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Short Communications

Orbital Electronegativity and Electron Affinity of Rare Earth Atoms Using Xα-Theory

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Slater's transition state concept and the relativistic numerical Hartree-Fock-Slater theory has been used to calculate the electronegativity and first ionization potential for the rare earth atoms. Based on these results the electron affinity has also been estimated. The theory predicts almost constant values of the electronegativity as ~2 eV, first ionization potential as ~8 eV and the electron affinity of ~ −(4–5) eV respectively.

Key Words: Rare earth atoms, Electronegativity, Ionization potential.

In a recent review of the binding energy of atomic negative ions Hotop and Lineberger [1] have pointed out that almost nothing is known about the negative ions of the rare earth (RE) elements. Binding energy of the negative ion by definition gives the electron affinity, E_A, of the corresponding neutral atom. Zollweg [2] has made a conservative estimate of E_A for the *RE* atoms as <0.5 eV. The electronegativity, χ, defined by Mulliken [3] as equal to $(I_p + E_A)/2$, where I_p gives the first ionization potential of the atom, ranges between 1.1–1.25 eV within the *RE* series. The purpose of the present communication is to report the results of calculations of χ, I_p, and E_A for the RE atoms Ce–Lu, using the transition state (TS) concept [4] within the relativistic Hartree–Fock–Slater (HFS) Xα theory [5]. In HFS-Xα theory, the one electron eigenvalues ε_i have the significance that

$$-\varepsilon_i = \left(\frac{\partial E}{\partial n_i}\right) \tag{1}$$

This work is dedicated to the memory of Prof. J. C. Slater.

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where E denotes the total electronic energy and n_i gives the orbital occupation number. It can be shown using Eq. (1) that for the transition process wherein the initial occupation numbers in the orbitals ϕ_i, ϕ_j, ... change from n_i, n_j, ... to n_i', n_j'... respectively, the energy of transition is given by [4]

$$\Delta E = \sum_i (n_i' - n_i)\varepsilon_i^{tr}, \tag{2}$$

where the ε_i^{tr}'s denote the Xα-eigenvalues corresponding to a transition state defined by the orbital occupation numbers $(n_i + n_i')/2$, $(n_j + n_j')/2 \ldots$. The predictive power of the method to calculate the first ionization potential [6], the two electron one photon X-ray transition energy [7], the shake up transition energy [8] and the electronegativity [9] of atoms has been tested successfully during the recent years. We note here that the TS results correspond to values averaged over the multiplets. We have used the relativistic numerical Hartree-Fock-Slater program [10], with the option of no Latter correction. The values of the exchange parameter have been taken from the work of Schwarz [11].

For each atom two separate TS calculations corresponding to the I_p and χ respectively have been carried out. For example in the case of Ce the process of ionization can be described by the electronic transition $\mathrm{Ce}(4f^2\,6s^2) \rightarrow \mathrm{Ce}^+(4f^3\,6s^0)$ leading to the TS as $\mathrm{Ce}^{0.5+}(4f^{2.5}\,6s^1)$. According to Eq. (2), I_p is given by $2\varepsilon_{6s}^{tr} - \varepsilon_{4f}^{tr}$. Similarly, the TS corresponding to the calculation of χ for Ce is obtained by considering the electronic configuration intermediate between the configurations $\mathrm{Ce}^+(4f^3\,6s^0)$ and $\mathrm{Ce}^-(4f^3\,6s^2)$ respectively i.e. $\mathrm{Ce}(4f^3\,6s^1)$. Using the Mulliken definition of χ and Eq. (2) it can be shown that χ for Ce is given by the quantity 1/2

Table 1. Values of the first ionization potential, electronegativity, and electron affinity in eV for the rare earth atoms. The two j values of 5/2 and 7/2 are denoted by $-$ and $+$ as the orbital subscripts respectively. For the $5d$ orbital $5d_-$ denotes $5d_{j=3/2}$. The atoms Yb and Lu show deviations due to the participation of the $5d$ orbital instead of the $4f$

	Ionization potential		Electronegativity		
Atom	Transition state	Transition energy	Transition state	Transition energy	Electron affinity
Ce	$4f_-^{2.5}6s^1$	8.73	$4f_-^3 6s^1$	1.80	−5.13
Pr	$4f_-^{3.5}6s^1$	8.36	$4f_-^4 6s^1$	1.84	−4.86
Nd	$4f_-^{4.5}6s^1$	8.10	$4f_-^5 6s^1$	1.90	−4.30
Pm	$4f_-^{5.5}6s^1$	7.89	$4f_-^6 6s^1$	1.93	−4.03
Sm	$4f_+^{0.5}6s^1$	8.24	$4f_+^1 6s^1$	1.96	−4.32
Eu	$4f_+^{1.5}6s^1$	8.17	$4f_+^2 6s^1$	1.95	−4.27
Gd	$4f_+^{2.5}6s^1$	8.16	$4f_+^3 6s^1$	2.02	−4.12
Tb	$4f_+^{3.5}6s^1$	8.15	$4f_+^4 6s^1$	2.00	−4.15
Dy	$4f_+^{4.5}6s^1$	8.27	$4f_+^5 6s^1$	2.01	−4.25
Ho	$4f_+^{5.5}6s^1$	8.39	$4f_+^6 6s^1$	2.03	−4.33
Er	$4f_+^{6.5}6s^1$	8.49	$4f_+^7 6s^1$	2.04	−4.41
Tm	$4f_+^{7.5}6s^1$	8.72	$4f_+^8 6s^1$	2.06	−4.60
Yb	$6s^{1.5}$	6.01	$5d_-^{0.5}6s^{1.5}$	1.85	−2.31
Lu	$5d_-^{1.5}6s^1$	2.45	$5d_-^2 6s^1$	3.87	+5.29

(ε_{6s}^{tr}). Due to the problem of nonconvergence associated with the TS calculation the values of E_A have been obtained according to the relationship $E_A = 2\chi - I_p$.

The numerical values of χ, I_p and E_A obtained in the present work are listed in Table 1. It is found that the results are in agreement with the experimental observation that the χ and I_p values remain almost constant within the rare earth series. The estimate of $E_A \sim -(4-5)$ eV suggests that the negative ions of the rare earth atoms are not likely to be stable. The present approach can be extended to calculate the group electronegativities using multiple scattering Xα theory [12].

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