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

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**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.
- Stage 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 , \( \Psi(t) = (H + \Delta)\Psi(t) \), 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

\[
\begin{align*}
(H + \Delta - i\nabla_{II})\Psi(t) &= \frac{\hbar}{i} \frac{\partial}{\partial t} \Psi(t) \\
(H + \Delta - i\nabla_{II})\Psi(t) &= \frac{\hbar}{i} \frac{\partial}{\partial t} \Psi(t) \\
(H + \Delta - i\nabla_{II})\Psi(t) &= \frac{\hbar}{i} \frac{\partial}{\partial t} \Psi(t) \\
(H + \Delta - i\nabla_{II})\Psi(t) &= \frac{\hbar}{i} \frac{\partial}{\partial t} \Psi(t)
\end{align*}
\]

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.

\[
\left( \frac{\hbar}{i} \frac{\partial}{\partial t} - H_{II} \right) \Psi_{II}(t) = \frac{\hbar}{i} \frac{\partial}{\partial t} \Psi_{II}(0) + \int_{t_0}^{t} dt' \left[ \frac{\hbar}{i} \frac{\partial}{\partial t'} H_{II} \right] \Psi_{II}(t')
\]

- The inhomogeneity 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 wavepacket arriving at Stage III.

**RESULTS**

- Computation 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 provide time dependent analytical potential.
- The Hamiltonian in terms of the generalized normal mode coordinates for the molecule is given by

\[
\mathbf{H} = \frac{1}{2} \sum_{\alpha} \left( \mathbf{\dot{Q}}_{\alpha}^{2} + k_{\alpha} \mathbf{Q}_{\alpha}^{2} \right) - k_{\alpha} \mathbf{Q}_{\alpha} \mathbf{r}^{\alpha} + V(\mathbf{r}, \mathbf{\dot{R}})
\]

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

**ACKNOWLEDGMENTS**

This research is supported by the National Science Foundation grant NSF CHE-0750326 and the Arnold and Mabel Beckman Foundation.

**REFERENCES**


**DESCRIPTION OF MODEL SYSTEM**

- 1D-wavepacket dynamics on an analytical potential,

\[
V(x) = \sum_{n=-\infty}^{\infty} \frac{1}{\sqrt{2\pi}\sigma} \exp \left[-(x-x_n)^2/2\sigma^2\right]; \sigma = 0.2, C = 0.15, \text{ A}
\]

- Modeled as Gaussians centered on the nuclear positions of an Al_{27}C_{7}–Al_{27}C_{7} nanowire with parameter \( C \) chosen to reproduce the well depth of the electrostatic potential around the nuclei.
- For imaginary absorbing potentials, we choose the Woods-Saxon potential.

\[
V_{abs}(R) = \frac{V_0}{1 + \exp(\alpha(R - R_0))}
\]

- The initial wavepacket, \( \Psi \), is chosen as a Gaussian centered at \( x_0 \), with width, \( \sigma \), and initial momentum, \( P_0 \),

\[
\Psi(x_0) = \frac{1}{\sqrt{2\pi\sigma}} \exp \left[-\frac{(x-x_0)^2}{2\sigma^2}\right] \times \exp(iP_0 x)
\]

**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 provide time dependent analytical potential.
- The flux-flux (or current-current) correlation function quantifies the flow of electrons through the molecular wire

\[
\sigma(\omega) = \int_{-\infty}^{\infty} dt \ exp(-i\omega t) \mathbf{F}(\mathbf{R})(0)
\]

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

\[
\mathbf{F}(\mathbf{R}) = \int_{-\infty}^{\infty} dt \ exp(-i\omega t) \mathbf{F}(\mathbf{R})(t)
\]

- 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 electron-nuclear dynamics by inclusion of oscillators at the nuclei positions is currently under progress.