

Relationes

A Relationship between Correlation Energies and Sizes: The Helium-Like Ions

Fernando Bernardi

Laboratorio CNR dei Composti del Carbonio contenenti eteroatomi, Ozzano E., Bologna, Italy

Imre G. Csizmadia

Department of Chemistry, University of Toronto, Ontario, Canada

Vedene H. Smith, Jr., M. H. Whangbo, and Saul Wolfe

Department of Chemistry, Queen's University, Kingston, Ontario, Canada

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The correlation energy (E_{corr}) is found to be inversely proportional to the product of the electron pair size ($\langle r^2 \rangle$) and the square of the effective nuclear charge (Z_{eff}) for the helium-like ions.

Key words: Helium-like ions – Correlation energies for helium-like ions

The correlation energy (E_{corr}) of an atomic or a molecular system is conveniently defined as the difference between the non-relativistic (E_{NR}) and the Hartree-Fock (E_{HF}) energies [1].

$$E_{\text{corr}} = E_{\text{NR}} - E_{\text{HF}} \quad (1)$$

For an isoelectric series, it has been observed [2, 3] that absolute values of correlation energies increase with increasing atomic number Z . For instance, $|E_{\text{corr}}|$ is larger for Ne^{8+} than it is for He. Another interesting observation made by Sinanoğlu and Pamuk [3] is that correlation energies of hydrocarbon isomers, in which there is no change in nuclear charges, are not the same. They interpreted this phenomenon in terms of changes in the volumes available for the electrons. It seems therefore that the correlation energies of an isoelectronic series should depend not only on Z but also on the volume occupied by the electrons. The purpose of the present investigation is to determine the nature of this relationship.

In this report we consider the simplest isoelectronic series, the helium-like ions in their ground states ($1S$).

To have a quantitative relation between correlation energy and the volume occupied by electrons, it is necessary to employ a rigorous definition of the volume. We choose the definition of *size* of an electron pair [4] which embodies the notion of the spatial extent of the charge distribution. The size is defined as the expectation value of the spherical quadratic operator, r^2 , (*viz.* $\langle r^2 \rangle$), for the helium-like ions.

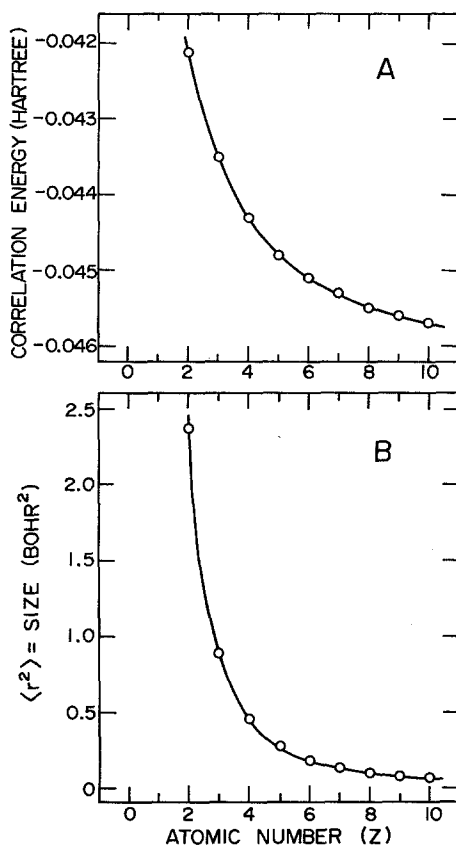


Fig. 1 A and B. Variation of correlation energy (A) and size (B) of He-like ions with their atomic numbers

In the following we will derive a simple empirical relationship between E_{corr} , Z , and $\langle r^2 \rangle$. It seems reasonable to suppose that the correlation interaction should increase as the volume occupied by an electron pair decreases [3], and that the size of an electron pair decreases with the increase in Z . In Fig. 1 A the dependence of E_{corr} on Z is shown. The hyperbolic behaviour of this relationship suggests that E_{corr} may be expanded in a power series of Z^{-1} , i.e., in terms of $\{Z^{-n}\}$. The first few terms of such an expansion can be written¹ as follows [5, 6].

$$E_{\text{corr}} = -0.04666326 + 0.00975430 Z^{-1} - 0.00042443 Z^{-2} + \dots \quad (2)$$

The relationship between $\langle r^2 \rangle$ and Z is shown in Fig. 1 B for the He-like ions. The hyperbolic behaviour of this relationship again suggests that $\langle r^2 \rangle$ can be expanded in terms of $\{Z^{-n}\}$. However, it is more appropriate to use $Z^2 \langle r^2 \rangle$ for the expansion, where $Z^2 \langle r^2 \rangle$ is the expectation value of the Z -scaled second moment operator $(Zr)^2$, since an electron coordinate r is scaled by Z in a given

¹ We employ atomic units throughout this paper.

isoelectronic series. This is particularly clear in the case of the hydrogen-like ions [7] for which the wavefunction includes Z explicitly.

$$\phi_{1s}(r) = \left(\frac{Z^3}{\pi}\right)^{\frac{1}{2}} e^{-Zr}. \tag{3}$$

The expansion of $Z^2 \langle r^2 \rangle$ is written as follows [6]

$$\begin{aligned} Z^2 \langle r^2 \rangle = & 6.0 + 4.7812500 Z^{-1} + 3.1005598 Z^{-2} \\ & + 1.9562260 Z^{-3} + \dots \end{aligned} \tag{4}$$

Multiplication of Eqs. (2) and (4) leads to the following expression

$$\begin{aligned} E_{\text{corr}} Z^2 \langle r^2 \rangle = & -0.27997956 - 0.16458291 Z^{-1} \\ & - 0.10059106 Z^{-2} \dots \end{aligned} \tag{5a}$$

which converges too slowly to have practical utility. A significant improvement is obtained by replacing Z by the effective nuclear charge Z_{eff} . This is a logical modification because the nuclear charge felt by an electron is not the nominal nuclear charge Z . An effective nuclear charge Z_{eff} may be chosen in such a way that in Eq. (5b), which is formally the same as (5a), the first term A will dominate and the coefficient of all subsequent terms ($B, C \dots$ etc.) will be negligible.

$$E_{\text{corr}} Z_{\text{eff}}^2 \langle r^2 \rangle = A + B Z_{\text{eff}}^{-1} + C Z_{\text{eff}}^{-2} + \dots \tag{5b}$$

The effective nuclear charge is defined as the nominal charge Z minus the screening due to all the other electrons. Its traditional definition is

$$Z_{\text{eff}} = (Z - \sigma) \tag{6}$$

which also serves as the basis of Slater's Rules [8]. In Eq. (6) σ is called the screening constant.

Our objective is, therefore, to choose σ in such a way that the product $E_{\text{corr}}(Z - \sigma)^2 \langle r^2 \rangle$ will be as constant as possible for the isoelectronic series. It is convenient to denote this product by the quantity $K(\sigma)$

$$K(\sigma) = E_{\text{corr}}(Z - \sigma)^2 \langle r^2 \rangle. \tag{7a}$$

Values of σ may be obtained in several ways. In one, we note that optimization of the total energy with respect to σ results in $\sigma_E = 5/16 = 0.3125$ for the helium-like ions [9]. In a second, the choice of Z_{eff} is made in such a way that the coefficient of the Z_{eff}^{-1} term in the expansion of $E_{\text{corr}} \langle Z_{\text{eff}}^2 r^2 \rangle$ vanishes. For this we obtain from Eq. (5a)

$$\begin{aligned} K_{\text{eff}} & \equiv E_{\text{corr}} \langle Z_{\text{eff}}^2 r^2 \rangle \\ & = -0.27997956 - 0.02802986 Z_{\text{eff}}^{-2} \dots \end{aligned} \tag{8}$$

wherein the corresponding screening constant, σ_{eff} , is 0.293920. It should be noted that this σ_{eff} is similar to the energy optimized value, $5/16$, and that Eq. (8) now quickly converges with increase in Z . A third procedure involves a statistical analysis of $K(\sigma)$, computed for helium-like ions of different Z values, with a

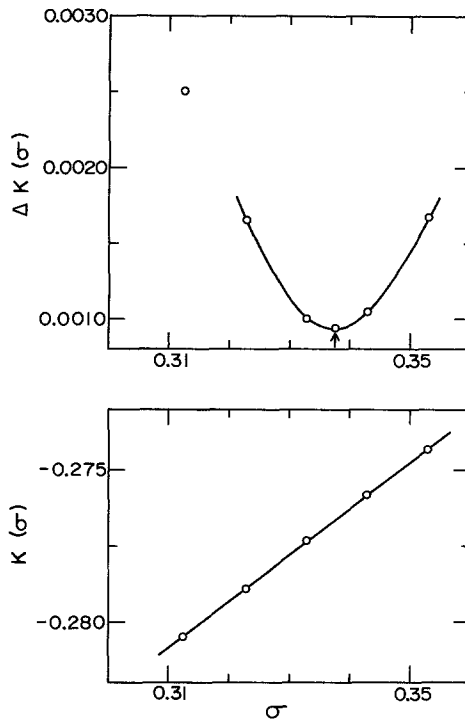


Fig. 2. Variation of $K(\sigma)$ and $\Delta K(\sigma)$ with σ as computed from $\langle r^2 \rangle_{\text{corr}}$

Table 1. K and ΔK values computed for the helium-like ions ($2 \leq Z \leq 8$) for various σ values

σ	K	ΔK
5/16	-0.280534	0.002514
(5/16 + 6/18)/2	-0.278926	0.001652
6/18	-0.277338	0.001003
(6/17 + 6/18)/2	-0.275846	0.001048
6/17	-0.274370	0.001671

simultaneous variation of σ . Minimization of the standard deviation in $K(\sigma)$, denoted by $\Delta K(\sigma)$, permits a choice of the best possible value for σ .

Table 1 collects the K values and the corresponding standard deviations for σ values between 0.3 and 0.4, and these results are illustrated in Fig. 2. The data were obtained by employing the correlation energies for the helium-like series ($2 \leq Z \leq 8$) given by Clementi [10] and the size values for the $1s^2$ pair computed by Knight and Scherr [11] using correlated wavefunctions. It can be seen that σ values between 0.3 and 0.4 yield a fairly constant product as judged from the standard deviation. The optimum value of the screening constant $\sigma_{\text{opt}}(\text{corr})$, i.e., the value which corresponds to the minimum standard deviation is 0.337541 and the corresponding average $K = -0.276698$.

Table 2. Correlation energies computed using $\langle r^2 \rangle_{\text{corr}}$ and $\langle r^2 \rangle_{\text{HF}}$ in Eq. 7b

Z	$\langle r^2 \rangle_{\text{corr}}^a$	$\langle r^2 \rangle_{\text{HF}}^b$	E_{corr}^c	E_{corr}^d	E_{corr}^e
2	2.3870	2.36960	-0.0421	-0.0419	-0.0420
3	0.89256	0.89036	-0.0435	-0.0437	-0.0437
4	0.46414	0.46365	-0.0443	-0.0444	-0.0444
5	0.28394	0.28376	-0.0448	-0.0448	-0.0448
6	0.19148	0.19140	-0.0451	-0.0451	-0.0451
7	0.13781	0.13778	-0.0453	-0.0452	-0.0452
8	0.10391	0.10389	-0.0455	-0.0454	-0.0454

^a Reference [11].

^b Banyard, K. E., Baker, C. C.: J. Chem. Phys. **51**, 2680 (1969)

^c Reference [10].

^d Obtained by using $K = 0.276698$, $\sigma_{\text{opt}}(\text{corr}) = 0.337541$ and $\langle r^2 \rangle_{\text{corr}}$.

^e Obtained by using $K = 0.27725394$, $\sigma_{\text{opt}}(\text{HF}) = 0.330672$ and $\langle r^2 \rangle_{\text{HF}}$.

From Eq. (7b)

$$E_{\text{corr}} = \frac{K}{(Z - \sigma)^2 \langle r^2 \rangle} \quad (7b)$$

with $\sigma = \sigma_{\text{opt}}(\text{corr})$ and $K = -0.276698$ the correlation energies for the helium-like ions can be computed to within one percent from the exact $\langle r^2 \rangle$, (i.e., $\langle r^2 \rangle_{\text{corr}}$) values, as can be seen in Table 2. However, there is a paucity of second moments computed from correlated wavefunctions, $\langle r^2 \rangle_{\text{corr}}$, whereas the corresponding values computed from Hartree-Fock wavefunctions, $\langle r^2 \rangle_{\text{HF}}$, are available for many neutral atoms, various ions and some molecular systems. It was therefore of interest to determine the effect on the above relationship caused by the use of $\langle r^2 \rangle_{\text{HF}}$. For this reason the computations of K for $2 \leq Z \leq 8$ were repeated at various values of σ with $\langle r^2 \rangle_{\text{HF}}$. These revealed that, for the same value of σ , the standard deviations are slightly smaller than those which resulted from use of $\langle r^2 \rangle_{\text{corr}}$. The optimum σ value in this case is $\sigma_{\text{opt}}(\text{HF}) = 0.330672$, and the corresponding $K = -0.277254$.

With these values Eq. (7b) provides correlation energies for the helium-like series which deviate by less than one percent from the exact values (see Table 2).

It is interesting to note that Fröman [12] has suggested a simple empirical relationship between E_{corr} , Z , and $\langle r_{12}^{-1} \rangle_{\text{HF}}$ which may be rewritten in a form similar to that of Eq. (7b), i.e.,

$$E_{\text{corr}} = -\frac{0.070702}{(Z - 0.32115)} \langle r_{12}^{-1} \rangle_{\text{HF}} \quad (8)$$

Extension of these empirical relationships to many-electron systems is now in progress.

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Prof. Dr. V. H. Smith, Jr.
Department of Chemistry
Queen's University
Kingston, Canada
K7L 3N6