The Unrestricted Local Properties as a Useful Tool for Nanoelectronics

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Introduction

The local ionization energy (IE_L) introduced by Sjoberg[1] and the local electron affinity (EA_L) introduced by Clark et al.[2] are local properties that are useful for predicting chemical reactivity depending on the electron donating and accepting properties of molecules.[3] EA_L is beginning to be more and more recognized as an important property for nanoelectronics by explaining their essential electronic properties, such as electron transport through molecular wires, direction and dynamics of electron transfer (ET) in donor-acceptor conjugates and most recently[4] a potential energy map for electron transport in self-assembling monolayer field-effect transistors (SAMFETs).[5]

IE_L and EA_L were used so far only to study closed-shell molecular species. Since electrons and/or holes are generated in electronic devices in their operating regimes, open-shell systems should also be studied. Thus, here we implement and use unrestricted Hartree–Fock (UHF) EA_L and IE_L to study electronic properties of several nanosystems.[5]

Theoretical Background

The UHF local electron affinity (UHF–EA_L) at some point **r** is defined as:[5]

$$EA_L^{UHF} = \frac{\sum_{i=N^\alpha+1}^{N_{orbs}} -\rho_i^\alpha(\mathbf{r})\varepsilon_i^\alpha + \sum_{i=N^\beta+1}^{N_{orbs}} -\rho_i^\beta(\mathbf{r})\varepsilon_i^\beta}{\sum_{i=N^\alpha+1}^{N_{orbs}} \rho_i^\alpha(\mathbf{r}) + \sum_{i=N^\beta+1}^{N_{orbs}} \rho_i^\beta(\mathbf{r})} \quad (1)$$

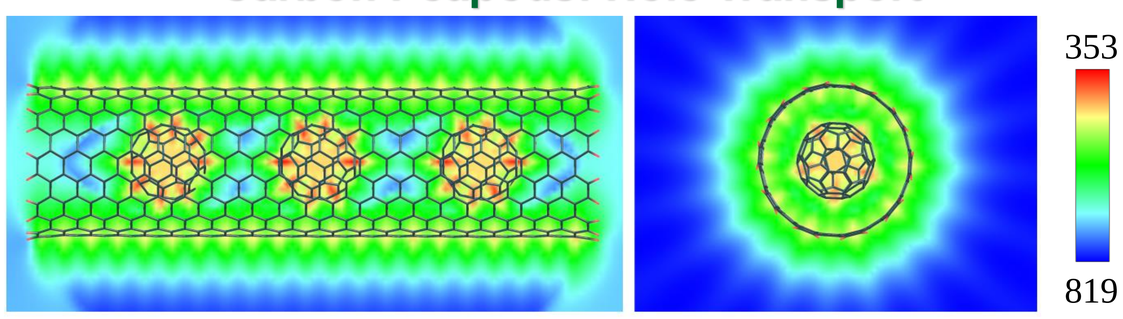
while the UHF local ionization energy (UHF–IE_L) as:

$$IE_L^{UHF} = \frac{\sum_{i=1}^{N^\alpha} -\rho_i^\alpha(\mathbf{r})\varepsilon_i^\alpha + \sum_{i=1}^{N^\beta} -\rho_i^\beta(\mathbf{r})\varepsilon_i^\beta}{\sum_{i=1}^{N^\alpha} \rho_i^\alpha(\mathbf{r}) + \sum_{i=1}^{N^\beta} \rho_i^\beta(\mathbf{r})} \quad (2)$$

where ε_i is the energy of the i^{th} molecular orbital (MO), ρ_i is electron density attributed to molecular orbital ψ_i at point **r**, N_{orbs} is the number of orbitals, the upper indices α and β correspond to electrons with spin up and down, and N_{orbs} are the number of electrons with spin up and down, respectively.

Calculations of UHF–EA_L and UHF–IE_L from UHF-AM1 wavefunction were implemented into the VWF2Cube 2013[6] utility. Molecular orbitals of all species were calculated using the parallel semiempirical MO program EMPIRE 2013[7].

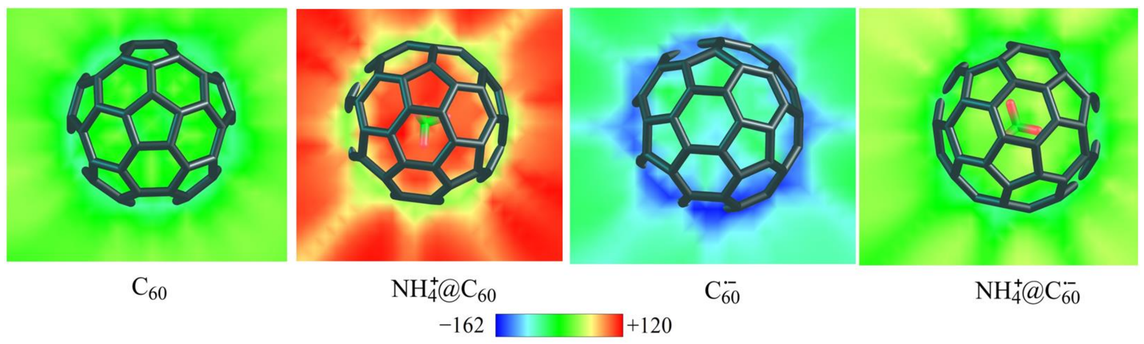
Carbon Peapods: Hole Transport



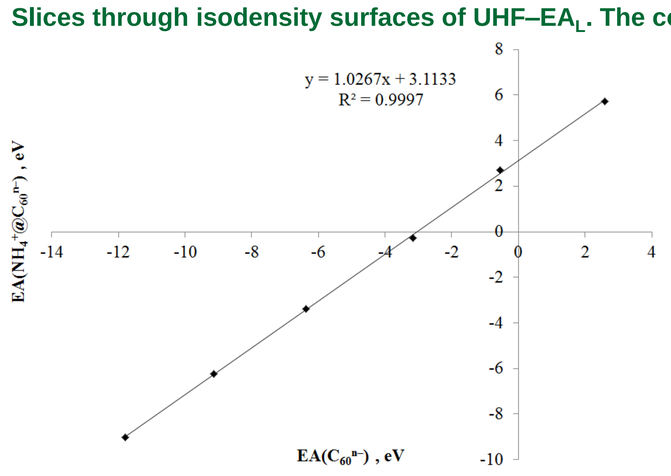
Slices through isodensity surface of UHF–IE_L of $3C_{60}$@(10,10) SWCNT. The color scale is in kcal mol^{-1}.

Lower UHF–IE_L values at the peapod are located around carbon nanotube and clearly represent nanotube's channel responsible for the hole transport mechanism observed in ambipolar transistors at very negative gate voltages.[8] Thus, IE_L can be seen as the local valence band.

C_{60} and $NH_4^+@C_{60}$ and Their Reduced Forms



Slices through isodensity surfaces of UHF–EA_L. The color scale is in kcal mol^{-1}.

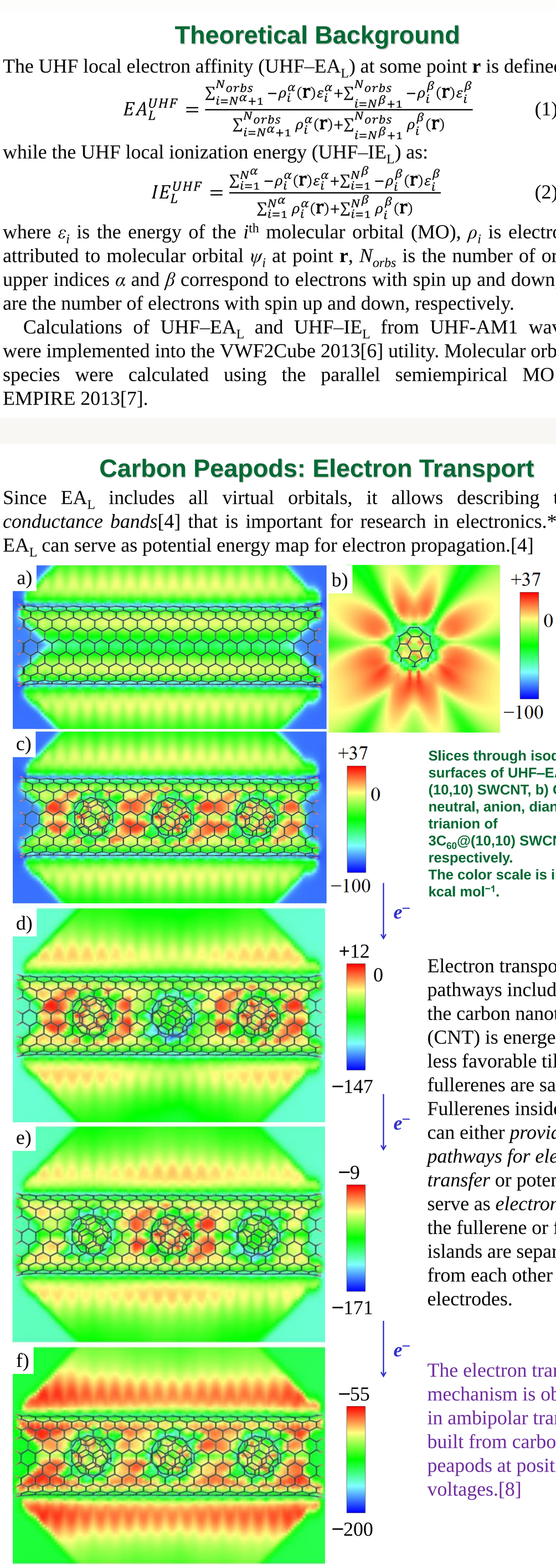


Encapsulating ammonium cation inside the C_{60} cage increases the electron accepting properties of C_{60} drastically. $NH_4^+@C_{60}^{n-}$ with n = 1…5 represent ion pairs rather than Rydberg radicals $[(NH_4^+)(e^-)_{Rydberg}]$ inside $C_{60}^{(n-1)-}$.[5]

Vertical EAs at B3LYP/6-311+G(d,p)// B3LYP/6-31G(d)

Carbon Peapods: Electron Transport

Since EA_L includes all virtual orbitals, it allows describing the local *conductance bands*[4] that is important for research in electronics.* Thereby EA_L can serve as potential energy map for electron propagation.[4]



Slices through isodensity surfaces of UHF–EA_L of a) (10,10) SWCNT, b) C_{60}, c–f) neutral, anion, dianion and trianion of $3C_{60}$@(10,10) SWCNT, respectively. The color scale is in kcal mol^{-1}.

Electron transport pathways including only the carbon nanotube (CNT) is energetically less favorable till all fullerenes are saturated. Fullerenes inside CNTs can either *provide pathways for electron transfer* or potentially serve as *electron traps*, if the fullerene or fullerene islands are separated from each other and the electrodes.

The electron transport mechanism is observed in ambipolar transistors built from carbon peapods at positive gate voltages.[8]

*Including all virtual orbitals is meaningful for minimal basis set used in semiempirical methods as AM1, but it represents a problem for non-minimal basis sets.[3,4] The latter problem has been solved by intensity-filtering technique.[3]

References

[1] P. Sjoberg, J. S. Murray, T. Brinck, P. Politzer, *Can. J. Chem.* **1990**, *68*, 1440.
[2] B. Ehresmann, B. Martin, A. H. C. Horn, T. Clark, *J. Mol. Model.* **2003**, *9*, 342.
[3] T. Clark, *J. Mol. Model.* **2010**, *16*, 1231.
[4] C. M. Jäger *et al. J. Am. Chem. Soc.* **2013**, *135*, 4893.
[5] P. O. Dral, *J. Mol. Model.* **2014**, *20*, 2134 *and references therein*.
[6] M. Hennemann, A. El Kerdawy A, T. Clark, P. O. Dral, *VWF2Cube 2013*. Universität Erlangen-Nürnberg and Cepos InSilico Ltd. **2013**.
[7] M. Hennemann, T. Clark, P. O. Dral, *EMPIRE 2013*. Universität Erlangen-Nürnberg and Cepos InSilico Ltd. **2013**.
[8] A. Guo *et al. Solid State Phenom.* 2007, *121-123*, 521.