems in the use of such expansions.[4,5] It does not appear that use of a Taylor-series expansion about a fixed nuclear charge Z_0 used in conjunction with virial and Hellmann-Feynman relations has been explored, although Clementi[6] showed that a polynomial in positive integer powers of Z was capable of giving an excellent representation of total electronic energies. We report here several new Z expansions of total electronic energies for an isoelectronic sequence. By the use of virial and Hellmann-Feynman theorems a method is proposed to derive values of $\bar{V}_{en}$, the average electron-nuclear attractive potential energy, and $\bar{V}_{ee}$, the average electron-electron repulsive potential energy, from total electronic energies alone. The theory is developed in Sec. II and numerical applications are discussed in Sec. III. The present techniques are applied to experimental total energies to deduce nonrelativistic estimates for $\bar{V}_{en}$ and $\bar{V}_{ee}$ for atoms from He through Ne. The relevance of these quantites to x-ray and electron scattering experiments, and quantum-mechanical calculations on atoms are detailed in Sec. IV.

II. THEORETICAL DEVELOPMENT OF Z EXPANSIONS

We express the virial theorem[7] as

$$E(Z)=\tfrac{1}{2}[\bar{V}_{en}(Z)+\bar{V}_{ee}(Z)]=-\bar{T}(Z) \qquad (1)$$

and a particular application of the Hellmann-Feynman theorem[8] written as

$$\frac{\partial E(Z)}{\partial Z}=\frac{\bar{V}_{en}(Z)}{Z}, \qquad (2)$$

where $E(Z)$ is the total atomic electronic energy, $\bar{T}(Z)$ is the average kinetic energy, and Z is the nuclear charge. Equation (2) can be expressed in integral form as

$$E(Z)=E(Z_0)+\int_{Z_0}^{Z} d\xi\, \bar{V}_{en}(\xi)/\xi \qquad (3)$$

which expresses the fact that if $\bar{V}_{en}(Z)$ is regarded as being a continuous function of Z then a knowledge of its Z dependence is sufficient to determine the total electronic energy. On the other hand, Eqs. (1) and (2) can be combined with some algebraic manipulation to obtain

$$E(Z)=\left[\frac{Z}{Z_0}\right]^2 E(Z_0)-Z^2\int_{Z_0}^{Z} d\xi\, \bar{V}_{ee}(\xi)/\xi^3 \qquad (4)$$

which shows that a knowledge of the Z dependence of $\bar{V}_{ee}(Z)$ is also sufficient, assuming it to be a continuous function of Z, to determine the total electronic energy.

It is possible, therefore, to develop three variants of Taylor-series expansions of $E(Z)$. The first is the obvious one

$$E(Z)=E(Z_0)+(Z-Z_0)\left.\frac{\partial E(Z)}{\partial Z}\right|_{Z=Z_0}+\frac{(Z-Z_0)^2}{2}\left.\frac{\partial^2 E(Z)}{\partial Z^2}\right|_{Z=Z_0}+\cdots, \qquad (5)$$

while the second variant consists of expanding $\bar{V}_{en}(Z)$ in a Taylor series about some nuclear charge Z_0 and then using Eq. (3) to obtain $E(Z)$. The third variant involves a Taylor-series expansion of $\bar{V}_{ee}(Z)$ about Z_0 used in conjuction with Eq. (4) to obtain $E(Z)$.

The results of these last two approaches through terms in second order in $Z-Z_0$ are

$$E(Z)=E(Z_0)+V_{en}^{(0)}(Z_0)\ln\left[\frac{Z}{Z_0}\right]+V_{en}^{(1)}(Z_0)\left[(Z-Z_0)-Z_0\ln\left[\frac{Z}{Z_0}\right]\right]+V_{en}^{(2)}(Z_0)\left[\frac{(Z^2-Z_0^2)}{4}-Z_0(Z-Z_0)+\frac{Z_0^2}{2}\ln\left[\frac{Z}{Z_0}\right]\right]+\cdots \qquad (6)$$

and

$$E(Z)=\left[\frac{Z}{Z_0}\right]^2 E(Z_0)+\frac{1}{2}\left[1-\frac{Z^2}{Z_0^2}\right]V_{ee}^{(0)}(Z_0)-V_{ee}^{(1)}(Z_0)\left[\frac{(Z-Z_0)^2}{2Z_0}\right]+V_{ee}^{(2)}(Z_0)\left[\tfrac{1}{2}(Z-Z_0)(3Z-Z_0)-Z^2\ln\left[\frac{Z}{Z_0}\right]\right]+\cdots, \qquad (7)$$

where $V_{en}^{(l)}(Z_0)$ and $V_{ee}^{(l)}(Z_0)$ are the lth derivatives with respect to Z evaluated at Z_0.[9]

Some comments concerning Eqs. (5)–(7) are in order. Equation (5) is a simple curve fitting with the possibility that its convergence properties might be superior to that of $1/Z$ expansions. Equations (6) and (7), on the other hand, introduce a very different dependence on Z in the total energy and enable one to immediately determine $\bar{V}_{ee}(Z)$ and $\bar{V}_{en}(Z)$ once a fit of experimental data is obtained and estimates of the parameters $\bar{V}_{en}^{(l)}(Z_0)$ or $\bar{V}_{ee}^{(l)}(Z_0)$ are known.[10] There is, however, a problem. Note that while both energy expressions contain logarithmic terms, they are not the same and if one uses Eq. (6) then $\bar{V}_{ee}(Z)$ will contain logarithmic terms while $\bar{V}_{en}(Z)$ will not and vice versa if Eq. (7) is employed.

Because it is known that the free-electron exchange potential contains logarithmic terms[11] it is tempting to assume that Eq. (6) is the more correct way to proceed. In fact, it can be shown that the use of Eq. (6) leads to an expansion for $\bar{V}_{ee}(Z)$ which contains no dependence on Z^2.[12] This is interesting since March and Parr[13] have shown that the Z expansion of $\bar{V}_{ee}(Z)$ in the free-electron limit is also devoid of any Z^2 terms. The result for $\bar{V}_{ee}(Z)$ in terms of $\bar{V}_{en}(Z)$ can be written as

$$\bar{V}_{ee}(Z)=V_{ee}^{(0)}(Z_0)+2V_{en}^{(0)}\left[(Z_0)\ln\left[\frac{Z}{Z_0}\right]\right]+V_{en}^{(1)}(Z_0)\left[(Z-Z_0)-2Z_0\ln\left[\frac{Z}{Z_0}\right]\right]$$
$$-V_{en}^{(2)}(Z_0)\left[Z_0(Z-Z_0)-Z_0^2\ln\left[\frac{Z}{Z_0}\right]\right]+\cdots \; . \qquad (8)$$

It is also of interest to note that all terms in Eqs. (6) and (7) can be summed vertically if one assumes the existence of convergent Taylor-series expansions of $\bar{V}_{en}(Z_0)$ and $\bar{V}_{ee}(Z_0)$ about the point $Z_0=0$ as

$$E(Z)=E(Z_0)+\ln\left[\frac{Z}{Z_0}\right]V_{en}^{(0)}(0)+(Z-Z_0)V_{en}^{(1)}(0)+\frac{(Z^2-Z_0^2)}{4}V_{en}^{(2)}(0)+\cdots \qquad (9)$$

and

$$E(Z)=\left[\frac{Z}{Z_0}\right]^2E(Z_0)-\frac{(Z^2-Z_0^2)}{2Z_0^2}V_{ee}^{(0)}(0)-\frac{Z(Z-Z_0)}{Z_0}V_{ee}^{(1)}(0)-\frac{Z^2}{2}\ln\left[\frac{Z}{Z_0}\right]V_{ee}^{(2)}(0)+\cdots \; . \qquad (10)$$

The exact significance of such a replacement is not clear but it is tempting to assume that the $V_{en}^{(l)}(0)$ and $V_{ee}^{(l)}(0)$ values are somehow related to a free-electron limit.

III. NUMERICAL INVESTIGATIONS WITH THEORETICAL AND EXPERIMENTAL RESULTS

A. Convergence properties

In order to test the applicability of the various possible Z expansions, Hartree-Fock (HF) values[14] of total electronic energies for various isoelectronic series were utilized. Constants were obtained by least-squares-fitting procedures for the expansions given by Eqs. (5)–(7), (9), and (10) along with a $1/Z$ expansion with an equivalent number of terms. The behavior of parameter variances, covariances, and goodness of overall fit as a function of adding new parameters was then used as a numerical test of convergence. All studied Taylor-series expansions displayed comparable fits of the total energy for an equivalent number of parameters. The variances obtained for the various cases are presented in Table I. For a rapidly converging series we would expect the change of variance to reach a plateau with the addition of new terms. An examination of the table reveals that for the ^1S state of Be, Eqs. (5)–(7), (9), and (10) definitely show superior convergence behavior from this point of view compared to the $1/Z$ expansion. For a system such as the ^3P state for S, the situation is not as clear cut but the Z expansions still exhibit slightly better convergence properties. Unlike previous observations[4,5] we were unable to detect any radical failure of the $1/Z$ expansion to converge with addition of higher-order terms. On the other hand, our least-squares derived values for the constant term ϵ_2 in the $1/Z$ expansion were not in good agreement with values derived from perturbation theory except for two- and three-electron systems. This may be indicative of convergence problems with the perturbation series approach. The limiting value of the variance is governed by the accuracy of the input energies while the actual value, if larger, can be regarded as a problem with the convergence. It is interesting to note that fits using either Eqs. (6) and (9) or (7) and (10) have essentially the same variance as might be expected since the latter series in each case is obtained by summing terms in the former. The fits using Eqs. (6) and (9) give poor results with only two coefficients. This could be because of the $\ln Z$ term which diverges as Z approaches zero. Other terms are finite at $Z=0$. However, when we include the next terms, these expressions are better representations than Eq. (5). We emphasize the fact

TABLE I. Variances[a] calculated from computed total energy E(comp) and input total energy E(input) for beryllium and sulfur isoelectronic series for different numbers of coefficients (NC) used in the fit. Numbers in parentheses are the powers of ten by which the number should be multiplied. Twenty energy values were used in each fit and the input energies were Hartree-Fock values.

	Beryllium (^1S) isoelectronic series			
Method	NC=2	NC=3	NC=4	NC=5
$1/Z$	2.51 (−2)	1.09(−5)	1.12(−7)	1.12(−9)
Eq. (5)	1.61(−5)	3.83(−6)	7.91(−7)	1.90(−7)
Eq. (6)	1.70(+2)	6.27(−7)	1.12(−7)	2.15(−8)
Eq. (7)	1.61(−5)	2.61(−6)	4.11(−7)	7.57(−8)
Eq. (9)	1.70(+2)	6.27(−7)	1.12(−7)	2.18(−8)
Eq. (10)	2.40(−4)	2.09(−5)	4.90(−6)	5.71(−7)
	Sulfur (^3P) isoelectronic series			
Method	NC=2	NC=3	NC=4	NC=5
$1/Z$	5.16(−3)	1.61(−3)	2.31(−5)	5.84(−6)
Eq. (5)	2.26(−3)	2.16(−4)	1.81(−5)	2.98(−6)
Eq. (6)	1.25(+2)	6.17(−5)	3.50(−6)	5.96(−7)
Eq. (7)	2.26(−3)	1.55(−4)	1.08(−5)	1.10(−6)
Eq. (9)	1.25(+2)	6.17(−5)	3.50(−6)	2.79(−5)
Eq. (10)	3.74(−3)	2.83(−4)	1.89(−5)	1.99(−6)

[a] Variance is defined as $\sum_{i=1}^{20}[E_i(\text{comp})-E_i(\text{input})]^2/19$.

that Eqs. (6)−(10) are derivable from Eq. (5) using Eqs. (1) and (2) by summing the series in different ways. It appears that for an isoelectronic sequence with a large number of electrons, Eq. (6) gives a slightly better fit than a $1/Z$ expansion.

It is of interest to note that the fits obtained with Eqs. (9) and (10) were *independent* of the *choice* of Z_0 within the *accuracy of the fits*. Unfortunately the values for $\bar{V}_{en}(0)$ and $\bar{V}_{ee}(0)$ turned out to be positive and negative, respectively, counter to physical expectations.

B. Calculation of $\bar{V}_{en}$ and $\bar{V}_{ee}$

An application of these fitting procedures which does not seem to have been made use of previously is the decomposition of total electronic energies into the parts $\bar{V}_{en}$ and $\bar{V}_{ee}$. A least-squares fit of the (HF) total energies of an isoelectronic sequence to Eq. (6) gives the coefficients $\bar{V}_{en}^{(l)}(Z_0)$. These are used to compute $\bar{V}_{en}$ directly for any element in the sequence. By the use of the virial relation, $\bar{V}_{ee}$ is also calculated. It is possible to calculate $\bar{V}_{ee}$ and $\bar{V}_{en}$ by using Eq. (7). Notice that one could also calculate these same quantities using Eq. (5) or the $1/Z$ expansion in conjuction with Eqs. (2) and (1). Again, the results obtained using Eq. (6) to obtain $\bar{V}_{en}(Z)$ and $\bar{V}_{ee}(Z)$ are slightly better than those obtained using the $1/Z$ expansion. Another advantage of using Eq. (6) or (7) is that the errors in $\bar{V}_{ee}$ and $\bar{V}_{en}$ can be estimated more directly since they can be obtained from the variances of $\bar{V}_{en}^{(l)}(Z_0)$ or $\bar{V}_{ee}^{(l)}(Z_0)$.

In Table II values of $\bar{V}_{en}$ and $\bar{V}_{ee}$ computed from the coefficients obtained by fitting Eq. (6) to accurate HF energies are compared to the exact HF values for these same quantities. This proves that $\bar{V}_{en}$ and $\bar{V}_{ee}$ can be recovered with reasonable accuracy from HF total energies. It only remains to show that the method also works when electron correlation is included in the total energy.

C. A test with very accurate nonrelativistic total energies: He isolectronic sequence

It is well known that the exact nonrelativistic total energy is lower than that calculated in the HF approximation. This energy difference is called the correlation energy. As a test, the present Z expansions were fitted to nonrelativistic total energies of the He isoelectronic sequence due to Thakkar and Smith.[15] These energies were chosen because highly accurate values of $\bar{V}_{en}$ and $\bar{V}_{ee}$ were given. The re-

TABLE II. Comparison of computed values (comp) of $\bar{V}_{en}$ and $\bar{V}_{ee}$ using Eq. (6) with Hartree-Fock (HF) values.[a] N signifies the number of electrons in the ion/atom. All values are in a.u.[b]

Z	N	$-\bar{V}_{en}$ Comp.	$-\bar{V}_{en}$ HF	$\bar{V}_{ee}$ Comp.	$\bar{V}_{ee}$ HF
5	4	54.5917±0.001	54.5932	6.1158±0.001	6.1181
7	4	111.4727±0.001	111.4733	9.3085±0.001	9.3087
9	4	188.3414±0.001	188.3402	12.4735±0.001	12.4721
16	4	614.8531±0.001	614.8540	23.4962±0.001	23.4968
6	6	88.1557±0.03	88.1376	12.7792±0.03	12.7604
16	6	715.7402±0.003	715.7410	45.8825±0.003	45.8834
24	6	1649.6703±0.003	1649.6712	72.0461±0.003	72.0475
17	16	1086.3403±0.02	1086.3313	168.2401±0.02	168.2345
22	16	1921.7185±0.02	1921.7001	247.2312±0.02	247.2124
27	16	2989.4573±0.02	2989.4674	324.5862±0.02	324.5964

[a] $\bar{V}_{en}$ and $\bar{V}_{ee}$ are calculated using the relations $\sum \epsilon_i = E + \bar{V}_{ee}$ and $2E = \bar{V}_{ee} + \bar{V}_{en}$ where both $\sum \epsilon_i$, the Hartree-Fock eigenvalue sum and E, the total HF electronic energy, are given in Ref. 14.

[b] Here 1 a.u. $= 2R_M$, where R_M is the Rydberg constant calculated with the reduced rest mass of the electron in relation to the nuclear mass of M.

sults obtained by fitting to Eq. (6) are given in Table III. This demonstrates the accuracy of the present method when electron correlation is included. The results given were from fits of the energies of He and the available heliumlike positive ions, but not the energy of H^-. Inclusion of H^- in the fitting set does not appreciably change the final result although the variance increases. Omission makes it possible to test the predictive ability of the Z expansion.

IV. APPLICATIONS OF THE PRESENT TECHNIQUES TO EXPERIMENTAL DATA

The formulations of the present Z expansions using Eqs. (1) and (2) are based on the nonrelativistic spin-independent Hamiltonian. Note that if relativistic or other effects are included then the form of the virial and Helmann-Feynman theorems will change and the formulation given here will be in-

TABLE III. Comparison of $\bar{V}_{en}$, $\bar{V}_{ee}$, and E determined by fitting to Eq. (6), $\bar{V}_{en}^{\text{fit}}$, $\bar{V}_{ee}^{\text{fit}}$, E^{fit}, respectively, with the exact values $\bar{V}_{en}^{\text{exact}}$, $\bar{V}_{ee}^{\text{exact}}$, and E^{exact} for the He isoelectronic sequence. Z denotes the nuclear charge. All quantities are in a.u.[a]

Z	$-E^{\text{fit}}$ [b]	$-E^{\text{exact}}$ [d]	$-\bar{V}_{en}^{\text{fit}}$ [c]	$-\bar{V}_{en}^{\text{exact}}$ [d]	$\bar{V}_{ee}^{\text{fit}}$ [c]	$\bar{V}_{ee}^{\text{exact}}$ [d]
2	2.903 724	2.903 724	6.753 318	6.753 267	0.945 869	0.945 818
4	13.655 565	13.655 565	29.502 003	29.502 002	2.190 873	2.190 872
6	32.406 245	32.406 245	68.251 383	68.251 386	3.438 893	3.438 893
8	59.156 594	59.156 594	123.001 05	123.001 06	4.687 864	4.687 865
10	93.906 803	93.906 802	193.750 83	193.750 85	5.937 222	5.937 244
12	136.656 940	136.656 944	280.500 76	280.500 71	7.186 871	7.186 821

[a] Here, 1 a.u. $= 2R_M$, where R_M is the Rydberg constant calculated with the reduced rest mass of the electron in relation to the nuclear mass of M.

[b] The estimated accuracy is ±0.000 0003.

[c] The estimated accuracy is ±0.000 007.

[d] The exact values quoted here are from Ref. 15.

valid. Successive experimental and very accurate theoretical ionization energies have been compiled by Moore.[16] For our purposes these must be corrected for relativistic effects and quantum electrodynamic effects in order to derive nonrelativistic energies.

A. Relativistic effects

An approximate formulation of the Dirac equation for a multielectron atom utilizes the Dirac-Breit Hamiltonian which, when formulated in the Hartree-Fock approximation, is known as the Dirac-Breit-Hartree-Fock approximation.[17] Another approximate formulation called the Dirac-Breit-Pauli-Hartree-Fock (DBPHF) method[18] involves the calculation of relativistic effects by first-order perturbation theory using nonrelativistic Hartree-Fock wave functions. We used the approximate relativistic corrections of the DBPHF method calculated by Fraga *et al.*[19] The accuracy of these values were checked by employing fitting procedures to determine a particular ionization potential, other than the K shell, by adding the difference in the relativistic corrections for the two states, before and after ionization, to the nonrelativistic result from the fits. The atom under study was excluded in the fits. The determined value agreed with the spectroscopic value in all cases studied, thus indicating that the Fraga *et al.*[19] values are consistent within the experimental uncertainties. The agreement also supports our assumption that the radiative corrections discussed below are similar for two states with the same nuclear charge and K shell.

B. Quantum electrodynamic effects

Although we have to correct for the interaction of electrons with the nuclear spin, the hyperfine interactions, these can be ignored because the correction to the energy is insignificant.[20] On the other hand, the vacuum fluctuations of the electromagnetic field that give rise to Lamb-shift (radiative) corrections[21] must be accounted for because these corrections can be as large as 1.4 eV as in the case of Ca^{18+}.

The radiative corrections are largest for $1s$ electrons. The radiative corrections for two-electron systems were determined from the difference between the accurate nonrelativistic total electronic energies due to Scherr *et al.*[22] and the experimental values corrected for relativistic effects. It was assumed that the total radiative correction for each atom was given completely by the $1s^2$ contribution. A check of this procedure was made in the cases of the neutral atoms Li,[23] Be,[24] C,[25] and Ne,[26] where accurate estimates of the total nonrelativistic energies are known. A comparison of present estimates of nonrelativistic energies with the literature values is presented in Table IV for these cases. The error in assuming that the $1s^2$ radiative correction is dominant is less than 0.02 eV in all cases. Strictly speaking, the good agreement confirms that the *sum* of the *relativistic* and *radiative* corrections is accurate.

C. Estimation of the accuracy of derived energy quantities

The experimental total energies for the atoms considered in this work, containing more than two

TABLE IV. Comparison of experimental total energies corrected for relativistic and radiation effects with literature values.

Atom	Literature value (eV)	Present estimate (eV)
Li[a]	203.482 29±0.000 03	203.483
Be[b]	399.114 30±0.000 03	399.083
C[c]	1029.75 ±0.04	1029.78
Ne[d]	3508.3 ±0.2	3508.35

[a] See Ref. 23.
[b] See Ref. 24.
[c] See Ref. 25.
[d] See Ref. 26.

electrons derived by adding up successive ionization energies,[16] should be accurate to $\pm 0.01\sqrt{N}$ eV where N is the number of electrons in the atom. We estimate that the relativistic and radiative corrections are each good to at least ± 0.03 eV. Hence the estimated nonrelativistic energies should be good to better than ± 0.1 eV for atoms with ten or fewer electrons.

D. Calculation of $\overline{V}_{en}$ and $\overline{V}_{ee}$ from experimental data and their significance in the study of electron correlation

The nonrelativistic total energies of isoelectronic sequences of the atoms He through Ne were derived from the experimental data corrected for relativistic and radiative effects by use of least-squares fit to Eq. (6). The estimated values of $\overline{V}_{en}^{\text{fit}}$, $\overline{V}_{ee}^{\text{fit}}$ for the elements are given in Table V along with the uncertainties and the nonrelativistic energies used. These quantities $\overline{V}_{en}^{\text{fit}}$ and $\overline{V}_{ee}^{\text{fit}}$ include electron correlation effects. The difference between these and the corresponding HF quantities $\Delta\overline{V}_{en}$ and $\Delta\overline{V}_{ee}$ show how the correlation energy is partitioned between these two quantities. A perusal of Table V shows that $\Delta\overline{V}_{ee}$ is negative and a monotonically decreasing function of the number of electrons, while $\Delta\overline{V}_{ne}$ shows oscillatory behavior. The observation concerning $\Delta\overline{V}_{ee}$ means that

$$\left\langle \frac{1}{r_{12}} \right\rangle_{\text{HF}} > \left\langle \frac{1}{r_{12}} \right\rangle_{\text{exact}} ,$$

where r_{12} is the interelectronic distance. If $\Delta\overline{V}_{ne}$ is negative then

$$\left\langle \frac{1}{r} \right\rangle_{\text{exact}} > \left\langle \frac{1}{r} \right\rangle_{\text{HF}}$$

while the opposite is true if $\Delta\overline{V}_{ne}$ is positive where r is the electron-nuclear distance. It is also of interest to note that $\Delta\overline{V}_{en}$ is positive when the total number of p electrons is greater than the number of s electrons, and negative when the total number of p electrons is less than the total number of s electrons.

As noted above $\overline{V}_{en}$ is a one-electron property while $\overline{V}_{ee}$ is a two-electron property. Until very recently, configuration-interaction (CI) calculations gave adequate descriptions of the second-order diagonal two-electron density, while the first-order density matrix was less satisfactorily determined because of the then usual custom of omitting the contributions from singly excited configurations. However, the values of Smith *et al.*[14] include all correlation effects in both density matrices and, using these, the authors have published reliable theoretical values for $\overline{V}_{ee}$ and $\overline{V}_{en}$ which have been used as a check on our procedures (see Table III). Our use of Z expansions of the electronic energy to determine $\overline{V}_{ee}$ and $\overline{V}_{ne}$ from total energies alone is of current interest because of the recent experimental measurements of $\Delta\overline{V}_{en}$ and $\Delta\overline{V}_{ee}$ reported by Duguet.[27]

We have attempted to compare our predictions for Ne with those of highly correlated wave functions and the results of Duguet. Unfortunately, no values appear to have been given in the literature for $\overline{V}_{ee}$ and $\overline{V}_{en}$ for such wave functions. On the other hand, Peixoto *et al.*,[28] and Naon and Cornille[29] have given results for the x-ray coherent scattering factor $F(s)$ and the incoherent scattering factor $S(s)$ from which $\Delta\overline{V}_{en}$ and $\Delta\overline{V}_{ee}$ values can be derived.[30] The results are summarized in Table VI.

For the 65-term CI wave function due to Bunge and Peixoto[26] we calculate from the form factors[28]

TABLE V. Values for $\overline{V}_{en}$ and $\overline{V}_{ee}$ obtained from total experimental electronic energies using Eq. (6) for atoms. All quantities are in a.u. (1 a.u. = 27.2107 eV).

element	$-E$	$-\overline{V}_{en}^{\text{fit}}$		$\overline{V}_{ee}^{\text{fit}}$		$\Delta\overline{V}_{en}$[a]	$\Delta\overline{V}_{ee}$[b]
He	2.903 72	6.753 27	±0.000 05	0.945 83	±0.000 05	−0.003 21	−0.080 09
Li	7.4781	17.157	±0.004	2.201	±0.004	−0.009	−0.08
Be	14.667	33.711	±0.004	4.376	±0.004	−0.074	−0.113
B	24.654	56.97	±0.01	7.67	±0.01	−0.07	−0.17
C	37.845	88.21	±0.01	12.52	±0.01	−0.07	−0.24
N	54.589	128.41	±0.02	19.23	±0.02	−0.05	−0.32
O	75.067	178.09	±0.02	27.96	±0.02	−0.01	−0.50
F	99.732	238.63	±0.02	39.17	±0.02	+ 0.04	−0.68
Ne	128.933	311.09	±0.025	53.22	±0.025	+ 0.05	−0.82

[a] $\Delta\overline{V}_{en} = \overline{V}_{en}^{\text{fit}} - \overline{V}_{en}^{\text{HF}}$, where $\overline{V}_{en}^{\text{HF}}$ is $\overline{V}_{en}$ in the HF approximation. The estimated error in $\Delta\overline{V}_{en}$ is the same as in $\overline{V}_{en}^{\text{fit}}$.

[b] $\Delta\overline{V}_{ee} = \overline{V}_{ee}^{\text{fit}} - \overline{V}_{ee}^{\text{fit}}$, where $\overline{V}_{ee}^{\text{HF}}$ is $\overline{V}_{ee}$ in the HF approximation. The estimated error in $\Delta\overline{V}_{ee}$ is the same as in $\overline{V}_{ee}^{\text{fit}}$.

the results $\Delta \bar{V}_{en} = +3.8$ eV and $\Delta \bar{V}_{ee} = -17.2$ eV. Unfortunately, the total correlation energy E_c of -6.7 eV falls well short of the 85% of the total correlation energy claimed for this wave function. It is possible that some smaller contributions to the form factors were omitted in the calculation or that there is an error in the calculation of the scattering factors. We also discovered that published curves for

$$\Delta\sigma(s) = -2Z\Delta F(s) + \Delta[F^2(s)] + \Delta S(s)$$

are given incorrectly for this wave function.[31] The Δ's signify correlated minus HF quantities.[31]

The Naon-Cornille form factors, on the other hand, lead to opposite results: $\Delta V_{en} = -6.2$ eV and $\Delta V_{ee} = -18.6$ eV. Comparison of $\Delta F(s)$ for the two wave functions immediately shows that they have totally different correlation corrections to the one-electron density function. The Peixoto-Bunge wave function[26] may leave out contributions from singly excited configurations which are known to make important contributions to the one-electron density[32] and, hence, one might assume that the Naon-Cornille results might be more reliable. However, the correlation energy calculated from the scattering factors is 19% larger than the correlation energy claimed for this wave function,[33] which is 10.4 eV. This also raises doubts as to the accuracy of these scattering factors. On the other hand, our fits of Hartree-Fock and correlated data, where $\Delta \bar{V}_{ee}$ and $\Delta \bar{V}_{en}$ are known, suggest that our Z-expansion predictions concerning correlation effects on $\Delta \bar{V}_{ee}$ and $\Delta \bar{V}_{en}$ should be better than ±0.7 eV in the case of Ne. The discrepancy between this uncertainty and that obtained in the case of He is due to the fact that the theoretical energies used in the He cases are more accurate than the experimental ones available for Ne. Within the accuracy of our estimate we are in better agreement with the results of Bunge and Peixoto than those of Naon and Cornille. Duguet[27] lists his experimental results for Ne as $\Delta \bar{V}_{en} = -7.3 \pm 7.0$ eV and $\Delta \bar{V}_{ee} = -7.6 \pm 7.0$ eV. These results yield a correlation energy of -7.5 ± 7.0 eV. He also lists a value of -9.0 ± 5.4 eV for the total correlation energy. The difference between these two estimates of E_c is due to the greater numerical uncertainties involved in determining the first value. Our results are $\Delta \bar{V}_{en} = +1.4 \pm 0.7$ eV and $\Delta \bar{V}_{ee} = -22.3 \pm 0.7$ eV with a total correlation energy of -10.5 ± 0.4 eV. This compares well with the generally accepted value of 10.36 eV for E_c. The smaller uncertainty in the case of the correlation energy is a reflection of the increase in uncertainty when the total energy is dissected into its component parts (i.e., compare the error estimates in footnotes b and c of Table III). It is clear that the Duguet experiment is not yet definitive but with further refinements it may be possible for work of this kind to yield very interesting information.

TABLE VI. Correlation effects on E, $\bar{V}_{en}$, and $\bar{V}_{ee}$ for Ne. All quantities are given in eV.

	Bunge, Peixoto, and Bonham	Naon and Cornille	Duguet (experimental)	This study
E_c	-6.7	-12.4	-9 ± 5.4	-10.5 ± 0.4
$\Delta \bar{V}_{ee}$	-17.2	-18.6	-7.6 ± 7.0	-22.3 ± 0.7
$\Delta \bar{V}_{en}$	$+3.8$	-6.2	-7.3 ± 7.0	$+1.4 \pm 0.7$

The obvious question is whether or not current diffraction experiments can possibly be expected to make reliable predictions about correlation effects. As far as we can tell, assuming that the Peixoto *et al.* data are correct, the answer is a qualified yes in the case of light elements such as Ne. While it is essential in the case of Ne to have values for the scattering quantities beyond $s = 40$ Å^{-1} to recover $\bar{V}_{ee}$ and $\bar{V}_{en}$, we find that we need accurate values only out to $s = 15$ Å^{-1} to recover $\Delta \bar{V}_{en}$ and $\Delta \bar{V}_{ee}$ energies. The accuracy with which relative scattered intensities must be measured simply depends on the magnitude of the difference between experimental and Hartree-Fock values. If the difference is of the order of 10% of the total experimental intensity and if the relative intensity is measured to 0.1% then $\Delta \bar{V}_{en}$ and $\Delta \bar{V}_{ee}$ might be determined experimentally to 10%. Considering the disagreements and uncertainties in currently available theoretical predictions even 10% accuracy would make a significant contribution to our understanding of electron correlation. It is not likely that diffraction experiments will be able to yield results as definitive as those given in this study. On the other hand, it appears that diffraction experiments could produce values better than those currently available from theory. Note that, for an order of magnitude improvement in the error estimate for our $\Delta \bar{V}_{en}$ value in Ne, the individual ionization potentials would all have to be known to an accuracy of 1 meV (i.e., ten times better than currently available values).

TABLE VII. Comparison of predicted ionization energies for high-Z atoms by extrapolation using different methods with the exact values. All values are in eV. The notation used here is the same as in Ref. 16.

State of ionization and atom	Exact value[a]	Fitting to Eq. (6) with $Z_0=14$	Fitting to Eq. (6) with $Z_0=8$	Fitting to Eq. (7) with $Z_0=14$	Fitting to Eq. (7) with $Z_0=8$	$1/Z$
P XIII	611.85	611.83	611.83	611.82	611.82	611.79
S XIV	707.14	707.07	707.06	707.01	707.01	706.98
Cl XV	809.39	809.21	809.18	809.07	809.06	809.05
Cl XIII	656.69	656.68[b]	656.68[c]	656.66[b]	656.66[c]	656.63
Ar XIV	755.73	755.67[b]	755.66[c]	755.61[b]	755.61[c]	755.55

[a] The exact values are from Ref. 16.

[b] Here the value of Z_0 used was 16.

[c] Here the value of Z_0 used was 10.

E. Calculation of electron affinities of H, F, and O from Z expansions

Fits of experimental energies of all the atoms for which data were available in an isoelectronic series, excluding negative ions, were determined. From the He isoelectronic sequence we calculated the nonrelativistic energy of H^- to be 0.52602 a.u. from Eq. (6) while the exact nonrelativistic energy is 0.52775 a.u.. This result is accurate to 0.001 a.u. but not *as accurate as we would have expected from the variance of the fit* (± 0.0000003). It was also discovered that when H^- was included in the fits the variance increased by a factor of 100. Further, it was found that the accuracy of the extrapolated energies of the negative ion improved when more points were used in the fit. We also fitted experimental first ionization energies[16] of isoelectronic species excluding the negative ions to Eqs. (5)–(7), (9), and (10). The ionization potential is the energy difference between two successive states of ionization of the atom $E(Z,N-1)-E(Z,N)$, where $E(Z,N)$ and $E(Z,N-1)$ are the total electronic energies for an atom of atomic number Z with N electrons before and $N-1$ electrons after ionization, respectively. The Z dependence for the ionization potential is, therefore, the same as that for the total electronic energy itself. No relativistic corrections were applied to the experimental ionization potential used since such corrections to the electron affinity are unknown. Note that relativistic corrections to the first ionization potential are of the order of 0.03 eV and we therefore would not expect the corrections to the electron affinity (EA) to be significantly greater. The EA's for the F and O atoms were then obtained by interpolation with a precision of ± 0.01 eV as deduced from the variance of the fit. As in the case of H^- the predicted value for the electron affinity of F^- and O^- were in error by a factor (30) much greater than the precision. In order to determine the source of this problem the high-Z member of the isoelectronic series was omitted from the fitting procedure and was then predicted by extrapolation. In all cases studied, the accuracy and precision for high-Z extrapolations were identical (± 0.01 eV). Variations in the choice of Z_0 did not qualitatively influence these conclusions. A summary of these results are given in Table VII. It is clear, as pointed out by others,[34] that there are problems uniquely associated with negative ions. The values predicted by different fits are given in Table VIII. It is also observed, as pointed out elsewhere,[34,35] that O^- has a negative EA suggesting that O^{2-} is unstable.

The EA for F and O atoms were also determined by calculating the total energies of F^- and O^- and

TABLE VIII. Values of the electron affinity EA for F and O atoms using different fits. The values from the fits are precise to ~0.01 eV.

Remark	EA of F (eV)	EA of O (eV)
$1/Z$	3.17	1.10
Eq. (5)	3.06	0.99
Eq. (6)	3.15	1.10
Eq. (7)	3.10	1.05
Eq. (9)	3.15	1.10
Eq. (10)	3.12	1.13
Exact[a]	3.445±0.005	1.46

[a] H. S. W. Massey, *Negative Ions* (Cambridge University Press, Cambridge, 1976), 3rd ed., pp. 31–65.

TABLE IX. Improved values for cetain ionization energies in Moore's tables as deduced from Eq. (6). All entries are in eV.

Entry[a]	Value in Moore's table	Suggested improved value
Ar XVI	918±1	918.61±0.01
K XVI	968±1	966.65±0.01
K XVII	1034±1	1034.81±0.04
Ca XVI	974±1	974.76±0.01
Ca XVII	1087±1	1085.47±0.01
Ca XVIII	1157±1	1157.97±0.02

[a] The notation used here is the same as in Ref. 16.

using the nonrelativistic experimental total energies of the neutral atoms. The difference in the total energy of the neutral atom and the negative ion is the electron affinity. The total energy of F^- was obtained by fitting the experimental total energies of the Ne isoelectronic sequence to Eqs. (5)–(7), (9), and (10). Similarly the F isoelectronic sequence was used to determine the total energy of O^-. The procedure, however, is subject to numerical difficulties because the electron affinity is a small difference between two large numbers. Although the results were essentially the same, the estimated precision was much larger (±0.3 eV) not only for the negative ion extrapolations but also for high-Z ionization potential extrapolations. Hence, we can conclude that, for the purpose of obtaining accurate estimates of high-Z ionization potentials by extrapolation, fits of ionization energies rather than total energies should be used, and that none of the studied methods are capable of predicting accurate values for electron affinities.

F. Determining more accurate estimates for some ionization energies

Fitting the experimental ionization energies of isoelectronic species can be used to determine, by extrapolation, improved values of ionization potentials for some high-Z ions. We believe that in certain cases our predictions are more reliable than those currently included in Moore's tables. As pointed out in Sec. IV E high-Z extrapolations to determine the next ionization potential in a series can be made with accuracies on the order of ±0.01 eV. We picked out those cases in Moore's table where all but one listed experimental value in an isoelectronic series of ionization potentials were given to an estimated accuracy of ±0.01 eV or better while the accuracy of the final high-Z member was given to only ±1.0 eV. We then used our fitting procedures to predict improved values for the final listed member of each series. Our recommendations for improved values are given in Table IX.

V. CONCLUSIONS

In summary, we conclude that other Z expansions, notably that in Eq. (6), offer equivalent or better fits to isoelectronic energies compared to the usually employed $1/Z$ expansions. We also propose that Z-expansion fits be used to decompose total energies into the constitutent parts $\bar{V}_{ee}$, $\bar{V}_{en}$ for the purpose of studying electron correlation contributions. Equation (6) appears capable of better than ±0.7 eV accuracy for such a purpose in the case of Ne. For Ne we predict the correlation corrections to $\bar{V}_{en}$ and $\bar{V}_{ee}$ to be $\Delta\bar{V}_{ne}=+1.4\pm0.7$ eV and $\Delta\bar{V}_{ee}=-22.3\pm0.7$ eV. These results are in better qualitative agreement with those derived from Ref. 28 than with the theoretical results of Naon and Cornille and the experimental results of Duguet.

All expansions yield excellent estimates of extrapolated positive ionization potentials from fits of experimental isoelectronic ionization potentials (±0.01 eV). Predictions of electron affinities from fits of total energies or ionization potentials appear to be unreliable by as much as 0.3 eV by any of the methods studied here.

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$$\bar{V}_{ne}(Z)=\bar{V}_{ee}(Z_0)+\sum_{l=0}^{\infty}\frac{\bar{V}_{en}^{l}(Z_0)}{l!}\times\int_{Z_0}^{Z}d\xi\left[2\frac{(\xi-Z_0)^{l}}{\xi}-l(\xi-Z_0)^{l-1}\right].$$

Binomial expansion of the two terms in the large parentheses does not contain terms proportional to ξ. Hence $\bar{V}_{ee}(Z)$ is devoid of terms proportional to Z^2.

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