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Isoelectronic changes in X-alpha theory using a Z-transition state approach

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Using a simple geometrical interpretation based on the Z-perturbation theory and the Hellman–Feynman theorem a Z-transition method is proposed for the calculation of total electronic energy difference of ions with respect to the isoelectronic neutral atoms. The method is particularly useful within the X-alpha like models wherein the negative ions are known to be inaccessible.

Key words: Local density functional theory — Negative ions

1. Introduction

Stillinger and coworkers [1] have analysed the total electronic energy $E(Z)$ as a function of Z within a given isoelectronic series of atoms and have discussed the role of correlation energy in the series. Levy [2] has shown that the exact relationship

$$E_B - E_A = \int_{Z_A}^{Z_B} \int \rho(r, Z)/r \, dr \, dZ \tag{1}$$

where $E_B - E_A$, to be denoted as ΔE, refers to the change in total electronic energy in going from an atom A with atomic number, Z_A, to the isoelectronic atom B with atomic number $Z_B(=Z_A+1)$, can be replaced by using the mean value theorem according to

$$\int \int \rho(r, Z)/r \, dr \, dZ = (Z_B - Z_A) \int \rho(r, \bar{Z})/r \, dr \tag{2}$$

where $\rho(r, \bar{Z})$ is the density for some nuclear charge between Z_A and Z_B. The approximation of the arithmetic mean

$$\rho(r, \bar{Z}) = 0.5[\rho_A(r) + \rho_B(r)] \tag{3}$$

led [2] to very satisfactory numerical estimates of ΔE.

The purpose of this paper is to associate a conceptually simple geometrical meaning to the result due to Levy [2] and suggest that the former leads to a new method of obtaining approximate isoelectronic changes in E within the local density functional (LDF) theory [3]. In particular, we show that E for the isoelectronic negative ions can be reliably calculated relative to the neutral atom. Such calculations are normally out of bounds of the LDF theories as negative ions are found to be unstable [4] unless the self interaction correction are properly included [5].

2. Method and calculations

We assume that the Lowdin Z-expansion [6] holds continuously in the region $Z_A \rightarrow Z_B$ and consider only the first three terms in the series as given by

$$E(Z) = a_0 Z^2 + a_1 Z + a_2 + \cdots \tag{4}$$

It has been shown [7] that the higher order terms are not significant and that within a given Z an extremely convergent series can be formed just containing the first three terms in Eq. (4). Under this assumption the variation of $E(Z)$ as a function of Z has been shown in fig. 1. Defining a Z-transition state at Z' given by $0.5(Z_A + Z_B)$ we obtain

$$\Delta E = (dE/dZ)_{Z'} = \langle 1/r \rangle_{Z'} \tag{5}$$

The last identity follows directly from the Hellman-Feynman theorem [8]. Eq. (4) is reminiscent of the well-known concept of Slater transition state [9] related to the continuous variation of E with the number of electrons, n_i, in the ith one

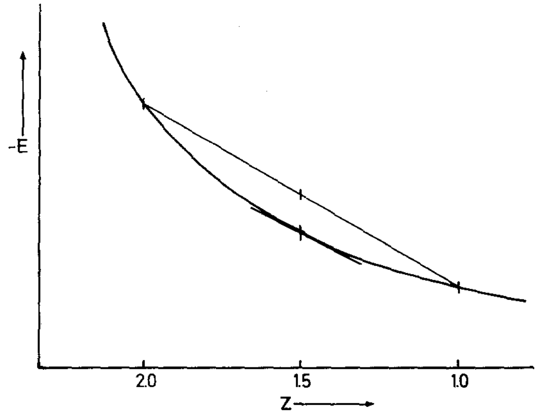

Figure 1

electron orbital wherein the slope at the intermediate transition state is calculated in terms of another one electron property in X-alpha theory namely the one electron eigenvalue which has the following significance

$$\varepsilon_i = (dE/dn_i) \tag{6}$$

In Eq. (5), the one electron property beomes $\langle 1/r \rangle$ evaluated at the intermediate Z. We note here that the variation of $\langle 1/r \rangle$ as a function of Z in the vicinity of integral Z values has been studied earlier by Levy [10] in the context of the discontinuous density functionals.

We have calculated the values of ΔE according to Eq. (5) for a number of atoms. For each calculation of ΔE, the self-consistent-field (SCF) calculations using the X-alpha potential were carried out corresponding to the suitable Z value as defined in Eq. (5). For example, Z is chosen to be 5.5 if E for B is to be calculated with respect to the energy of C atom. The integrals $\langle 1/r \rangle$ were evaluated using the finite difference method which includes the differences up to fourth. Our results have been presented in Table 1 along with the estimates of ΔE based on the Hartree–Fock (HF) calculations [11]. A comparison of the two sets of results shows that Eq. (5) provides a reliable approximation to ΔE within the local density functional of X-alpha type. The only case of slight disagreement is found in the $Cl \rightarrow S^-$ pair and this might be due to insufficient flexibility in the basis set chosen in the HF calculation of S^- ion [11]. The estimates based on Eq. (5) are obtained by means of a single SCF calculation performed on a well defined Z-transition state which is computationally more attractive than the conventional SCF method [12]. In addition the energy difference is obtained directly in terms of the electron density corresponding to the transition state. Indeed, we find a

Table 1. A comparison of the values of ΔE as calculated using the Z-transition method with the Hartree–Fock estimates for atoms. The value of Z corresponding to the transition state is given in column 2. All values are in a.u.

Atoms	Z'	$\langle 1/r \rangle_Z$	ΔE^{HF}
$C \rightarrow B^-$	5.5	13.16	13.17
$C \rightarrow N^+$	6.5	16.19	16.20
$N \rightarrow C^-$	6.5	16.66	16.69
$N \rightarrow O^+$	7.5	19.95	19.97
$O \rightarrow N^-$	7.5	20.47	20.49
$O \rightarrow F^+$	8.5	24.02	24.02
$F \rightarrow O^-$	8.5	24.62	24.62
$F \rightarrow Ne^+$	9.5	28.42	28.41
$P \rightarrow Si^-$	14.5	51.83	51.83
$P \rightarrow S^+$	15.5	56.46	56.45
$S \rightarrow P^-$	15.5	56.82	56.81
$S \rightarrow Cl^+$	16.5	61.57	61.54
$Cl \rightarrow S^-$	16.5	61.97	61.73
$Cl \rightarrow Ar^+$	17.5	66.81	66.80

lot of similarities between the transition potentials corresponding to the Slater and the present Z-transition state calculations respectively.

Several interesting applications of Eq. (5) can be considered. At smaller ΔZ values it is possible to calculate the isoelectronic energy changes in the speculated quark atoms defined by atomic number increments $\pm 1/3$, and $\pm 2/3$ relative to the integral values. It would be also interesting to combine the concept of Z-transition state with the conventional Slater transition state to calculate isoelectronic changes in a given electronic transition, in other words utilize the approximately paraboloid nature of the $E(Z, n_i)$ surface. Such calculations would be particularly useful in the cases of negative ions. In conclusion, we have shown that the simple geometric interpretation of Eq. (4) as in Fig. 1 enlarges the scope of application of the existing approximate atomic local density functionals to the negative ions as far as the calculations of E are concerned.

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References

1. Stillinger FH (1966) J Chem Phys 45:3623; Stillinger FH, Stillinger DK (1974) Phys Rev 10:1109; Stillinger FH, Weber TA (1974) Phys Rev 10:1122; Stillinger FH, Weber TA (1975) J Chem Phys 62:4360
2. Levy M (1978) J Chem Phys 68:5298
3. Parr RG (1984). In: Dahl JP, Avery J (eds) Local density approximations in quantum chemistry and solid state physics. Plenum Press, New York-London
4. Shore HB, Rose JH, Zaremba E (1977) Phys Rev B15:2858; Schwarz K (1978) Chem Phys Lett 57:605
5. Sen KD (1980) Chem Phys Lett 74:201
6. Löwdin PO (1959) J Mol Spectosc 3:46
7. Levy M (1979) J Chem Phys 70:1573
8. Hellman H (1937) Quantenchemie. Deuticke, Leipzig, p 285; Feynman RP (1939) Phys Rev 56:340
9. Slater JC (1974) The self-consistent field for molecules and solids. McGraw-Hill, New York
10. Levy M (1982) J Chem Phys 77:3140
11. Clementi E, Roetti C (1974) At Data Nucl Data Tables 14:177
12. Bagus PS (1965) Phys Rev 139:619