Computational Quantum Mechanics-Based Study of Conduction in Iodine Doped Polyethylene

A. Huzayyin[1], S. Boggs[1,2], R. Ramprasad[2]
[1]ECE Department, University of Toronto, Canada
[2]Institute of Materials Science, University of Connecticut, USA

***Abstract* - Interaction between iodine and polyethylene relevant to conduction has been studied through the use of density functional theory. The interaction between I_2 and polyethylene was characterized on an atomic level, and the role of I_2 in linking the polymer chains electronically was demonstrated. The viability of a previously proposed conduction process in iodine doped polyethylene was demonstrated using quantum mechanical parameters.**

***Keywords*- Polythylene, Conduction, Iodine, DFT.**

I. INTRODUCTION

Polymers are used widely as insulation in power apparatus such as capacitors and cables. As a result of the ever increasing design electric fields at which polymer dielectrics are employed, understanding of high field phenomena is increasingly important. The present understanding of the physical basis of high field conduction in common insulating polymers, such as polyethylene (PE), is incomplete [1,2] in that an atomic level understanding of the role played by chemical impurities is lacking. The effect of chemical impurities on high field conduction is generally explained in terms traps and ionizable species which provide carriers and hopping sites for carriers [1,3]. Little physical basis for the concept of traps has been provided in spite of extensive effort [1,2,4]. An atomic level characterization of the role of chemical impurities in high field conduction in insulating polymers such as PE is a major goal still to be achieved.

The effect of iodine on the conductivity of PE is a good place to start an investigation of the effect of chemical impurities, as iodine is weakly bound to the PE and yet increases its conductivity by about four orders of magnitude [5,6,7,8], whether the iodine is introduced through diffusion of iodine vapor into the PE [7,8] or through diffusion from an aqueous solution employed as electrodes [5,6]. The experimental data suggest that the main factor behind increased conductivity is an interaction between iodine molecules and PE chains [5,6]. The literature suggests that iodine in PE exists in the form of neutral I_2 [5-8] with the possibility of charged species [5] or molecular aggregates I_n [6].

Our objective is to identify interactions between I_2 and PE chains at an atomic level through the use of density functional theory (DFT), on the basis of which we hope to demonstrate the role of I_2 in linking the polymer chains electronically. Our computations support the conduction mechanisms proposed by Lewis and Taylor [6].

II. METHODOLOGY

While DFT involves numerous approximations, it remains the most successful implementation of computational quantum mechanics for systems involving hundreds of atoms, as it represents the best tradeoff between the computational time and accuracy [9,10]. The limitations of DFT are reasonably well understood as a result of its wide use. The ground state configuration of a system of electrons and nuclei forming a molecule or solid can be determined though a combination of DFT (for the electronic structure) and optimization of the nuclei positions based on energy minimization using atomic forces calculated according to the Hellman-Feynman theorem. Using this procedure, the atomic structure of systems can be computed to within about 1% of experimental values [11]. However, DFT tends to underestimate the band gap of insulators by about 30%; still, trends in the changes of band gaps, and qualitative descriptions of the energy of impurity states in the band gap near the conduction band minimum (CBM) or valence band maximum (VBM) are rendered accurately [12]. The band structure of PE as determined using DFT agrees qualitatively with experimental data [13,14].

In SIESTA, the DFT code employed in the present research [15], the unit cell containing the system of interest is repeated periodically in space by applying periodic boundary conditions. In the present work, unit cells are made large enough to ensure little interaction between neighboring cells. Pseudopotentials (of the Troullier-Martins type [16]) are used to eliminate the core electrons, and wavefunctions are expanded using a double zeta plus polarization (DZP) basis set. Geometry optimizations were accomplished by requiring each component of the forces on each atom to be smaller than 0.04 eV/Å. SIESTA determines the electronic eigenvalues and wavefunctions (i.e., eigenstates) from which various electronic properties and atomic features of the system can be determined including the electron density, density of states (DOS), and the projected density of states (PDOS). The DOS is the number of states available for electrons to occupy per unit energy and unit cell, as a function of energy. The PDOS is defined as the contribution of any orbital, atom or group of atoms to the DOS of the system. The square of the absolute value of an eigenstate (i.e., the wavefunction) represents the probability of finding an electron occupying that state at a given point in space.

978-1-4244-4559-2/09/$25.00

III. APPLICATION OF DFT TO I_2 IN PE

Application of DFT to complex systems requires a systematic, incremental approach which assures agreement with available experimental data at each step along the way. First an isolated I_2 molecule is studied to verify various DFT approximations used in modeling iodine. In addition, the isolated I_2 energy and electron state wavefunctions are used in studying the interaction of I_2 with PE chains. To study I_2 in PE, a "core-shell" model was employed, as this allows the PE to deform in the region of the iodine. We feel that this approach represents the best approximation to amorphous PE which can be implemented with a reasonable number of atoms and periodic boundary conditions. Next, the I_2 binding energy in PE-I_2 model is determined. Using the DOS and PDOS, I_2 states most relevant to conduction in PE-I_2 are identified, and their wavefunctions are compared to those of the isolated I_2 molecule. The binding energy, wavefunctions, and the contribution of PE chains to I_2 states (determined by PDOS) are used to identify the interaction of I_2 with PE chains. In addition to the above, the overlap of the I_2 wavefunctions with the CBM and VBM of the PE chains is used to demonstrate the likely role of I_2 in linking the polymer chains electronically and to assess the viability of conduction mechanisms proposed by Lewis and Taylor [6].

A. Isolated I_2 Molecule

The calculated bond length of I_2 was 2.66 Å, within 1% of the experimental value of 2.67 Å [17]. The I_2 highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are expected to play an important role in enhancing conduction in PE. The PDOS and wavefunction plots show that the HOMO is a π anti-bonding 2p (π^*_{2p}) orbital and the LUMO is a σ anti-bonding 2p (σ^*_{2p}) orbital in agreement with the theoretical I_2 molecular orbital energy diagram [18]. Based on bond lengths and the relevant orbitals of I_2, the DFT results for I_2 are satisfactory in the context of the present work.

B. I_2 in Polyethylene

The model employed for I_2 in PE consists of seven PE chains terminated by methyl groups, each consisting of 40 carbon atoms. Past experimental and theoretical results [2], as well as the present DFT calculations, indicate that a 40 carbon atom chain is a good approximation to an infinite PE chain. The PE-I_2 model consists of a core chain surrounded by six chains with PE crystal structure spacing and orientation. The I_2 molecule is inserted between chains. The chains are held together by attractive electrostatic forces but still have freedom to accommodate the I_2 molecule. The minimum energy structure determined through DFT and geometry optimization is shown from two perspectives in Figure 1. The PE-I_2 model is more amorphous like than crystalline in that it allows the chains deform to create space for the I_2.

Comparison between the DOS of crystalline PE and the PE-I_2 model shows good agreement in CBM, VBM, band structure, and band gap. The PE-I_2 DOS (Fig. 2) has a band gap of 6.7 eV in agreement with DFT estimates of PE band gap [13]. I_2 introduces three impurity states into the band gap, two of which are occupied states and one unoccupied. These states were identified as I_2 states through comparison with the DOS of pure PE chains and the PDOS which determines how much each atom and orbital in the structure contributes to each state in the DOS. A FORTRAN code was developed to assess the relative degree of overlap between the I_2 unoccupied impurity state and the CBM and VBM states within a specified energy range. The two CBM states which overlap most with the I_2 unoccupied impurity state belong to differing PE chains. The PDOS and wavefunction plots of the CBM states were used to identify the relevant PE chains. Since DFT determines the energy of I_2 unoccupied impurity state with respect to the CBM accurately [12], the UV absorption spectrum of iodine in PE [5] can be used to verify the analysis of the overlap. The energy difference between the I_2 unoccupied states and the CBM state with greatest overlap to these I_2 states agrees well with two peaks in the UV absorption spectrum of iodine in PE [5] with errors of 5% and 1%. Based on the above the PE-I_2 model is considered appropriate for the present study.

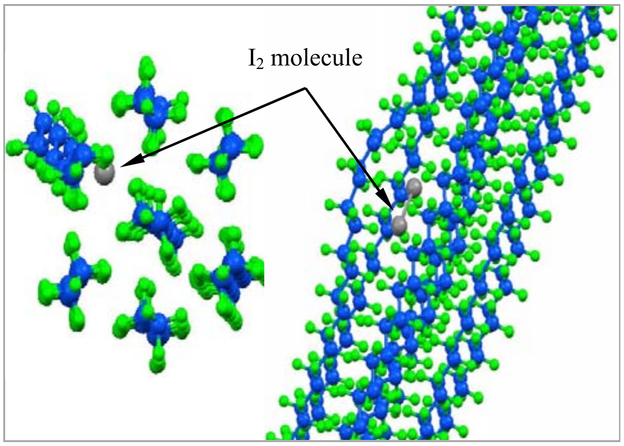

Fig. 1. PE-I_2 model showing I_2 residing in between deformed PE chains.

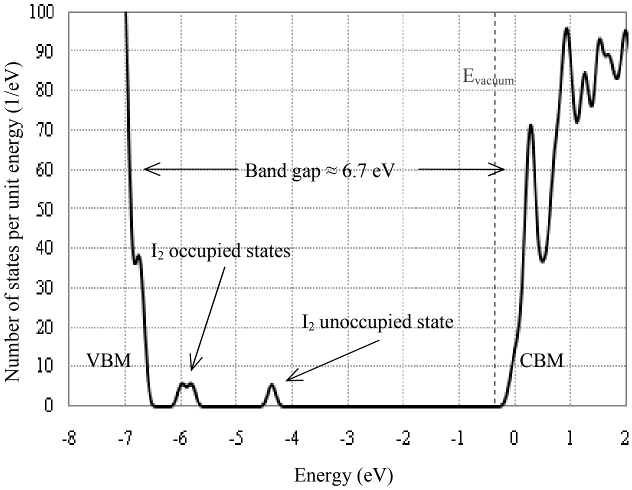

Fig. 2. DOS of PE-I_2 structure showing I_2 impurity states.

IV. DISCUSSION

Iodine-PE interaction: The I_2 binding energy in the PE-I_2 structure is defined as the sum of ground state energies of the isolated I_2 molecule and the pure PE chains minus the ground state energy of the PE-I_2 structure [19]. At less than 1 eV, the calculated binding energy indicates a relatively weak interaction between the I_2 and the PE chains. The PDOS reveals that the I_2 orbitals are the main contributors to the band gap impurity states (Fig 2), with a minor contribution from orbitals in the PE chains adjacent to the I_2, which also attests to the weak interaction between I_2 and PE chains. Plots of the impurity state wavefunctions and PDOS analysis confirm that the I_2 impurity states in the PE-I_2 band gap are modified π^*_{2p} HOMO and σ^*_{2p} LUMO of the isolated I_2 molecule. The modification is due to I_2 interaction with the PE chains as revealed in the binding energy and PDOS analysis.

Electronic linking of polymer chains: Inter-chain separation is a barrier to carrier transport in PE. The interaction between I_2 and PE chains as described above can link the polymer chains electronically, which could decrease the inter-chain barrier to charge transfer and thereby increase conduction. The PDOS analysis shows that I_2 band gap impurity states (wavefunctions) have contributions from multiple PE chains, which indicates that electron location, while concentrated on the I_2, is spread among several PE chains.

We can compare the wavefunctions of the LUMO of the isolated I_2 and the I_2 unoccupied impurity state in PE-I_2 which is expected to play a role in linking the polymer chains. The wavefunction of the unoccupied I_2 impurity state is basically the LUMO of the isolated I_2 molecule modified by interaction with PE chains. The square of wavefunctions for the above state in isolated I_2 and I_2-PE model are shown in Figure 3. The square of a state wavefunction indicates the spatial distribution of the electron location probability. As shown in Figure 3, the wavefunction of the isolated I_2 molecule is localized around the molecule, while the wavefunction of the I_2 in PE-I_2 is extended in space with low amplitude peaks centered around two neighboring PE chains. Analysis of the overlap between the I_2 unoccupied state wavefunctions and PE chain CBM and VBM state wavefunctions is required to demonstrate the role of I_2 linking of polymer chains.

VBM states belonging to differing PE chains show relatively high overlap with the I_2 unoccupied impurity state. Accordingly, the I_2, through its unoccupied state, links the VBM and CBM states of differing chains electronically. An electron captured by the I_2 unoccupied state has a probability of being transferred to various surrounding chains. The above provides an atomic level computational basis for the role of iodine in linking polymer chains electronically and for some aspects of the conduction mechanisms proposed in [5,6]. Details of the linking of polymer chains through I_2 unoccupied states requires further investigation.

The role of iodine in the conduction process proposed by Lewis and Taylor [6] (Fig. 4) includes two main mechanisms; (i) iodine formation of donor/acceptor (DA) complexes with PE chains, which promotes electron transfer from the polymer to the I_2 and creates a vacancy in the polymer chain which promotes hole conduction along the chain, and (ii) electrons captured by iodine pass through iodine states to reach electron vacancy (EV) sites on adjacent PE chains where recombination can occur to maintain conduction.

As characterized in this work, the relation between I_2 and PE chains and I_2 unoccupied states linking polymer chains agrees with DA complex formation as discussed above. The possibility of charge transfer through iodine states to EV sites is supported by the I_2 unoccupied impurity state overlap with VBM states of PE chains. The I_2 unoccupied impurity state is very well suited to capture of an electron, as a result of I_2 electronegativity and the spread of the unoccupied impurity state wavefunction towards PE chains, as demonstrated above. If the PE chain VBM states which overlap with the I_2 have a vacancy (EV site), the captured electron can recombine with that vacancy as proposed by Lewis and Taylor. Thus the mechanisms by which iodine enhances conduction suggested by Lewis and Taylor are supported by the present DFT computations.

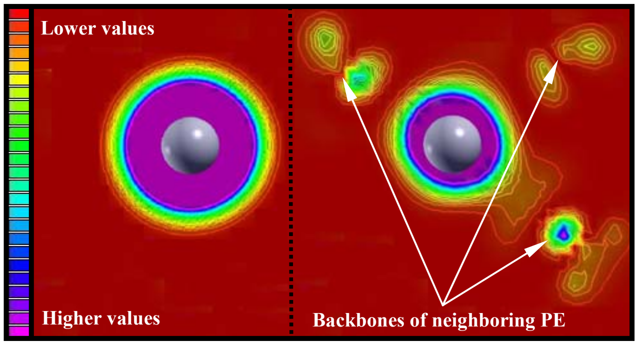

Fig. 3. Square of the wavefunction of the unoccupied I_2 impurity state in the PE-I_2 structure (right) and LUMO in the isolated I_2 molecule (left). Plots are in the XY plane at a Z location between the two iodine atoms. Z location and the plot scale were selected to demonstrate the difference between the two wavefunctions.

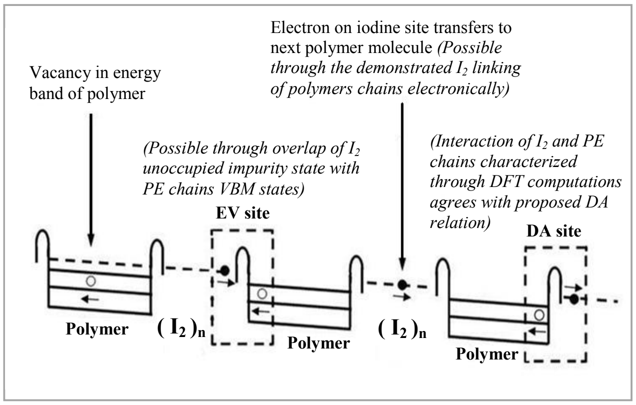

Fig. 4. Model of enhanced conduction in the presence of iodine by Lewis and Taylor [6]. "Vacancies and electrons, created by a DA charge transfer process, migrate in the electric field through polymer and iodine regions respectively and then recombine at EV sites" [6]. Figure taken from [6] with the present authors' comments in italics.

V. SUMMARY AND FUTURE WORK

DFT was used to study an isolated I_2 molecule to demonstrate accurate computation of bond length and molecular orbitals, in particular the HOMO and LUMO. A core-shell model for iodine in PE was developed, on the basis of which the atomic level interaction between I_2 and PE chains was identified. The interaction between I_2 and PE chains was characterized through binding energy, PDOS and the change in I_2 unoccupied impurity state wavefunction. The linking of polymer chains through the I_2 unoccupied impurity state overlap with CBM and VBM states from neighboring PE chains was demonstrated. Our computations demonstrate the viability of the two mechanisms proposed by Lewis and Taylor [6] by which iodine enhances the conductivity of PE.

Further work is required to confirm various aspects of the conduction process proposed by Lewis and Taylor [6]. Future work will include investigating the effect of other stable forms of iodine on conduction mechanisms in PE. In the long term, we hope to incorporate the results of DFT computations into quantitative models for conduction in polymers.

REFERENCES

[1] S. Boggs, "Very High Field Phenomena in Dielectrics", *IEEE Transactions on Dielectrics and Electrical Insulation* vol. 12, no. 5, October 2005, pp.929-938.

[2] G. Teyssedre and C. Laurent, "Charge Transport Modeling in Insulating Polymers: From Molecular to Macroscopic Scale", *IEEE Transactions on Dielectrics and Electrical Insulation* vol. 12, no. 5, October 2005, pp.857-874.

[3] M. Meunier, N. Quirke and A. Aslanides, "Characterisation of Charge Carrier Traps in Polymeric Insulators", *Proceedings of IEEE Conference on Electrical Insulation and Dielectric Phenomena*, 2000, pp.21-24.

[4] H. J. Wintle, "Charge Motion and Trapping in Insulators Surface and Bulk Effects", *IEEE Transactions on Dielectrics and Electrical Insulation* vol. 6, no. 1, February 1999, pp.1-10.

[5] D. W. Swan, "Electrical Conductivity of Iodine-Doped Polyethylene", *Journal of Applied Physics,* vol. 38, no. 13, December 1967, pp.5051-5057.

[6] T. J. Lewis and D. M. Taylor, "Electrical Conduction in Iodine-Doped Polyethylene", *Journal of Physics D: Applied Physics,* vol.5, 1972, pp.1664-1670.

[7] D. K. Davies, "Carrier Transport in Polythene", *Journal of Physics D: Applied Physics,* vol.5, 1972, pp.162-168.

[8] T. Mizutani, K. Mitani and M. Ieda "Electric Conduction of Iodine-Doped Polyethylene", *Journal of Physics D: Applied Physics,* vol.17, 1984, pp.1477-1484.

[9] K. Capelle, "A Bird's-Eye View of Density Functional Theory", *Brazilian J. of Physc.*, vol. 36, no. 4a, 2006, pp.1318-1343.

[10] M. H. Gordon and E. Artacho, "Chemistry on the Computer", *Physics Today*, April 2008, pp.58-63.

[11] W. Kohn, "Nobel Lecture: Electronic Structure of Matter-Wave Functions and Density Functionals", *Reviews of Modern Physics,* vol. 71, no. 5, 1999, pp.1253-1266.

[12] Richard M. Martin, *Electronic Structure Basic Theory and Practical Methods*, Cambridge University Press, 2004.

[13] M. S. Miao, M. L. Zhang, V. E. Van Doren, C. Van Alsenoy, J. L. Martins, "Density Functional Calculations on the Structure of Crystalline Polyethylene Under High Pressures, *J. of Chemical Physics,* vol. 115, no. 24, December 1999, pp.11317-11324.

[14] M. S. Miao, P. E. Van Camp, V. E. Van Doren, J. J. Ladik, J. W. Mintmire, "Conformation and Electronic Structure of Polyethylene: A Density-Functional Approach", *Physical Review B*, vol. 54, no. 15, October 1996-I, pp.10430-1043X.

[15] SIESTA 2.0 User Guide, 2006.

[16] N. Troullier and J. L. Martins, "Efficient Pseudopotentials for Plane-Wave Calculations", vol. 43, no. 3, 1991, pp.1993-2006.

[17] S. Nakashima, M. Norimoto, H. Harima, Y. Hamanaka, L. S. Grigoryan and M. Tokumoto, "Raman Scattering of Iodine Intercalated C_{60} Crystal", vol. 268, no. 5-6, 1997, pp.359-364.

[18] P. H. Svensson and L. Kloo, "Synthesis, Structure, and Bonding in Polyiodide and Metal Iodide-Iodide Systems", *Chemical Reviews,* vol. 103, no.5, 2003, pp.1649-1684.

[19] N. L. Tran and A. C. Kummel, "A Density Functional Theory Study on the Binding of NO onto FePc films", Journal of Chemical Physics, vol. 127, 2007, pp.214701.