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Electronegativities and isoelectronic energy and electronegativity differences for monatomic systems with nonintegral nuclear charges: Local-spin-density-functional calculations

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A relativistic self-consistent-field self-interaction-corrected local-spin-density functional, with electronic correlation included, has been used to compute the electronegativities of monatomic systems with nonintegral nuclear charges. We focused specifically upon quark atoms related to the halogens, having nuclear charges of $Z\pm 1/3$. Two different methods for calculating electronegativities were found to give results in good agreement with each other and with an earlier empirical approach. It was also shown that accurate energy and electronegativity differences for the isoelectronic quark-atom pairs $Z+1/3, Z-1/3$ and $Z+2/3, Z-2/3$ can be determined using only the electrostatic potentials at the nuclei of the isoelectronic atoms and ions with integral nuclear charges.

I. INTRODUCTION

In an important recent development, Lackner and Zweig have generalized the concept of electronegativity to quark atoms.[1] The latter are defined as having integral numbers of electrons but nuclear charges that differ by $\pm\frac{1}{3}$ or $\pm\frac{2}{3}$ from integral values. Lackner and Zweig used the Mulliken formula for electronegativity [Eq. (1)],[2] in which I and A denote the ionization potential

$$\chi=\frac{I+A}{2} \tag{1}$$

and electron affinity, respectively, to calculate χ for quark atoms in their ground states. I and A were obtained by isoelectronic interpolation of the experimentally measured values for the neutral atoms.

In density-functional theory, the electronegativity has been defined as[3]

$$\chi=-\left(\frac{\partial E}{\partial N}\right)_Z . \tag{2}$$

The total energy E is treated as a continuous function of the number of electrons N and the nuclear charge Z. Equation (2) has been the basis for a number of quantitative determinations of electronegativities.[4]

In this paper, we shall compare several different approaches for computing the electronegatives of quark atoms. We will also show that energy and electronegativity differences for the isoelectronic quark pairs $Z+\frac{1}{3}$, $Z-\frac{1}{3}$ and $Z+\frac{2}{3}$, $Z-\frac{2}{3}$ can be determined from a single calculation of the electrostatic potential at the nucleus of the isoelectronic neutral atom with nuclear charge Z. As examples, we shall use quark atoms related to the halogens (F, Cl, Br, and I).

II. METHOD

A. Notation

A ground-state monatomic system X with nuclear charge Z will be denoted by $X(0)$. Isoelectronic quark atoms with nuclear charges $Z\pm\frac{1}{3}$ and $Z\pm\frac{2}{3}$ shall be represented by $X(\pm\frac{1}{3})$ and $X(\pm\frac{2}{3})$. Thus $\mathrm{F}(-\frac{1}{3})$ corresponds to a quark with nine electrons in the $1s^2 2s^2 2p^5$ configuration and a nuclear charge of $8\frac{2}{3}$; $F^-(+\frac{2}{3})$ indicates a quark atom with ten electrons ($1s^2 2s^2 2p^6$) and nuclear charge equal to $9\frac{2}{3}$.

B. Computational approach

We have used a relativistic self-consistent-field procedure within the self-interaction-corrected local-spin-density approximation to compute total and orbital energies and electrostatic potentials.[5,6] This method has been used successfully to calculate atomic ionization potentials and electron affinities over a large portion of the periodic table,[5,6] indicating that it is effective in taking account of electron correlation.

C. Calculation of electronegativities

Two approaches were used to compute quark-atom electronegativities. One of these involved the application of Eq. (1), with the ionization potentials and electron affinities being obtained from the calculated total energies of the ionic and nonionized systems. These results shall be denoted by χ_M.

The second method is based upon the concept of the Slater transition state.[7,8] Taking an analogous approach, we expanded the total energy of a quark atom about the energy of E_0 of the neutral atom:

$$E=E_0+\sum_i (n_i-n_{i0})\frac{\partial E}{\partial n_i}+\frac{1}{2!}\sum_{ij}(n_i-n_{i0})(n_j-n_{j0})\frac{\partial^2 E}{\partial n_i\,\partial n_j}+\cdots \;. \tag{3}$$

n_i is the number of electrons in the ith atomic orbital. If δ electrons are transferred from the jth orbital of one atom to the ith of another, the energy difference is

$$E(N+\delta)-E(N-\delta)=\delta\left[\frac{\partial E}{\partial n_i}+\frac{\partial E}{\partial n_j}\right]+O(\delta^2)+\cdots \;. \tag{4}$$

In local-spin-density-functional theory, the energy of orbital i, represented by ε_i, satisfies Eq. (5):

$$\varepsilon_i=-\frac{\partial E}{\partial n_i} \;. \tag{5}$$

Combining Eqs. (2), (4), and (5),

$$\chi=-\left[\frac{\partial E}{\partial N}\right]_Z=-\lim_{\delta\to 0}\frac{E(N+\delta)-E(N-\delta)}{2\delta}\approx\frac{\varepsilon_i+\varepsilon_j}{2} \;. \tag{6}$$

If the same orbital is involved in both the gain and loss of an electron, as is the case for the halogens, then $\varepsilon_i=\varepsilon_j$ and

$$\chi=\varepsilon_i \;. \tag{7}$$

Since the computational approach that we are using does retain the orbital formulation, we can use Eq. (7) to estimate electronegativities. The results shall be represented by χ_S.

In this work, we have calculated χ_M and χ_S for the quark atoms $X(\pm\frac{1}{3})$, where X=F, Cl, Br, and I. In order to obtain χ_M for $X(-\frac{2}{3})$, Eq. (1) would require computing the energies of nearly doubly charged negative ions. Since this presents severe convergence problems in the self-consistent-field procedure, χ_M and χ_S were not calculated for the systems $X(\pm\frac{2}{3})$.

D. Calculation of electronegativity differences

Levy has shown that the energy difference between adjacent members A and B of an isoelectronic atomic series is given rigorously by[9]

$$\Delta E=E_B-E_A=(Z_B-Z_A)V_0^* \;. \tag{8}$$

Z_A and Z_B are the nuclear charges of A and B, and V_0^* is the electrostatic potential at the nucleus of an isoelectronic system with a nuclear charge Z^* that is intermediate between Z_A and Z_B; thus $V_0^*=-\langle 1/r\rangle_{Z^*}$. Levy *et al.* subsequently used a recursion relationship derived from Eq. (8) in studying atomic binding energies and chemical potentials.[10,11] Kumar and Sen modified this relationship by defining[12]

$$Z^*=0.5(Z_A+Z_B) \;. \tag{9}$$

We have recently used Eq. (8) and this definition of Z^* to compute the differences in energy within isoelectronic pairs of atomic and molecular systems.[13] This approach, which requires calculating wave functions and electrostatic potentials for nonintegral nuclear charges, has been called the Z transition state (ZTS) method.[12,13]

For the quark-atom pairs $X(+\frac{1}{3})$, $X(-\frac{1}{3})$ and $X(+\frac{2}{3})$, $X(-\frac{2}{3})$, Eq. (9) gives

TABLE I. Calculated electronegativities, in atomic units, for quark atoms related to the halogens.

Atoms	χ_M [Eq. (1)]	χ_S[a] [Eq. (7)]	χ (Lackner-Zweig)[b]
F$(+\frac{1}{3})$	0.6366	0.6105	0.6077
F(0)	0.4060	0.3848	0.3826
F$(-\frac{1}{3})$	0.2078	0.1914	0.1873
Cl$(+\frac{1}{3})$	0.4700	0.4542	0.4548
Cl(0)	0.3207	0.3052	0.3050
Cl$(-\frac{1}{3})$	0.1880	0.1727	0.1720
Br$(+\frac{1}{3})$	0.4241	0.4137	0.4090
Br(0)	0.2941	0.2823	0.2789
Br$(-\frac{1}{3})$	0.1749	0.1634	0.1605
I$(+\frac{1}{3})$	0.3573	0.3696	0.3631
I(0)	0.2458	0.2567	0.2484
I$(-\frac{1}{3})$	0.1438	0.1531	0.1452

[a] No self-interaction correction was used in calculating χ_S.

[b] Reference 1.

TABLE II. Calculated energy differences for isoelectronic pairs of quark atoms related to halogens. All values are in hartrees.

Atoms A, B	Differences of total calculated energies, $E_B - E_A$	ZTS [Eqs. (12) and (13)]	Eq. (8)[a]
$F(+\frac{1}{3})$, $F(-\frac{1}{3})$	17.7423	17.7423	17.7415
$F(+\frac{2}{3})$, $F(-\frac{2}{3})$	35.4827	35.4847	35.4777
$Cl(+\frac{1}{3})$, $Cl(-\frac{1}{3})$	43.2018	43.2020	43.2011
$Cl(+\frac{2}{3})$, $Cl(-\frac{2}{3})$	86.4020	86.4040	86.3969
$Br(+\frac{1}{3})$, $Br(-\frac{1}{3})$	119.8970	119.8965	119.8555
$Br(+\frac{2}{3})$, $Br(-\frac{2}{3})$	239.7940	239.7930	239.7848
$I(+\frac{1}{3})$, $I(-\frac{1}{3})$	217.2672	217.2649	217.2639
$I(+\frac{2}{3})$, $I(-\frac{2}{3})$	434.5352	434.5298	434.5282

[a] V_0^* is set equal to $0.5(\langle 1/r\rangle_{Z_A} + \langle 1/r\rangle_{Z_B})$.

$$Z^* = 0.5(Z+\tfrac{1}{3}+Z-\tfrac{1}{3}) = Z \qquad (10)$$

and

$$Z^* = 0.5(Z+\tfrac{2}{3}+Z-\tfrac{2}{3}) = Z\ . \qquad (11)$$

Equation (8) then becomes

$$E(Z+\tfrac{1}{3})-E(Z-\tfrac{1}{3}) = (Z+\tfrac{1}{3}-Z+\tfrac{1}{3})V_{0,z} = -\tfrac{2}{3}\langle 1/r\rangle_Z \qquad (12)$$

and

$$E(Z+\tfrac{2}{3})-E(Z-\tfrac{2}{3}) = (Z+\tfrac{2}{3}-Z+\tfrac{2}{3})V_{0,Z} = -\tfrac{4}{3}\langle 1/r\rangle_Z . \qquad (13)$$

Thus the energy differences within these pairs of isoelectronic quark atoms, $X(\pm\frac{1}{3})$ and $X(\pm\frac{2}{3})$, can be expressed in terms of the electrostatic potential at the nucleus of the isoelectronic neutral (nonquark) atom $X(0)$. Furthermore, the energy difference for the pair $X(\pm\frac{2}{3})$ should be twice that of $X(\pm\frac{1}{3})$.

Applying Eq. (2),

$$\chi(Z+\tfrac{1}{3})-\chi(Z-\tfrac{1}{3}) = -\frac{2}{3}\frac{\partial}{\partial N}\left\langle\frac{1}{r}\right\rangle_Z \qquad (14)$$

and

$$\chi(Z+\tfrac{2}{3})-\chi(Z-\tfrac{2}{3}) = -\frac{4}{3}\frac{\partial}{\partial N}\left\langle\frac{1}{r}\right\rangle_Z . \qquad (15)$$

The derivatives on the right-hand sides of Eqs. (14) and (15) shall be approximated by finite differences:

TABLE III. Calculated energy differences for isoelectronic pairs of quark atoms related to halogen ions. All values are in hartrees.

Ions A, B	Differences of total calculated energies, $E_B - E_A$	ZTS [Eqs. (12) and (13)]	Eq. (8)[a]
$F^-(+\frac{1}{3})$, $F^-(-\frac{1}{3})$	18.1021	18.1034	18.0992
$Cl^-(+\frac{1}{3})$, $Cl^-(-\frac{1}{3})$	43.4496	43.4505	43.4476
$Br^-(+\frac{1}{3})$, $Br^-(-\frac{1}{3})$	120.1191	120.1195	120.1164
$I^-(+\frac{1}{3})$, $I^-(-\frac{1}{3})$	217.4599	217.4563	217.4546
$F^+(+\frac{1}{3})$, $F^+(-\frac{1}{3})$	17.2444	17.2443	17.2440
$Cl^+(+\frac{1}{3})$, $Cl^+(-\frac{1}{3})$	42.8857	42.8857	42.8855
$Br^+(+\frac{1}{3})$, $Br^+(-\frac{1}{3})$	119.6207	119.6198	119.6198
$I^+(+\frac{1}{3})$, $I^+(-\frac{1}{3})$	217.0328	217.0300	217.0307

[a] V_0^* is set equal to $0.5(\langle 1/r\rangle_{Z_A} + \langle 1/r\rangle_{Z_B})$.

TABLE IV. Comparison of calculated electronegativity differences, in atomic units, for isoelectronic pairs of quark atoms related to the halogens.

Isoelectronic pair	$\Delta\chi_M$ [Eq. (1)]	$\Delta\chi_S$ [Eq. (7)]	$\Delta\chi_{\mathrm{ZTS}}$ [Eq. (16)]	$\Delta\chi$ (Lackner-Zweig)[a]
$\mathrm{F}(+\frac{1}{3})$, $\mathrm{F}(-\frac{1}{3})$	0.4289	0.4296	0.4191	0.4204
$\mathrm{Cl}(+\frac{1}{3})$, $\mathrm{Cl}(-\frac{1}{3})$	0.2819	0.2842	0.2815	0.2828
$\mathrm{Br}(+\frac{1}{3})$, $\mathrm{Br}(-\frac{1}{3})$	0.2492	0.2499	0.2503	0.2484
$\mathrm{I}(+\frac{1}{3})$, $\mathrm{I}(-\frac{1}{3})$	0.2135	0.2131	0.2165	0.2179

[a] Reference 1.

$$\begin{aligned}\Delta\chi(Z\pm\tfrac{1}{3})&=\chi(Z+\tfrac{1}{3})-\chi(Z-\tfrac{1}{3})\\&=-\frac{2}{3}\left[\frac{\left[\left\langle\frac{1}{r}\right\rangle_{Z,N+1}-\left\langle\frac{1}{r}\right\rangle_{Z,N-1}\right]}{2}\right]\\&=-\frac{1}{3}\left[\left\langle\frac{1}{r}\right\rangle_{Z,N+1}-\left\langle\frac{1}{r}\right\rangle_{Z,N-1}\right], \qquad (16)\end{aligned}$$

$$\begin{aligned}\Delta\chi(Z\pm\tfrac{2}{3})&=\chi(Z+\tfrac{2}{3})-\chi(Z-\tfrac{2}{3})\\&=-\frac{4}{3}\left[\frac{\left[\left\langle\frac{1}{r}\right\rangle_{Z,N+1}-\left\langle\frac{1}{r}\right\rangle_{Z,N-1}\right]}{2}\right]\\&=-\frac{2}{3}\left[\left\langle\frac{1}{r}\right\rangle_{Z,N+1}-\left\langle\frac{1}{r}\right\rangle_{Z,N-1}\right]. \qquad (17)\end{aligned}$$

Equations (16) and (17) can be used to obtain electronegativity differences for isoelectronic pairs of quark atoms.

III. RESULTS AND DISCUSSION

Table I contains our calculated electronegativities χ_M and χ_S for the halogen quark atoms $X(\pm\frac{1}{3})$, obtained using Eqs. (1) and (7), respectively. The values are in good agreement with each other and with the empirical ones of Lackner and Zweig, which were calculated with Eq. (1) and interpolated ionization potentials and electron affinities.[1] These results demonstrate that the density-functional treatment of electronegativity can satisfactorily be extended to atoms with nonintegral nuclear charges.

Table II compares energy differences within the isoelectronic halogen quark pairs $X(\pm\frac{1}{3})$ and $X(\pm\frac{2}{3})$, as computed by (a) taking total energy differences; (b) the ZTS method [i.e., Eqs. (12) and (13)]; and (c) Eq. (8), with V_0^* taken to be $0.5[\langle 1/r\rangle_{Z_A}+\langle 1/r\rangle_{Z_B}]$ as originally suggested by Levy.[9] Both the ZTS approach and Eq. (8) produce energy differences that are extremely close to those obtained directly, the average discrepancies being only 0.002% for the ZTS method and 0.009% for Eq. (8).

Analogous results are presented in Table III for the quark forms of the halogen ions $X^+(\pm\frac{1}{3})$ and $X^-(\pm\frac{1}{3})$. The agreement with the directly calculated energy differences is again excellent, with average discrepancies of 0.002% (ZTS) and 0.004% [Eq. (8)]. It should be noted that the ZTS results presented in Tables II and III involved no new computations, since they require only $\langle 1/r\rangle$ values for nonquark atoms and ions and these are already available.[14,15]

Table IV compares the electronegativity differences $\Delta\chi_M$ and $\Delta\chi_S$ with those calculated by the ZTS approach [Eq. (16)] for the isoelectronic quark pairs $X(\pm\frac{1}{3})$. The Lackner-Zweig predictions are also included. All of these values agree very well with each other. Again, the ZTS electronegativity differences can be obtained from existing $\langle 1/r\rangle$ data.[14,15]

IV. SUMMARY

This paper has demonstrated the feasibility of using local-spin-density-functional theory to compute the electronegativities of monatomic systems with nonintegral nuclear charges. Two different approaches were used and found to produce results that are in good agreement with each other and with an earlier empirical treatment. It was also shown that energy and electronegativity differences within the isoelectronic quark atom pairs $X(+\frac{1}{3})$, $X(-\frac{1}{3})$ and $X(+\frac{2}{3})$, $X(-\frac{2}{3})$ can be obtained accurately from a knowledge only of the electrostatic potentials at the nuclei of the isoelectronic neutral atom $X(0)$ and ions $X^+(0)$ and $X^-(0)$.

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