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Louisiana Alliance for Simulation-Guided Materials Applications

Electronic Structure Determination of Charge Transfer within Electrolyte Solutions

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Abstract 1

Data regarding the basic chemical and physical characteristics of supercapacitors is sought for in attempts to improve capacitor function and energy storage. Using *ab initio* calculations, we have computed amounts of charge transfer occurring in Electric Double Layer Capacitors utilizing Carbon Nanotube Forests filled with a propylene carbonate (*PC*) tetraethylammonium-tetrafluorborate solution ($TEA^+BF_4^-$). Analysis of charge transfer taking place between pairs of particles present in the solution (PC and BF_4^-, TEA^+ and BF_4^-) is the focus of this research.

Charge transfer was calculated employing a range of theory regarding electron density (DFT, MP2, and HF/SCF) for gas-phase-minimum-energy structures of the pairs. The computations show small amounts of charge transfer (on the order of 0.01e and 0.1e depending upon the computational method), which reduces as the molecules are separated. This work will help in the design and understanding of electrolyte solutions used not only in double layer capacitors, but in other devices as well, including batteries.

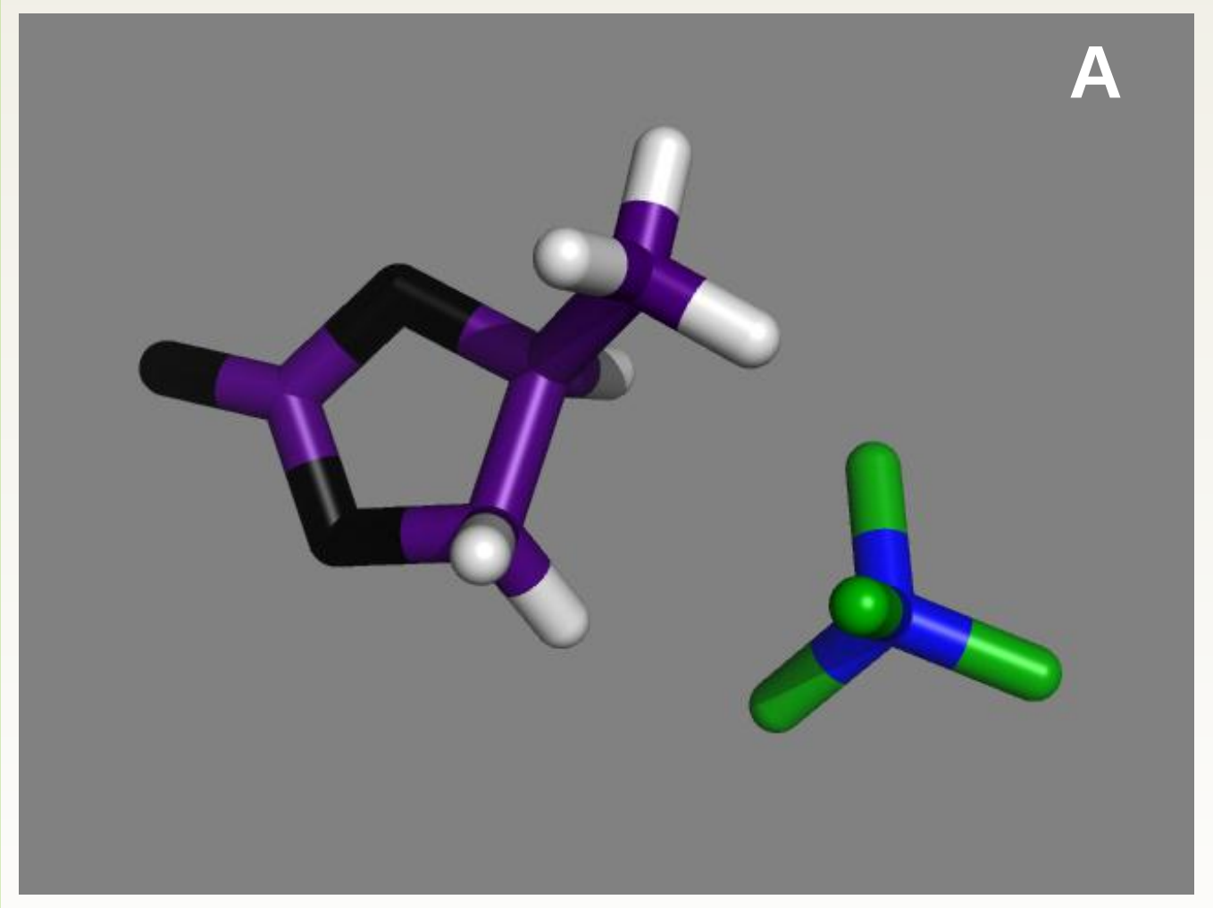

Figure A: *PC* and BF_4- gas-phase-minimum-energy structure. BF_4- is green/blue.

The Focus 2

- Charge Transfer Between:
  - TEA^+ and BF_4^- neutral net charge
  - PC and BF_4^- net charge of -1

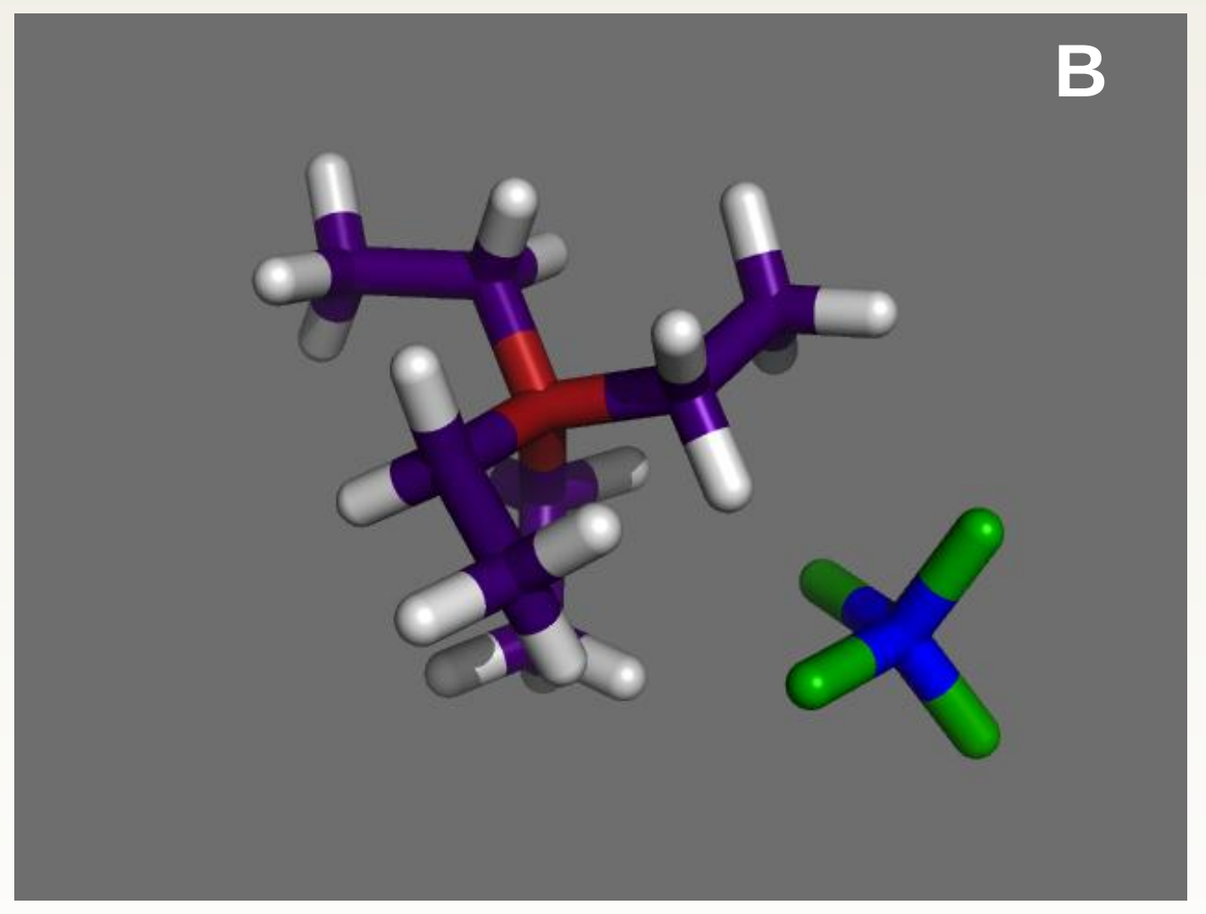

Figure B: TEA^+ and BF_4^- gas-phase-minimum-energy structure. BF_4^- is green/blue.

Introduction/Background 3

The diminishing supply of fossil fuels, increased energy consumption, and increased green house gas emissions have stressed the need for clean, efficient, and renewable energy sources. Many renewable energy sources are intermittent (solar and wind) and require effective energy storage.[1] High energy density and high power density electrical-energy-storage devices (such as batteries, fuel cells, and supercapacitors) are a solution. In particular, supercapacitors are of interest for boasting a high energy density—relative to regular capacitors—while retaining capacitor advantages: incredibly longer life cycles and higher power output. Though progress has been made in the development of EDLCs using a *PC-*$TEA^+BF_4^-$ solution, several basic physical-chemical properties of the device have not been characterized at a molecular level.[1] The goal of this research is to understand the role of the electrolyte solution present in these capacitors. Specifically, this research looks at charge transfer between the molecules of the solution.

Charge transfer can be described as the shifting of small amounts of electron density in non-bonded interactions. This results in ionic charges that deviate from integer values and that affect short-range interactions through the relocation of charge. Charge transfer terms have been reported as accounting for as much as 20% of total interaction energy. Therefore, charge transfer has significant implications for solvation, and EDLCs or any device using an electrolytic solution.[2]

Acknowledgements

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4. Dr. Matthew Tarr at the University of New Orleans

Methods 4

- Molecular structures were loaded into NWChem—an *ab initio* computational software package—where quantum mechanical calculations determined the electron density of the system using several theories:
  - Hartree-Fock (HF)
  - second order Moller-Plesset perturbation theory (MP2)
  - Density Functional Theory (DFT).

  Once in possession of the electron density, Electrostatic Potential (ESP) and Atoms in Molecules (AIM) methods were employed to determine the amount of electron density distributed to each atom.
- BF_4^- atomic charges (as distributed by ESP and AIM) were summed. Then the absolute value of the difference between the "actual" charge (-1) and the ESP or AIM calculated charge was taken to determine how much charge shifted to or away from the BF_4^-. (see Figure D)
- Refinement of electron density box—"dplot". This refinement allowed for more accurate calculations.
- Each pair was separated along a central axis, analyzing charge transfer as a function of distance at select intervals, until charge transfer became minimal.

Results 5

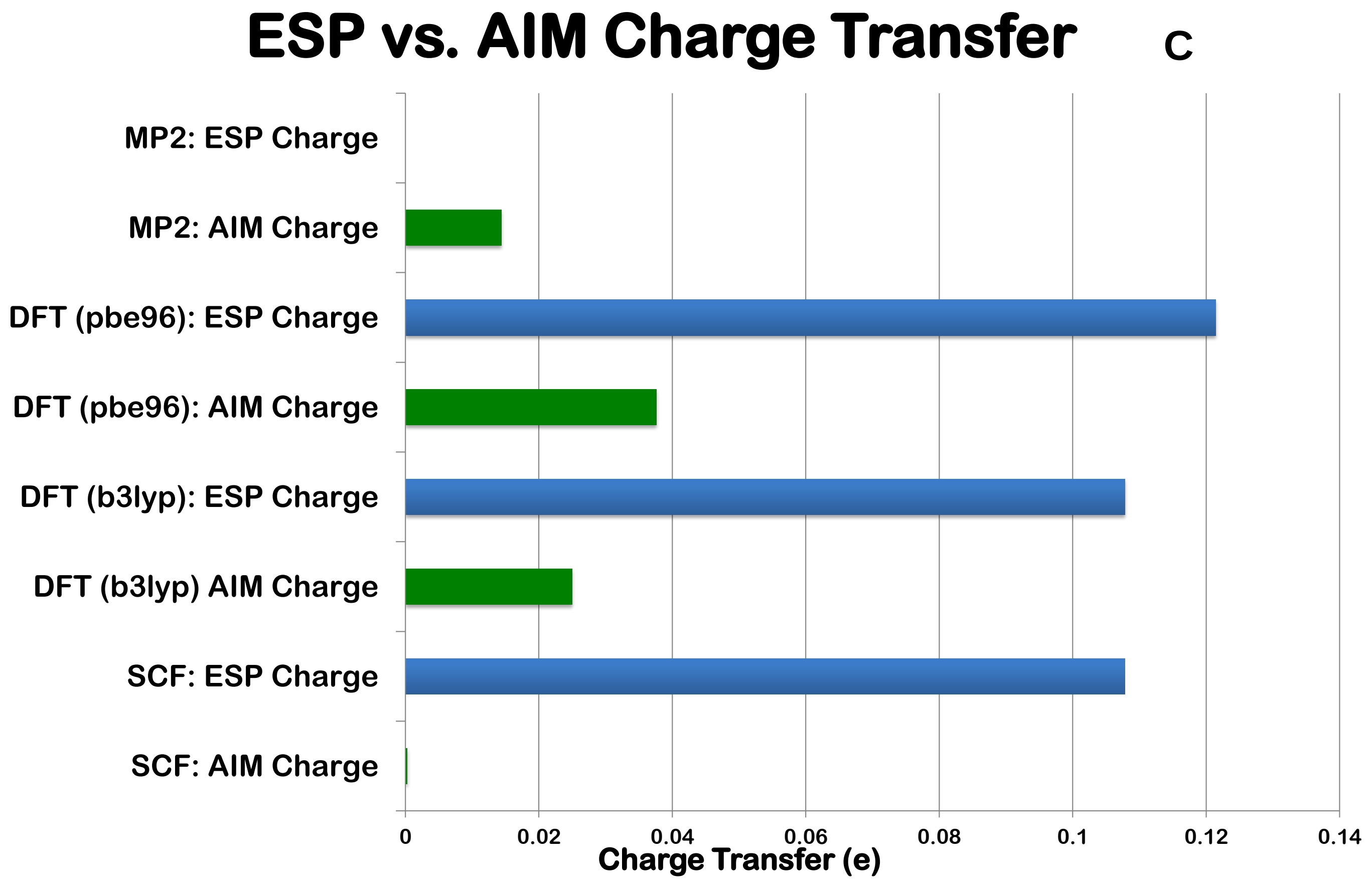

Figure C: Graphical comparison of charge transfer values produced by different theories and methods for the gas-phase-minimum-energy structure of the ion pair. AIM is in green and ESP is in blue. The DFT functional is specified in parentheses.

References

1. Pratt, Lawrence R.; Migliori, Albert; Fishbine, Brian H.; Yang, Lu. *Molecular Simulation of Electric Double-Layer Capacitors on Carbon Nanotube Forests*. J. AM. CHEM. SOC., Vol 131, NO. 34, 2009.
2. Soniat, Marielle and Rick, Steve W. *Charge Transfer Potential Models for Ions.* Department of Chemistry, University of New Orleans.

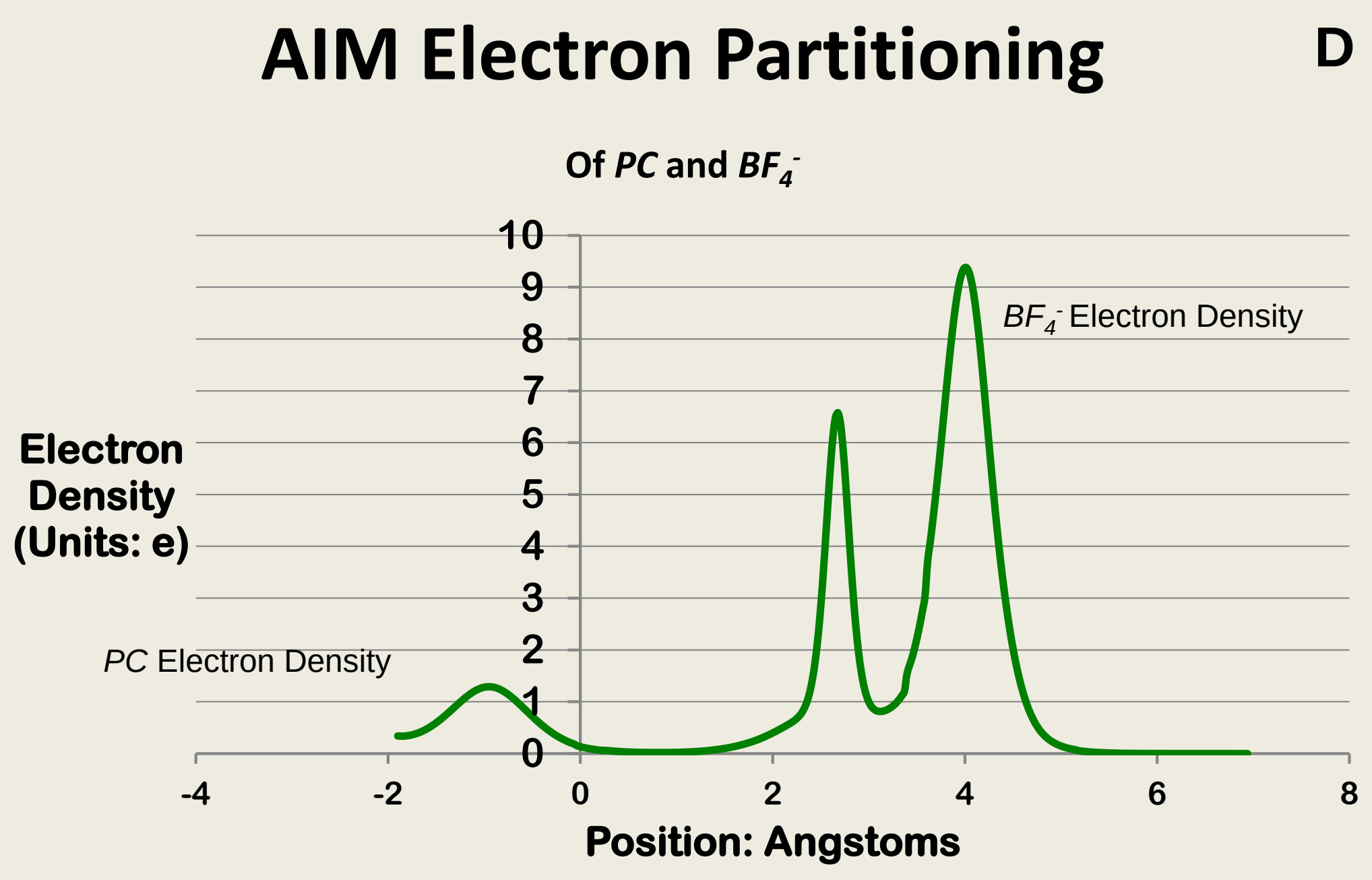

Figure D: Provided as an example of AIM electron partitioning. The program calculates the clear minimum between the two major hubs of data, then partitions all electrons on each side to the corresponding molecule.

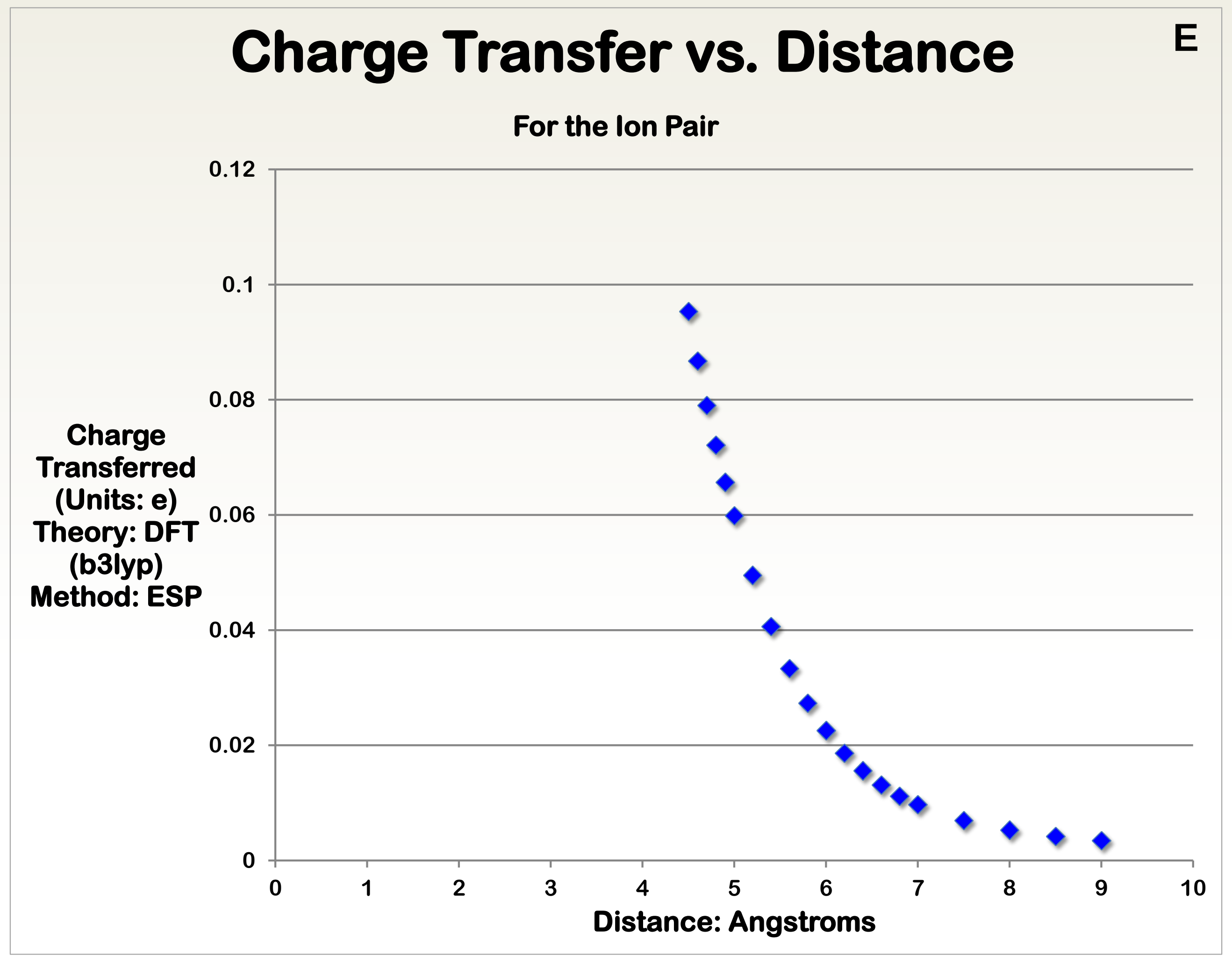

Figure E: Amount of charge transfer away from *BF4-* as the ion pair is separated.

Summary and What Else? 6

- Appreciable charge transfer between the ion pair which drops off as they are separated.
- Exponential dependence of charge transfer on distance as shown in Figure E and in corresponding log-scale graphs (not shown here).
- More charge transfer in ESP than AIM as shown in Figure C.
- DFT, MP2, and HF methods produce similar values of charge transfer as shown in Figure C.

- Charge transfer between several other molecule pairs still needs to be accounted for (such as carbon molecules from the nanotubes with the solution molecules).