Charge patching method for electronic structure of organic systems

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Abstract

The development of the charge patching method for the calculation of the electronic structure of organic systems containing a large number of atoms was presented. The method was tested on a range of systems including alkane and alkene chains, polyacenes, polythiophenes, polypyrroles, polyfuranes, polyphenylene vinylene, and poly(amidoamine) dendrimers. The results obtained by the method are in very good agreement with direct calculations based on density functional theory, since the eigenstate errors are typically of the order of a few tens meV.

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There is a widespread interest to understand the optical and transport properties of organic semiconducting polymers and macromolecules, which have a range of applications including solar cells,[1] field-effect transistors,[2] luminescent devices,[3,4] and drug delivery.[5] The main step towards this goal on the theoretical side would be to have a reliable and efficient method for calculation of their electronic structures. However, for such systems containing a large number of atoms, the direct calculations based on density functional theory (DFT) are often not feasible. Here, we present the development of the charge patching method for the calculations of organic systems.

The charge patching method[6–9] is based on a general idea to predict the behavior of a large system based on the properties of its small constituents. Similar ideas were in the past applied by partitioning a molecule into interacting fragments,[10] into atomic like regions,[11] and combined with the idea of molecular similarity in quantitative structure-activity relationships analysis.[12,13] The charge patching method exploits the fact that in systems with covalent bonds, the distribution of charge density around a given atom depends mainly on its local environment. One can therefore define a charge density motif corresponding to a given atom in a particular environment. In order to find the motif, one performs the DFT calculation on a small system where a given atom has a similar environment and extracts the motif from such a calculation. The charge density of the large system can then simply be found by adding together the motifs corresponding to each of the atoms in the system, rather than performing a self-consistent DFT calculation. Such method has recently been successfully applied to inorganic semiconductor systems, such as diluted nitrogen alloys,[6] quantum dots and wires,[7] impurities,[8] as well as carbon nanotubes and fullerenes.[9] Due to presence of covalent bonding, one expects that the charge patching approach should be applicable in organic systems as well. However, in organic systems, there is a variety of bonding types and local environments that a given atom can exhibit within the same molecule, in contrast to inorganic semiconductors where all atoms of the same element usually have the same environment. Therefore, there is a need to develop the appropriate schemes for the classification of atoms, their environment and motifs. A systematic methodology for performing charge patching calculations on organic systems will be presented, and tested by comparing the results obtained on a range of different systems with DFT results.

In order to classify the atoms and the motifs, we follow the idea present in the classification of atoms for force field calculations that the atoms of the same physical element are of

different type if their bonding environments differ. For example, in an alkane chain, there are two types of carbon atoms, one corresponding to the atoms at the end of the chain (which are connected to three H atoms and one C atom) and one corresponding to the rest of carbon atoms (which are connected to two H atoms and two C atoms), which we can label for example as C_3 and C_2, respectively. A charge density motif is defined by the type of the central atom of the motif, the type of atoms connected to the central atom (its nearest neighbors) and the corresponding bonds (single bond, double bond, conjugated bond,...). In the case of atoms that are connected to one atom only (for example H atoms), this definition is extended to include next nearest neighbors. To illustrate this, in the case of an alkane chain there are six different motifs: $(C_3 - C_2, H, H, H)$, $(C_2 - C_3, C_2, H, H)$, $(C_2 - C_2, C_2, H, H)$ (in this notation the first atom is the central atom of the motif and the others are the atoms it is connected to), $(H - C_3 - C_2, H, H)$, $(H - C_2 - C_3, C_2, H)$, and $(H - C_2 - C_2, H, H)$ (in this notation the first atom is the central motif atom, the second one is its neighbor, and the others are next nearest neighbors).

The motif corresponding to central atom A is extracted from a small system used to generate the motifs, using the formula

$$m_A(\boldsymbol{r} - \boldsymbol{R}_A) = \frac{w_A(\boldsymbol{r} - \boldsymbol{R}_A)}{\sum_B w_B(\boldsymbol{r} - \boldsymbol{R}_B)} \rho(\boldsymbol{r}), \tag{1}$$

where $\rho(\boldsymbol{r})$ is the charge density calculated using DFT and $\boldsymbol{R}_A$ is the position of atom A. Atomic charge density multiplied by an exponentially decaying function was used as w_A. The charge density of a large system can then be found as

$$\rho_{\text{patch}}(\boldsymbol{r}) = \sum_A m_A(\boldsymbol{r} - \boldsymbol{R}_A). \tag{2}$$

The DFT calculations in the local density approximation (LDA) were performed using the plane-wave pseudopotential code PEtot.[14] Troullier-Martins norm-conserving pseudopotentials with a kinetic energy cutoff of 60 Ry were used. One should note that all results obtained here are susceptible to a well known LDA band gap problem. At this stage, no attempt was made to correct this problem, although semiempirical methods which correct it do exist. Once the charge density is obtained using the charge patching procedure, the single particle Hamiltonian can be generated by solving the Poisson equation for the Hartree potential and using the LDA formula for the exchange-correlation potential. The single-particle states and wavefunctions were then found using the folded spectrum method[15]

as implemented in the ESCAN code.[16] We have compared the energies of the Kohn-Sham single-particle states, as well as the total charge densities obtained using the charge patching method and the direct self-consistent LDA calculation. The results of the calculation are presented in Tables I and II. The average and the maximum value of the absolute difference of eigen-energies were used for comparison of energies, while for the charge density the quantity $\delta\rho = \int |\rho(\boldsymbol{r}) - \rho_{\text{patch}}(\boldsymbol{r})| d^3\boldsymbol{r} / \int \rho(\boldsymbol{r}) d^3\boldsymbol{r}$ is used as the measure of error.

Throughout the paper, an idealized molecule geometry where all bond lengths and angles are equal to the ideal bond lengths and angles, and to those of the corresponding motifs, was enforced. Although the main features of the electronic structure are certainly defined by the torsion angles, the changes in bond lengths and angles have some effect on the electronic structure. Such effects can be taken into account by using bond length and angle derivative motifs.[9] In the current paper, we will focus on the main challenge of the charge patching method, which is to describe the dependence of the electronic structure on the overall structure of the molecule, defined by its torsion angles and the molecule length. It should be also mentioned that the present version of the method is limited to charge neutral systems.

In the calculations of alkane chains, an idealized geometry was assumed with all bond angles equal to 109.47^0, $C - C$ bond lengths of 1.54Å, and $C - H$ bond lengths of 1.09Å. There are six motifs which were generated from an alkane chain in all trans configuration containing six carbon atoms (Fig. 1a). The comparison was then made for alkane chains in all trans configuration containing 4, 6, 8 and infinite number of atoms (polyethylene). From the results shown in Table I, one can see that an excellent agreement of the charge patching results with direct DFT results is obtained, with eigen-energy errors being typically less than 10 meV and all being less than 30 meV.

Next set of calculations was done for alkene chains with alternating single and double bonds. The single and double bond length were set to the values of 1.44 Åand 1.36 Å, respectively[17] and bond angles of 120^0 were assumed. The motifs were generated from the chain with 6 carbon atoms in all trans configuration (Fig. 1b). Using these motifs, the calculations were performed for the trans (Fig. 1b), the cis configuration (Fig. 1c) and the combined trans-cis configuration (Fig. 1d). The agreement between DFT and charge patching results is overall good. However, one should note that for longer chains in the trans or combined trans-cis configuration, the agreement becomes worse with eigen-energy errors

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being as large as 100 meV for infinite polymers. In these cases, the band gap is small and the signs of metallic behavior of the system start to appear. The main assumption of the charge patching method that the charge density feels mainly the local environment is not fulfilled in metallic systems.[6] Therefore, the error of the charge patching method becomes progressively larger as the band gap decreases. To further verify this conclusion, the calculations for alkene chain of length 6 and infinite length (polyacetylene) in trans configuration were performed with increased bond length alternation (1.54Å and 1.36Å). It is known[18] that the gap of polyacetylene is proportional to bond length alternation. Therefore, the band gap is bigger in this case, and as we have expected, the charge patching method performs better.

We would further like to study the polymers containing closed rings. Therefore we first test the method for the acene molecules. The idealized geometry was assumed with all conjugated bond lengths of 1.40 Å, $C-H$ bonds of 1.09 Å and bond angles of 120^0. The motifs were extracted from DFT calculation on an anthracene molecule (Fig. 1e). The average eigen-energy error for each of the molecules is less than 15 meV and all errors are less than 40 meV. Next, we study the oligomers of thiophene, furane and pyrrole molecule. They can be all described by the same chemical formula, shown in Fig. 1f, where X should be replaced with S (thiophenes), O (furanes), or N-H (pyrroles). For each of these systems, the motifs are generated from the oligomer containing three rings. For furanes and thiophenes, the experimental bond lengths and bond angles of furane and thiophene molecule, summarized in Ref. 19, were assumed and the lengths of bonds connecting the rings were taken from Ref. 20. For pyrroles, these parameters were taken from Refs. 21 and 22, respectively. From the results presented in Table II, one can see that average energy errors are less than 30 meV. The charge patching method was also tested for the polyphenylene vinylene (PPV) polymer. Charge density motifs were calculated on an oligomer consisting of three rings, shown in Fig. 1g. All bond angles were taken to be equal to 120^0, conjugated bond lengths 1.40Å, while the same values for single and double bonds as in the case of alkene chains were assumed. A good agreement with DFT results was again obtained, with eigen-energy errors at all $\boldsymbol{k}$-points being below 40 meV.

The results obtained so far establish a good performance of the charge-patching method for systems with a small number of atoms in the supercell. As an example of the calculation involving a larger number of atoms, we choose an alkane chain with 50 carbon atoms (152 atoms in total), where we can still obtain the direct DFT results for comparison. Fur-

thermore, the applicability of the motifs generated from an all trans configuration (with all torsion angles of 180^0) to chains where a different distribution of torsion angles is present, should be tested. The geometry of the alkane chain was therefore generated from a classical molecular dynamics (MD) simulation at 300 K. The simulation was performed for 100 ps, where the initial state in the simulation was an all trans state. The structure obtained was then relaxed to a local minimum. At the end of MD simulation, force field coefficients for the bond length and angle terms were increased to enforce the ideal bond length and angle values. Both the MD simulation and relaxation were performed using the TINKER code[23] where MM3(2000) classical force field[24] was used. The motifs used to generate the charge density are the same that have been used for short alkane chains. The results of the comparison presented in Table I and Fig. 2a and b indicate that charge patching method works well for this folded alkane chain.

Next, we would also like to establish the method in the case of larger systems, where the direct DFT approach is not feasible. As a first example, we choose an alkane chain with 1000 carbon atoms (3002 atoms in total). The geometry of the chain (which was generated in the same manner as in the previous case except that MD simulation was run for 400 ps) and the isosurface plots of the wavefunctions of the HOMO and LUMO orbitals are presented in Fig. 2c. The calculated HOMO-LUMO gap is 4.90 eV. The calculation of one state using 32 processors of the IBM POWER 5 system takes about one hour. Bearing in mind that both the charge patching procedure and the folded spectrum method scale linearly to the size of the system,[6,15] this implies that the states of the systems with as much as even ten thousand atoms could be calculated in reasonable amount of time with present day available computational resources.

Finally, the charge patching method was applied to poly(amidoamine) (PAMAM) dendrimers, widely investigated organic macromolecules with drug delivery and biomedical applications.[5] The coordinates of atoms in the molecule were taken from MD snapshots reported in Ref. 25 and were further relaxed using a similar procedure as in the case of alkane chains. There are 17 different motifs which were generated from a generation 0 dendrimer (containing 84 atoms). For a generation 0 dendrimer, the average error of eigen-energies of the first 5 states below and above the gap is 59 meV, while the charge density error is 1.2%. While these errors are slightly bigger than in previous cases, it is important to note that wavefunctions calculated by the two methods resemble each other and are localized in

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the same regions of space. The generated motifs were then applied to calculate the states of a generation 3 dendrimer containing 1092 atoms. The obtained HOMO – LUMO gap is 1.64 eV, while the wavefunctions of several states are shown in Fig. 3.

In summary, the charge patching method for the calculation of electronic states in organic systems was developed. This methodology should enable theoretical studies of properties of a wide range of organic systems, which were so far beyond the reach of present day computational resources.

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TABLE I: The comparison of eigen-energies and charge densities obtained by DFT and charge patching in the case of alkanes, alkenes and acenes. The average and the maximal value of the absolute error in eigen-energies $\Delta\varepsilon_{\mathrm{av}}$ and $\Delta\varepsilon_{\mathrm{max}}$, the relative charge density error $\delta\rho$ (defined in the text), and the energy gap obtained by DFT E_g^{DFT} and charge patching E_g^{CP} are presented. All eigenstates in the valence band and several first eigenstates in the conduction band are used in the comparison. The numbers in the first column denote the length of the chain.

system	$\Delta\varepsilon_{\mathrm{av}}$ (meV)	$\Delta\varepsilon_{\mathrm{max}}$ (meV)	$\delta\rho$ (%)	E_g^{DFT} (eV)	E_g^{CP} (eV)
alkanes					
4, trans	8.7	14.3	0.12	6.882	6.892
6, trans	5.5	13.2	0.16	6.362	6.357
8, trans	6.4	28.3	0.13	6.049	6.035
∞, trans	14.4	24.6	0.11	5.267	5.247
50, MD	7.6	27.8	0.34	5.651	5.621
alkenes					
4, trans	20.5	35.5	0.24	3.742	3.749
6, trans	12.3	36.1	0.15	2.909	2.907
8, trans	20.5	75.7	0.27	2.415	2.408
∞, trans	40.0	97.3	0.53	0.707	0.680
4, cis	20.3	34.9	0.24	3.742	3.749
8, cis	13.6	29.2	0.43	2.575	2.572
∞, cis	16.0	48.7	0.65	1.458	1.450
8, trans-cis	14.4	68.8	0.68	1.983	1.973
∞,trans-cis	41.2	111.1	0.94	0.371	0.322
alkenes with increased bond length alternation					
6, trans	7.1	17.9	0.15	3.234	3.232
∞, trans	27.3	56.7	0.30	1.488	1.476
acenes					
benzene	11.9	35.4	0.49	5.049	5.011
naphtalene	13.0	28.2	0.35	3.154	3.167
anthracene	11.4	29.5	0.33	2.036	2.053
tetracene	9.9	30.1	0.37	1.337	1.354
pentacene	10.0	31.2	0.38	0.874	0.889

TABLE II: The comparison of eigen-energies and charge densities obtained by DFT and charge patching for oligomers and polymers of thiophene, furane and pyrrole, as well as for PPV polymer. The numbers in the first column denote the number of closed rings present in a molecule. The same notation as in Table I was used.

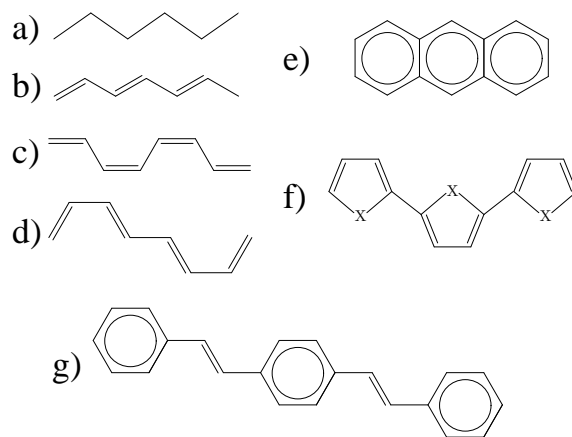| system	$\Delta\varepsilon_{\mathrm{av}}$ (meV)	$\Delta\varepsilon_{\max}$ (meV)	$\delta\rho$ (%)	E_g^{DFT} (eV)	E_g^{CP} (eV)
thiophenes					
2, trans	5.5	19.8	0.14	2.974	2.973
4, trans	11.4	36.6	0.12	2.101	2.096
6, trans	15.9	37.7	0.13	1.827	1.822
∞, trans	1.6	6.9	0.12	1.449	1.444
furanes					
2, trans	13.0	40.5	0.17	3.405	3.403
4, trans	20.7	78.5	0.15	2.503	2.492
6, trans	27.9	83.4	0.15	2.207	2.193
∞, trans	8.5	35.2	0.15	1.822	1.809
pyrroles					
2, trans	5.4	21.2	0.12	3.419	3.417
4, trans	22.7	68.2	0.11	2.542	2.532
6, trans	27.5	76.1	0.12	2.266	2.252
∞, trans	20.0	44.5	0.12	1.923	1.909
PPV					
∞	19.8	38.9	0.23	1.161	1.155

Figure captions

Fig. 1: Structural formulas of the molecules and polymers investigated in this work.

Fig. 2: The probability density of the HOMO (blue) and LUMO (red) of the alkane chain with 50 carbon atoms calculated using DFT (part a), as well as with 50 (part b) and 1000 (part c) carbon atoms calculated using charge patching. The isosurfaces correspond to the probability of finding an electron inside the surface of 50%.

Fig. 3: The probability density of the HOMO-1 (light blue), HOMO (dark blue), LUMO (red) and LUMO+1 (pink) orbitals of the generation 3 PAMAM dendrimer. The isosurfaces corresponds to the probability of finding an electron inside the surface of 90%.

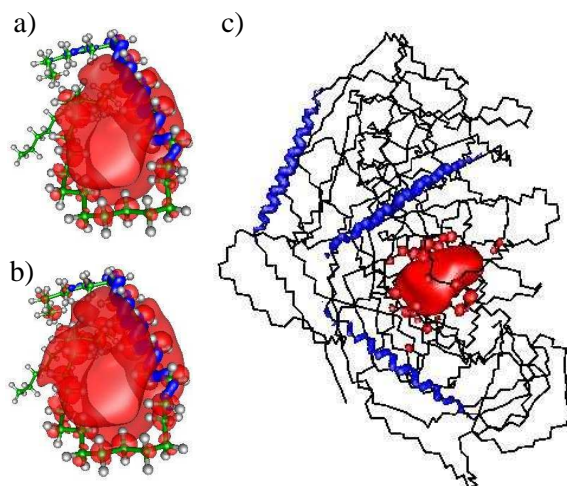FIG. 1: Structural formulas of the molecules and polymers investigated in this work.

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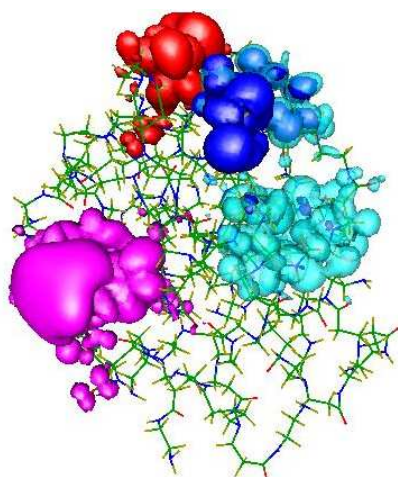
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