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Modelling organic molecular crystals by hybrid quantum mechanical/molecular mechanical embedding

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ABSTRACT

We present a hybrid quantum mechanical/molecular mechanical (QM/MM) embedding scheme to model organic molecular materials. The method employs specialist QM and MM codes as modules in an integrated way that enables the dynamic simulation of large numbers of molecules at a MM level with a smaller fraction treated at a higher QM level of theory. In this preliminary study our QM/MM methodology is applied to the high performance organic (opto)electronic material dithiophene–tetrathiafulvalene (DT–TTF). The QM/MM methodology is tested and confirmed with respect to experiment and previous cluster calculations. The effects of the more realistic treatment of the molecular environment are highlighted.

1. Introduction

Organic molecular crystals (OMCs) promise to form the basis for a wide range of new inexpensive (opto)electronic technologies, especially where structural flexibility and/or high surface areas are sought. Essential for such applications is the improvement of the performance of OMCs at realistic operating temperatures. Although it is largely agreed that at ambient temperatures, the charge mobility in OMCs is likely to be dominated by intermolecular hopping rather than band-like transport [1,2] a full understanding of the charge transport mechanism and the nature of charge carriers in this regime is still lacking [3]. The explicit theoretical treatment of the microscopic details of finite temperature phenomena in OMCs is complicated by the combination of (i) electronic effects (e.g. delocalisation, charge transfer) requiring quantum mechanical (QM) methods, and (ii) the timescales of thermally induced effects together with the weak dispersive intermolecular interactions, both favouring the use of more computationally efficient classical molecular mechanics (MM) methods. Recent efforts using both QM and MM methods separately (i.e. using MM methods to obtain reasonable thermally excited OMC configurations which can then be evaluated afterwards by QM methods) have lead to significant steps forward in our understanding of the finite temperature transport of localised carriers in a few important OMCs [4,5]. In the present investigation we employ both QM and MM methods combined in an fully integrated manner enabling an appropriately tailored treatment of an OMC in a single calculation. Such hybrid QM/MM calculations have been extensively used for dealing with numerous complex systems in many fields (e.g. organic and organometalic chemistry, solvation, biochemistry, and solid-state chemistry and catalysis) [6–8]. In all these cases the common feature is that is it desirable to treat a relatively small localised region of the system at a high (usually QM) level of theory whereas the effects of the remainder of the system can be adequately calculated using computationally efficient lower level methods (often MM). In such cases the main advantage of hybrid methods over pure QM approaches is in the significant gain in computational efficiency with very little loss in accuracy. Compared to the use of QM calculations as separate post-refinements to MM-derived system geometries, hybrid QM/MM methods also have the benefit of simultaneously accounting for both QM and MM interactions in a self-consistent manner. In this way QM/MM calculations use QM methods to account for geometric changes in the sub-system due to electronic effects (inherently poorly reproduced by MM calculations) while at the same time still allowing the use of MM methods for the efficient representation of any additional environmental influences on the local sub-system geometry. In this study our QM/MM methodology (described in detail below) is applied to dithiophene–tetrathiafulvalene (DT–TTF), an OMC with one of the highest reported room temperature field effect mobilities [9,10]. As far as we are aware this is the first attempt to describe the properties of an OMC by means of a hybrid QM/MM method. As such, the main objective of the present work is to validate our QM/MM approach with respect to both experimental data, where available,

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and to previous pure QM cluster calculations on the DT–TTF system. In particular we have previously shown that estimates of important parameters from a simple embedding approach using small QM cluster calculations are significantly different to those from an isolated DT–TTF molecule [11]. Especially with respect to comparison with these calculations, in this preliminary study, we focus only on very low temperature QM/MM simulations (i.e. effectively relaxed systems) on systems prepared by higher temperature annealing. We find that our method is able to reproduce a range of data and provides new results that further confirm the significant role of the molecular environment on parameters important to charge transport in DT–TTF.

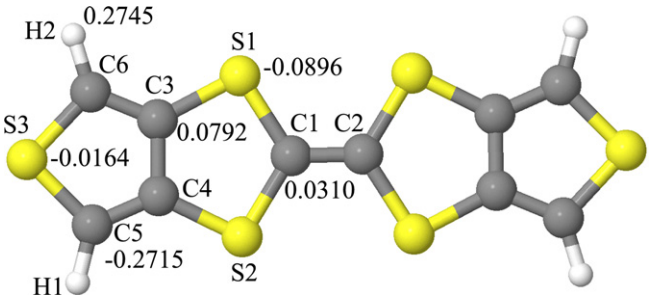

Fig. 1. Atomic structure of the neutral isolated DT–TTF molecule together with selected RESP charges for all symmetrically non-equivalent atoms.

2. Computational methodology

To study the crystallographic system of DT–TTF we used a periodic supercell simulation box of $6 \times 10 \times 4$ unit cells containing a total of 480 DT–TTF molecules with initial molecular geometries and cell parameters obtained from experimental crystallographic data [12,13]. In the hybrid QM/MM calculations the QM sub-system was taken to be either (i) a single DT–TTF molecule, or (ii) three DT–TTF molecules lying face-to-face in one-dimensional stack along the crystallographic *b*-axis (the interfacial DT–TTF interaction being by far the main intermolecular interaction [14]).

The QM forces on atoms were computed in a small sub-region of the system using Density Functional Theory (DFT) using the Gaussian 03 QM package [15], with the intra- and intermolecular forces of the remaining molecules in the MM region calculated using the General Amber force field parameters (GAFF) [16] employing the DL-POLY code [17]. Important for the success of a QM/MM method is the choice of interface (i.e. where and how and to divide the whole system into a QM sub-system and the MM environment) and further how and which information (e.g. forces, energies) is passed through this interface. In our calculations the passage of information between the QM and MM zones was achieved via the automated interoperation of Gaussian and DL-POLY MD via the PUPIL (Program for User Package Interface and Linking) framework [18–20]. PUPIL is a free, open source package created to facilitate the interfacing of MM-based molecular dynamics (MD) and QM programs. In PUPIL, the dynamics is carried exclusively by the MD program with the QM program providing the forces for the QM region. The forces from the QM region were calculated employing the B3LYP [21] functional evaluated taking into account all internal interactions of the molecule together with the effects of an electrostatically represented environment of the remaining molecules in the crystal. The electrostatic embedding environment is constructed by substituting the instantaneous positions of the classical atoms with partial charges. To help ensure a consistent treatment of the atomic charge distribution in the QM and MM zones the atomic partial charges were adjusted from the original GAFF values using the RESP strategy (Restrained ElectroStatic Potential) [22,23]. RESP derives atom-centered point charges from a fit to the QM-computed electrostatic potential at the molecular surface. In our case the geometry and the electrostatic potential of the isolated DT–TTF molecule optimised at a Hartree-Fock level of theory with a 6-31G(d) basis set were used to fit the RESP atomic partial charges (see Fig. 1).

For the calculations employing a QM-embedded charged DT–TTF molecule we also obtained the partial charges for the optimised DT–TTF molecular cation at the same level of theory. Under this scheme the electronic structure in the QM zone is polarized by, and adapts to, changes in the atomic charge distribution of the MM environment leading to changes in the molecular geometry in the QM zone. In the MM region the motion of the atomic centres in each molecule is determined by the inter- and intramolecular interactions given by the Amber force field (GAFF parameterization using the RESP-derived partial atomic charges). Both electrostatic and dispersive intermolecular terms in the Amber force field control the relative crystal positions of the molecules in the MM zone and further provide an interaction channel through which the MM region can respond to the instantaneous configuration of the QM-embedded region (which is seen by the MM region as a classical-treated region). The Ewald summation was applied to calculate the long-ranged electrostatics interactions in the crystal.

Purely classical MD simulations of the periodic supercell simulation box were first carried out employing an initial combination of short MD runs using both the NVT (constant number of molecules, system volume and temperature) and NPT (constant number of molecules, external pressure and temperature) ensembles to equilibrate the system in order to obtain an acceptable point to initiate the QM/MM simulation. At first, the initial configuration with the crystallographic geometries was allowed to relax at near to 0 K for 20 ps of NVT MD with an integration time step of 1 fs. The resulting system was then gradually warmed up to 300 K by 20 ps of NVT MD with an integration time step of 1 fs. The temperature of the system in each case was set using the Nosé-Hoover thermostat [24]. Finally, a NPT simulation was carried out for 100 ps to equilibrate the final volume of the supercell. Once the system volume is equilibrated and before starting with the hybrid QM/MM simulation, a further near-0 K MD relaxation was carried out for 75 ps keeping the new system volume constant. At the end of these relaxation steps the volume of the simulation supercell increased by only 5.38% (with respect to the volume of the supercell using the experimental crystal data) confirming an acceptably accurate performance of the MD (GAFF/RESP parameterization) setup (see Table 1). The aim of the relaxations is to prepare the simulation cell in a suitable starting configuration from which further relaxation using the more computationally expensive full QM/MM method is minimised. Two different classical systems were considered for this relaxation procedure, each starting from the last system configuration of the NPT simulation: (i) the system where all the DT–TTF molecules are neutral, and (ii) the system with one ionic $DT–TTF^{+}$ molecule. In order to maintain

Table 1
Comparison of DT–TTF crystal parameters between experimental crystallographic data (Refs. [13,14]) and the values from the classical MD(GAFF/RESP parameterization) NPT simulation at 300 K

DT-TF crystal parameters	Experimental (Refs. [13,14])	GAFF/RESP MD	Δ% deviation
a (Å)	10.906	11.098	1.76
b (Å)	3.991	4.061	1.75
c (Å)	14.030	14.278	1.77
α (°)	90	90	0.0
β (°)	110.82	110.82	0.0
γ (°)	90	90	0.0
Volume (Å^3)	570.792	601.476	5.38