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Isoelectronic changes in energy of quark atoms and molecules via the Levy equation

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Summary. Z-transition state calculations based on the Levy equation suggest that the isoelectronic changes in energy of quark atoms, Q, (ordinary atoms with extra nuclear charge in units of $\pm 1/3$ and/or $\pm 2/3$) can be expressed quantitatively in terms of the electrostatic potential at the nucleus of an isoelectronic ordinary atom. Numerical tests within the local density functional theory are presented for the quark atoms of Li–F. The *ab initio* MO (molecular orbital) calculations using STO-5G basis on the C_2 molecule and its quark derivatives lead to similar conclusions.

Key words: Quark atoms and molecules—Levy equation—Isoelectronic energy changes

Quark atoms, Q, are defined [1] as the ordinary atoms with extra nuclear charge in units of $\pm 1/3$ and $\pm 2/3$, respectively. The estimates of isoelectronic changes in the energy ΔE_Q^{iso}. of quark atoms pairs $Q(\pm 1/3)$ and/or $Q(\pm 2/3)$ would be useful in understanding physical and chemical changes involving these atoms. The purpose of this paper is to show that the Levy equation [2] can be used to obtain reliable estimates of ΔE_Q^{iso} directly from the electrostatic potential at the nucleus, $\langle 1/r \rangle$, of an isoelectronic, ordinary atom. These arguments can be extended to calculate the isoelectronic change in energy of quark molecules which are defined as ordinary molecules with one or more atoms replaced by the quark atoms.

Within an isoelectronic series of atoms containing N electrons the variation in total energy E is related to the electrostatic potential at the nucleus, $\langle 1/r \rangle_N$, according to the Hellman–Feynman theorem as

$$\left(\frac{\partial E}{\partial Z}\right) = \left\langle \frac{1}{r} \right\rangle_N. \tag{1}$$

Levy [2] has shown that for adjacent members in the series defined by the atomic numbers Z_A and $Z_B(=Z_A+1)$, respectively, the isoelectronic change in energy ΔE^{iso} is given by

$$E_B - E_A = \frac{\Delta Z}{2}\left[\left\langle\frac{1}{r}\right\rangle_{Z_A} + \left\langle\frac{1}{r}\right\rangle_{Z_B}\right] \tag{2}$$

In subsequent papers, Levy et al. [3] have used the recursion relationship

$$E(K+1, N) - E(K-1, N) = -2\int dr\, r^{-1}\varrho(r, K, N) \tag{3}$$

where ϱ denotes the one electron density function. Kumar and Sen [4] have used the Levy equation, Eq. (3), with half integral Z^* in the following form

$$E(Z^*+0.5, N) - E(Z^*-0.5, N) = \int dr\, r^{-1}\varrho(r, Z^*, N) \tag{4}$$

to calculate the isoelectronic changes in ordinary atoms of Li–Ar within the $X\alpha$-theory [5]. Due to its resemblance to the concept of the Slater transition state [5] (STS), the method of calculations of ΔE^{iso} defined by Eq. (4) is called the Z-transition state (ZTS) method. Very recently, it has been shown [6] that the ZTS method gives excellent estimates of ΔE_{iso} in ordinary atoms and molecules. As an illustration of the computational steps involved in the ZTS method we consider the isoelectronic process $\text{Ne} \rightarrow \text{Na}^+$. The value of ΔE^{iso} is obtained by carrying out an SCF calculation on a fictitious atom with the nuclear charge $Z^* = 10.5$ in the electronic configuration $(1s^2 2s^2 2p^6)$. The calculated value of $\langle 1/r \rangle$ gives the estimate of ΔE^{iso} according to Eq. (4). A similar calculation of $\langle 1/r \rangle$ with $Z^* = 9.5$ gives the energy of the process $\text{Ne} \rightarrow \text{F}^-$. In the molecular calculations corresponding to the process $\text{C}(-2/3)\text{–C}(-2/3) \rightarrow \text{C}(-2/3)\text{–C}(+2/3)$ the electrostatic potential at the ordinary carbon atom in $\text{C}(-2/3)\text{–C}$ gives ΔE^{iso}. The nuclear center at which the nuclear charge undergoes a change in the isoelectronic process will be denoted as the active nucleus. The molecular calculations are carried out at a fixed geometry.

In this paper we show how the ZTS method is particularly useful in the calculation of ΔE_Q^{iso} of the quark atoms and molecules. We first consider the isoelectronic processes involving the quark atoms pairs $[Q(+1/3) \rightarrow Q(-1/3)]$ and $[Q(+2/3) \rightarrow Q(-2/3)]$, respectively. Equation (4) then assumes the form

$$\Delta E_Q^{\text{iso}}(\pm 1/3) = 2/3 \int dr\, r^{-1}\varrho(r, Z, N) \tag{5}$$

and

$$\Delta E_Q^{\text{iso}}(\pm 2/3) = 4/3 \int dr\, r^{-1}\varrho(r, Z, N) \tag{6}$$

where Z has integral values corresponding to the isoelectronic ordinary neutral atom.

In Table 1, we have calculated the values of total energy for the quark atoms of Li–F using the relativistic self-interaction-corrected (SIC) local spin density

Table 1. Isoelectronic energy changes (ΔE) in the quark atom pair in terms of electrostatic potential at the nucleus of the isoelectronic ordinary atom (ZTS). All values are given in a.u.

Isoelectronic pair	ΔSCF(LSD)	ZTS
[Li(+1/3), Li(−1/3)]	3.8225	3.8214
[Li(+2/3), Li(−3/2)]	7.6305	7.6429
[Be(+1/3), Be(−1/3)]	5.6197	5.6198
[Be(+2/3), Be(−3/2)]	11.2384	11.2396
[B(+1/3), B(−1/3)]	7.6065	7.6068
[B(+2/3), B(−2/3)]	15.2112	15.2135
[C(+1/3), C(−1/3)]	9.8215	9.8217
[C(+1/3), C(−2/3)]	19.6414	19.6433
[N(+1/3), N(−1/3)]	12.2606	12.2607
[N(+2/3), N(−2/3)]	24.5197	24.5214
[O(+1/3), O(−1/3)]	14.8874	14.8876
[O(+2/3), O(−2/3)]	29.7729	29.7752
[F(+1/3), F(−1/3)]	17.7423	17.7423
[F(+2/3), F(−2/3)]	35.4827	35.4847

(LSD) functional including correlation energy developed by Perdew and coworkers [7]. The conventional method of obtaining ΔE_Q^{iso} via the difference of two total energy values [8] is denoted by ΔSCF(LSD). The ZTS estimates of ΔE_Q^{iso} are obtained via an independent calculation of $\langle 1/r \rangle$ corresponding to the isoelectronic neutral atom. The two sets of values are found to be in excellent agreement with each other.

In order to illustrate the utility of Eqs. (5) and (6) we have carried out *ab initio* molecular orbital calculations using GAUSSIAN 86 [9] for C_2 and its quark derivatives. In Table 2 we have compared the values of ΔE_Q^{iso} obtained via the ΔSCF calculations with those based on the electrostatic potential at the

Table 2. A comparison of the ΔSCF calculations of isoelectronic changes in the energy of the quark derivatives of the C_2 molecule with those derived from the Z-transitions using Eqs. (5), (6). All values are in a.u. The band length is kept fixed at 1.3 Å

Isoelectronic pair	ΔSCF	ZTS
C(−2/3)–C(−2/3); C(−2/3)–C(+2/3)	20.1140	20.2749
C(−2/3)–C(−2/3); C(−2/3)–C(+1/3)	10.0464	10.1375
C(−1/3)–C(−2/3); C(−1/3)–C(+2/3)	19.8877	20.0010
C(−1/3)–C(−1/3); C(−1/3)–C(+1/3)	9.9264	10.0005
C–C(−2/3); C–C(+2/3)	19.6461	19.7097
C–C(−1/3); C–C(+1/3)	9.8126	9.8548
C(+1/3)–C(−2/3); C(+1/3)–C(+2/3)	19.3914	19.4065
C(+1/3)–C(−1/3); C(+1/3)–C(+1/3)	9.6921	9.7032
C(+1/3)–C(−1/3); C(+2/3)–C(+2/3)	19.1214	19.7097
C(+2/3)–C(−1/3); C(+2/3)–C(+1/3)	9.5501	9.8548

active nucleus of the C_2 molecule as given by Eqs. (5) and (6), respectively. The two set of values are in good agreement with each other. In the molecular calculations for the quark atoms we have used a Z scaled STO-5G basis using the method described earlier [6]. The prediction, based on Eqs. (5) and (6), that $\Delta E_Q^{\text{iso}}(\pm 2/3) = 2\,\Delta E_Q^{\text{iso}}(\pm 1/3)$ is evident from Tables 1 and 2, respectively. In conclusion, the concept of ZTS via Eqs. (5) and (6) proposed originally by Levy et al. [2, 3] provides the interesting result that the isoelectronic energy changes in quark atoms and molecules can be estimated reliably from the electrostatic potential at the nucleus of an isoelectronic ordinary atom. It is to be noted here that very accurate data on $\langle 1/r \rangle$ for the light atoms and molecules is already available [10, 11] and can be used to obtain the estimates of $\Delta E_Q^{\text{iso}}(\pm 1/3)$ and $\Delta E_Q^{\text{iso}}(\pm 2/3)$, respectively. We are presently extending our calculations of ΔE_Q^{iso} to the polyatomic quark molecules.

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