A multilayer multiconfigurational time-dependent Hartree study of vibrationally coupled electron transport using the scattering state representation

Haobin Wang

Department of Chemistry and Biochemistry, MSC 3C,
New Mexico State University, Las Cruces, NM 88003, USA and
Beijing Computational Science Research Center,
No. 3 He-Qing Road, Hai-Dian District, Beijing 100084, P.R. China

Michael Thoss

Institute for Theoretical Physics and Interdisciplinary Center for Molecular Materials,
Friedrich-Alexander-Universität Erlangen-Nürnberg,
Staudtstr. 7/B2, D-91058, Germany

Abstract

The multilayer multiconfiguration time-dependent Hartree method is employed to study vibrationally coupled charge transport in models of single molecule junctions. To increase the efficiency of the simulation method, a representation of the Hamiltonian in terms of the scattering states of the underlying electronic Hamiltonian is used. It is found that with an appropriate choice of the scattering states the artificial electron correlation present in the original representation of the model is greatly reduced. This allows efficient simulation of the steady-state currents in a wide physical parameter space, which is demonstrated by several numerical examples.
I. INTRODUCTION

Charge transport in single-molecule junctions has raised a great deal of interest recently. Experimental studies on transport properties of molecular junctions revealed a variety of interesting phenomena, e.g., Coulomb blockade, Kondo effect, negative differential resistance, switching and hysteresis. This has stimulated many theoretical developments for understanding quantum transport at the molecular scale. Examples of approximate methods employed in this regard include the scattering theory, nonequilibrium Green’s function (NEGF) approaches, and master equation methods. To the other end, a variety of (in principle) numerically exact methods have been developed to obtain more reliable results for nonequilibrium transport in model systems. These include the numerical path integral approach, real-time quantum Monte Carlo simulations, the numerical renormalization group approach, the time-dependent density matrix renormalization group approach, and the hierarchical equations of motion method. Our work in this direction is the development of the multilayer multiconfiguration time-dependent Hartree (ML-MCTDH) theory in the second quantization representation (SQR), a systematic, numerically exact methodology to study quantum dynamics and quantum transport including many-body effects. For a generic model of vibrationally coupled electron transport, we have demonstrated the importance of treating the vibronic coupling accurately. Comparison with approximate methods such as NEGF revealed the necessity of employing accurate methods such as the ML-MCTDH-SQR approach, in particular in the strong coupling regime.

The ML-MCTDH-SQR method employs a recursive, layered representation of the overall wave function and captures correlation effects through a converged multiconfigurational expansion in all the corresponding layers. Like any other methods, the efficiency of the ML-MCTDH-SQR theory depends on how the problem is approached, e.g., the choice of the an appropriate coordinate system. Consequently, the term “correlation” also depends on such a choice. For example, the quantum dynamics of a quadratic Hamiltonian, where a full Hessian is present, is highly correlated. On the other hand, when this Hamiltonian is transformed to the normal mode representation, there is no correlation at all between different degrees of freedom. In this sense we can term the former correlation as “artificial correlation” due to the inappropriate representation of the Hamiltonian. Finding an op-
nal representation is thus crucial for solving the problem efficiently. Unfortunately, this is typically not an automatic procedure and requires a clear physical understanding of the problem. In most cases, a simple analytic reduction of the problem as the example above is not available. Instead, one has to transform the Hamiltonian according to the physical intuition and known experiences. One of the most frequently used criterion is to ensure that this transformation reduces the problem in a certain physical limit.

In a previous ML-MCTDH-SQR study of vibrationally coupled electron transport, we had found that in some regimes the configuration space required to achieve convergence is quite large. We noticed, however, that these regimes are not necessarily characterized by a strong correlation in the usual sense. In fact, it was often relatively easy to converge the simulation when the electron-nuclear coupling is strong (i.e., easier to capture the “real” correlation effect induced by electronic-vibrational coupling), but not otherwise (i.e. more difficult to capture artificial electron correlation effects), especially when the source-drain bias voltage is high. This has motivated us to examine other representations of the Hamiltonian for studying nonequilibrium charge transport. One promising choice is to employ the scattering states of the underlying electronic Hamiltonian. The resulting scattering states representation of the model has been used before to describe quantum transport in combination with different methods. In this paper we discuss our implementation of the scattering state representation within the framework of the ML-MCTDH-SQR theory.

The paper is organized as follows. Section II outlines the original, tight-binding type model for describing the vibrationally coupled electron transport. Section III then discusses the scattering state representation of the same problem and our specific choice of the reference frame. Section IV illustrates the performance of our approach by numerical examples for a variety of parameter regimes. Section V concludes with a summary.

II. MODEL FOR VIBRATIONALLY COUPLED ELECTRON TRANSPORT

A. Model Hamiltonian

A model that is frequently adopted to study vibrationally coupled electron transport through a single-molecule junction is based on tight-binding description for the two metal leads. It comprises one discrete electronic state at the molecular bridge, two electronic
continua describing the left and the right metal leads, respectively, and a distribution of harmonic oscillators that models the vibrational modes of the molecular bridge. The Hamiltonian reads

\[ \hat{H} = \hat{H}_{\text{el}} + \hat{H}_{\text{el-\text{nuc}}}, \]  
(2.1a)

where \( \hat{H}_{\text{el}} \) and \( \hat{H}_{\text{el-\text{nuc}}} \) describe the pure electronic degrees of freedom and the nuclear vibrations with their coupling terms to the electronic part, respectively

\[ \hat{H}_{\text{el}} = E_{d}d^{+}d + \sum_{k_L} E_{k_L} c_{k_L}^{+} c_{k_L} + \sum_{k_R} E_{k_R} c_{k_R}^{+} c_{k_R} \]
\[ + \sum_{k_L} V_{dk_{L}} (d^{+} c_{k_L} + c_{k_L}^{+} d) + \sum_{k_R} V_{dk_{R}} (d^{+} c_{k_R} + c_{k_R}^{+} d), \]  
(2.1b)

\[ \hat{H}_{\text{el-\text{nuc}}} = \frac{1}{2} \sum_{j} (P_{j}^{2} + \omega_{j}^{2} Q_{j}^{2}) + d^{+} d \sum_{j} 2c_{j} Q_{j}. \]  
(2.1c)

Thereby, \( d^{+}/d, c_{k_L}^{+}/c_{k_L}, c_{k_R}^{+}/c_{k_R} \) are the fermionic creation/annihilation operators for the electronic states on the molecular bridge, the left and the right leads, respectively. The corresponding electronic energies \( E_{k_L}, E_{k_R} \) and the molecule-lead coupling strengths \( V_{dk_{L}}, V_{dk_{R}} \), are defined through the energy-dependent level width functions

\[ \Gamma_{L}(E) = 2\pi \sum_{k_{L}} |V_{dk_{L}}|^{2} \delta(E - E_{k_{L}}), \quad \Gamma_{R}(E) = 2\pi \sum_{k_{R}} |V_{dk_{R}}|^{2} \delta(E - E_{k_{R}}). \]  
(2.2)

In principle, the parameters of the model can be obtained for a specific molecular junction employing first-principles electronic structure calculations. In this paper, which focuses on the methodology and general transport properties, however, we will use a generic parameterization. Employing a tight-binding model, the function \( \Gamma(E) \) is given as

\[ \Gamma(E) = \begin{cases} \frac{\alpha_{e}^{2}}{\beta_{e}^{2}} \sqrt{4\beta_{e}^{2} - E^{2}} & |E| \leq 2|\beta_{e}| \\ 0 & |E| > 2|\beta_{e}| \end{cases}, \]  
(2.3a)

\[ \Gamma_{L}(E) = \Gamma(E - \mu_{L}), \quad \Gamma_{R}(E) = \Gamma(E - \mu_{R}), \]  
(2.3b)

where \( \beta_{e} \) and \( \alpha_{e} \) are nearest-neighbor couplings between two lead sites and between the lead and the bridge state, respectively. I.e., the width functions for the left and the right leads are obtained by shifting \( \Gamma(E) \) relative to the chemical potentials of the corresponding leads.

We consider a simple model of two identical leads, in which the chemical potentials are given by

\[ \mu_{L/R} = E_{f} \pm V/2, \]  
(2.4)
where $V$ is the source-drain bias voltage and $E_f$ the Fermi energy of the leads. Since only the difference $E_d - E_f$ is physically relevant, we set $E_f = 0$.

Similarly, the frequencies $\omega_j$ and electronic-nuclear coupling constants $c_j$ of the vibrational modes of the molecular junctions are modeled by a spectral density function:

$$ J(\omega) = \frac{\pi}{2} \sum_j \frac{c_j^2}{\omega_j} \delta(\omega - \omega_j). $$

(2.5)

In this paper, the spectral density is chosen in Ohmic form with an exponential cutoff

$$ J_O(\omega) = \frac{\pi}{2} \alpha \omega e^{-\omega/\omega_c}, $$

(2.6)

where $\alpha$ is the dimensionless Kondo parameter.

Both the electronic and the vibrational continua can be discretized by choosing a density of states $\rho_e(E)$ and a density of frequencies $\rho(\omega)$ such that

$$ \int_0^{E_k} dE \rho_e(E) = k, \quad |V_{dk}|^2 = \frac{\Gamma(E_k)}{2\pi \rho_e(E_k)}, \quad k = 1, \ldots, N_e, $$

(2.7a)

$$ \int_0^{\omega_j} d\omega \rho(\omega) = j, \quad \frac{c_j^2}{\omega_j} = \frac{2}{\pi} \frac{J_O(\omega_j)}{\rho(\omega_j)}, \quad j = 1, \ldots, N_b. $$

(2.7b)

where $N_e$ is the number of electronic states (for a single spin/single lead) and $N_b$ is the number of bath modes in the simulation. In this work, we choose a constant $\rho_e(E)$, i.e., an equidistant discretization of the interval $[-2\beta_e, 2\beta_e]$, to discretize the electronic continuum.

For the vibrational bath, $\rho(\omega)$ is chosen as

$$ \rho(\omega) = \frac{N_b + 1}{\omega_c} e^{-\omega/\omega_c}. $$

(2.8)

Within a given time scale the numbers of electronic states and bath modes are systematically increased to reach converged results for the quantum dynamics in the extended condensed phase system.

**B. Initial state and calculation of current**

In this paper the observable of interest for studying transport through molecular junctions is the current for a given source-drain bias voltage, given by (we use atomic units where $\hbar = e = 1$)

$$ I_L(t) = -\frac{dN_L(t)}{dt} = -\frac{1}{\text{tr}[\hat{\rho}]} \text{tr} \left\{ \hat{\rho} e^{i\hat{H}t} i[\hat{N}_L, \hat{N}_L] e^{-i\hat{H}t} \right\}, $$

(2.9a)
\[
I_R(t) = \frac{dN_R(t)}{dt} = \frac{1}{\text{tr}[\hat{\rho}]} \text{tr} \left\{ \hat{\rho} e^{i\hat{H}t} i[\hat{H}, \hat{N}_R] e^{-i\hat{H}t} \right\}.
\]  \quad (2.9b)

Here, \( N_{L/R}(t) \) denotes the time-dependent charge in each lead, defined as

\[
N_{\zeta}(t) = \frac{1}{\text{tr}[\hat{\rho}]} \text{tr}[\hat{\rho} e^{i\hat{H}t} \hat{N}_{\zeta} e^{-i\hat{H}t}],
\]  \quad (2.10)

and \( \hat{N}_{\zeta} = \sum_{k\zeta} c_{k\zeta}^+ c_{k\zeta} \) is the occupation number operator for the electrons in each lead \((\zeta = L, R)\). For Hamiltonian \((2.11)\) the explicit expression for the current operator is given as

\[
\hat{I}_{\zeta} \equiv i[\hat{H}, \hat{N}_{\zeta}] = i \sum_{k\zeta} V_{d\zeta}(d^+ c_{k\zeta} - c_{k\zeta}^+ d), \quad \zeta = L, R.
\]  \quad (2.11)

In the expressions above, \( \hat{\rho} \) denotes the initial density matrix representing a grand-canonical ensemble for each lead and a certain preparation for the bridge state

\[
\hat{\rho} = \hat{\rho}_0^d \exp \left[ -\beta (\hat{H}_0 - \mu_L \hat{N}_L - \mu_R \hat{N}_R) \right],
\]  \quad (2.12a)

\[
\hat{H}_0 = \sum_{k_L,\sigma} E_{k_L} \hat{n}_{k_L,\sigma} + \sum_{k_R,\sigma} E_{k_R} \hat{n}_{k_R,\sigma} + \hat{H}_0^{\text{mac}}.
\]  \quad (2.12b)

Here \( \hat{\rho}_0^d \) is the initial reduced density matrix for the bridge state, which is usually chosen as a pure state representing an occupied or an empty bridge state, and \( \hat{H}_0^{\text{mac}} \) defines the initial bath equilibrium distribution.

Various initial states can be considered. For example, one may choose an initially unoccupied bridge state and the nuclear degrees of freedom equilibrated with this state, i.e. an unshifted bath of oscillators with

\[
\hat{H}_0^{\text{mac}} = \frac{1}{2} \sum_j \left[ P_j^2 + \omega_j^2 Q_j^2 \right].
\]  \quad (2.13)

On the other hand, one may also start with a fully occupied bridge state and a bath of oscillators in equilibrium with the occupied bridge state

\[
\hat{H}_0^{\text{mac}} = \frac{1}{2} \sum_j \left[ P_j^2 + \omega_j^2 \left( Q_j + \frac{c_j}{\omega_j^2} \right)^2 \right].
\]  \quad (2.14)

Other initial states may also be prepared. The initial state may affect the transient dynamics profoundly. The dependence of the steady-state current on the initial density matrix is a more complex issue. Recent investigations for a model without electron-electron interaction seem to indicate that different initial states may lead to different (quasi)steady states, \(72-74\).
although this has been debated.\textsuperscript{75} In this paper, we limit our discussion to physical regimes where the steady state current does not depend on the initial state. When comparing the time-dependent current from the scattering state representation with that from the original Hamiltonian discussed above, we typically choose initial conditions that are close to the final steady state, e.g., an unoccupied initial bridge state if its energy is higher than the Fermi level of the leads and an occupied bridge state otherwise. We also use the average current

\[ I(t) = \frac{1}{2} [I_R(t) + I_L(t)], \]  

(2.15)

for such a purpose, which minimizes transient effects.

In our simulations the continuous set of electronic states of the leads is represented by a finite number of states. The number of states required to properly describe the continuum limit depends on the time \( t \). The situation is thus similar to that of a quantum reactive scattering calculation in the presence of a scattering continuum, where, with a finite number of basis functions, an appropriate absorbing boundary condition is added to mimic the correct outgoing Green’s function.\textsuperscript{76–79} Employing the same strategy for the present problem, the regularized electric current is given by

\[ I_{\text{reg}} = \lim_{\eta \to 0^+} \int_0^\infty dt \frac{dI(t)}{dt} e^{-\eta t}. \]  

(2.16)

The regularization parameter \( \eta \) is similar (though not identical) to the formal convergence parameter in the definition of the Green’s function in terms of the time evolution operator

\[ G(E^+) = \lim_{\eta \to 0^+} (-i) \int_0^\infty dt e^{i(E+i\eta-H)t}. \]  

(2.17)

In numerical calculations, \( \eta \) is chosen in a similar way as the absorbing potential used in quantum scattering calculations.\textsuperscript{76–79} In particular, the parameter \( \eta \) has to be large enough to accelerate the convergence but still sufficiently small in order not to affect the correct result. While in the reactive scattering calculation \( \eta \) is often chosen to be coordinate dependent, in our simulation \( \eta \) is chosen to be time dependent

\[ \eta(t) = \begin{cases} 
0 & (t < \tau) \\
\eta_0 \cdot (t - \tau)/t & (t > \tau).
\end{cases} \]  

(2.18)

Here \( \eta_0 \) is a damping constant, \( \tau \) is a cutoff time beyond which a steady state charge flow is approximately reached. As the number of electronic states increases, one may choose a
weaker damping strength $\eta_0$ and/or longer cutoff time $\tau$. The former approaches zero and the latter approaches infinity for an infinite number of states. For the systems considered in this work, convergence can be reached with a typical $\tau = 30-80$ fs (a smaller $\tau$ for less number of states) and $1/\eta_0 = 3-10$ fs.

III. SCATTERING STATE REPRESENTATION OF THE MODEL

In previous work\textsuperscript{58,59} we have used the above Hamiltonian with the ML-MCTDH-SQR theory for studying vibrationally coupled electron transport through molecular junctions. It provided important benchmark results to guide further development of the approximate theories. However, it was also found that upon increasing the bias voltage the number of configurations required in the ML-MCTDH representation of the wave function to achieve convergence becomes very large. This is so even without including the contribution from the nuclear bath, Eq. (2.1c), i.e. for the so-called noninteracting model. In fact, in many cases, including the vibrational coupling accelerates the convergence of the ML-MCTDH-SQR simulation within a given time scale (see below for a physical explanation).

Such a performance is not surprising if one considers the electronic Hamiltonian in Eq. (2.1b). Similar to the example of a quadratic Hamiltonian with full Hessian, all the electronic degrees of freedom in Eq. (2.1b) may be strongly coupled, thus creating significant artificial correlations in the quantum dynamics of the model. Including the vibronic contribution in Eq. (2.1c) may suppress such artificial correlations, though it also introduces vibrationally induced ‘true’ electronic correlation effect. Within the current form of the Hamiltonian, these artificial correlations are real and cannot be removed in a variational calculation.

To circumvent this problem and to reduce the artificial correlation, we take advantage of the fact that the Green’s function and also the steady state current for the noninteracting model defined by Eq. (2.1b) can be obtained analytically. Thus, the electronic Hamiltonian Eq. (2.1b) can be represented in the basis of its eigenstates, which are scattering states. The resulting scattering states representation of the model has been used before to describe quantum transport in combination with different methods.\textsuperscript{60–64}
A. General formulation

In the scattering state representation\[^{60-64}\] a set of scattering state operators are introduced to diagonalize the Hamiltonian (2.1b). These operators $\gamma_{k\zeta}^+$ satisfy the Lippmann-Schwinger equation ($\zeta = L, R$)

$$
\gamma_{k\zeta}^+ = c_{k\zeta}^+ + \frac{1}{E_{k\zeta} + i\eta - L_0} [\hat{V}, \gamma_{k\zeta}^+], \tag{3.1a}
$$
or the equivalent Heisenberg equation

$$
[\hat{H}_{el}, \gamma_{k\zeta}^+] = E_{k\zeta} \gamma_{k\zeta}^+ + i\eta (\gamma_{k\zeta}^+ - c_{k\zeta}^+). \tag{3.1b}
$$

Here $\hat{H}_{el} = \hat{H}_0 + \hat{V}$, $\hat{L}_0 = [\hat{H}_0, .]$ is a Liouville operator, $\eta$ is an infinitesimal, and

$$
\hat{H}_0 = E_d d^+ d + \sum_{k,\zeta} E_{k\zeta} c_{k\zeta}^+ c_{k\zeta}, \tag{3.2a}
$$
$$
\hat{V} = \sum_{k,\zeta} V_{dk\zeta} (d^+ c_{k\zeta} + c_{k\zeta}^+ d). \tag{3.2b}
$$

The scattering state operators $\gamma_{k\zeta}^+/\gamma_{k\zeta}$ fulfill the usual fermionic commutation relations. They can be expanded in terms of $d^+$ and $c_{k\zeta}^+$, and the formal solution to the Lippmann-Schwinger equation is given by

$$
\gamma_{k\zeta}^+ = c_{k\zeta}^+ + V_{dk\zeta} g_d^0(E_{k\zeta}) \left[ d^+ + \sum_{k',\zeta'} \frac{V_{dk'\zeta'}}{E_{k\zeta} + i\eta - E_{k'\zeta'}} c_{k'\zeta'}^+ \right], \tag{3.3}
$$

where $g_d^0(E_{k\zeta})$ is the retarded Green’s function for the bridge state

$$
g_d^0(E_{k\zeta}) = \frac{1}{E_{k\zeta} + i\eta - E_d - \Sigma(E_{k\zeta})}, \tag{3.4a}
$$
$$
\Sigma(E_{k\zeta}) = \sum_{k',\zeta'} \frac{|V_{dk'\zeta'}|^2}{E_{k\zeta} + i\eta - E_{k'\zeta'}}. \tag{3.4b}
$$

For the tight-binding parameterization, Eq. (2.3), the self energy $\Sigma(E) = \Sigma_L(E) + \Sigma_R(E)$ has the following analytic form

$$
\Sigma_\zeta(E) = -\frac{i}{2} \Gamma_\zeta(E) + \Delta_\zeta(E), \quad \zeta = L, R, \tag{3.5}
$$

where $\Gamma_\zeta(E)$ is given by Eq. (2.3), and

$$
\Delta_\zeta(E) = \begin{cases} 
\frac{\alpha^2}{2\beta_c^2} (E - \mu_\zeta) & |E - \mu_\zeta| \leq 2\beta_c \\
\frac{\alpha^2}{2\beta_c^2} \left[ (E - \mu_\zeta) \mp \sqrt{4\beta_c^2 - (E - \mu_\zeta)^2} \right] & \pm (E - \mu_\zeta) > 2\beta_c
\end{cases}, \tag{3.6}
$$
In the following, we assume that the purely electronic problem defined by the Hamiltonian Eq. (2.1b) does not possess bound states, so that the set of the scattering states provide a complete basis. As a result, the electronic Hamiltonian is diagonal in the scattering representation and has the form

$$\hat{H}_{el} = \sum_{k,\zeta} E_{k\zeta} \gamma_{k\zeta}^+ \gamma_{k\zeta} = \sum_{kL} E_{kL} \gamma_{kL}^+ \gamma_{kL} + \sum_{kR} E_{kR} \gamma_{kR}^+ \gamma_{kR}. \quad (3.7)$$

For the vibronic part of the Hamiltonian in Eq. (2.1c) and the current operator in Eq. (2.11), one applies the inverse relation of Eq. (3.3)

$$d^+ = \sum_{k,\zeta} \gamma_{k\zeta}^+ \left[ g_0^0(E_{k\zeta}) V_{dk\zeta} \right]^* \quad (3.8a)$$

and

$$c_{k\zeta}^+ = \gamma_{k\zeta}^+ + \sum_{k',\zeta'} \gamma_{k'\zeta'}^+ \left[ g_0^0(E_{k'\zeta'}) \frac{V_{dk\zeta'} V_{dk\zeta}}{E_{k'\zeta'} + i\eta - E_{k\zeta}} \right]^*, \quad (3.8b)$$

which, when substituting into Eq. (2.1c) and Eq. (2.11), yields the necessary expressions for implementation. It is noted that both the number operator $d^+ d$ and the current operator $\hat{I}_\zeta$ are more complex in the scattering state representation. This is the price for reducing the artificial correlation effect in the quantum dynamics simulation.

Finally, the initial density matrix, which will be used in the current simulation based on the scattering state representation, is given by

$$\hat{\rho} = e^{-\beta(\hat{H}_1 - \hat{Y})} \frac{\text{tr}[e^{-\beta(\hat{H}_1 - \hat{Y})}]}{\text{tr}[e^{-\beta(\hat{H}_1 - \hat{Y})}]}, \quad (3.9)$$

where $H_1$ is the Hamiltonian without the vibronic coupling

$$\hat{H}_1 = \sum_{kL} E_{kL} \gamma_{kL}^+ \gamma_{kL} + \sum_{kR} E_{kR} \gamma_{kR}^+ \gamma_{kR} + \hat{H}_{nuc}^0 \quad (3.10)$$

$$= \hat{H}_{el} + \hat{H}_{nuc}^0$$

and $Y$ is the bias operator

$$\hat{Y} = \mu_L \sum_{kL} \gamma_{kL}^+ \gamma_{kL} + \mu_R \sum_{kR} \gamma_{kR}^+ \gamma_{kR}. \quad (3.11)$$

The density matrix in Eq. (3.9) can be factorized

$$\hat{\rho} = \hat{\rho}_{el} \hat{\rho}_{nuc}, \quad (3.12)$$
into an electronic part

\[ \hat{\rho}_{\text{el}} = \frac{e^{-\beta(\hat{H}_{\text{el}} - \hat{Y})}}{\text{tr}[e^{-\beta(\hat{H}_{\text{el}} - \hat{Y})}]}, \tag{3.13} \]

and a nuclear part

\[ \hat{\rho}_{\text{nuc}} = \frac{e^{-\beta \hat{H}_{0\text{nuc}}}}{\text{tr}[e^{-\beta \hat{H}_{0\text{nuc}}}]}. \tag{3.14} \]

The electronic density matrix \( \hat{\rho}_{\text{el}} \) describes the steady state of the purely electronic model (without electron-vibrational coupling), i.e.

\[ \lim_{t \to \infty} \text{tr}\{\rho_0 e^{i\hat{H}_{\text{el}} t} \hat{A} e^{-i\hat{H}_{\text{el}} t}\} = \text{tr} \left\{ \frac{e^{-\beta(\hat{H}_{\text{el}} - \hat{Y})}}{\text{tr}[e^{-\beta(\hat{H}_{\text{el}} - \hat{Y})}]} \hat{A} \right\}, \tag{3.15} \]

holds for a given density matrix \( \rho_0 \) and electronic operator \( \hat{A} \). In particular, the steady state current for vanishing electronic-vibrational coupling is given by

\[ \lim_{t \to \infty} I_{L/R}(t) = \mp \text{tr} \left\{ \frac{e^{-\beta(\hat{H}_{\text{el}} - \hat{Y})}}{\text{tr}[e^{-\beta(\hat{H}_{\text{el}} - \hat{Y})}]} \hat{I}_{L/R} \right\}, \tag{3.16} \]

Assuming a unique steady state, both initial states, Eqs. (3.9) and (2.12), will result in the same steady-state current, however, the transient dynamics will be different.

**B. Optimization of the transport calculation including vibronic coupling**

It is straightforward to implement the above Hamiltonian in the scattering state representation for the ML-MCTDH-SQR simulation of the current. Without vibronic coupling, the model corresponds to a non-interacting system. We have verified that with a sufficient number of states used in the discretization of the electronic continua of the leads, the steady state current agrees with the Landauer formula, which is exact in this noninteracting case. Moreover, the ML-MCTDH-SQR only needs one configuration to obtain the numerically exact result, as it should be.

Including vibronic coupling, this is no longer the case because the systems represents a true many-body problem. In this case, we have found that the direct application of the scattering state representation as introduced above may result in serious numerical problems except for a range of positive energies for the original bridge state \( E_d > E_f \) where limited success is achieved. In particular, when \( E_d \) approaches zero or becomes negative, the simulated steady-state current sometimes becomes negative even with a relatively large
number of scattering states and configurations in the ML-MCTDH-SQR calculation, which is clearly unphysical.

This numerical problem may be understood from the technical aspects of applying a finite basis set representation to study dynamics. In principle, an infinite basis expansion can solve the problem exactly, but in practice one wants to keep the number of basis functions as small as possible to make the simulation feasible. To achieve this, it is advantageous to keep the (complete) basis sets as close as possible to the eigenfunctions of the overall Hamiltonian. If this is not done appropriately, one may need a prohibitively large number of basis functions (i.e., an “infinite” basis in a practical sense) to obtain numerical convergence, such as what we have observed here. In the discretized scattering state representation, the overall current comes from the contribution of all the scattering channels. The weight of each channel/scattering state is determined properly from the solution to the pure electronic Hamiltonian. However, when including the vibrational degrees of freedom in the Hamiltonian and electron-vibrational coupling, such a basis set may be far from optimal. The channels that contribute the most to the original, non-interacting electronic system may not be important at all to the overall true many-body transport problem. On the other hand, other channels that were insignificant previously may now become important.

According to our investigations, this numerical problem can be circumvented by noticing the fact that the scattering state representation is not unique. In particular, there is an arbitrariness in defining the bridge state energy, e.g., one can rewrite Eq. (2.1) as

\[
\hat{H}_{el} = (E_d - \Delta E)d^+d + \sum_{k_L} E_{k_L} c^+_k c_{k_L} + \sum_{k_R} E_{k_R} c^+_k c_{k_R} + \sum_{k_L} V_{d k_L} (d^+ c_{k_L} + c^+_k d) + \sum_{k_R} V_{d k_R} (d^+ c_{k_R} + c^+_k d),
\]

\[
\hat{H}_{el-nuc} = \frac{1}{2} \sum_j (P_j^2 + \omega_j^2 Q_j^2) + d^+d(\Delta E + \sum_j 2c_j Q_j).
\]

With a different choice of \(\Delta E\), the scattering state operators are different and so will be the performance of the vibronic transport calculation. Our numerical tests show that choosing specifically the value of \(\Delta E\), which is obtained by completing the square in the vibronic
\[ \hat{H}_{el} = \left( E_d - \sum_j \frac{2c_j^2}{\omega_j^2} \right) d^+ d + \sum_{kL} E_{kL} c_{kL}^+ c_{kL} + \sum_{kR} E_{kR} c_{kR}^+ c_{kR} \] (3.18a)
\[ + \sum_{kL} V_{dkL} (d^+ c_{kL} + c_{kL}^+ d) + \sum_{kR} V_{dkR} (d^+ c_{kR} + c_{kR}^+ d), \]
\[ \hat{H}_{el-nuc} = \frac{1}{2} \sum_j \left[ P_j^2 + \omega_j^2 \left( Q_j + d^+ d \frac{2c_j}{\omega_j^2} \right)^2 \right], \] (3.18b)

corresponding to \( \Delta E = \sum_j 2c_j^2/\omega_j^2 \), results in a particularly good performance of the transport calculations. It is recognized that for this choice of \( \Delta E \), the correction to the bridge state energy, \( \sum_j 2c_j^2/\omega_j^2 \), is the reorganization energy (polaron shift) for electron transfer between the bridge and the lead states and thus this selection also has a clear physical meaning.

With the choice of the scattering state operators that diagonalize the \( H_{el} \) in Eq. 3.18a, the effective Hamiltonian for the overall vibronic model performs well in all regimes we have tested. The numerical examples presented below will illustrate this point.

**IV. SIMULATION OF TRANSPORT IN THE SCATTERING STATE REPRESENTATION USING THE ML-MCTDH-SQR METHOD**

To simulate transport in the model described above, we employ the Multilayer Multiconfiguration Time-Dependent Hartree Theory in Second Quantization Representation (ML-MCTDH-SQR) \(^{80}\), which allows a numerically exact treatment of the many-body problem. The method has been described in detail elsewhere. It is based on the ML-MCTDH theory \(^{21}\), which is a rigorous variational method to propagate wave packets in complex systems with many degrees of freedom. In the ML-MCTDH theory \(^{21}\), the wave function is represented by a recursive, layered expansion,

\[
|\Psi(t)\rangle = \sum_{j_1} \sum_{j_2} \ldots \sum_{j_p} A_{j_1j_2\ldots j_p}(t) \prod_{\kappa=1}^p |\varphi_{j_\kappa}(t)\rangle, \]
(4.1a)
\[
|\varphi_{j_\kappa}(t)\rangle = \sum_{i_1} \sum_{i_2} \ldots \sum_{i_{Q(\kappa)}} B_{i_1i_2\ldots i_{Q(\kappa)}}(t) \prod_{q=1}^{Q(\kappa)} |v_{i_q}(t)\rangle, \]
(4.1b)
\[
|v_{i_q}(t)\rangle = \sum_{\alpha_1} \sum_{\alpha_2} \ldots \sum_{\alpha_{M(\kappa,q)}} C_{\alpha_1\alpha_2\ldots \alpha_{M(\kappa,q)}}(t) \prod_{\gamma=1}^{M(\kappa,q)} |\xi_{\alpha_{\gamma}}(t)\rangle, \]
(4.1c)
where $A_{j_1j_2...j_p}(t)$, $B_{i_1i_2...i_Q(\kappa)}^{\kappa}(t)$, $C_{i_{\alpha_1}i_{\alpha_2}...i_{M(\kappa,q)}}(t)$ and so on are the expansion coefficients for the first, second, third, ..., layers, respectively; $|\varphi_j^{(\kappa)}(t)\rangle$, $|v_{i_q}^{(\kappa,q)}(t)\rangle$, $|\xi_{\alpha,\gamma}^{(\kappa,q)}(t)\rangle$, ..., are the “single particle” functions (SPFs) for the first, second, third, ..., layers. In Eq. (4.1a), $p$ denotes the number of single particle (SP) groups/subspaces for the first layer. Similarly, $Q(\kappa)$ in Eq. (4.1b) is the number of SP groups for the second layer that belongs to the $\kappa$th SP group in the first layer, i.e., there are a total of $\sum_{\kappa=1}^{p} Q(\kappa)$ second layer SP groups. Continuing along the multilayer hierarchy, $M(\kappa,q)$ in Eq. (4.1c) is the number of SP groups for the third layer that belongs to the $q$th SP group of the second layer and the $\kappa$th SP group of the first layer, resulting in a total of $\sum_{\kappa=1}^{p} \sum_{q=1}^{Q(\kappa)} M(\kappa,q)$ third layer SP groups.

Each summation in the expressions above is over the number of SPFs in that single particle group and the total combination defines the size of the configurational space in that layer, e.g., if there are 4 SP groups and we use 10 SPFs per group, the configurational space is $10^4 = 10000$. If there is no correlation at all between different degrees of freedom, only one SPF is required for each group, resulting in one overall configuration. As the correlation becomes stronger, more SPFs are required to achieve convergence, which results in a larger configuration space. Thus, the number of SPFs is a good indicator of the correlation strength and will be used for analysis purposes below.

V. RESULTS AND DISCUSSION

In this section, we apply the methodology discussed above to study vibrationally-coupled charge transport. In particular, we discuss for selected examples the performance of the simulation in the scattering-state representation as compared to the original representation. Without specifying otherwise, we will use the tight-binding parameterization for the electronic part of the model, as described in Sec. II and used equivalently in the scattering state representation, Sec. III. The tight-binding parameters for the function $\Gamma(E)$ are $\alpha_e = 0.2$ eV, $\beta_e = 1$ eV, corresponding to a moderate molecule-lead coupling an a bandwidth of 4 eV.
A. Transport without vibronic coupling

If the Hamiltonian only contains the pure electronic part, i.e. without electronic vibrational coupling, it corresponds to the non-interacting transport model. Employing the scattering-state representation, in this case one SPF for each SP group, i.e., one overall configuration representing the wave function, gives the numerically exact steady-state current. This was verified by comparing the numerical results obtained with one configuration of the wave function to the Landauer formula. In contrast, for the original representation of the model described in Sec. II, there is significant artificial correlation, especially for a large source-drain bias voltage, such that a large configurational space is required to achieve convergence.

B. Vibrationally coupled electron transport for $E_d > E_f$

Including electronic-vibrational coupling, the model becomes a many-body problem with “true” correlation. We first consider a physical regime where, without vibronic coupling, the electronic energy of the bridge state is located above the Fermi level of the leads, $E_d - E_f = 0.5 \text{eV}$. For small bias voltages, this corresponds to the non-resonant transport regime. Fig. 1a shows the converged time-dependent currents obtained with the original model Hamiltonian in Sec. II and with the scattering state Hamiltonian. Thereby, the characteristic frequency of the bath has been chosen as $\omega_c = 500 \text{ cm}^{-1}$ and the overall electronic-nuclear coupling strength is determined by the reorganization energy, $\lambda = 2\alpha\omega_c = 2000 \text{ cm}^{-1}$. The source-drain bias voltage is 0.1V. Despite the difference in the transient behavior of $I(t)$, which is expected due to the difference in the initial states between the two model representations, the stationary values of the current agree within 1% relative difference. This small numerical error is remarkable considering the two drastically different representations of the model and the wave function. Fig. 1b shows the convergence behavior of $I(t)$ versus the number of SPFs for each electronic SP group, where 6 SPFs for each nuclear SP group provides a converged solution. It is seen that the result obtained with 8 SPFs per each electronic SP group agrees perfectly with a larger 12 SPFs simulation. Even 6 SPFs per electronic SP group gives a result that is within 10% relative error of the converged answer. On the other hand, to achieve convergence for the original model requires 40 SPFs per electronic
SP group to generate the result in Fig. 1a.

This shows that by using the Hamiltonian in the scattering state representation much of the artificial correlation has been removed. This results in a significantly smaller configuration space than that required for the original model Hamiltonian. A comparison of results obtained with different number of SPFs also reveals the extent of the “true” correlation effect, which is helpful for analyzing the physics of the problem.

It is also interesting to consider the result obtained with 1 SPF, i.e., only one overall configuration. Within the scattering state representation, this corresponds to the Hartree-Fock approximation for the present vibronic model. Fig. 1b shows that in this case: (i) there is no transient dynamics in the simulated $I(t)$ and (ii) the stationary current is approximately three times as large as the true result. Further inspection shows that the one-configuration result agrees with a pure electronic model (Landauer formula), where the bridge state energy is shifted by the bath reorganization energy, i.e., $E_d' = E_d - \lambda$. For this particular example, this brings the level closer to the chemical potential of the electrodes. As a result, the current is enhanced compared with that without vibronic coupling. Although the one-configuration result captures this effect qualitatively, it is not quantitative at all, being a factor of three too large.

Figure 2 shows the time-dependent current for larger bias voltages, 0.5V and 1V, where all other parameters are the same as in Fig. 1. For $V = 0.5V$, as depicted in Fig. 2a, about 6-8 SPFs per electronic SP group gives the converged result that is in good agreement with that obtained with the original model Hamiltonian. The stationary current obtained with 4 SPFs is 20% larger, which does not satisfy our convergence criterion but is still reasonable. The single configuration (1 SPF) result is approximately four times as large as the true result. For this bias voltage the artificial correlation effect in the original model becomes quite large. It requires 60 SPFs per electronic SP group to obtain the converged result in Fig. 2a for the original model.

For an even higher bias voltage of $V = 1V$, it becomes difficult to converge the steady-state current for the original model due to the even increased artificial electronic correlation. On the other hand, this also makes the vibrational contribution (relatively) less important. Figure 2b shows that within the scattering state representation of the Hamiltonian, the steady state current is easily converged, although the transient behavior is different with different number of SPFs. In this case, the single configuration result is very accurate, thus
the steady-state current is very well approximated by the purely electronic model. This is due to the rather large voltage. It is known that in the limit of large voltages (within the wide-band-approximation), the steady-state current becomes independent of the vibronic coupling. For the voltage considered here, the polaron shifted energy level \((E_d - \lambda \approx 0.25 \text{ eV})\) is already well within the bias window given by the chemical potential of the two electrodes.

C. **Vibrationally coupled electron transport for** \(E_d = E_f\)

Here we consider a model where the energy of the bridge state is located at the Fermi energy of the leads. This parameter regime is particularly interesting, because already for small bias voltage the transport mechanism corresponds to resonant tunneling and involves mixed electron/hole transport.

In this parameter regime and for a relatively large reorganization energy (e.g., \(\lambda = 2000 \text{ cm}^{-1}\)), it is found that when transforming to the effective Hamiltonian in the scattering state representation, the naive procedure outlined in Sec. III A sometimes gives negative steady-state currents, which is unphysical. This numerical problem persists even with a relatively large number of scattering channels and a large configuration space. Employing the modification described in Sec. III B, on the other hand, gives excellent performance. As shown in Figure 3 for a typical range of bath reorganization energies, 1000-2000 cm\(^{-1}\), results obtained with 10 SPFs per electronic SP group are in good agreement with those obtained with the original model Hamiltonian, which requires 40 SPFs per electronic SP group.

The results depicted in Figs. 3, 4 for different values of voltage and electron-vibrational coupling strength, all show the same qualitative behavior: a strong increase of the current for short time, which is followed by a decrease to a very small steady-state current. As was discussed in detail in Ref. 59, this suppression of the steady state current is a manifestation of the phonon blockade effect, which is particularly pronounced for larger electronic-vibrational coupling.

The phonon blockade of the current is usually, qualitatively rationalized by considering the energy level of the bridge state. For any finite bias voltage, the bare energy of the bridge state \((E_d - E_f = 0)\) is located between the chemical potential of the leads and thus, within
a purely electronic model, current can flow. The coupling to the vibrations results in a polaron shift of the energy of the bridge state. For electronic-vibrational coupling strengths $\lambda > |V|/2$ the polaron-shifted energy of the bridge state is below the chemical potentials of both leads and thus the current is blocked.

The comparison between the converged results and those obtained employing only a single SPF for the electronic degrees of freedom (which agree with the results for the purely electronic model), demonstrate that this simple picture based on the static energy shift is at best qualitatively correct. It is seen from Fig. 3 that the 1 SPF (single configuration) approach, i.e., the Hartree-Fock limit in the scattering state representation, significantly overestimates the steady state current. The discrepancy becomes larger for stronger electron-nuclear couplings.

It is noted that the results obtained with 1 SPF, which neglect true correlation between electronic and vibrational degrees of freedom, are very similar to the results obtained with a NEGF method (see, e.g., the data shown in Fig. 9 of Ref. 59). In this method, a factorization of the electronic and vibrational Green’s function is employed. As a consequence, correlations between electronic and vibrational degrees of freedom are only treated on a very approximate level. This results, in this case, in a significant overestimation of the current, similar to what would be obtained with a very small (unconverged) number of configurations in the ML-MCTDH-SQR method.

Similar to the examples discussed in Sec. VI B the single configuration limit becomes a better approximation for a higher bias voltage when the vibronic coupling is fixed. For the parameters displayed in Fig. 3, the single configuration result becomes very good for, e.g., a bias voltage of 1 V (data not shown), similar to that illustrated in Fig. 2b. Again, in this regime, the NEGF approach or the Landauer formula with the shifted bridge state energy becomes accurate.

It should be emphasized, though, that this also depends on the relative strength between the vibronic coupling and the bias voltage. Only for voltages $|V| \gg |2(E_d \pm \lambda - E_f)|$, can it be expected that vibronic effects, and thus also vibrationally induced correlation, are negligible in the steady state current. As an example, Figure 4a shows the simulation for a higher voltage of 0.5 V but also a larger reorganization energy 4000 cm$^{-1}$. In this case 12 SPFs per electronic SP group are required to obtain the result in the scattering state representation, where the single configuration result is approximately a factor of three too
large. Convergence in the original model Hamiltonian also becomes more expensive, which requires 64 SPFs per electronic SP group.

D. Vibrationally coupled electron transport with \( E_d < E_f \)

We finally consider in Fig. 5 an example with a bridge state located at \( E_d - E_f = -0.5 \) eV., i.e. well below the Fermi energy. All other parameters are the same as in Fig. 1. For the voltage considered, this case corresponds to non-resonant transport. Similar to the case \( E_d - E_f = 0 \), when transforming to the effective Hamiltonian in the scattering state representation, the naive procedure outlined in Sec. IIIA gives a negative steady-state current. On the other hand, Figure 5 shows the result obtained with employing the modification described in Sec. IIIB, which gives excellent agreement with the result obtained with the original model Hamiltonian. The former requires 8 SPFs to converge, whereas the latter require 40 SPFs. The performance with other voltage/vibronic coupling is similar to the previous figures.

VI. CONCLUDING REMARKS

In this paper, we have shown that the scattering state representation of the underlying electronic Hamiltonian represents a promising approach for studying vibrationally coupled electron transport through molecular junctions. Within the ML-MCTDH-SQR theory\(^{58,59}\), much less configurations are required to achieve convergence than when using the original representation of the Hamiltonian. This is because the transformation to the scattering state representation effectively diagonalizes the underlying electronic Hamiltonian and, therefore, much artificial correlation present in the original model is removed. We have also shown that the definition of the scattering states is not unique. This can be used to optimize the simulation. Our numerical studies suggest that the form of the Hamiltonian outlined in Sec. IIIB performs best in all the physical regimes investigated.

The results of our studies also give physical insight into the importance of correlation effects in vibrationally coupled nonequilibrium transport. While for small voltages and/or transient effects, electronic-vibrational correlation is often of utmost importance, for higher voltages correlation effects are less pronounced in the steady state current. This finding
is also of relevance for the validity of NEGF calculations for vibrationally coupled electron transport, in particular, methods that employ an effective factorization between electronic and vibrational degrees of freedom.\textsuperscript{29,33}

To conclude this paper, we discuss the computational costs of the simulations in the two different representations. As was shown above, much less SPFs are needed when using the scattering state representation as compared to the original model. However, the transformation used to generate the number operator $d^+d$ and the current operator $\hat{I}_{\zeta}$, Eq. (3.8), scales quadratically versus the number of the electronic states. This is in contrast to the original model where the number of electronic operators scales linearly versus the number of electronic states. As a result, there are many more operators to evaluate in the scattering state Hamiltonian, which makes the simulation more expensive. For the examples considered in this paper, using 10 SPFs per electronic SP group in the scattering model has a similar computational cost to using 40 SPFs in the original model. Therefore, when studying vibrationally coupled electron transport at a lower bias voltage, the original model Hamiltonian may be more efficient.

However, things are quite different when the bias voltage becomes higher, where significant artificial correlation exists in the original model, which makes convergence difficult or even impossible. The scattering state representation, on the other hand, requires typically a smaller configuration space to converge as demonstrated by the numerical examples in this paper. This makes the scattering state representation a valuable tool for multiconfigurational study of current-voltage characteristics where the bias voltage spans a larger range. Such work is currently in progress.

Our current implementation of the scattering state representation has not yet exploited its full potential. It is possible that a different energy shift from that of the reorganization energy is more efficient for solving the problem in some physical regimes. This may be achieved by designing a self-consistent procedure in the convergence tests. Furthermore, a different initial condition for the vibrational bath or even a correlated electronic-vibrational initial density matrix may be helpful in reducing the transient peaks of the current, and thus making the calculation of the steady-state current more stable numerically. Work on these issues is in progress.
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FIG. 1: (a) Time-dependent current $I(t)$ for different representations of the model Hamiltonian (scattering state vs. original representation), (b) Convergence of $I(t)$ versus the number of SPFs for the electronic part, where 6 SPFs are used for each nuclear SP group. The model parameters are: $\alpha_e = 0.2eV$, $\beta_e = 1eV$, and $E_d - E_f = 0.5eV$ for the electronic part; $\lambda = 2000cm^{-1}$ and $\omega_c = 500cm^{-1}$ for the vibrational bath. The source-drain voltage is $V = 0.1V$. 
FIG. 2: Convergence of $I(t)$ versus the number of SPFs. The parameters are the same as Fig. 1 except for the bias voltage: (a) $V = 0.5\,\text{V}$, (b) $V = 1\,\text{V}$.
FIG. 3: Time-dependent current $I(t)$ versus the number of SPFs for the source-drain voltage $V = 0.1V$. Six SPFs are used for each nuclear SP group. The model parameters are: $\alpha_e = 0.2eV$, $\beta_e = 1eV$, and $E_d - E_f = 0$ for the electronic part; $\omega_c = 500cm^{-1}$ for the vibrational bath and (a) $\lambda = 2000cm^{-1}$, (b) $\lambda = 1000cm^{-1}$. 
FIG. 4: Time-dependent current $I(t)$ versus the number of SPFs for the source-drain voltage $V = 0.5V$. Six SPFs are used for each nuclear SP group. The model parameters are: $\alpha_e = 0.2eV$, $\beta_e = 1eV$, and $E_d - E_f = 0$ for the electronic part; $\omega_c = 500 cm^{-1}$ for the vibrational bath and $\lambda = 4000 cm^{-1}$. 
FIG. 5: Time-dependent current $I(t)$ versus the number of SPFs for the source-drain voltage $V = 0.1V$. Six SPFs are used for each nuclear SP group. The model parameters are: $\alpha_e = 0.2eV$, $\beta_e = 1eV$, and $E_d - E_f = -0.5eV$ for the electronic part; $\lambda = 2000cm^{-1}$ and $\omega_c = 500cm^{-1}$ for the vibrational bath.