Theoret. Chim. Acta (Berl.) 57, 179–180 (1980)

THEORETICA CHIMICA ACTA

Short Communication

Isoelectronic Changes in Total Hartree–Fock Energy of Atoms

K. D. Sen[*]

Institut fur Physikalische Chemie, Physikalische Chemie III, Technische Hochschule Darmstadt, D-6100 Darmstadt, Federal Republic of Germany

It is shown numerically that to a reasonably good accuracy, the isolectronic changes in total Hartree–Fock energy of atomic systems can be predicted, in terms of the energy ratio between the adjacent members in a given isoelectronic series, simply as a function of atomic numbers.

Key words: Isoelectronic changes in Hartree–Fock energy – Hartree–Fock energy of atoms.

Recently, two approximate energy density functionals proposed by Politzer [1] and Levy [2], respectively, have been used to derive [3] a very simple relationship involving only the atomic numbers to predict the total Hartree–Fock (HF) energy in the neighbouring atomic systems. The relationship is given by

$$\frac{E_B}{E_A} \approx \frac{Z_B(Z_A - 7Z_B)}{Z_A(Z_B - 7Z_A)}, \tag{1}$$

where E and Z denote the total HF energy and the atomic numbers, respectively, and the subscripts A and B refer to two isoelectronic atomic systems such that $Z_A = Z_B + 1$. For example, considering Ne-like ions in ground state, if B represents Ne with $Z_B = 10$ then A would refer to Na^+ with $Z = 11$. The purpose of this note is to numerically test the general validity of Eq. (1). For this purpose we have chosen the Ne and Ar-like ions in ground state and Ne^+ and Ar^+-like ions in which an electron is removed from the various orbitals one by one, respectively. The calculations of E have been carried out in each case using the numerical HF

---

[*] Alexander von Humboldt Fellow, on leave from School of Chemistry, University of Hyderabad, India.

Table 1. Comparison of the energy ratio predicted from Eq. (1), given in the last column with the actual HF values. Ground states for Ne and Ar are given by $1s^22s^22p^6$ and $1s^22s^22p^63s^23p^6$ respectively. Hole-states are represented as − 1 over the active orbital

El. conf. / Ions[a]	Ground st.	$1s^{-1}$	$2s^{-1}$	$2p^{-1}$	$3s^{-1}$	$3p^{-1}$	Eq. (1)
F^-/Ne	0.7737	0.7713	0.7777	0.7777			0.7820
Ne/Na^+	0.7951	0.7960	0.7990	0.7988			0.8005
Na^+/Mg^{2+}	0.8131	0.8123	0.8162	0.8165			0.8162
Mg^{2+}/Al^{3+}	0.8280	0.8280	0.8310	0.8310			0.8296
Cl^-/Ar	0.8724	0.8703	0.8735	0.8738	0.8731	0.8731	0.8751
Ar/K^+	0.8795	0.8777	0.8806	0.8809	0.8802	0.8802	0.8815
K^+/Ca^{2+}	0.8859	0.8844	0.8870	0.8873	0.8867	0.8867	0.8872
Ca^{2+}/Sc^{3+}	0.8918	0.8905	0.8928	0.8930	0.8925	0.8925	0.8924

[a] For the hole-states, an additional positive charge should be considered. Energies refer to the average over multiplets

program [4]. In Table 1 we have listed the values of the ratio E_B/E_A as calculated from the actual HF energy values and Eq. (1), respectively. Eq. (1) is found to be in general a good approximation. Its practical utility in predicting the ionization energy, however, is limited [5] due to the deviations in the energy ratio corresponding to the hole-states with respect to the parent system in the ground state. Nevertheless, within a given isoelectronic series, Eq. (1) can be used to obtain reasonably good approximations of E, simply from the knowledge of energy E of just one member and the relevant atomic numbers in the isoelectronic series under consideration.

Acknowledgement. The author is grateful to Prof. Dr. Alarich Weiss for encouragement.

References

1. Politzer, P.: J. Chem. Phys. **64**, 4239 (1976)
2. Levy, M.: J. Chem. Phys. **68**, 5298 (1978)
3. Sen, K. D.: J. Chem. Phys. **70**, 5334 (1979)
4. Froese Fischer, C.: The Hartree–Fock method for atoms. New York: J. Wiley 1977
5. The ratio of ionization energy for the inner shells approximately follows Eq. (1). For example, in the case of 1s electron in Ne series, the actual HF values are F^-/Ne = 0.7811, Ne/Na^+ = 0.7993, Na^+/Mg^{2+} = 0.8156 and Mg^{2+}/Al^{3+} = 0.8299 which should be compared with the predicted values of 0.7820, 0.8005, 0.8162 and 0.8296 respectively. The ratio of ionization energy for the outer shells deviates considerably from Eq. (1), particularly in the small Z region

Received June 20, 1980