

# Fullerenes, Carbon Nanotubes and Graphene as Tetrel Bond Donors and Acceptors of Electrophiles

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## Supplementary Information

### S.1 The Descriptors of the Molecular Electrostatic Surface Potential: Their Implications in Describing Assembly Between Molecules

The molecular electrostatic surface potential (MESP) model is increasingly recognized as a tool to insightfully describe the chemical bonding environment (and reactivity) between interacting molecules.<sup>1-6</sup> However, its calculation requires an appropriate isoelectron density envelope.<sup>7-9</sup> In particular, for molecules containing atoms with high electronegativity and low polarizability, such as, for example, fluorine in CF<sub>4</sub><sup>10</sup> and chlorine in CH<sub>3</sub>Cl,<sup>11,12</sup> it is necessary to calculate the electrostatic potential using a higher isoelectron density envelope.<sup>7-13</sup> This has been supported by several studies.<sup>14-16</sup> Storer and Hunter showed in a recent study that the 0.002 a.u. ( $e \text{ bohr}^{-3}$ ) isosurface gives a reasonably good correlation with experimental measurements (viz. with the empirical non-covalent interaction parameters  $\alpha$  and  $\beta$ <sup>17</sup>). They then suggested that the 0.002 a.u. isosurface approximates a van der Waals surface, a view that agrees with that of Bader and co-workers.<sup>18</sup> The view developed in this study was previously discussed in a number our studies.<sup>7,10,19-21</sup>

Although the MESP calculations in this study were performed on a 0.001 a.u. isodensity surface as suggested by Politzer et al.,<sup>22</sup> we show in a few cases that a higher isodensity envelope is necessary to understand the detailed nature of the chemical surface reactivity of each and every atomic region in a molecule. It should be borne in mind that the 0.001 a.u. isodensity envelope is arbitrary,<sup>7,23</sup> although it does approximate the van der Waals surfaces of most molecules as reported by many research groups; however, its use

sometimes provides misleading information about the electrophilicity and nucleophilicity of some molecules.<sup>7, 8, 12</sup> To this end, the very recent work of de Azvedo Santos and coworkers<sup>24</sup> is informative. They argue that the  $\sigma$ -hole model, which emerges from the MESP model, may be an oversimplification, leading to an incorrect understanding of the nature of pnictogen bonds (PnBs),<sup>25, 26</sup> chalcogen bonds (ChBs),<sup>27</sup> and halogen bonds (HaBs),<sup>28</sup> since the model assumes that a bond donor (D) is an electrostatic potential on a molecular surface and a bond acceptor (A) is a point charge. We expect that a great deal of debate and contrary views will appear based on the testing of a variety of chemical model systems that will clarify whether or not there are underlying potential pitfalls associated with the model.

The equation describing the MESP at a given point  $r$  has been extensively covered in many studies.<sup>4, 6, 29-31</sup> Briefly, the MESP model computationally generates two physical descriptors. They are the local minima and maxima of the potential on the electrostatic surface of a molecule, represented by  $V_{S,min}$  and  $V_{S,max}$ , respectively. Their signs (positive and negative) represent the electrophilicity or nucleophilicity of a particular region on the electrostatic surface of the molecular domain. When either of them on the surface is positive ( $V_{S,min} > 0$  or  $V_{S,max} > 0$ ), the region is electrophilic; when either of them on the surface is negative ( $V_{S,min} < 0$  or  $V_{S,max} < 0$ ), the region is nucleophilic. Their magnitude determines the strength of the potential; this has been shown to correlate linearly with the strength of intermolecular interactions<sup>14, 32, 33</sup> and the Hammett electronic parameters<sup>34</sup> in complex systems. It has also been shown that the magnitude of  $V_{S,min}$  may directly reflect the strength of the interaction between an anion and a cation.<sup>35, 36</sup> Wang et al. have demonstrated that  $V_{S,max}$  on a proton-donating atom can be used to estimate the excited-state acid dissociation constant ( $pK_a^*$ ) based on simple TD-DFT calculations for a broad range of hydroxyl-substituted aromatic compounds.<sup>37</sup>

The sign of  $V_{S,min}$  or  $V_{S,max}$  that appears at specific portions on the molecular surface was the basis for the development of the concepts  $\sigma$ -hole<sup>38, 39</sup> and  $\pi$ -hole,<sup>40</sup> as well as the definition of PnBs<sup>25, 26</sup> and tetrel bonds (TtBs).<sup>41, 42</sup> When  $V_{S,max}$  appears on the surface of an atom A on the extension of a R–A covalent or coordination bond, it is called a  $\sigma$ -hole (R is the remainder of the molecule). Thus, the  $\sigma$ -hole can be negative or positive<sup>9</sup> depending on whether the sign of  $V_{S,max}$  is negative or positive. Similarly, a  $\pi$ -hole appears on the surface of the bonding (or centroid) region in a molecule. It can be positive or negative depending on the sign and the location of  $V_{S,min}$  (or  $V_{S,max}$ ). For instance, for the centroid of  $C_6F_6$  and other fluorinated arenes,<sup>9, 43, 44</sup>  $V_{S,max}$  is positive, which corresponds

to a positive  $\pi$ -hole; the  $V_{S,min}$  is negative at the centroid of  $C_6H_6$ <sup>45</sup> and  $C_6H_5F$ <sup>9</sup> ( $V_{S,min} < 0$ ), which represents a negative  $\pi$ -hole. The mid-points of  $HC\equiv CH$ <sup>45, 46</sup> ( $V_{S,min} < 0$ ),  $P_2$  ( $V_{S,min} < 0$ <sup>43</sup>),  $As_2$  ( $V_{S,min} < 0$ <sup>47</sup>), and  $N_2$  ( $V_{S,max} > 0$ <sup>48</sup>), represent a negative  $\pi$ -hole and a positive  $\pi$ -hole, respectively. Thus, a positive  $\pi$ -hole is electron-density deficient (electrophilic), whereas a negative  $\pi$ -hole is electron-density rich (nucleophilic).

A tetrel bond donor atom Tt in R–Tt can be a  $\sigma$ -hole donor; examples include the C atom in  $CF_4$ <sup>10</sup> and  $CH_3Cl$ .<sup>12</sup> When the  $\sigma$ -hole, or the  $\pi$ -hole, on the tetrel derivative in a molecule has a negative potential, it is nucleophilic, and hence can act as a tetrel bond acceptor. The centroid region of the  $C_6$  ring in  $C_6H_6$ , and the mid-point of the  $C\equiv C$  bond in  $HC\equiv CH$ , for examples, are not only  $\pi$ -centered tetrel bond acceptors, but also an acceptor of an electrophile (viz. a halogen bond, a chalcogen bond, a pnictogen bond, or a hydrogen bond).

## S.2 Computational Details

The geometries of all molecular model fullerene derivatives, carbon nanotubes (CNTs), and graphene (and some of their allotropes) considered in this study were energy-minimized with the  $\omega B97X-D$  functional,<sup>49</sup> which uses Grimme's D2 dispersion model, in combination with the Dunning-type correlation-consistent basis set cc-PVTZ.<sup>50</sup> Default cut-off criteria were used for the convergence of geometry (maximum and RMS forces of  $10^{-5}$  hartrees bohr<sup>-1</sup> and  $10^{-4}$  hartrees radians<sup>-1</sup>, respectively). An ultrafine integration grid was used for frequency calculations. According to Chai and Head-Gordon, the functional is superior for the study of non-bonded interactions.<sup>49</sup> Other studies that demonstrate the usefulness of the functional can be found elsewhere.<sup>51, 52</sup>

The MESP and quantum theory of atoms in molecules (QTAIM) calculations were performed at the same level of theory as above. The bond path topology of QTAIM was used to show the connectivity of the atoms that make up each molecule. The delocalization index, a two-electron property,<sup>53-55</sup> was determined to investigate the delocalized nature of chemical bonds between the bonded carbon atoms in the systems examined.<sup>56</sup> Each energy-minimized system was identified to be at a local minimum on its potential energy surface, evidenced by the positive eigenvalues of the Hessian (second derivative) of the energy with respect to the atom-fixed nuclear coordinates. Gaussian 16<sup>57</sup> was used for the geometry optimization and frequency calculations, while both

AIMAll<sup>58</sup> and Multiwfn<sup>59, 60</sup> were used for the computation of the properties of QTAIM and MESP, and subsequent analyses. We used a reasonable size basis set of triple- $\zeta$  quality for our investigation of the potential, which is also supported by a previous study.<sup>61</sup> Analysis of the reduced charge density based isosurfaces was performed using the actual density computed within the framework of Independent Gradient Model (IGM- $\delta g^{inter}$ ).<sup>62</sup>

The dimer models of some fullerene systems with some diatomic and triatomic molecules were examined using the same level of theory described already above. The uncorrected and basis set superposition error (BSSE) corrected energies ( $\Delta E$  and  $\Delta E(\text{BSSE})$ , respectively) were calculated using Eqns. (1) and (2), respectively.  $E_T$  in Eqn (1) and  $E(\text{BSSE})$  in Eqn. (2) are the electronic total energy of respective species and the error in total electronic energy due to the effect of the basis set superposition, respectively.

$$\Delta E (\text{dimer}) = E_T(\text{dimer}) - [E_T(\text{monomer 1}) + E_T(\text{monomer 2})] \dots\dots\dots(1)$$

$$\Delta E(\text{BSSE}) = \Delta E(\text{dimer}) + E(\text{BSSE}) \dots\dots\dots(2)$$

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