A COMBINED MODEL TO STUDY CONDUCTIVE PROPERTIES OF POLYMERS WITH ATOMIC RESOLUTION

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Abstract

High level quantum mechanical simulations are able to predict the relationship between geometry and composition of molecular systems and their electronic properties but are limited to just a few atoms (ca 100). A combination of semiempirical geometry calculations and Density Functional Theory (DFT) electronic structure predictions is used here to study the evolution of the electronic structure of different polymers with the number of units in the chain. Polyacetylene (PA) and Poly(2-methoxy-5-(2,9-ethyl-hexyloxy)-1,4-phenylenevinylene (MEH-PPV) were studied. Semiempirical predictions of the HOMO-LUMO gap (HLG) follow the right trend but this property is overpredicted by several eV. DFT predictions however seem to converge to acceptable values when compared to available experimental information

Introduction

Since plastic materials (organic compounds) were first introduced, the number of applications has grown so much that plastic is one of the most common materials in everyday life. The main reason for the increasing utilization of organic compounds is the set of unique characteristics they have, such us[1,2] low cost, simple fabrication techniques, and mechanical and electronic versatility, giving the possibility of chemically tuning their properties, within a wide range of values.[3]

Plastics, once assumed to be exclusively insulators, are now know to be able to conduct electricity[4] extending their utilization to electronic and photonic application supplementing traditional inorganic materials. Organic compounds, particularly π-conjugated polymers and oligomers, are being employed in an increasing number of applications including transistors,[5-8] capacitors,[9,10] transducers,[11,12] filters,[13] sensors,[14-16] displays,[16,17] and switches,[18,19] among others.

Flexibility, one of the main characteristics of plastics, is at the same time a limiting factor for conductivity, conductivity was observed to decrease several orders of magnitude in systems with configurational disorder.[1,20]
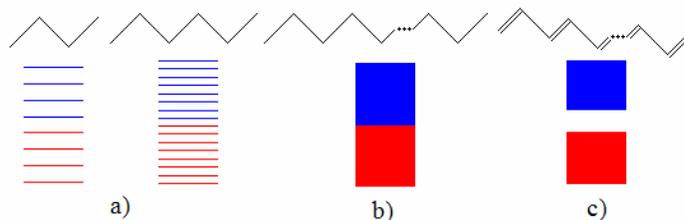
Carbon atoms in conjugated polymers are characterized by an sp^2 hybridization what leaves a p electron free to delocalize along the polymer.[20] A polymer chain with atoms located equidistant from each other would have a semi-filled π band formed from the extra p level in each atom. Peierl distortion, however prevents this from happening and the polymer chain show alternating single and double bonds

Figure 1: Evolution of electron energy levels with polymer size. a) As more monomers are added more molecular energy levels are formed with smaller gaps between them. b) For a long polymer with equal bond lengths between its atoms, energy levels are so close to each other that they form a half full band c) Due to Peierl's distortion, alternate single and double bonds are formed in conjugated polymers that separate occupied (red) and unoccupied (blue) energy levels into two bands, one full and the other empty.

what localize the electrons and breaks the π into one full and one empty band (see figure 1).[21]

Similar to semiconductor materials, polymers become conductive with the addition of electron donor and electron withdrawing groups. For example, polyacetylene's (PA) conductivity was found to continuously increase over 11 orders of magnitude by doping with AsF_5, a strong electron acceptor.[3,4,22] However, unlike semiconductors, polymer's structure bends around the charge what results in a localized charge state known as polaron. [23] The hole state in the valence band or the electron state in the conduction band moves to the gap and remain isolated. Conduction thus occurs when this localize state jumps from one site to another.[20,23,24]

Available theories to study conduction through polymers use ad-hoc parameter to represent polymer electronic properties, for instance, the density of states is represented by a normal distribution, what somewhat hides the atomic nature of the polymer. This paper describes how Quantum Chemistry-based modeling of the electronic structure of polymers can be performed to provide parameters to later model conduction in polymers and polymeric devices. Since the techniques used here are at the atomic level, changes on the composition or conformation of polymers will directly affect the parameters thus modifying conductive properties. This work is the basal part of a larger model to study conductivity in polymers with atomic resolution.

Theory

Quantum chemistry methods are methods to solve the Schrödinger equation in different conditions. Different methods differ from each other on the approximations to formulate the Hamiltonian and the approximations followed to solve it. Two different families of methods are relevant to this work, methods of Density Functional Theory (DFT) and Semiempirical Methods.

The characteristic of Density Functional Theory is that the Schrödinger equation is solved for the electron density rather than individual electrons; thus the problem is solved for just 3 spatial coordinates rather than $3N$ coordinates (N being the number of electrons) as in full electron methods.[25-27] This is justified by a theorem due to Hohenberg and Kohn,[28] that proves that all electronic properties of a molecular system can be obtained from the electron density. The gain in simulation time is used to increase the accuracy of the functionals, particularly the exchange and correlation terms. Results provided with DFT have accuracy comparable to high level all electron ab initio methods at the computational cost comparable to that of HF.[26,27] In this work the Becke 3 Perdew-Wang 91[29-31] was used in combination with the 6-31++G** basis set.

Semiempirical methods instead, are obtained by adding approximations to the HF formalism but accuracy is partially recovered by using fitting parameters. Well-parameterized semiempirical methods can usually predict certain molecular properties with more precition than HF, at least for the family of molecules used to parameterize the method or similar ones.[26] Semiempirical methods are obtained from the HF formalism by: a) considering only valence electrons and representing core electrons in an approximate way, b) using a small basis set, c) neglecting some of the integrals, and d) making the other integrals equal to parameters that can be obtained from experiments.[26]

Austin Model 1 (AM1) and the Modified Neglect of Diatomic Overlap-Parametric Method Number 3 (MNDO-PM3 or simply PM3) are semiempirical methods that belong to the MNDO general set of methods and were developed to avoid the need of parameterize for every application. Molecular properties such us ionization potential and excitation energies of a set of training molecules are calculated in terms of parameter that are then optimized using least

square fit for a large set of experimental values.[26] With these parameters, now fixed for usage, these methods produce accurate results for large number of molecular systems.

Semiempirical methods provide a good estimation for the geometrical structure of polymer but they perform poorly when electronic structures are of interest. Particularly, energy of unoccupied levels is greatly overestimated and thus HLG is very poorly predicted. Calculations reported below show that the HLG predicted by semiempirical methods AM1, MNDO, and PM3 are in good qualitative agreement with the same property predicted by DFT for short chains, but semiempirical methods overpredict this property by several eVs. This disagreement is unacceptable if conductive and photoconductive properties are of interest. DFT instead seems to asymptotically converge to the right results when compared to experimentally available values.

In summary semiempirical method allow calculation of fairly large chains but will not be accurate while DFT is more accurate but will not work on large systems. Both methods are then combined using the fact that semiempirical methods do indeed produce accurate geometries. Geometries are first optimized at a semiempirical level and then used calculate electronic structure at a DFT level.

Results

Comparison of geometry prediction

Using semiempirical geometries to calculate electronic properties at the DFT level of theory is only valid if the geometries predicted by semiempirical methods are acceptably close to those predicted by DFT.   For Polyacetylene (PA), AM1 and DFT were used to optimize the geometry of oligomers with 1 to 10 monomers. Table I shows minimum, maximum, and average values for bond lengths and angles as well as the maximum, minimum and average difference between the predictions of these two methods, as a function of the number of monomers in the chain. In all the cases the error induced by using the AM1 geometry is within 2% of the bond or angle values, although in most cases this error is around 1%.

Table 1: Maximum, minimum, and average difference between the AM1 and DFT predictions of bond lengths and angles for PA oligomer of 1 to 10 units. Maximum, minimum, and average bond lengths and angles, as predicted by DFT are also reported for comparison.   In all cases the difference is within 2% of the corresponding magnitude with most cases being around 1%.

| Nº	Bond Length						Angle					
	Values			AM1-DFT Diff			Values			AM1-DFT Diff		
	Max	Min	Avrg	Max	Min	Avrg	Max	Min	Avrg	Max	Min	Avrg
1	1.112	1.112	1.112	0.019	0.019	0.019	104.5	104.5	104.5	0.0	0.0	0.0
2	1.333	1.087	1.136	0.007	0.011	0.010	121.7	116.6	120.0	2.094	1.047	1.396
3	1.497	1.086	1.173	0.023	0.004	0.016	125.3	106.6	114.7	2.217	0.119	1.021
4	1.455	1.086	1.185	0.014	0.004	0.010	124.2	116.4	120.0	1.848	0.478	1.061
5	1.495	1.086	1.198	0.023	0.004	0.014	125.2	106.5	116.5	2.620	0.208	1.095
6	1.448	1.085	1.204	0.014	0.000	0.010	124.4	116.5	120.0	1.854	0.456	1.140
7	1.494	1.085	1.210	0.025	0.000	0.012	125.2	106.4	117.4	2.584	0.085	1.195
8	1.446	1.085	1.213	0.014	0.002	0.010	124.5	116.5	120.0	1.928	0.477	1.191
9	1.494	1.085	1.217	0.023	0.002	0.012	125.1	106.4	117.9	2.609	0.232	1.189
10	1.445	1.085	1.219	0.014	0.003	0.011	124.5	116.5	120.0	1.997	0.448	1.220
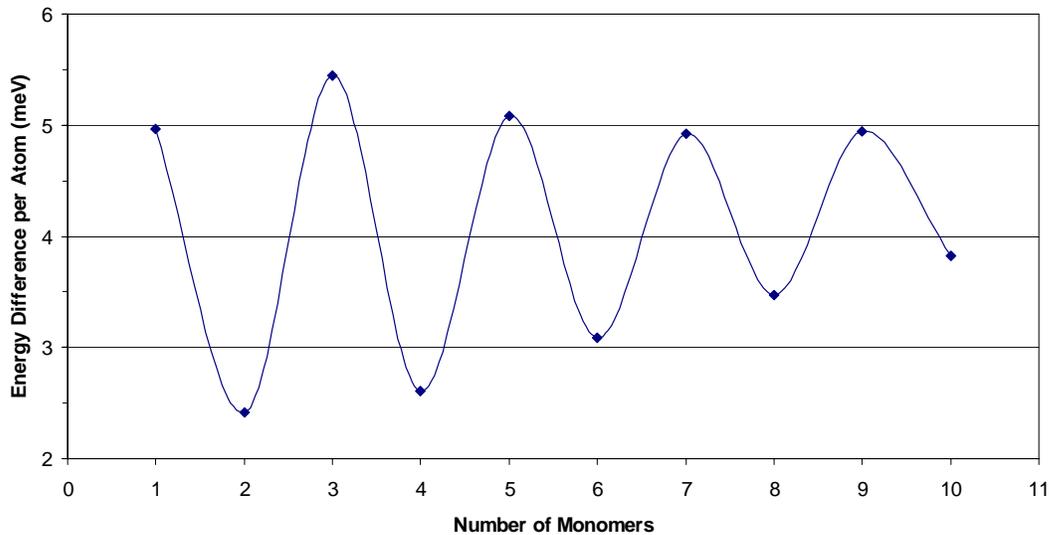
Figure 2: Difference in energy per atom calculated at a DFT level on a DFT geometry vs.
AM1 geometry

   As shown in table I, the geometry predicted by semiempirical methods are reasonable and
can be used to obtain electronic properties from DFT. To further study the agreement the total
energy of both geometries, calculated at a DFT level was compared and found to be in
agreement with 0.5% for all the cases. Figure 2 show the difference in energy per atom.
Notice that the vertical scale is in meV.
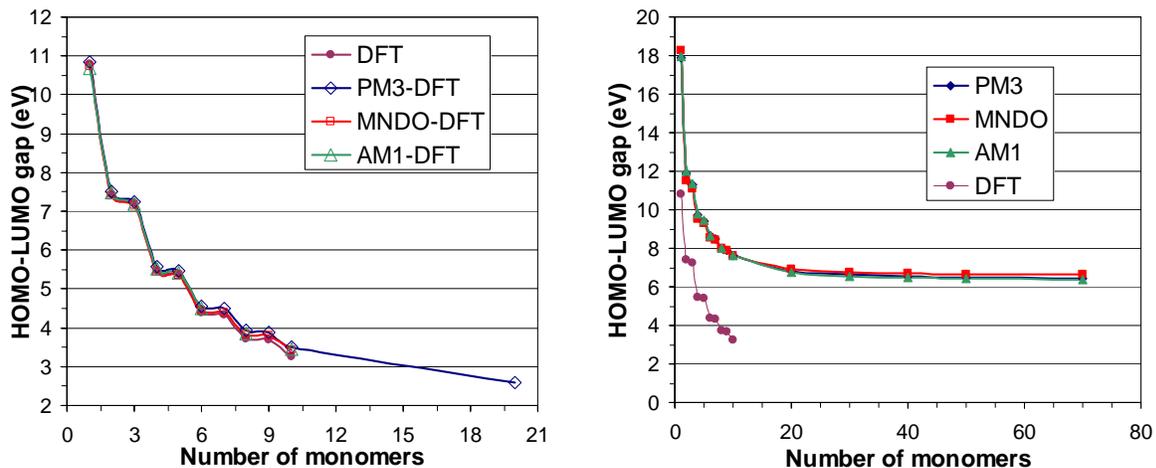
Electronic Structure

Figure 3: HLG for PA vs. Number of monomers in the chain. a) Optimization and electronic
structure calculated at the same level of theory. b) Electronic structure is calculated at a DFT level,
geometry is optimized with four different methods

Figure 3a shows the HLG of PA as a function of the number of monomers according to semiempirical
AM1, PM3, and MNDO methods compared to the DFT prediction of the same property. DFT predicts a
HLG that seems to converge to about ~2 eV, which is in good agreement with experiments that predict
to be above 1.7eV.[32] Qualitatively, the semiempirical methods show a similar trend to that of DFT but

they predict a HLG value ~6.3eV. Both methods are then combined, using the fact that semiempirical do indeed produce good geometries. Thus, the polymer geometry is optimized at a semiempirical level and the electronic structure is then calculated at a DFT level on the semiempirical geometry. Figure 3b shows the HLG at the DFT level over AM1, PM3, and MNDO geometries compared to HLG obtained with the optimized DFT geometry. The agreement is remarkable especially considering that the simulation time decreases tremendously. For the nanomer, the structure that took longer to converge, the simulation time for the full DFT optimization was 14 hours 46 minutes, instead, with the combined method the total simulation time was less than 28 minutes (37" for the AM1 optimization and 26' 52" for the DFT single point). For all the other cases, the total simulation time was from a few seconds to a couple of minutes.

Study of Optical properties of MEH-PPV

Similar results were obtained for MEH-PPV. Semiempirical calculations were done up to 20 monomers, while DFT single point calculations on AM1 semiempirical geometries were done up to the pentamer, with a total of 225 atoms. Attempts to optimize this system at a DFT level failed for chains larger than the dimer. The results show that the HLG predicted by semiempirical is about 6.9eV. DFT prediction for the monomer is 4.41 eV and the HLG decreases with the number of monomers, for the pentamer (the largest system calculated by us) its value is 2.9eV (Figure 5). This is again in good agreement with experiments; this polymer is observed to absorb visible light at 2.5-2.1 eV.[33]
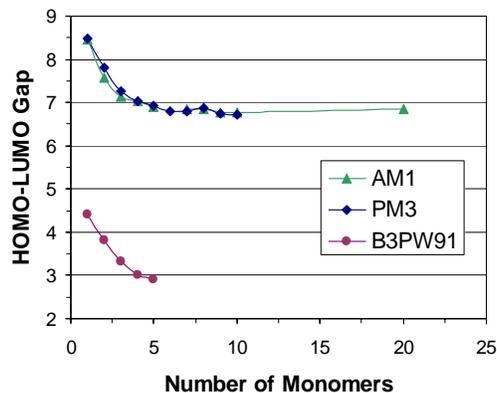

Figure 4: HLG for PA vs. Number of monomers in the chain.

This result is of a practical importance. Ultra-violet photoelectron spectroscopy is used (UPS) predict a HLG for this polymer to be above 7 eV by,[33] furthermore, previous semiempirical calculations predicted HLG in that range explaining the absorption properties of this polymer to local disorder structures in the polymer layer.[33] The results reported here clearly indicate that this polymer indeed has an optical gap thus its optical activity is not due to disorder but to the polymer itself.

Conclusions

Electronic properties of polymers clearly change as the polymer size increases, experimental information refers to large polymers and thus calculations on monomers have little chance to be able to describe the experimental observation. Using an approximate method in increasingly larger structures gives the possibility to observe the evolution of the polymer properties as the polymer molecular weight increases. As shown here semiempirical results can be used to determine qualitative behavior while DFT (on semiempirical geometries) allows for a more quantitative analysis. The results reported here showed that electronic structure calculations on semiempirical geometries are viable alternative to study electronic structure of polymer. This work is the initial step to a method under development to study electron transport in polymers and polymeric devices. The method needs accurate electronic structure calculations to calculate the Hamiltonian. This Hamiltonian is fed into a Green Function's Formalism that produces a density of states for the polymer. Finally this density of states is used in a Monte Carlo algorithm implementing transport by hopping. The entire model is worthless if HLG and other electronic properties are not well described, thus the result of this study showing combined semiempirical-DFT calculations at a very low computational cost is of a fundamental importance.

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