# A Multi-Stage *Ab-initio* Quantum Wavepacket Dynamics Formalism for Electronic Structure and Dynamics in Open Systems

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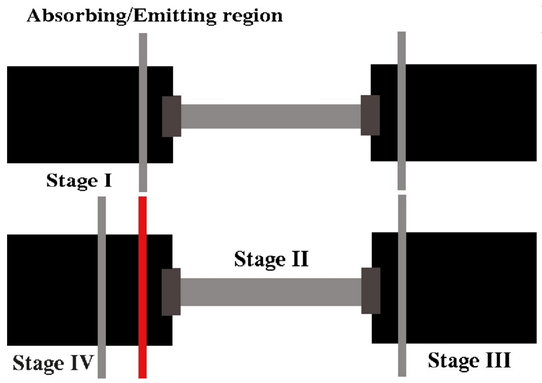
$$\imath\hbar\frac{\partial}{\partial t}\Psi = \mathbf{H}\Psi$$




## Outline

- Multi-Stage quantum Wavepacket *Ab-initio* Dynamical (MS-AIWD) treatment for the study of delocalized electronic systems as well as electron transport through donor-bridge-acceptor systems.
- The *full* donor-bridge-acceptor system is treated through a rigorous partitioning scheme.
- Computationally efficient and potentially accurate treatment for long-range coupling interactions and open-system boundary conditions.
- The quantum dynamics using an accurate and efficient representation of the discretized quantum-mechanical free-propagator.
- Transmission probability is obtained directly from the probability density.
- Conductivity through the molecular wire is computed using a wavepacket flux correlation function.

## MS-AIWD Formalism

- The full system is partitioned into local domains through the inclusion of *offsetting absorbing/emitting potentials*[1].
- Imaginary components allow the introduction of coupled dissipative/regenerative behavior .
- Multiple stages allows for computational simplicity and accuracy.
- Stage I: propagation of an initial wavepacket in the donor region.
- Stages IV and III: propagating the wavepacket back into the donor and acceptor respectively.
- Stage II: region of primary interest consisting of the electron tunneling through the bridge system.
- MS-AIWD accounts for the coupling, eigenstate broadening and the associated non-equilibrium conditions.
- Model system: electron transport in molecular wire.
- The total wavefunction $\Psi(t)$ is partitioned as follows

$$\Psi(t) = \Psi_I(t) + \Psi_{II}(t) + \Psi_{III}(t) + \Psi_{IV}(t)$$

satisfying , $i\hbar\frac{\partial}{\partial t}\Psi(t) = (H+\Delta)\Psi(t)$, where $\Delta$ is an applied external bias and the subscripts denote the Stages in which the wavepacket is localized.

- We introduce absorbing potentials which are localized in space, and rewrite the TDSE as,

$$(H + \Delta - \imath V_{I-II})\,|\Psi_I\rangle = i\hbar\frac{\partial}{\partial t}|\Psi_I\rangle$$

$$(H + \Delta - \imath V_{II-III} - \imath V_{II-IV})\,|\Psi_{II}\rangle + \imath V_{I-II}|\Psi_I\rangle = i\hbar\frac{\partial}{\partial t}|\Psi_{II}\rangle$$

$$(H+\Delta)|\Psi_{III/IV}\rangle + \imath V_{II-III/IV}|\Psi_{II}\rangle = i\hbar\frac{\partial}{\partial t}|\Psi_{III/IV}\rangle$$

where $V_{I-II}$ is the absorbing potential in the interface region between Stages I and II, etc.
- The Stage I wavepacket at time $t$, is obtained as

$$\Psi_I(t) = \exp\left[-\imath\,(H+\Delta-\imath V_{I-II})\,t/\hbar\right]\Psi_I(t=0),$$

- The Stage II wavepacket is given by,

$$\Psi_{II}(t) = \exp\left[-\frac{i}{\hbar}\int_0^t dt'\,H_{II}\right]\{\Psi_{II}(0) + \frac{1}{\hbar}\int_0^t dt' \exp\left[-\frac{i}{\hbar}\int_{t'}^0 dt''\,H_{II}\right]V_{I-II}\Psi_I(t')\Big\}$$

with similar equations for Stages III and IV.

- The differential form of $\Psi_{II}(t)$ is similar to the Dyson equation in the Kadanoff-Baym Formalism.

$$\left(i\hbar\frac{\partial}{\partial t} - H_{II}\right)\Psi_{II}(t) = \frac{\imath}{\delta t}\exp\left[-\frac{i}{\hbar}H_{II}\delta t\right] \int_t^{t+\delta t} dt' \exp\left[-\frac{i}{\hbar}H_{II}(t-t')\right]V_{I-II}\Psi_I(t')$$

- The inhomegeniety in the Schrödinger equation for the Stage II wavepacket arises from the dynamics in Stage I.
- The transmission probability is given by probability density of the Stage III wavepacket while the energy-dependent cross-section of waves arriving in Stage III is given by

$$|\xi_{III}(x;E)|^2 = \left|\int dt \exp\left(-\imath Et/\hbar\right)\Psi_{III}(x;t)\right|^2$$

## Description of Model System

- 1D-wavepacket dynamics on an analytical potential,

$$V(x) = \sum_i \frac{-1}{\sqrt{a_i\pi}}\exp\left[-(x-x_i)^2/a\right];\, a = \begin{cases}0.2, & C\\ 0.15, & Al\end{cases}$$

modeled as Gaussians centered on the nuclear positions of an $Al_{27}-C_7-Al_{27}$ nanowire with parameter $a$ chosen to reproduce the well depths of the electrostatic potential around the nuclei.
- For imaginary absorbing potentials, we choose the Woods-Saxon potential.

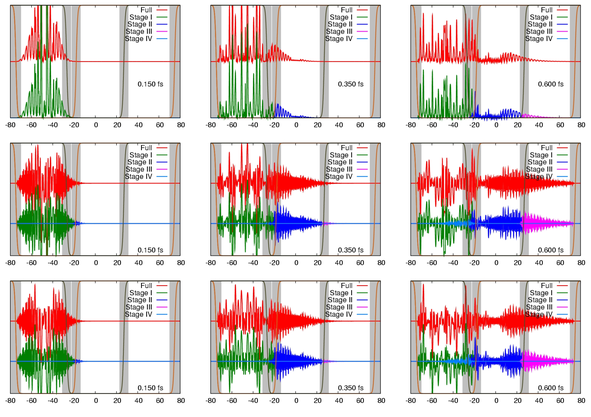
$$V_{abs}(R) = \frac{V_0}{1+\exp(\alpha*(R-R'))}$$

- The initial wavepacket, $\Psi$, is chosen as a Gaussian centered at $x_0$, with width, $\sigma$ and initial momentum, $P_x$.

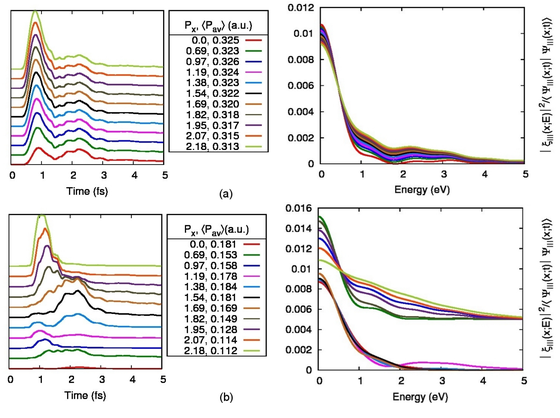
$$_\sigma\Psi_{P_x}(x) = \frac{1}{\sqrt{2\pi\sigma}}\exp\left[-\frac{(x-x_0)^2}{2\sigma^2}\right]\times\exp(\imath P_x\times x)$$

## Results

- Comparison between the probability density (top) and the real (middle) and imaginary (bottom) part of the wavepacket with $\sigma = 0.4\mathring{A}$, $x_0 = 48\mathring{A}$ and $P_x = 0.0\,a.u.$ for the Full and the Multi-Stages dynamics as a function of distance [1, 2].




- Evolution of the transmission probability and the energy dependent cross section for $\sigma = 0.4\mathring{A}$ (top) and $\sigma = 4.0\mathring{A}$ (bottom) and initial momenta $P_x\,(a.u.)$.




- The wider wavepacket has contributions from different momentum states leads to the associated complex behavior of the energy different cross-sections.

## Coupled Electron-Nuclear Dynamics: Work in Progress

- The coupling between the electron transfer and the vibrational modes of the donor-bridge-acceptor leads to inelastic scattering and breakdown of the Frank-Condon approximation.
- Harmonic oscillators on nuclear positions providea time dependent analytical potential.

$$V(\vec{r},\vec{R}) = \sum_i \frac{-1}{\sqrt{a_i\pi}}\exp\left[\frac{-(\vec{r}-\vec{R}_i)^2}{a_i}\right]$$

- The Hamiltonian in terms of the generalized normal mode coordinates for the nuclei is given by,

$$H = \frac{1}{2}\sum_i\left(\dot{Q}_i^2 + k_iQ_i^2\right) - \frac{\hbar^2}{2m_e}\nabla^2 + V(\vec{r},\vec{R})$$

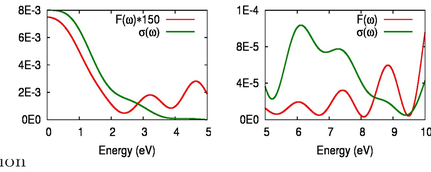
- The MS-AIWD formalism for this Hamiltonian will account for the nuclear dynamics in response to the tunneling electron.
- The flux-flux (or current-current) co lation function quantifies the flow of e trons through the molecular wire

$$\sigma(\omega) \propto \int_{-\infty}^{+\infty} dt e^{-\imath\omega t}\langle\mathbf{J}(t)\mathbf{J}(0)\rangle$$

while the force-force correlation function quantifies the energy transferred to the molecular vibrations by the tunneling electron

$$\mathcal{F}(\omega) \propto \int_{-\infty}^{+\infty} dt e^{-\imath\omega t}\langle\mathbf{F}(t)\mathbf{F}(0)\rangle$$

where $\vec{F}_i(t) = -\frac{dV(\vec{R};t)}{d\vec{R}_i(t)}$ is the force on the $i^{\text{th}}$ nuclei.




- The correlation between the electron and the nuclear dynamics can be seen from the coupling in the 5-10 eV range in the above spectra.

## Conclusions

- Multi-Stage *Ab-initio* Wavepacket Dynamics is an effective tool to study electron transfer in infinite system.
- An infinite system is decomposed into multiple "stages" through introduction of offsetting (imaginary) absorbing-emitting potentials.
- An effective reduction of computational complexity while reproducing the dynamical behavior of the full system.
- Study of coupled electon-nuclear dynamics by inclusion of oscillators at the nuclei positions is currently under progress.

## Acknowledgments

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## References

[1] A. B. Pacheco and S. S. Iyengar,*submitted J. Chem. Phys.* (2010).
[2] http://www.indiana.edu/~ssiweb/outbox/MS-AIWD/animations/