# From Atomic Orbitals to Nano-scale Charge Transport with mixed Quantum/Classical Non-Adiabatic Dynamics: Method, Implementation and Application

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# Abstract

An efficient computational method to perform fully atomistic mixed quantum/classical non-adiabatic molecular dynamics in nano-scale organic semiconductors is presented and its implementation discussed. The methodology is termed fragment orbital-based surface hopping (FOB-SH) and rests on a DFT-parametrized tight-binding representation of the Hamiltonian (updated on-the-fly along the molecular dynamics) as well as an efficient calculation of nuclear gradients to propagate the coupled electron-nuclear dynamics. Common algorithmic extensions to the original surface hopping algorithm, such as the adjustment of the velocities along the non-adiabatic vectors upon successful non-adiabatic transitions and a decoherence correction, allow FOB-SH to reach total energy conservation, detailed balance and internal consistency. Further improvements and optimizations applied to FOB-SH to deal with a high density of electronic states characterizing condensed phase systems are discussed. Trivial crossing detection and a removal of decoherence correction-induced spurious charge transfers are particularly important for accurate dynamics and the convergence of charge carrier mobility and wavefunction delocalization with increasing system size. The application of FOB-SH to the calculation of charge mobilities and transport mechanism across the 2D high-mobility planes of experimentally well-known molecular crystals is presented.

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# 1 Introduction

Many physical processes require a theoretical treatment that goes beyond the Born-Oppenheimer or adiabatic approximation. Photophysical processes, photochemical reactions, electron and exciton transfer are well-known examples. Over the past few decades a plethora of different non-adiabatic dynamics methods have been developed and the choice depends, as usual, on the particular question under investigation and, in particular, on the size of the system under study.<sup>1-3</sup> Fully quantum dynamical methods treating both electrons and nuclei at the quantum level are available, e.g. multi-configuration time-dependent Hartree (MCTDH)<sup>4</sup> and its multi-layer version,<sup>5,6</sup> or full multiple spawning (FMS).<sup>7</sup> These methods can give accurate results for small photoactive molecules. For larger systems approximations have to be made but they can often be improved, sometimes systematically. A common approximation is the classical treatment of the nuclei leading to so-called mixed quantum-classical nonadiabatic molecular dynamics methods (MQC-NAMD), where the electronic wavefunction is propagated quantum mechanically in the time dependent potential of the classical nuclei. Ehrenfest dynamics<sup>8</sup> and Fewest Switches Surface Hopping<sup>9-12</sup> are prominent examples, and another method, the classical  $limit^{13}$  of exact factorization<sup>14</sup> has quietly joined the team in recent years.

MQC-NAMD methods still require relatively efficient solvers for the electronic structure problem, e.g. time-dependent density functional theory (TDDFT).<sup>15,16</sup> While the combination of MQC-NAMD with TDDFT offers a powerful approach for the study of the photophysics and chemistry of medium-sized systems, typically molecules or small clusters of molecules in the gas phase, it becomes too expensive for large nano-scale or condensed phase materials. Here one usually resorts to quantum mechanics/molecular mechanics (QM/MM) or a QM/continuum embedding methodology where MQC-NAMD/TDDFT is only done in the QM region. Such embedding approaches are often very useful but they are only suitable in situations where the electronic excitation is relatively local, i.e. confined to one or a few molecules. There are, however, very important electronic processes that are not, or cannot *a priori* be assumed to be local. In that case all parts of the system need to be treated as electronically active and a separation into QM and MM parts is no longer possible. Examples are charge and exciton transport as well as exciton dissociation in organic materials with very little structural and energetic disorder. Such materials are of interest for next generation organic field effect transistors, solar cells and light emitting diodes. Another example is electron transport across biomolecular junctions where the charge mediating orbitals may be delocalized over the whole biomolecule and, in addition, the coupling to the electrode needs to be included at the QM level.

Several cost-effective strategies have been devised to deal with such scenarios. Some of the most promising are the use of density-functional tight-binding (DFTB) methods (e.g. self-consistent charge/density functional tight binding (SCC-DFTB)<sup>17,18</sup>) and other semiempirical electronic structure methods (e.g. Pariser-Parr-Pople (PPP) Hamiltonians<sup>19</sup> and fragment molecular orbital methods (FMO)<sup>20</sup>), which significantly reduce the computational complexity while maintaining reasonable accuracy. Depending on the problem under investigation, the atomic resolution can be given up altogether and non-adiabatic dynamics is done for a few selected nuclear degrees of freedom in combination with model electronic Hamiltonians, e.g. Holstein-Peierl Hamiltonian for charge transport.<sup>21,22</sup>

Our group has recently developed a semiempirical all-atom MQC-NAMD method termed fragment orbital-based surface hopping (FOB-SH), that is geared towards highly efficient time propagation of charge carriers or excitons in "soft" nano-scale materials and biomolecules. The FOB-SH methodology rests on a DFT-parametrized tight-binding representation of the electronic Hamiltonian that is updated on-the-fly along the MQC molecular dynamics trajectory to incorporate local and non-local electron-phonon couplings and their fluctuations. This approach enables fast (yet sufficiently accurate) calculation of the important quantities, such as site energies, electronic couplings and related nuclear gradients, in condensed matter systems subject to strong thermal fluctuations. Polaronic and localization/delocalization of charges and excitons are paramount to accurately describe transport properties and wavefunction delocalization, are naturally included in this description. Until now we have applied FOB-SH to charge transport in organic crystals and we will frequently refer to this problem when explaining our methodology in subsequent sections. Yet, FOB-SH provides a general framework that can be relatively straightforwardly extended to exciton transport and exciton dissociation to charge carriers, which is currently a work in progress.

In Section 2 we will introduce the tight-binding molecular orbital representation of the electronic Hamiltonian used in FOB-SH, exemplified on  $\pi$ -conjugated organic molecules, and explain the efficient calculation of the matrix elements, site energy and electronic coupling, respectively. In Section 3 we introduce the working equations of fewest switches surface hopping and present expressions for all the quantities needed to do FOB-SH dynamics, including non-adiabatic coupling elements and vectors, hopping probability and nuclear forces on the manifold of electronic states. To keep the presentation not too cumbersome with regard to technical details, we shall refer to our recent publications  $2^{3-28}$  for some derivations. Important properties that any surface hopping molecular dynamics simulations should fulfil are defined including energy conservation, detailed balance and internal consistency. In Section 4 we present the tricks of the trade, improvements to Tully's original fewest switches surface hopping algorithm, that make FOB-SH work. These are trivial crossing detection, decoherence correction and treatment of decoherence-correction induced spurious (long-range) charge transfer. In this section we also explain how we could speed-up our original implementation at virtually no loss in accuracy. This enabled us to carry out FOB-SH simulation of charge transport in very large systems of more than 1,000 organic molecules ( $\approx 100,000$ atoms) and to converge charge mobility, as described in Section 5. In this section we also briefly explain the new picture of charge transport in organic crystals that has emerged from FOB-SH simulations. In Section 6 we conclude with an outlook on ongoing and future extensions of FOB-SH.

# 2 Coarse-graining of electronic structure

#### 2.1 Hamiltonian and basis set

The electronic structure of typical organic semiconductors exhibits narrow bands across the entire Brillouin zone and a minimal band dispersion. In fact, the interaction between different molecular sites of the system (electronic coupling) is usually small, in the range of 10-200 meV. By analysing a set of 40,000 molecular semiconductors extracted from the Cambridge Structural Database (CSD), it was recently found in Ref.<sup>29</sup> that the median energy separation between HOMO and HOMO-1 energy levels is 0.66 eV (i.e. much larger than typical electronic coupling values). Hence, it is possible to conclude that band energies do not overlap effectively and that the electronic Hamiltonian constructed in the space of the relevant frontier orbitals of the molecules forming the crystal e.g. highest occupied molecular orbital (HOMO) for hole transport (or lowest unoccupied orbital (LUMO) for electron transport),  $\phi_k$ , is expected to give a good approximation to the true band structure of the highest valence (or lowest conduction band).<sup>30–32</sup> As an example we show the rubrene crystal in Figure 1(A), where the HOMO band state of the crystal (Figure 1(C)) closely resembles a linear combination of HOMO orbitals of single molecules (Figure 1(B)): the molecular identity is preserved in the crystal.

These considerations motivate the use of simplified one-particle electronic Hamiltonians for hole or excess electron transport,

$$H = \sum_{k} \epsilon_{k} |\phi_{k}\rangle \langle \phi_{k}| + \sum_{k \neq l} H_{kl} |\phi_{k}\rangle \langle \phi_{l}|$$
(1)

where,  $\phi_k = \phi_k(\mathbf{R}(t))$  is the orthogonalized HOMO (LUMO) of molecule k for hole (electron) transport,  $\mathbf{R}(t)$  are the time-dependent nuclear coordinates,  $\epsilon_k = H_{kk}(\mathbf{R}(t))$  is the site energy, that is, the potential energy of the state with the hole (excess electron) located at site k and  $H_{kl} = H_{kl}(\mathbf{R}(t))$  is the electronic coupling between  $\phi_k$  and  $\phi_l$ . All Hamiltonian matrix elements, i.e. site energies and couplings, depend on the nuclear coordinates which, in turn, depend on time,  $\mathbf{R} = \mathbf{R}(t)$  as determined by the nuclear dynamics (see Section 3).

The orthogonalized basis,  $\{\phi_l\}$ , used to represent the Hamiltonian in Eq. 1, is obtained via Löwdin orthogonalization of the non-orthogonal orbital basis,  $\{\varphi_k\}$ , whose elements are the HOMO (LUMO) orbitals of isolated fragments (calculated as explained in Section 2.2),

$$\phi_l(\mathbf{R}) = \sum_{k=1}^{M} T_{kl} \varphi_k(\mathbf{R})$$
(2)

where  $T_{kl} = [\mathbb{S}^{-1/2}]_{kl}$ , with  $\mathbb{S}$  the overlap matrix of the fragment orbital basis set (with elements  $[\mathbb{S}]_{kl} \equiv \bar{S}_{kl} = \langle \varphi_k | \varphi_l \rangle$ ). The efficient calculation of the overlap matrix and associated orbital reconstruction along FOB-SH dynamics will be presented in Section 2.2.

#### 2.2 Site energies and electronic couplings

A cornerstone of the FOB-SH is an efficient computation of the electronic tight-binding Hamiltonian in Eq. 1 (and related forces acting on the atoms of the system).<sup>23</sup> The Hamiltonian matrix elements are effectively evaluated at each step along the dynamics by using a combination of parametrized force-field and approximate electronic coupling computations. This avoids explicit expensive electronic structure calculations and allows the simulation of charge transport in realistic nano-scale systems over relatively long (picoseconds) time scales. In particular, the diagonal elements  $H_{kk} = \langle \phi_k | H | \phi_k \rangle$ , are calculated *via* force-field energy contribution where the molecule k is charged and all the other M - 1 molecules are neutral (with M total number of molecules whose orbitals contribute to form a basis for Eq. 1). The force-field parameters for the charged state are suitably parametrized to reproduce the intramolecular reorganization energy from DFT calculations as done, e.g., in Refs.<sup>27,33</sup> for several OSs. The off-diagonal elements  $H_{kl} = \langle \phi_k | H | \phi_l \rangle$ , that correspond to the electronic coupling matrix elements, are calculated using the recently developed analytic overlap method (AOM).<sup>34</sup> The AOM relies on two assumptions: (i) a linear relationship between off-diagonal  $H_{kl}$ and the overlap  $\bar{S}_{kl}$  (overlap between the projected (non-orthogonal) fragment orbitals into Slater-type functions) and (ii) an analytical expression to calculate  $\bar{S}_{kl}$  (see below). The AOM coupling is written as:

$$H_{kl} = C\bar{S}_{kl} \tag{3}$$

C is a fitting parameter and can be obtained by correlating the overlap  $\bar{S}_{kl}$  against DFT calculations, e.g. scaled fragment orbital DFT (sFODFT)<sup>35–37</sup> as done in Refs.,<sup>27,34</sup> or wavefunction-based methods.<sup>38</sup> AOM allows the calculation of  $H_{kl}$  for a cost several orders of magnitude lower than explicit electronic structure calculations.<sup>34</sup>

In the first step of the parametrization of AOM couplings, the (non-orthogonal) molecular frontier orbital,  $\varphi_k$  is obtained by DFT calculation on an isolated molecule (HOMO is used for hole transfer and LUMO for electron transfer). This orbital is then projected on a minimum Slater basis of p orbitals with optimized Slater decay coefficients as proposed in Ref.<sup>34</sup> For  $\pi$ -conjugated systems, it is usually sufficient to include only one optimized Slater p-orbital per atom contributing to  $\pi$ -conjugation, in this case:

$$\varphi_k = \sum_{i \in k}^{atoms} c_{p\pi,i} p_{\pi,i} \tag{4}$$

where *i* runs over all  $\pi$ -conjugated atoms in molecule *k* and  $p_{\pi,i}$  is the Slater type orbital *p* on atom *i*,  $c_{p\pi,i}$  is the corresponding (normalized) expansion coefficient obtained by projection of the DFT molecular frontier orbital. In this minimum Slater basis the overlap between the (non-orthogonal) HOMO (LUMO) orbitals ( $\varphi_k, \varphi_l$ ) of two monomers forming a dimer,  $\bar{S}_{kl}$ , is calculated analytically and is very fast due to the small number of basis functions involved:

$$\bar{S}_{kl} = \langle \varphi_k | \varphi_l \rangle = \sum_{i}^{atoms} \sum_{j}^{atoms} c_{p\pi,i} c_{p\pi,j} \langle p_{\pi,i} | p_{\pi,j} \rangle.$$
(5)

The overlap  $\langle p_{\pi,i} | p_{\pi,j} \rangle$  can be calculated extremely efficiently using the analytic formulas

provided by Mulliken.<sup>39</sup>

The second step in the AOM procedure involves the calculation of electronic couplings to use as a reference for the parametrization of C on a set of molecular dimer geometries along MD. We note in passing that the results presented therein are obtained by using reference couplings from sFODFT calculations.<sup>35–38,40</sup> Importantly, good linear correlation in Eq. 3 between  $\bar{S}_{kl}$  and  $H_{kl}$  from sFODFT was found for different organic molecules<sup>27,34</sup> and the HAB7- database for electronic couplings.<sup>38</sup>

Possible shortcomings of AOM arise from the fact that, although atomic orbitals comprising the HOMO (LUMO) follow the motion of the atoms during the dynamics, the expansion coefficients in Eq. 5 are otherwise frozen. However, some checks indicated that this is a very good approximation, especially for rigid molecules, where orbitals are stable against intermolecular vibrations. To improve reconstruction of the orbitals along the dynamics, for example for flexible molecules, AOM could be supplemented with more sophisticated interpolation schemes (e.g. machine-learning techniques), nowadays used to develop a new generation of force-fields.<sup>41,42</sup>

The quality of the coarse-grained Hamiltonian in Eq. 1 (supplemented with sFODFT and AOM couplings) can be assessed by comparing the density of its eigenstates (DOS) against the DOS obtained from Kohn-Sham DFT band structure calculations.<sup>28</sup> To this end, a static electronic Hamiltonian (with zero site energies all coupling the same in a given direction) of the form of Eq. 1 is constructed and diagonalized for the high-mobility plane of rubrene, comprised of 5,000 sites and using the atomic coordinates from the experimental crystal structure. Notably, we find that the DOS of sFODFT and AOM Hamiltonians (dashed red and green lines respectively) in Figure 1(D) are in good agreement with the results from standard band structure calculations (performed on the crystallographic unit cells with k-point sampling as explained in Ref.<sup>28</sup>) with regards to both peak positions and bandwidth, thus attesting to the reliability of the Hamiltonian in Eq. 1. When thermal disorder is included through the fluctuations of the Hamiltonian matrix elements along finite temperature trajectories, the DOS becomes much broader (data in solid green lines) and the sharp band edges change into smooth tails, while the asymmetry in the DOS is still clearly visible. Temperature-related volume increases (not taken into account here) can partly reverse this situation and could lead to a decrease in the band width.

The typical asymmetry in the DOS of a given OS is a direct consequence of the coupling sign relationship characterizing the Hamiltonian of the two dimensional herringbone layer plane.<sup>43,44</sup> This relative sign of the electronic couplings for different crystal pair directions is of particular importance for the correct description of the electronic band dispersion of OS solids and, thus, for electronic transport properties and band states delocalization.  $^{44}$  For a more detailed discussion on why the sign combination is essential for the charge transport dynamic we refer to Refs.<sup>28,43,44</sup> It is important to point out that, in DFT calculations the relation between electronic coupling  $H_{kl}$  and overlap  $\bar{S}_{kl}$  is commonly antisymmetric for OSs, i.e. C is negative in AOM. When performing excess electron transport from FOB-SH, the site energies obtained from the force-field correspond to electronic energy levels, hence the sign of C is the same sign as in DFT calculations, C < 0. For hole transport dynamics, the site energies obtained from the force-field correspond to hole energy levels and therefore the sign of C obtained from DFT calculations needs to be inverted in FOB-SH simulations,  $C \rightarrow -C$ (see also Refs.<sup>28,43</sup>). Consequently, along FOB-SH dynamics the energy levels for both excess electron and hole transport are consistently populated according to  $\exp[-E_i/(k_{\rm B}T)]$  where  $E_i$  are the excess electron or hole energy levels.<sup>28</sup>

### **3** FOB-SH: basic equations

#### 3.1 Electronic propagation

The surface hopping (SH) method uses a swarm of totally independent classical trajectories propagated with the velocity-Verlet algorithm and representing a nuclear wavepacket (see Figure 2 for a scheme of the FOB-SH algorithm). Each trajectory carries a wavefunction,  $\Psi(t)$ . In the FOB-SH approach the hole (excess electron) is described by a time-dependent 1-particle wavefunction,  $\Psi(t)$ , expanded in the same orthogonal orbital basis,  $\{\phi_l\}$ , that is used to represent the Hamiltonian in Eq. 1,

$$\Psi(t) = \sum_{l=1}^{M} u_l(t)\phi_l(\mathbf{R}(t)), \tag{6}$$

where  $u_l$  are the expansion coefficients. Insertion of Eq. 6 in the time-dependent Schrödinger equation gives the time-evolution of the charge carrier wavefunction in the valence (conduction) band,

$$i\hbar\dot{u}_k(t) = \sum_{l=1}^M u_l(t) \left( H_{kl}(\mathbf{R}(t)) - i\hbar d_{kl}(\mathbf{R}(t)) \right)$$
(7)

where  $H_{kl}$  are the Hamiltonian matrix elements computed as explained in Section 2.2 and  $d_{kl} = \langle \phi_k | \dot{\phi}_l \rangle$  are the non-adiabatic coupling elements (NACEs) of the localized orbital basis. As those NACEs are generally very small compared to the Hamiltonian elements,<sup>28</sup> we refer to this basis as diabatic.  $H_{kl}$  and  $d_{kl}$  terms can be calculated at t and then at  $t + \Delta t$  when the nuclear positions have been updated by the first half of the velocity-Verlet algorithm. The expansion coefficients of the charge carrier wavefunction in the diabatic basis,  $u_k$ , are propagated according to Eq. 7 from time t to  $t + \Delta t$  in N steps of length  $\delta t$  (with N=5 in our simulations) using the fourth-order Runge-Kutta algorithm. At each electronic integration time step m, the  $H_{kl}$  and  $d_{kl}$  elements are linearly interpolated between t and  $t + \Delta t$ ,  $H_{kl}(t + m\delta t) = H_{kl}(t) + [H_{kl}(t + \Delta t) - H_{kl}(t)](m\delta t/\Delta t)$  for  $m = 1, ..., (\Delta t/\delta t)$ , and similarly for  $d_{kl}$ .<sup>23</sup>

The  $d_{kl}$  in the diabatic basis can, in practice, be evaluated using the AOM approach from the overlap  $\bar{S}_{kl}$ , Eq. 5, as detailed in Ref.<sup>23–25</sup> and briefly explained here. In particular, they are related to the NACEs in the non-orthogonal basis,  $\{\varphi_k\}$   $(d'_{kl} = [\mathbb{D}']_{kl} = \langle \varphi_k | \dot{\varphi}_l \rangle)$  by,

$$d_{kl} = \left[\mathbb{T}^{\dagger}\mathbb{D}'\mathbb{T}\right]_{kl} + \left[\mathbb{T}^{\dagger}\mathbb{S}\dot{\mathbb{T}}\right]_{kl} , \qquad (8)$$

Both  $\mathbb{D}'_{kl}$  and  $\dot{\mathbb{T}}$  are obtained from finite difference between t and  $t + \Delta t$  (note that  $\mathbb{T} = \mathbb{S}^{-1/2}$ , where  $\mathbb{S}$  is formed by  $\bar{S}_{kl} = \langle \varphi_k | \varphi_l \rangle$ ). If Eq. 8 allows the calculation of  $d_{kl}$  terms and to integrate exactly Eq. 7, we will show in Section 4.6 that neglecting them gives essentially the same dynamics but for much smaller simulation cost. This is somewhat expected as the  $d_{kl}$  (NACEs in the diabatic basis) are always small with a smooth evolution along the entire dynamics. Avoiding the calculation of  $d_{kl}$ , means bypassing a matrix-matrix-matrix multiplication (Eq. 8) at each nuclear time step and it permits a speed-up of almost a factor of 1.5 compared to the usual interpolation scheme when the system size reaches more than a thousand molecules (see Section 4.6).

#### **3.2** Non-adiabatic transitions

When the electronic propagation is completed, the core of any method based on SH is the choice of the active adiabatic potential energy surface (PES)  $E_a$  on which the nuclei evolve and the inclusion of the feedback from the electronic dynamics onto the nuclear motion. The energy of the active PES a is  $E_a = [\mathbb{H}^{ad}]_{aa}$ , with  $\mathbb{H}^{ad} = \mathbb{U}^{\dagger}\mathbb{H}\mathbb{U}$  and  $\mathbb{U}$  the unitary transformation matrix that diagonalizes  $\mathbb{H}$  in the diabatic representation to  $\mathbb{H}^{ad}$  in the adiabatic representation (eigenvectors basis).

In Tully's approach,<sup>9</sup> the active surface is decided in two steps: (i) a tentative new state is chosen *via* a stochastic process and (ii) the energy conservation requirement is applied to determine whether the change of active state is energetically possible. At step (i), the tentative new state is chosen with a probability  $g_{ja}(t)$ , where  $g_{ja}(t)$  are the hopping probabilities calculated at each timestep t between the active surface and all the other states j:

$$g_{ja} = -\frac{2\operatorname{Re}(c_j^* c_a d_{ja}^{\operatorname{ad}})}{|c_a|^2} \Delta t \tag{9}$$

where  $d_{ja}^{\rm ad} = \left\langle \psi_j | \dot{\psi}_a \right\rangle$  are the adiabatic NACEs. They are calculated from the diabatic

NACEs  $(d_{kl} \equiv [\mathbb{D}]_{kl})$  and the transformation matrix  $\mathbb{U}$ ,

$$d_{ja}^{\mathrm{ad}} = \left[\mathbb{U}^{\dagger}\mathbb{D}\mathbb{U}\right]_{ja} + \left[\mathbb{U}\dot{\mathbb{U}}\right]_{ja} \,. \tag{10}$$

The adiabatic coefficients  $c_j$  are the expansion coefficients of the electronic wavefunction in the adiabatic basis,  $\{\psi_i\}, \ \psi_i = \sum_{k=1}^M U_{ki}\phi_k$ , namely,

$$\Psi(t) = \sum_{i=1}^{M} c_i(t)\psi_i(\mathbf{R}(t)).$$
(11)

The probability to remain on state a is simply  $g_{aa} = 1 - \sum_{j \neq a} g_{ja}$ . After the calculation of the probabilities  $g_{ja}$  all states  $j \neq a$ , a random number is drawn to decide whether a hop can be attempted to a new state n. If so, the following condition should hold to ensure energy conservation,

$$E_{\text{tot}}(\mathbf{R}) = T_a(\mathbf{R}) + E_a(\mathbf{R}) = T_n(\mathbf{R}) + E_n(\mathbf{R})$$
(12)

where  $E_a$  and  $E_n$  are the potential energies and  $T_a$  and  $T_n$  are the nuclear kinetic energies before and after the hop. To ensure Eq. 12 is satisfied, the only quantity that can be adapted is the nuclear kinetic energy (and thus the nuclear velocities) after the hop,  $T_n = T_a + E_a - E_n$ . Based on the theoretical work of Pechukas<sup>45</sup> and Herman,<sup>46</sup> Tully prescribes to adjust the velocity component in the direction of the non-adiabatic coupling vectors (NACVs)  $\mathbf{d}_{I,an}^{\text{ad}} = \langle \psi_a | \nabla_I \psi_n \rangle$ .<sup>9</sup> But if there is not enough kinetic energy along the NACVs to satisfy Eq. 12, the hop is rejected, the active state remains state a and the velocity components along the NACVs direction are reversed<sup>47</sup> (see Section 4.1 for a discussion on the accuracy of this adjustment).

To apply the NACV-oriented adjustment in the FOB-SH framework, we derived in Ref.<sup>24</sup> an exact expression for the adiabatic NACVs ( $\mathbf{d}_{I,ij}^{\mathrm{ad}}$ ) in terms of the corresponding diabatic NACVs, the nuclear gradient of  $\mathbb{H}$  and the diabatic to adiabatic transformation matrix ( $\mathbb{U}$ ). Namely,

$$\mathbf{d}_{I,ij}^{\mathrm{ad}} = \frac{1}{E_j - E_i} [\mathbb{U}^{\dagger}(\nabla_I H)\mathbb{U}]_{ij} + [\mathbb{U}^{\dagger}\mathbb{D}_I\mathbb{U}]_{ij}$$
(13)

where  $E_j$  and  $E_i$  are adiabatic energies. We also showed that the last term in Eq. 13 is numerically small and can be ignored, which has led to the efficient "Fast NACV" approximation (see Section 4.1).

#### **3.3** Forces and nuclear equation of motion

We now turn to the propagation of the nuclei along the molecular dynamics and to the force calculation (see the related box in Figure 2). In the SH algorithm, the nuclei evolve on one adiabatic energy surface  $E_a$  chosen as described in Section 3.2. The nuclear force acting on nucleus I,  $\mathbf{F}_{I,a} = -\nabla_I E_a$  is obtained from the Hellmann-Feynman theorem as

$$\mathbf{F}_{I,a} = -\langle \psi_a | \nabla_I H | \psi_a \rangle = - \left[ \mathbb{U}^{\dagger} (\nabla_I \mathbb{H}) \mathbb{U} \right]_{aa}$$
(14)  
$$= -\sum_{k,l} \left[ \mathbb{U}^{\dagger} \right]_{ak} [\nabla_I \mathbb{H}]_{kl} [\mathbb{U}]_{la}$$
  
$$= -\sum_k |U_{ka}|^2 [\nabla_I \mathbb{H}]_{kk} - \sum_{k \neq l} U_{ka} U_{la} [\nabla_I \mathbb{H}]_{kl}$$

where  $[\nabla_I \mathbb{H}]_{kl} = \nabla_I \langle \phi_k | H | \phi_l \rangle$ . We refer to our previous paper<sup>24</sup> for an explicit derivation of Eq. 14. Importantly, the nuclear forces on a given adiabatic state *a* obtained in Eq. 14 consist of a linear combination of the diagonal forces ( $\nabla_I H_{kk}$  which are the forces related to the classical force-field potentials  $H_{kk}$ ), and off-diagonal forces on the diabatic states ( $\nabla_I H_{kl} = C \nabla_I \bar{S}_{kl}$  which are obtained using AOM). The weighting  $U_{ka}U_{la}$  is proportional to the projection of the active adiabatic states on the diabatic states. It therefore incorporates the effect of wavefunction delocalization on the adiabatic forces.

These forces permit the update of the nuclear positions with the second half of the velocity Verlet and carry on the dynamics at the next nuclear time step (see Figure 2). As the number of atoms in the system and the number of off-diagonal elements increase, the calculation of the off-diagonal gradients of the Hamiltonian becomes the time-limiting step. To reduce this computational cost, we have introduced a multiple time step algorithm (MTS).<sup>28</sup> In particular, all the gradients  $\nabla_I H_{kl}$ , with  $k \neq l$ , are updated only every N MD time steps and kept unchanged between two updates. N must be chosen to be small enough to reproduce the time oscillations of the off-diagonal gradients well. Since the electronic couplings in OSs generally fluctuate with an oscillation period of  $\approx 1$  ps,<sup>48</sup> one can expect the gradients of the couplings to oscillate on the same time scale. It is worth mentioning that similar MTS approaches are often used in MD codes to efficiently speed-up different parts of the computation.<sup>49,50</sup> The quality of this algorithm will be assessed in Section 4.6. Unfortunately, the same approach cannot be applied to the diagonal gradients without biasing the whole dynamics, as the site energies fluctuate in the order of the aromatic carbon stretching frequencies ( $\approx 20 - 30$  fs).

#### **3.4** Adiabatic populations and internal consistency

Tully's hopping probability (Eq. 9) was designed to ensure, for a two-states model system, that –within the fewest number of switches– the population of an adiabatic potential energy surface is equal to the amplitude of the corresponding adiabatic wavefunction. However, the energy conservation criteria leads to rejecting some hops along the dynamics (so-called frustrated hops). Without any correction, the electronic wavefunction will over-populate excited states that are high in energy and therefore unreachable for the classical nuclei. In addition to the presence of frustrated hops, that are necessary to maintain detailed balance and energy conservation, a more fundamental problem affecting SH is the overcoherent propagation of the off-diagonal elements of the density matrix (i.e., the coherence terms  $c_i^*c_j$ ) along the classical trajectory.<sup>51</sup> In reality, after leaving an avoided crossing where the adiabatic states mix, the center and/or the phase of each wavepackets evolving on different potential energy surfaces should diverge in phase space, decreasing the wavefunction coherence. This effect is not taken into account in standard SH where the coherence terms remain finite. This yields the so-called SH internal inconsistency, i.e. a divergence between  $\Psi(t)$  and  $\psi_a(t)$ . Importantly, due to this internal inconsistency, two different adiabatic populations coexist in the SH algorithm, the quantum amplitude averaged over many trajectories,

$$P_i^{\rm ad-wf}(t) = \frac{1}{N_{\rm traj}} \sum_{n=1}^{\rm traj} |c_{in}(t)|^2$$
(15)

and the surface population,

$$P_i^{\text{ad-surf}}(t) = \frac{1}{N_{\text{traj}}} \sum_{n=1}^{\text{traj}} \delta_{i,a_n(t)} , \qquad (16)$$

where  $a_n(t)$  is the index of the active state at time t of the trajectory n, and  $\delta_{i,a_n(t)} = 1$  if the state i is the active state a on which the nuclear dynamics is running at time t. The internal inconsistency of SH leads to a divergence of these two adiabatic populations. For this reason, as illustrated in Figure 2, before propagating the nuclear dynamics further, a decoherence correction (DC) is applied to attenuate the inconsistency between adiabatic wavefunction and surface populations as explained in Section 4.4.

#### 3.5 Mobility calculation and inverse participation ratio

Solving Eq. 7, gives the charge carrier wavefunction as a function of time,  $\Psi(t)$ . This gives access to key dynamical properties: the mobility tensor (Eq. 17), the extent of localization or delocalization (Eq. 20) of the charge carrier as a function of time and the mechanism by which the charge carrier moves within the material. The charge mobility can be expressed as a 2<sup>nd</sup> rank tensor using the Einstein relation,

$$\mu_{\alpha\beta} = \frac{eD_{\alpha\beta}}{k_{\rm B}T} \tag{17}$$

where  $\alpha(\beta)$  represent Cartesian coordinates, x, y, z. e is the elementary charge,  $k_{\rm B}$  the Boltzmann constant and T the temperature. The diffusion tensor components,  $D_{\alpha\beta}$ , is defined as the time derivative of the mean squared displacement (MSD) along the nine Cartesian components (MSD<sub> $\alpha\beta$ </sub>),

$$D_{\alpha\beta} = \frac{1}{2} \lim_{t \to \infty} \frac{\mathrm{dMSD}_{\alpha\beta}(t)}{\mathrm{d}t}$$
(18)

We note that different definitions of MSD have been used in the literature for the calculation of charge mobility from explicit wavefunction propagation depending on whether the center of charge motion (termed MSD<sup>coc</sup> in Ref.<sup>25</sup>), the spreading of the wavefunction (termed MSD<sup>var</sup> in Ref.<sup>25</sup>) or both effects at the same time (termed MSD), are considered (these different approaches have been compared and discussed in Refs.<sup>25,27</sup>). We concluded that MSD<sup>coc</sup> and MSD lead to the same diffusion coefficient, while MSD<sup>var</sup> will always lead to a null diffusion coefficient and mobility in the case of finite size polarons. In particular, MSD (which is our recommended definition<sup>24</sup>) is defined as the expectation value of the operator  $[(\alpha - \alpha_{0,n})(\beta - \beta_{0,n})]$ ,

$$MSD_{\alpha\beta}(t) = \frac{1}{N_{traj}} \sum_{n=1}^{N_{traj}} \langle \Psi_n(t) | (\alpha - \alpha_{0,n}) (\beta - \beta_{0,n}) | \Psi_n(t) \rangle$$
(19)

In Eq. 19,  $\Psi_n(t)$  is the time-dependent charge carrier wavefunction in FOB-SH trajectory n,  $\alpha(\beta)$  are the Cartesian coordinates,  $\alpha_{0,n}(\beta_{0,n})$  are the initial positions of the center of charge in trajectory n,  $\alpha_{0,n} = \langle \Psi_n(0) | \alpha | \Psi_n(0) \rangle$ , and the square displacements are averaged over  $N_{\text{traj}}$ FOB-SH trajectories.

A common measure to describe the delocalization of the charge carrier wavefunction  $\Psi(t)$ is the inverse participation ratio (IPR),

$$IPR(t) = \frac{1}{N_{\text{traj}}} \sum_{n=1}^{N_{\text{traj}}} \frac{1}{\sum_{k=1}^{M} |u_{k,n}|^4(t)}.$$
(20)

The IPR value corresponds to the number of molecules the wavefunction is delocalized over.

With a simple calculation one can show that a wavefunction (of a single trajectory) fully localized on a single molecule gives an IPR of 1, while a wavefunction homogeneously delocalized over N molecules gives an IPR of N.

### 4 FOB-SH: technical details

A plethora of variants have appeared in the literature<sup>1,2,12,52,53</sup> to systematically improve the standard SH method and to ensure that crucial requirements such as energy conservation, thermal Boltzmann population of the adiabatic states (i.e. detailed balance) and internal consistency are satisfactorily achieved. Common issues such as the correct rescaling of the velocities after a successful hop (related to the energy conservation and detailed balance) and the decoherence correction (DC) (necessary to attain internal consistency) have been largely investigated.<sup>1,51,54-60</sup> Yet several questions, especially in relation to the effect of the DC on the equilibrium properties and charge mobilities of condensed phase systems were, until recently, almost unexplored.<sup>1,22,25,26</sup>

In relation to the simulation of large systems with a high density of states, SH presents another less known shortcoming: the presence of trivial crossings hampering the solution of the electronic Schrödinger equation and causing unphysical long-range charge transfers (i.e. charge transfer events between states localized far away in space).<sup>21,22,61–63</sup> We will discuss this problem and possible solutions to restore the correct dynamics in Section. 4.3

Only very recently, we have discovered in Ref.<sup>26</sup> that along with these trivial crossing events, an additional source of spurious long-range charge transfers comes from the common DC schemes applied to SH. Wang and coworkers<sup>64</sup> independently reported the same issue in their simulations. We will discuss the problem in Section 4.5 and we will explain that, if not removed, the decoherence-induced spurious long-range charge transfer (DCICT) will render any mobility calculation and the dynamics erroneous. We will also discuss a possible correction algorithm for this problem, called spurious (long-range) charge transfer correction

#### $(SCTC).^{25,26}$

Finally, all semiclassical approaches, like SH, do not account for nuclear quantum effects that are particularly important at low temperatures, such as zero-point energy and tunneling. We will not discuss this problem in any depth in this contribution, since soft organic semiconducting materials are generally characterized by slow and low-frequency vibrations, that can to some extent be approximated by classical dynamics at least at room temperature.<sup>32</sup> Nevertheless, we refer the interested reader to our recent work about a possible way of including nuclear quantum effects in FOB-SH hole transfer simulations by combining it with ring-polymer molecular dynamics (RPMD).<sup>65</sup>

Improvements	Energy conservation	Detailed balance	Internal consistency	Mobility	IPR
Velocity rescaling	$\checkmark$	$\checkmark\checkmark$	-	$\checkmark\checkmark$	$\checkmark\checkmark$
Velocity reversal	-	-	$\checkmark$	-	-
Decoherence correction	-	-	$\checkmark$	$\checkmark\checkmark$	$\checkmark\checkmark$
Spurious charge transfer correction	-	-	-	$\checkmark$	$\checkmark$
Trivial crossings detection	$\checkmark$	$\checkmark$	-	$\checkmark$	$\checkmark$

Table 1: Importance of various improvements for accurate properties.

 $\checkmark \checkmark$ , the correction is very important for a given property.  $\checkmark$ , the correction is reasonably important for a given property. – the correction has no effect on a given property. The best FOB-SH set-up includes all the above corrections.

In what follows we discuss the application of the aforementioned improvements to the FOB-SH approach and their impacts on energy conservation, detailed balance, internal consistency for an accurate dynamics and transport properties such as mobility and IPR. A summary about the importance of each of these algorithms on different properties is given in Table 1 and it will be commented in the next Sections. The best FOB-SH set-up will then be used for the calculation of mobility in real nano-scale systems and comparison with experiments in Section 5.

In the following, we will show results for two different classes of systems. On the one hand, an atomistic OS model made of a dimer of ethylene-like molecules (ELMs) Figure 3(A), which have the same geometry as real ethylene molecules, but whose couplings and site-energies were chosen to explore the wide range of physical behaviours present in realistic materials. On the other hand, we consider real applications to relevant organic semiconducting crystals that are well-characterized by experiments (e.g. anthracene in Figure 4(A)). For a discussion on simulation details and system set-up we refer to our previous works.<sup>24,25,27</sup>

#### 4.1 Energy conservation after a successful hop

As prescribed by Tully,<sup>9,66</sup> whenever a surface hop occurs the velocities must be adjusted in the direction of the non-adiabatic coupling vectors (NACVs),  $\mathbf{d}_{I,an}^{\mathrm{ad}} = \langle \psi_a | \nabla_I \psi_n \rangle$ , between the adiabatic electronic states in order to conserve energy cf. Eq. 12. In FOB-SH the calculation of the NACVs is done according to Eq. 13. The energy drift in FOB-SH is  $\approx 10^{-7} - 10^{-8}$  Ha ps<sup>-1</sup> QMatoms<sup>-1</sup>, which is good compared to the drift of standard *abinitio* molecular dynamics ( $\approx 10^{-5}$  Ha ps<sup>-1</sup> atoms<sup>-1</sup>), albeit still larger than that in normal MD with standard force-field ( $10^{-12}$  Ha ps<sup>-1</sup> atoms<sup>-1</sup> (e.g. with CP2K software<sup>49,50</sup>) due to the presence of surface hops along the dynamics.

The adjustment of the velocities, not only allows the conservation of energy, but it permits one to attain detailed balance.<sup>12,24</sup> We compare the effect of velocity adjustment along the NACVs (Eq. 13) with an alternative commonly used, isotropic rescaling, where the velocities are all rescaled by the same value  $\kappa = \sqrt{1 - \frac{E_n - E_a}{T_a}}$ , for the excited state population of the ELM dimer system. The results are reported in Figure 3(B). The excited state surface population (Eq. 16) follows the exact Boltzmann population for all the coupling values investigated when the NACV adjustment (blue line) is applied, whereas the same population diverges from the correct result when the isotropic rescaling is used (red line) as too many hops are allowed.<sup>24</sup> A detailed discussion of this behaviour is given in Ref.<sup>24</sup> We also found that Tully's suggestion<sup>47</sup> to reverse velocity after an unsuccessful hop slightly improves internal consistency (see Table 1).<sup>24</sup>

#### 4.2 Stable electronic propagation in the diabatic basis

We highlight here that, in contrast with common SH approaches in which both the electronic and the nuclear equation of motion are often solved in the adiabatic basis (due to the fact that energy and forces are a common output of electronic structure calculations),<sup>16</sup> in FOB-SH only the nuclear propagation is carried out in the adiabatic basis while the electronic propagation is solved in the diabatic site basis (see Section 3.1). This has some advantages, most notable is the fact that, at avoided crossings, the adiabatic NACE,  $d_{ji}^{ad}$ , can be strongly peaked (because of the strong mixing of the adiabatic PESs). Thus, they could be easily missed unless the nuclear time step is chosen to be very small. This could lead to serious trivial crossing artifacts as we will point out in Section 4.3. By contrast, the NACEs between the diabatic states,  $d_{kl}$ , remain by definition small and negligible at avoided crossings ensuring a more stable and accurate propagation.<sup>67,68</sup> This practical advantage has led to the development of "local diabatization" in quantum chemical applications of SH.  $^{67,68}$  At each nuclear time step, the adiabatic states obtained from quantum chemistry are transformed to a diabatic basis in which the electronic wavefunction is propagated, followed by transformation back to the adiabatic basis. The first transformation is not needed in the FOB-SH approach as the Hamiltonian is directly constructed in a diabatic basis. Nevertheless, an additional issue comes from the fact that, although the electronic propagation is accurately carried out in the diabatic basis taking advantage of the smoothness of the NACEs, the probability to hop (Eq. 9) is still calculated in the adiabatic basis where NACEs peak in avoided crossing regions, in some cases causing trivial crossings that can easily go undetected and other important consequences. In Section 4.3, we will discuss approaches to overcome these issues.

#### 4.3 Trivial crossings and state-tracking

Trivial or unavoided crossings occur when two (or more) adiabatic potential energy surfaces with vanishing couplings cross between subsequent time steps. This causes a change in the state ordering that, if undetected, gives rise to serious problems: continuation of the nuclear dynamics on an incorrect active state, discontinuity in the nuclear forces deteriorating energy conservation, erroneous calculation of time derivatives, especially  $d_{ji}^{ad}$ , deteriorating excited state population and detailed balance, and most seriously in the context of charge transport, spurious and unphysical long-range charge transfer events between spatially distant states of similar energy.<sup>25,26</sup> The problem is magnified in the case of large systems with hundreds or more electronic states as e.g. in organic semiconductors, where adiabatic states very close in energy may be localized and spatially distant (hence have a small derivative coupling).

Different solutions have been proposed to deal with this issue: state-tracking algorithms between subsequent time-steps,<sup>61,66</sup> reduction of the state space involved in the transfer,<sup>21</sup> improved interpolation of the  $d_{ji}^{ad}$  terms<sup>69</sup> or improved hopping probabilities.<sup>70</sup> For example, the self-consistent fewest-switches SH (SC-FSSH) proposed by Wang and Prezhdo<sup>70</sup> introduces a simple self-consistency test to the calculation of the hopping probability from the current state to the energetically closest state. Trivial unavoided crossings are detected as a significant discrepancy between the summation of probabilities to hop from the current state to all other states according to the SH prescription, and the value of the effective change in population of the current state evaluated at the same time interval.

In our previous work we found this correction to be quite effective in improving detailed balance, energy drift and allowing for a larger time-step in a small 2-state ELM dimer system.<sup>24</sup> However for larger system with a higher density of states, where more than two states may cross with each other, SC-FSSH alone could not completely solve the trivial crossing problem.<sup>26</sup> Therefore, we adopted a combination of the SC-FSSH and a tracking procedure for the identity of the states along the dynamics to more effectively tackle this problem in large systems.<sup>25–28,33</sup> In particular, a map  $\mathcal{M}$  between the adiabatic states j at time t and adiabatic states i at time  $t - \Delta t$  with a maximum overlap criteria is built. First, the overlap  $O_{ij}$  is calculated as,

$$O_{ij} = \langle \psi_i(t - \Delta t) | \psi_j(t) \rangle \quad . \tag{21}$$

For each state j = l, the state  $i_l$  with the maximum overlap,  $|O_{i_ll}| = \max_i |O_{il}|$  is identified. If  $|O_{i_ll}| > 1 - \epsilon$  ( $\epsilon$  is a constant set to 0.1), the state l at time t is mapped with state  $i_l$  at time  $t - \Delta t$ ,  $\mathcal{M}(l) = i_l$ . After that step, all remaining states j = k at time t that could not be mapped to states at  $t - \Delta t$  (since  $|O_{i_k}| < 1 - \epsilon$  for all unmapped states i) are arranged by index (i.e. by increasing adiabatic energy) and mapped onto one another. As the function map  $\mathcal{M}$  is a bijection between states at t and states at  $t - \Delta t$ , the reverse map  $\mathcal{M}^{-1}$  (that associates states at  $t - \Delta t$  with states at t) is easily found. We can track the index of the active state at t, knowing its value at  $t - \Delta t$ ,  $a_t = \mathcal{M}^{-1}(a_{t-\Delta t})$ . This step allows one to change the index of the active state at eadiabatic NACEs (Eq. 10) and in particular the second term  $\left[\mathbb{U}^{\dagger}\dot{\mathbb{U}}\right]_{ia}$  is finally determined.<sup>25,26</sup>

We note at this point that the tracking procedure is essential to converge the MSD (and therefore the charge mobility) with system size (see Table 1). This is exemplified in Figure 4(C) and (D) for an embedded chain of anthracene molecules in a crystal (different colors represent the MSD for different chain lengths). When the state-tracking is switched on (Figure 4(C)), the MSDs are identical for the different chain lengths (except for the chain with 12 molecules where the MSD is slightly below the MSD of longer chains as the diffusive charge starts to feel the non-periodic boundary and to bounce back at the end of the chain).<sup>25</sup> On the other hand, when the state-tracking is switched off (Figure 4(D)), the MSDs for different chain lengths reach a plateau in a few femtoseconds that depends on the size of the system (i.e., the larger the system the larger the plateau value). In that uncorrected case, the numerous missed trivial crossings yield an unphysical, ultrafast and stochastic motion of the charge along the chain.

#### 4.4 Decoherence correction

A well known problem of SH is the overcoherence of the electronic wavefunction  $^{51,53,55}$  (see Section 3.4). Adopting a decoherence correction (DC) is fundamental to reach good internal consistency between surface and wavefunction population and to avoid unphysical delocalization of the wavefunction.

We have thoroughly investigated the effect of the decoherence corrections on transport properties (such as mobility and IPR) and equilibrium properties (such as energy conservation, detailed balance of the adiabatic states) as well as internal consistency in our previous works.<sup>25,26</sup> We have explored in detail: different flavours of collapsing approaches in which the electronic wavefunction is reset to the active state whenever a given criteria is fulfilled;<sup>55,60</sup> the exponential damping approach where the damping time,  $\tau_{ia}$ , (also referred to as decoherence time) can be calculated solely using energies, within the notorious energy-based decoherence correction (EDC) scheme<sup>51,56</sup> as  $\tau_{ia} = \frac{\hbar}{|E_i - E_a|} \left(C_0 + \frac{E_0}{T_a}\right)$  and choosing empirical parameters ( $C_0, E_0$ ), or using forces, within the force-based decoherence (FDC) scheme.<sup>58</sup> The latter decoherence time is more rigorous but also more expensive (see Ref.<sup>25</sup>). Finally we have investigated the stochastic damping approach, which rely on random numbers to determine whether the wavefunction should be collapsed onto the active state.<sup>71</sup> We found that generally damping approaches give better equilibrium properties (and internal consistency) than instantaneous collapsing schemes and the results are reasonably independent on the specific damping time.<sup>25,26</sup>

These effective damping algorithms consist of rescaling the adiabatic coefficients of all except the active (subscript "a") adiabatic electronic states  $(i \neq a)^{56}$  as:

$$c_i \to c_i \exp(-\Delta t/\tau_{ia})$$
 (22)

The coefficient for state a,  $c_a$ , is scaled appropriately to ensure norm conservation.<sup>51</sup> Beside the EDC and FDC decoherence times already mentioned, a further simplification of the former allows one to define a, parameter free, Heisenberg principle-related decoherence time:  $\tau_{ia} = \hbar/|E_i - E_a|$  (referred herein as EDC for simplicity as it corresponds to the choice of  $C_0 = 1$  and  $E_0 = 0$ ).

The impact of the decoherence on the internal consistency is shown in Figure 3(C), by means of defining the RMSE<sub>i</sub> =  $\left(\frac{1}{T}\int_0^T dt \left(P_i^{\text{ad-surf}}(t) - P_i^{\text{ad-wf}}(t)\right)^2\right)^{1/2}$  as a measure of the goodness of the internal consistency criteria. Without decoherence there is no longer internal consistency at any coupling value (red line). While FDC (dark orange line) and EDC with Heisenberg decoherence time (blue line) give similar results. In Figure 4(B), we show results for hole transport in a larger system (i.e. anthracene embedded chain, Figure 4(A)) as a function of state index. First we note that there is no longer internal consistency when the decoherence correction is switched off: the quantum population (Eq. 15), dashed red line, is almost the same for all electronic states, which corresponds to an infinite temperature for the electronic subsystem, the infamous problem of the original Ehrenfest and SH methods.<sup>12</sup> As a consequence, the polaron size (IPR) and the mobility are strongly overestimated because most of the high lying electronic states that are now occupied are more delocalized than the lower lying states (see Figure 1(E) for the extension of the adiabatic states as a function of energy). In this uncorrected case, the IPR and charge mobility will also be size-dependent, an unphysical feature, whereas when DC is included the quantum population (dotted blue line) follows the surface population (solid blue), and both these populations agree with the correct Boltzmann population (dashed green line). For all these reasons it is of utmost importance to apply a decoherence correction, otherwise the energy level population and the charge transport dynamics becomes unphysical (see Table 1).

# 4.5 Decoherence correction-induced spurious long-range charge transfer

In small systems with only a few electronic states surface hops between localized but spatially distant electronic states are unlikely due to the small NACEs (entering the probability Eq. 9). In large systems with a high density of electronic states the probability for a single transition is still small, but since many of these transitions are attempted, they are more likely to take place (because of the stochasticity of the surface hopping algorithm). If such unlikely transitions occur, the active adiabatic electronic state is reassigned from an adiabatic wavefunction localized in one region of space, say  $\psi'_a(t)$ , to another adiabatic wavefunction localized in a different region of space,  $\psi_a(t + \Delta t)$ . While such transitions are not an artefact of the SH algorithm *per se*, the problem is that the decoherence correction (DC), Eq. 22, tends to quickly collapse the charge carrier wave function (Eq. 6) from  $\Psi' \approx \psi'_a$  to  $\Psi \approx \psi_a$ . This results in unphysical long-range charge transfer and yields charge mobilities that increase with system size. This is shown in Figure 4(D), when the correction for the so-called decoherence-induced spurious long-range charge transfer correction (SCTC) is switched off (together with the state-tracking procedure) the MSD no longer converges with increasing chain length.

The SCTC is implemented using a simple three-step strategy:<sup>26</sup> (i) at each timestep, an "active" region that encloses 99 % of the electronic density  $|\Psi(t)|^2$  is determined, (ii) the DC is applied and (iii) any change of diabatic population  $\Delta |u_l|^2$  outside the active region is reset to zero, while the diabatic populations inside the active region are scaled accordingly to preserve the norm. Consequently, the wavefunction  $\Psi(t)$  propagates physically (i.e. according to the time-dependent Schrödinger equation) towards the adiabatic wavefunction on the new surface, and not near-instantaneously (i.e. unphysically) via the DC. In practice, SCTC amounts to a local DC within the active region, while outside the active region the diabatic populations remain unchanged. All decoherence-induced spurious charge transfers (DCICTs) are removed while DC is still applied at each time step. Note that the propagation of the wave function according to Eq. 7 remains unaffected by the presence of the active region.

#### 4.6 Code speed-up and cost

An efficient multiple time step (MTS) algorithm as well as the possibility of neglecting the NACEs in the diabatic basis,  $d_{kl}$ , in the electronic propagation have been introduced before in Sections 3.3 and 3.1 respectively. Here we validate the quality of these two important

algorithmic optimizations for charge transport in a large 2D crystal of anthracene with 378 molecules forming the active plane and we assess their impacts on the efficiency of the code.<sup>28</sup> We run 600 trajectories, 1 ps long with a 0.1 fs nuclear time step for different combinations with increasingly optimized FOB-SH. The different combinations are: "FULL" which represents the complete calculation in which the diabatic NACEs,  $d_{kl}$ , are evaluated at each nuclear time step (as in Eq. 8) and linearly interpolated when solving the electronic equation of motion, Eq. 7, and the MTS algorithm is inactive; "no  $d_{kl}$ " in which these NACEs are neglected and the MTS is still inactive; "MTS+ $d_{kl}$ " in which the MTS algorithm is activated and the off-diagonal gradients are updated only every 100 MD time steps (namely, every 10 fs using a 0.1 fs MD time step), and "MTS+no  $d_{kl}$ ", in which NACEs are not calculated and the MTS algorithm is activated.

Importantly in Figure 5(A-C) we show that the number of (successful and rejected) hops, the mobilities along a and b crystallographic directions of the herringbone layer of anthracene and the IPR, all remain virtually unchanged (within statistical errors) when going from "FULL" scheme to "MTS+no  $d_{kl}$ " (the latter being the most approximate). As expected, upon activation of the MTS algorithm the energy conservation decreases from  $2.1 \times 10^{-8}$ to  $6.0 \times 10^{-7}$  Ha/ps/atoms, but it remains well below the typical energy conservation of ab - initio MD of about  $10^{-5}$  Ha/ps/atoms. Figure 5(D) illustrates the big advantage of "MTS+no  $d_{kl}$ " optimization: a significant speed-up of the FOB-SH code (almost factor of 3 when the system becomes larger than a thousand molecules). This makes the code capable of affording almost twice as large a system at the same computational cost without sacrificing the accuracy of the actual dynamics and to propagate around a ps/day in systems with several tens of thousands atoms.

# 5 Charge mobilities in nano-scale organic semiconductors

We present here the application of FOB-SH to the calculation of room temperature charge mobility tensors across the 2D herringbone planes of a series of experimentally well-known molecular organic crystals for which reliable experimental mobilities have been measured. The OSs investigated are 1,4-bis(4-methylstyryl)benzene (pMSB-h<sup>+</sup>), naphthalene (NAPh<sup>+</sup>), anthracene (ANT-h<sup>+</sup>), perylene (PER-e<sup>-</sup>), rubrene (RUB-h<sup>+</sup>) and pentacene (PEN-h<sup>+</sup>) The appendix -h<sup>+</sup> and -e<sup>-</sup> is used to distinguish between hole and electron transfer systems and the crystallographic direction of the transport in the a - b mobility plane is also given (note that for perylene mobility is shown along the perpendicular direction to this plane as well). Simulation details and system set-ups are given in Ref.<sup>28</sup>

In Figure 6 we report the convergence of charge mobilities along the different crystallographic directions obtained from the Einstein relation (Eq. 17) and the wavefunction delocalization (or polaron size) in the form of average IPR (Eq. 20), as a function of number of molecules in the 2D herringbone layer of the investigated OSs and time step. It is worth noting at this point that there is an excellent agreement between polaron size calculated from FOB-SH, which gives an IPR of about 17-18 molecules in pentacene, and data based on experimental electron spin resonance data (ESR) for the same system, which estimates a polaron extension of 17 molecules at 290 K,<sup>72</sup> also with other experimental measurements that point to charge carriers localized over a few molecules.<sup>73-75</sup> On a more technical note, we point out that the good convergence of mobility and IPR with system size as well as with time step implies that spurious long-range charge transfer due, for example, to trivial crossings have been largely eliminated.

The computed converged charge mobilities are shown against the experimental mobilities in Figure 7(A) for the different systems (data in blue). They are in excellent agreement with experiment or within the experimental uncertainty, with typical deviations of less than a factor of two for mobilities spanning three orders of magnitude. Importantly, traditional hopping and band models (data in green and red, respectively) fail to provide a uniformly good description of charge transport in different regimes (e.g. localized or delocalized) for the OSs investigated. The hopping results are obtained by solving the master equation with a Marcus-like rate as described in Ref.,<sup>28</sup> while the band theory data are taken from the literature with references given in Ref.<sup>27</sup> In contrast, FOB-SH describes all relevant transport regimes accurately and seamlessly bridges the gap between small polaron hopping and band transport. We also note that the mobilities obtained from FOB-SH simulation for the full 2D plane<sup>28</sup> are by a factor of 2-3 higher than the corresponding values obtained from calculations on 1D chains<sup>27</sup> This is in line with the finding of Fratini et al. who concluded that 2D systems with isotropic couplings exhibit higher mobilities than anisotropic systems and noting that the 1D models are perfectly anisotropic.<sup>44</sup>

Local and non-local electron-phonon coupling fluctuations have a profound impact on the delocalization of the states and the subsequent formation of a polaronic charge state extended over several molecules in the most conductive crystals, and thus on the charge dynamics.<sup>27,28</sup> In this regard, in Figure 7(B) we show, for the highly conductive rubrene crystal, that thermal intra-band excitations (exemplified by the active state index, a, black dashed line) from modestly delocalized band edge states, up to 5 nm or 10-20 molecules in this system, to highly delocalized tail states, up to 10 nm or 40-60 molecules, give rise to short bursts of the charge carrier wavefunction that drives the spatial displacement of the polaron. This results in carrier diffusion and mobility (note the correlation between the peaks of the dashed black line and the solid blue IPR line). We refer to these wavefunction displacements, that are at the heart of the transport mechanism in OSs, as "diffusive jumps" and we show one of such wavefunction jump in Figure 7(C-E).<sup>28</sup> These findings reconcile the experimental view of a coexistence between delocalized and localized carriers in OSs<sup>76</sup> and give insights into the actual charge carrier dynamics in these materials.

# 6 Conclusion and Outlook

In conclusion, we have described a powerful and computationally efficient non-adiabatic molecular dynamics simulation methodology termed fragment-orbital based surface hopping (FOB-SH). This approach allows us to propagate a 1-particle approximation of the charge carrier wavefunction in large nano-scale systems (100-1,000 molecules) at a rate of about 1 ps/day on a single compute core. Moreover, since SH trajectories are independent, parallelization is trivial and the different trajectories are farmed on several computer cores. Our implementation conserves total energy and approximately fulfils detailed balance and internal consistency in the presence of a high density of states. This is possible thanks to important extensions to the original SH algorithm, namely a correction for missing electronic decoherence, detection of trivial crossings and removal of decoherence correction-induced spurious charge transfer. If any one of these corrections is not included, the charge mobility diverges with system size for different physical reasons. We have also reported the calculation of the full 2D charge mobility tensors for six organic crystals and briefly discussed the real-time dynamics of the charge carriers.

Based on these findings, a number of avenues for further research are currently being explored in our laboratory and they will hopefully provide further advance in the field of nano-scale optoelectronic organic materials. With regards to charge transport simulations, we believe that FOB-SH is now efficient and accurate enough to gain fresh insight into structure-mobility relationships of organic semiconductors. For instance, we are interested to understand how different solid-state morphologies of one and the same molecule (crystal, thin film, amorphous), how interfaces between crystalline and amorphous domains and how crystal defects (e.g. Schottky or line dislocations) impact the charge carrier propagation.

Another important goal currently being tackled in the group is the use of FOB-SH as a tool for the discovery of high-mobility OSs. Scaffolding and conformational locking of conjugated molecules are expected to boost mobility and efficiency of OSs (as predicted by us in Ref.<sup>27</sup> by artificially freezing the thermal fluctuations of the electronic coupling). A recent experimental study on rubrene reported a strong, anisotropic enhancement of the mobility under compressive strain,<sup>77</sup> which might be regarded as an alternative way to improve charge mobility. Molecular simulations will play a key role in understanding the relationship between strain and mobility at an atomistic level. Such knowledge might open up ways to use the mechano-electric response as a new means of enhancing the mobility in organic materials.

Finally, the main goal in the future is to extend FOB-SH to simulate the electronic processes occurring in excitonic solar cells: exciton transport, exciton dissocation into charge carriers and charge recombination. Such simulations will be free of the many limiting model assumptions of Golden-rule rate theories (e.g. Marcus or Marcus-Levich-Jortner) that are hard to justify in the context of excitonic solar cells. For instance, these rate theories assert thermal equilibrium on the ultrafast time scales involved, small electronic perturbations which are clearly incompatible with the relatively large electronic couplings in many organic semiconductors and strong localization of excitons and charges. We are currently extending the FOB-SH formalism to increase the state space of the tight-binding DFT Hamiltonian to include charge separated states as well as singlet Frenkel excited states. The future of FOB-SH is bright!

# Figure and Table captions



Figure 1: (A) a - b high mobility planes for rubrene crystal. The crystallographic directions along a, b, c are shown in red, green and blue. Panels (B) and (C) show a representative DFT HOMO orbital of a single rubrene molecule and the HOMO band state of a perfect crystal. (D) Normalized density of states (DOS) of the HOMO band of rubrene. DOS for sDFT (dashed black), sFODFT (dashed red) and AOM (dashed green) are calculated for the static crystal structure as described in the text. DOS for AOM (300 K), indicated with solid green lines, are computed from Hamiltonians extracted from a representative FOB-SH trajectory and including the effect of thermal disorder. The latter DOS are smoother than the DOS of the static (frozen) Hamiltonian, due to the fluctuations of electronic couplings and site energies. (E) Displays 2D histograms correlating the delocalization of the band states, quantified by the inverse participation ratio IPR (Eq. 8 in Ref.<sup>28</sup>), and their energies. Dashed red lines are used to indicate time averages of the band active state energy  $E_a$  and the active state delocalization IPR<sub>a</sub>, with a being the active state index. Double white arrows indicate the thermally accessible (valence) band tail regions for the excess hole or electron. (A), (D), (E) Adapted from Ref.<sup>28</sup> Copyright 2020 Wiley Online Library.



Figure 2: Scheme of the FOB-SH (fragment orbital-based surface hopping) algorithm. Different colors represent improvements of the algorithm necessary to fulfil: trivial crossings detection, detailed balance and energy conservation and internal consistency. RK: Runge-Kutta algorithm, AOM: Analytic overlap method, SC-FSSH: self-consistent surface hopping, FSSH: fewest switches surface hopping, NACV: non-adiabatic coupling vectors, SCTC: Spurious charge transfer correction, MSD: mean squared displacement, IPR: inverse participation ratio. Adapted from Ref.<sup>25</sup> Copyright 2019 Royal Society of Chemistry.



Figure 3: (A) Graphical representation the two fragment orbitals for an ELM dimer and adiabatic energy surfaces against site energy difference. Three electronic coupling values are indicated with different colours (red 100 meV, blue 50 meV, green 2 meV), reorganization energy  $\lambda = 100$  meV in each case. Corresponding diabatic curves are given in dashed black lines. (B) Influence of the rescaling prescription used to ensure energy conservation on excited state population for different diabatic electronic couplings. "Isotropic" results use the isotropic rescaling as described in the text. "Fast NACV" and "total NACV" refer to rescaling along the direction of the NACV, Eq. 13. In the former case, NACVs are calculated neglecting the second term on the RHS of Eq. 13, while in the latter case all terms in Eq. 13 are considered. Error bars are shown for our default option (fast NACV) and represent standard deviations over five independent blocks of 200 trajectories. Error bars for the exact population (calculated from free energy surfaces as in Ref.<sup>24</sup>) indicate standard deviation over three blocks of 20 ps. Adapted from Ref.<sup>24</sup> Copyright 2017 American Institute of Physics (AIP). (C) Internal consistency (in the form of RMSE between surface and wavefunction populations) as a function of coupling strength. Two well-known electronic decoherence corrections (DCs) are compared: damping of adiabatic electronic populations with forcebased (FDC) damping time and energy-based with Heisenberg decoherence times (EDC) against no DC. Adapted from Ref.<sup>25</sup> Copyright 2019 Royal Society of Chemistry.



Figure 4: Supercell and electronically active chain along the *b* direction for anthracene. A snapshot of a polaron with typical delocalization over three molecules is shown. Adapted from Ref.<sup>25</sup> Copyright 2019 Royal Society of Chemistry. (B) Importance of decoherence correction for the charge transport in FOB-SH hole transport trajectories for anthracene crystal, wavefunction (Eq. 15) and surface (Eq. 16) population with DC (data in blue) and without DC (dashed red). In the latter case the electronic eigenstates (also denoted adiabatic states) are almost equally populated, i.e. the electronic temperature tends to infinity. Adapted from Ref.<sup>27</sup> Copyright 2019 Springer Nature content. (C) and (D) Importance of state reordering and spurious charge transfer correction in FOB-SH simulations of hole transport along embedded chains of anthracene molecules. MSD (Eq. 19) for hole transport with chain lengths as indicated (12, 24, 36 and 48 molecules). Adapted from Ref.<sup>25</sup> Copyright 2019 Royal Society of Chemistry.



Figure 5: Different algorithmic optimizations ("FULL", "no  $d_{kl}$ ", "MTS+ $d_{kl}$ ", "MTS+no  $d_{kl}$ ") are compared for anthracene 2D crystal. (A) Average number of successful and rejected hops for 600 trajectories. (B) and (C) represent, respectively, the mobilities along the eigendirections and average IPR. (D) On the lest vertical axis time taken in (s) to complete a nuclear time step as a function of total number of molecules in the system on a single CPU core, on the right vertical axis time of ps done per day (assuming 0.1 fs time step). The inset shows the overhead of the "MTS+no  $d_{kl}$ " compared to a standard MD run in CP2K. Processor used for the timing: Intel(R) Xeon(R) x86\_64 CPU E5-2687W v4 3.00GHz. Adapted from Ref.<sup>28</sup> Copyright 2020 Wiley Online Library.



Figure 6: Convergence of charge mobility (A), (B) and IPR (C), (D) for the investigated OSs with respect to number of molecules and the MD nuclear time step, respectively. The experimental estimate for polaron size of pentacene is indicated by dashed green lines in (C) and (D).<sup>72</sup> Adapted from Ref.<sup>28</sup> Copyright 2020 Wiley Online Library.



Figure 7: (A) Computed versus experimental charge mobilities for the investigated OSs. Charge mobilities from FOB-SH (data in blue) are taken from Ref.<sup>28</sup> and obtained by averaging the MSD of the charge carrier wavefunction (t) over at least 300 trajectories and inserting the corresponding diffusion tensor component in the Einstein relation (Eq. 17). Statistical error bars indicate the standard deviations over 3 independent blocks of at least 100 trajectories. Predictions from band theory calculations are taken from the literature (data in red, see Ref.<sup>27</sup> and references therein). Charge mobilities from a small polaron hopping model (data in green) are obtained by solving a chemical Master equation for nearest neighbour hopping in the specified direction using semi-classical electron transfer rates (see Ref.<sup>28</sup>). As a guide to the eye, perfect agreement is indicated by a thick solid line and deviations in mobility by a factor of 2 by thin dotted lines. (B) Correlation between IPR (blue line) and active state index, a, (dashed black line) for a representative FOB-SH trajectory on a large rubrene crystal. Horizontal dashed blue line represents the average polaron size (average IPR) over many trajectories. Panels (C)-(E) depict a representative "diffusive jump" of the charge carrier wavefunction  $\Psi(t)$  resulting in drift velocity and charge mobility. Initially the polaron is of average size, about 5 nm (C); upon thermal excitation it extends to about 10 nm (D) and finally re-localizes at a position about 5 nm apart from the original position (E). For comparison, the unit cell of rubrene is schematically indicated in (D). Adapted from Ref.<sup>28</sup> Copyright 2020 Wiley Online Library.

# Abbreviations

AOM	Analytic Overlap Method
CSD	Cambridge Structural Database
DC	Decoherence Correction
DCICT	Decoherence Correction-Induced Spurious Charge Transfers
DFT	Density Functional Theory
DFTB	Density-Functional Tight-Binding
DOS	Density Of States
EDC	Energy-based Decohererence time
ELM	Ethylene Like Molecule
ESR	Electron Spin Resonance
FDC	Force-based Decoherence Correction
FOB-SH	Fragment Orbital-Based Surface Hopping
sFODFT	Scaled Fragment Orbital DFT
FMO	Fragment Molecular Orbital
FMS	Full Multiple Spawning
SH	Fewest Switches Surface Hopping
НОМО	Highest Occupied Molecular Orbital
IPR	Inverse Participation Ratio
LUMO	Lowest Unoccupied Molecular Orbital

MCTDH Multi-Configuration Time-Dependent Hartree

MD Molecular Dyna	amics
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- MM Molecular Mechanics
- MQC Mixed Quantum-Classical
- MSD Mean Squared Displacement
- MTS Multiple Time Step algorithm
- NACE Non-Adiabatic Coupling Element
- NACV Non-Adiabatic Coupling Vector
- NAMD Non-Adiabatic Molecular Dynamics
- OSs Organic Semiconductors
- PES Potential Energy Surface
- PPP Pariser-Parr-Pople
- QM Quantum Mechanics
- RK Runge-Kutta algorithm
- RPMD Ring-Polymer Molecular Dynamics
- RMSE Root Mean Square Error
- SC-FSSH Self Consistent Fewest Switches SH
- SCTC Spurious Charge Transfer Correction
- TDDFT Time Dependent Density Functional Theory

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