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Transmission eigenchannels from nonequilibrium Green’s functions

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The concept of transmission eigenchannels is described in a tight-binding nonequilibrium Green’s function (NEGF) framework. A simple procedure for calculating the eigenchannels is derived using only the properties of the device subspace and quantities normally available in a NEGF calculation. The method is exemplified by visualization in real space of the eigenchannels for three different molecular and atomic wires.

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I. INTRODUCTION

Electronic transport properties of atomic-scale conductors have been investigated intensively in the past decade.1,2 Examples of interest include molecular wires connected to metal electrodes, atomic metal wires, and nanotubes. First-principles transport calculations on these systems give results that are, in general, difficult to interpret due to the multichannel nature of the scattering problem and the fact that the scattering states are generated from the atomic valence orbitals. The free-electron type of reasoning normally used in mesoscopic quantum transport is, thus, not adequate. It is, therefore, useful to analyze the conduction in terms of eigenchannels. Eigenchannels are particular scattering states1 with a well-defined transmission probability, \(0 \leq T_n \leq 1\), where the individual eigenchannel transmissions add up to the total transmission \(T = \sum_n T_n\). In addition to being useful for analyzing theoretical calculations, the eigenchannel transmissions may be obtained experimentally (i) with superconducting electrodes connecting the atomic-scale conductor, as shown by Scheer et al.,3 or (ii) from shot noise measurements,4 where information about the individual channel contributions can be obtained since the Fano factor involves the sum \(T_n(1-T_n)/T_n\).

Eigenchannels have previously been calculated for atomic metal wires5,7 and molecular contacts8 by directly solving for the scattering states in the leads. This type of analysis breaks up the transmission into the “nonmixing” channels3,9 and gives an intuitive picture of electron transport. The ability to plot the eigenchannel wave functions is especially useful, since it gives a direct spatially resolved picture of the orbitals involved in the transport. Another possibility is to consider projections of eigenchannel wave functions onto, for example, molecular orbitals.

An increasingly popular theoretical approach to calculate transport properties is the nonequilibrium Green’s function (NEGF) formalism.10 This is normally used in combination with a tight-binding type or linear combination of atomic orbitals electronic structure description.12–15 In this approach, it is straightforward to calculate the single particle (retarded) Green’s function (matrix) including coupling to the infinite electrodes by introducing self-energies. The Green’s function is, thus, the fundamental quantity in these calculations, and scattering states are normally not considered. Interpretation of the results in terms of scattering states is, therefore, nontrivial.10 In contrast, the scattering states are the fundamental quantity in approaches based on the Lippmann-Schwinger equation, where jellium models are normally used to describe the electrodes.12–20

The aim of this paper is to show how the eigenchannels can be easily generated within the NEGF approach without solving for the scattering states in the leads. The eigenchannel wave functions are here obtained directly from quantities readily available in the NEGF calculation, e.g., the retarded Green’s function matrix, \(G_D\) of the device region, and the \(G_{LR}\) matrices describing the coupling of the device region to the two electrodes (“left” \(L\) and “right” \(R\), see Fig. 1). In the case of atomistically defined electrodes, this approach is especially advantageous since solving for the scattering states requires calculating the Bloch waves in the electrodes (complex band structure), which may be a nontrivial numerical task for large unit cells.21 Related to our approach is the so-called (left and/or right) open “channel functions” of Inglesfield et al. based on the “embedding potential” in the real-space formulation22 and the Korringa-Kohn-Rostoker-based formulation by Bagrets et al.23,24 In addition to providing a simple way to calculate the eigenchannels, the method presented here offers an intuitive understanding of the one-particle NEGF equations; e.g., it may be used to understand propensity rules for the effect of phonon scattering on the electronic transport.25,26

The paper is organized as follows. Section II starts with the definition of eigenchannels and a summary of the standard one-particle NEGF equations. Our method to obtain the eigenchannels without solving for the full transmission matrix is then derived. The usefulness of the eigenchannels is
II. EIGENCHANNELS

We consider transport through a device region $D$ coupled to two semi-infinite leads, left and right ($L,R$), and limit ourselves to leads built from periodic cells. The solutions in the corresponding infinite leads are Bloch states $|u_l\rangle$ (in $|u_r\rangle$) denoted by band index $l$ ($r$) for the left (right) lead. In order to obtain the transmission amplitude matrix $t_{r,l}$ at a given energy $E$, we consider the solutions to the Schrödinger equation, $|\Psi_l\rangle$, with scattering boundary conditions and incoming waves in the left lead,

$$|\Psi_l\rangle = \frac{|u_l\rangle}{\sqrt{\cal V}_l} + \text{reflected, left lead,}$$

$$|\Psi_r\rangle = \sum_r \frac{|u_r\rangle}{\sqrt{\cal V}_r} t_{r,l} + \text{decaying, right lead,}$$

where $|u_l\rangle$ is an incoming Bloch wave from the left lead, i.e., right-moving, with energy $E$ and group velocity $v_l > 0$, and $|u_r\rangle$ is an outgoing Bloch wave ($v_r > 0$). At a certain energy, the number of such incoming channels, $N_l(E)$, is determined by the band structure of the lead. Likewise, there are $N_r(E)$ such outgoing channels on the right. In Eq. (1), we explicitly state the flux normalization by dividing the Bloch state by $\sqrt{\cal V}_l$, where the Bloch waves $|u_l\rangle$ are normalized in the conventional manner over the infinite leads $\sum_k |u_l(k)|^2 = \delta_{ll'} \delta(k-k')$. The relected and transmitted parts may contain evanescent decaying waves which have zero velocity, and for those states, we use normal integral normalization. With these considerations, we find that the flux-normalized states fulfill the normalization,

$$\frac{1}{\sqrt{\cal V}_l} \langle u_l(k)|u_{l'}(k') \rangle \frac{1}{\sqrt{\cal V}_{l'}} = \hbar \delta_{ll'} \delta(E-E'),$$

since the velocity is related to the energy as $v_l = 1/\hbar dE_l(k)/dk$. The scattering states generated from the flux-normalized incoming waves will also be flux normalized, see the Appendix,

$$\langle \Psi_l|\Psi_{l'}\rangle = \hbar \delta_{ll'} \delta(E-E'),$$

and likewise for $r,r'$ while $\langle \Psi_l|\Psi_r\rangle = 0$.

The advantage of using flux-normalized states is that we can make any unitary transformation between the incoming scattering states from the left lead at a particular energy,

$$|\psi_l\rangle = \sum_{l'} \frac{|u_{l'}\rangle}{\sqrt{\cal V}_l} (U_L)^{l',l}.$$

These new states will again solve the Schrödinger equation, only contain incoming waves in the left lead, and be flux normalized. However, the mix of Bloch waves will no longer have Bloch symmetry. Naturally, we can apply a similar transformation of the outgoing right channels with $U_R$. Especially, we can choose the transformations $(U_L, U_R)$ such that the transmission matrix $t$ becomes a diagonal matrix, $^9 t_{r,l}$, at a specific energy

$$t_r = U_R^t U_L = \text{diag} (\sqrt{T_1}, \sqrt{T_2}, \ldots).$$

This corresponds to a singular value decomposition of the transmission amplitude matrix, or a diagonalization of the Hermitian (left to right) transmission probability matrix,

$$T_r = t_r^t U_r^t U_L^t U_R = \text{diag} (T_1, T_2, \ldots),$$

where there will be a maximum of $\min(N_L(E),N_R(E))$ non-zero eigenvalues $0 \leq T_a \leq 1$.

The diagonalization of the transmission matrix defines the transmission eigenchannels $|\Phi_{a}\rangle$ of the system as the unitary mix of left incoming flux-normalized scattering states (“channels”) given by $U_L$; i.e., the left eigenchannels are given by $|\Phi_{a}\rangle = \sum_r |\Psi_{r}\rangle (U_L)^{l,r}$. The eigenchannels have the special property of being nonmixing in the sense that the transmission of a sum of 2 is the sum of individual fluxes or transmissions (equal for flux-normalized states). For example, consider the alternative channels given by the scattering states defined by the two first eigenchannels as $|\psi_a\rangle = a_1 |\Phi_1\rangle + a_2 |\Phi_2\rangle$, with transmission $T_a = |a_1|^2 T_1 + |a_2|^2 T_2$, and similarly, $|\psi_b\rangle$ with transmission $T_b$. Now the total transmission $|\psi_{a+b}\rangle = |\psi_a\rangle + |\psi_b\rangle$ will be $T_{a+b} = T_a + T_b + I$, with the interference term $I = 2T_1 \text{Re}(a_1 b_1^* ) + 2T_2 \text{Re}(a_2 b_2^* )$. It will, thus, not simply be the sum of the two transmissions, $T_k \neq T_k^a + T_k^b$. Since the purpose of this paper is to calculate the eigenchannels without solving for the complex band structure in the leads, we will use the fact that the eigenchannels also maximize the transmission through the device; i.e., the first eigenchannel from the left contact maximizes the transmission probability over the space of incoming states from the left, the next channel maximizes the transmission while being orthogonal to the first channel, etc.

In the following, we will, instead of flux normalization, make use of energy normalization $\langle \Psi_{a}(E)|\Psi_{a}(E)\rangle = \delta_{\text{en}} \delta(E-E')$, with the trivial difference from flux normalization being a factor $\sqrt{\cal V}$. Energy normalization is advantageous when working with energy resolved quantities since the natural continuous quantum number for this normalization is the energy. In addition, we can interpret the energy-normalized states as a density of states; i.e., $|\Psi_{a}(x)|^2 = |\langle x|\Psi_{a}\rangle|^2$ is the projected (local) density of states at $x$.

A. Preliminaries

The one-particle Hamiltonian for the tight-binding scattering problem shown in Fig. 1 can be written

$$H = H_0 + V = H_L + H_D + H_R + V_L + V_R,$$

where the isolated leads $H_{L,R}$ and device $H_D$ are coupled...
together by the interactions between leads and device \( (V = V_L + V_R) \) without any direct coupling between the leads. Using projection operators onto the device \( P_D \) and left and/or right leads \( P_{L,R} = P_{L} + P_{D} + P_{R} \), we can also define \( \tau_{L,R} = P_{D}V_{L,R}P_{L,R} \), where \( V_{L,R} = \tau_{L,R} + \tau_{L,R}^{-1} \). The rest of this section provides a short summary of the standard definitions of one-particle Green’s functions, self-energies, and the notation we will use throughout the paper.\(^{11,27}\)

From the definition of the retarded Green’s function (operator) for the whole system, we can find the expansion of the Green’s function in an eigenbasis, \( H|\Psi_m(E)\rangle = E|\Psi_m(E)\rangle \),

\[
G(E) = (E + i\delta - H)^{-1} = \int dE' \sum_{m} \frac{\langle \Psi_m(E') | \Psi_m(E) \rangle}{E + i\delta - E'},
\]

where the infinitesimal imaginary part \( \delta = 0^+ \) ensures that the Green’s function yields the retarded response of the system. The device part of the Green’s function can further be written

\[
G_D = (E + i\delta - H_D - \Sigma_L - \Sigma_R)^{-1},
\]

where we have introduced the self-energies, \( \Sigma_{L,R} = \tau_{L,R}V_{L,R}^{\dagger}V_{L,R} \) given by the Green’s functions of the isolated leads \( V_{L,R} = (E + i\delta - H_{L,R})^{-1} \). In addition to the Green’s function, the spectral functions \( A(E) = \text{Im} \left\langle \Gamma L \right| G(E) - G^d(E) \right\rangle \) and \( \text{Im} \left\langle \Gamma R \right| G(E) - G^d(E) \right\rangle \) and broadening \( \Gamma_{L,R} = \text{Im} \left\langle \Sigma_{L,R} - \Sigma_{L,R}^{-1} \right\rangle = \tau_{L,R}V_{L,R}^{\dagger}V_{L,R} \) will be needed. The fact that these matrices live on different subspaces will be used repeatedly, e.g., \( \Gamma_L = PD\Gamma_L^dP_D \), etc.

For the scattering problem, see Fig. 1, we know that the time independent discrete Schrödinger equation has a complete set of solutions. These solutions can be divided into a continuous set of solutions \( |\Psi_n(E)\rangle \) (where there may be several solutions at any given energy) and localized states \( |\Psi_n^{\text{loc}}\rangle \) with energy \( E_n^{\text{loc}} \). We use the energy as the continuous quantum number together with a discrete quantum number \( n \), i.e., subbands. Since we are only interested in the transport properties, we will, from here on, ignore localized states.\(^{32}\)

In the following, we will describe a method to determine the eigenchannel scattering states inside the device region using the information contained in \( G_D \), \( \Gamma_L \), and \( \Gamma_R \). The spectral function \( A \) is a central quantity in the following discussion. It can be obtained from the expansion of the retarded Green’s function in eigenfunctions to the Hamiltonian [Eq. (8)].

\[
A(E) = \text{Im} \left\langle \Gamma L \right| G(E) - G^d(E) \right\rangle = 2\pi \sum_n \left| \langle \Psi_n(E) | \Psi_n(E) \rangle \right|.
\]

**B. Scattering states from the leads**

We may choose to express the solutions to the Schrödinger equation as solutions consisting of waves originating in the left or right lead. These scattering states can be generated from the spectral function, as will be shown here. Decomposing the spectral function of the device \( \Delta P = P_D\Delta P_D \) using Eq. (9), we find

**B. Scattering states from the leads**

with energy \( E \), \( |\Psi_0\rangle \), originating from \( L \) from the original incoming (standing) wave \( |\tilde{u}_i\rangle \), can be written

\[
A_D = iG_D(G_D^d - G_D^d)^{-1} G_D^d = G_D\Gamma_L G_D^d + G_D\Gamma_R G_D^d,
\]

where we, in the following, wish to show that \( A_{L,R} = G_D\Gamma_{L,R} G_D^d \) is generated by the scattering states with incoming waves in the left (right) lead.

Viewing the coupling between device and leads as a perturbation, we can start with a set of orthogonal and normalized eigenfunctions, \( |\tilde{u}_i\rangle \), of the isolated left lead (and similarly for the right), which are totally reflected solutions since they are solutions for the isolated semi-infinite leads. From these states, the full solutions \( |\Psi_i\rangle \) can be generated,

\[
|\Psi_i\rangle = GVL|\tilde{u}_i\rangle + |\tilde{u}_i\rangle.
\]

The response given by the retarded Green’s function only contains waves traveling outward from the device region. These solutions to the Schrödinger equation, thus, have the required property of being incoming from the left lead. In addition, the solutions are energy normalized and orthogonal; see the Appendix.

We can then express the device part of the spectral function from the solutions generated by Eq. (12),

\[
A_L = 2\pi \sum_l P_D|\Psi_l\rangle\langle\Psi_l| P_D
\]

\[
= 2\pi \sum_l P_D(GVL|\tilde{u}_l\rangle + |\tilde{u}_l\rangle)(|\tilde{u}_l\rangle + \langle\tilde{u}_l|VG_lG^d)P_D
\]

\[
= P_DGV_l|\tilde{u}_l\rangle|\tilde{u}_l\rangle G^dP_D = G_D\Gamma_L G_D^d,
\]

where we have used Eq. (10) for the whole system and for the isolated lead. Apart from rederiving Eq. (11), we have proven that the two parts of the device spectral function \( A_{L,R} = G_D\Gamma_{L,R} G_D^d \) are built up of scattering states originating from the respective leads. This immediately leads to the well known formula for the density matrix in nonequilibrium (excluding localized states)

\[
\rho = \frac{1}{2\pi} \int_{-\infty}^{\infty} [f_L(E)A_L(E) + f_R(E)A_R(E)]dE,
\]

where \( f_{L,R} \) is the Fermi function of the leads.

**C. Current operator**

To find the eigenchannels of the system, we will need the current operator. The number of electrons in lead \( R \) is described by the projection operator \( P_R \). The operator for current into \( R \) is, thus, determined as the time derivative of \( P_R \),

\[
\dot{J}_R = 2eP_R = \frac{i2e}{\hbar} [H, P_R] = \frac{i2e}{\hbar} (\tau_R - \tau_R^d),
\]

where we have evaluated the commutator using the Hamiltonian, Eq. (7), and included a factor of 2 for spin.

The current into lead \( R \) due to the scattering state with energy \( E \), \( |\Psi_i\rangle \), originating from \( L \) from the original incoming (standing) wave \( |\tilde{u}_i\rangle \), can be written
\[ j_H = \left\langle \Psi_l | \hat{J} | \Psi_r \right\rangle. \] (16)

To simplify this expression, we extract the right lead part of the wave function using the Lippmann-Schwinger Eq. (A2), which gives

\[ P_R | \Psi_r \rangle = P_R G_0 | \Psi_r \rangle + P_R \tilde{\alpha} \tilde{\alpha} | \Psi_r \rangle = \frac{s_R \tau_R^l | \Psi_r \rangle}{\tau_R}. \] (17)

where all quantities are evaluated at energy \( E \). The current carried by the scattering state \( | \Psi_r \rangle \) is then given by

\[ j_H = \frac{i 2 e}{\hbar} \langle \Psi_l | \tau_R^l - \pi_R^l | \Psi_r \rangle \]
\[ = \frac{i 2 e}{\hbar} ( \langle \Psi_l | \tau_R^l \pi_R^l | \Psi_r \rangle - \langle \Psi_l | \pi_R^l \tau_R^l | \Psi_r \rangle ) \]
\[ = \frac{e}{\pi \hbar} 2 \pi \langle \Psi_l | \Gamma_R | \Psi_r \rangle. \] (18)

Summing the current over all the orthogonal, energy-normalized scattering states originating in \( L \) at the specific energy yields the net current or total transmission and, thus, the Landauer formula,

\[ j = \sum_j J_{ij} = \frac{e}{\pi \hbar} 2 \pi \sum_j \langle \Psi_l | \Gamma_R | \Psi_r \rangle \]
\[ = \frac{e}{\pi \hbar} \text{Tr}(A_L \Gamma_R) = \frac{e}{\pi \hbar} \text{Tr}(G_D \Gamma_L G_D \Gamma_R). \] (19)

From Eq. (18), we notice that the transmission probability for any scattering state from the left \( | \Psi_r \rangle \) is given by

\[ T_{ij} = 2 \pi \langle \Psi_l | \Gamma_R | \Psi_r \rangle. \] (20)

since we consider energy-normalized (flux normalized except for the factor of \( \hbar \)) scattering states, \( | \Psi \rangle \), for which the current is equivalent to the transmission.

**D. Scattering states in the device region**

To find the eigenchannels from the left lead, \( | \Phi \rangle = \sum_j (U_L^j)_j^j | \Psi_j \rangle \), we need to diagonalize the transmission probability matrix. Since we do not, in this paper, explicitly calculate the Bloch states in the leads, we will diagonalize the transmission probability matrix in an abstract basis formed by incoming waves from the left lead. Another, equivalent, formulation is to find the eigenchannels by maximizing the transmission at a given energy while keeping the eigenchannels orthogonal \( (U_L^j U_L^j \dagger = 1) \).

\[ \text{max} \ 2 \pi \langle \Phi_l | \Gamma_R | \Phi_r \rangle. \] (21)

The main problem in finding the eigenchannels is that we do not have access to the wave functions, Green’s functions, or spectral functions of the entire system in a typical calculation. We, therefore, have to find a method using only properties from the device part of the system.

We will now show that optimizing the current by varying the scattering state over spanned by the incoming states from the left lead, \( \{ | \Psi_r \rangle \} \), is equivalent to varying over the states \( | \chi \rangle \) defined on the device subspace; see Fig. 2. We begin by diagonalizing the device part of the spectral function from the left lead,

\[ A_L(E) = \sum_i | \chi_i \rangle \lambda_i \langle \chi_i | = 2 \pi \sum_i | \chi_i \rangle \langle \chi_i |, \] (22)

where the eigenvectors on the finite device space are orthogonal \( \langle \chi_i | \chi_j \rangle = \delta_{ij} \). Each \( | \chi_i \rangle = \sqrt{\lambda_i / 2 \pi} | \chi \rangle \) with nonzero eigenvalues \( (\lambda_i \neq 0) \) is the device part of a specific state \( | \tilde{\Psi}_i \rangle \), i.e., \( | \chi \rangle = P_D | \tilde{\Psi}_i \rangle \), where the \( | \tilde{\Psi}_i \rangle \) states are normalized and orthogonal linear combinations of the scattering states \( | \Psi_r \rangle \),

\[ | \tilde{\Psi}_i \rangle = \sum_j \frac{2 \pi}{\lambda_j} \langle \Psi_j | \chi \rangle | \chi \rangle = \sum_j W_{ij} | \Psi_j \rangle. \] (24)

This shows that the states \( | \tilde{\Psi}_i \rangle \) are spanned by the incoming scattering states from the left lead. We further wish to show that these states are normalized in the same manner as the original scattering states; i.e., we want to show that \( W_{mm} \) is unitary,

\[ \sum_n W_{mn} W_{mn}^\dagger = \frac{2 \pi}{\lambda_m \lambda_m'} \sum_n \langle \chi_m | \Psi_n \rangle \langle \Psi_n | \chi_m \rangle \]
\[ = \frac{1}{\lambda_m \lambda_m'} \langle \chi_m | A_L \chi_m \rangle \]
\[ = \frac{\lambda_m}{\lambda_m \lambda_m'} \langle \chi_m | \chi_m \rangle = \delta_{mm'}, \] (25)

using Eqs. (13) and (22).

In addition, any scattering states outside the space spanned by \( | \tilde{\Psi}_i \rangle \) are orthogonal to the device subspace. This
can be seen from the fact that we can write the spectral function on the device subspace as

$$A_L = 2\pi \sum_l P_D |\tilde{\psi}_l\rangle\langle\tilde{\psi}_l| P_D = 2\pi \sum_l P_D |\psi_l\rangle\langle\psi_l| P_D.$$  (26)

Comparing the two equations reveals that $P_D |\psi\rangle\langle\psi| P_D$ must be zero for any $|\psi\rangle$ which is orthogonal to the space spanned by $|\tilde{\psi}_l\rangle$.

In this section, we have shown that the wave functions $|\tilde{\chi}_l\rangle$ span the device part of any scattering state generated from lead $L$; see Fig. 2. To find the left eigenchannels, we can, therefore, maximize the current through the device with respect to a linear combination of $|\tilde{\chi}_l\rangle$ instead of maximizing with respect to the full scattering states $|\Psi\rangle$. This is equivalent to diagonalizing the transmission matrix [Eq. (20)] in the basis formed by $|\tilde{\chi}_l\rangle$.

### E. Finding the eigenchannels

In general, the basis $\{|e_i\rangle\}$ used in the calculations is nonorthogonal with the overlap matrix defined by $[S]_{ij} = \langle e_i | e_j \rangle$. Although the eigenchannels may be calculated directly in this nonorthogonal basis, we will make use of Lövdin orthogonalization to simplify the algebra. The orthogonalized matrices (denoted by a bar) are given by $\Gamma_R = S^{-1/2} \Gamma_0 S^{-1/2}$ and $\bar{A}_L = S^{1/2} A_L S^{1/2}$. The eigenchannels obtained in the Lövdin orthogonalized basis can, at the end of the calculation, simply be transformed back into the nonorthogonal basis for further visualization or projection.

From the previous section, we learned that it is enough to diagonalize the transmission probability matrix [Eq. (20)] $T_{i'i} = 2\pi \langle \tilde{\chi}_{i'j} | \bar{\Gamma}_{R|j} | \tilde{\chi}_l \rangle$ in the abstract basis $\{|\tilde{\chi}_l\rangle\}$. To transform $2\pi \bar{\Gamma}_R$ into the basis $\{|\tilde{\chi}_l\rangle\}$, we first need to calculate the eigenvectors of $\bar{A}_L = \bar{\Gamma}_L \bar{\Gamma}_R$, where $U$ is unitary. We then obtain the transformation matrix to the $\{|\tilde{\chi}_l\rangle\}$ basis,

$$\sum_n \bar{A}_{Lmn} [U]_{nl} = \lambda_n [U]_{nl},$$  (27)

which gives the explicit expression for the matrix we want to diagonalize

$$T_{i'i} = 2\pi \langle \tilde{\chi}_{i'j} | \bar{\Gamma}_R | \tilde{\chi}_l \rangle = 2\pi [\bar{U}^\dagger \bar{\Gamma}_R \bar{U}]_{i'i}. $$  (29)

The eigenproblem is, therefore,

$$\sum_n 2\pi [\bar{U}^\dagger \bar{\Gamma}_R \bar{U}]_{mn} [e]_{na} = \lambda_n [e]_{na},$$  (30)

where the eigenchannel vectors $[e]_{na}$ are given in the basis described by the columns of $\bar{U}$, and the eigenvalues $\lambda_n$ are the transmission probabilities of the individual eigenchannels, $\alpha$. Finally, transforming back to the original nonorthogonal basis (from $\bar{U}$ basis to the Löwdin basis, and from Löwdin basis to normal nonorthogonal basis), we find that the eigenchannels on the device subspace are given by

$$P_D |\phi_{al}\rangle = \sum_{i,a} [\bar{S}^{-1/2} \bar{U}]_{ia} [c]_{na} |e_i\rangle.$$  (31)

Equations (27)–(31) provide a recipe for calculating the eigenchannels of a specific scattering problem using only properties available in standard NEGF calculations. In contrast to Ref. 16, these eigenchannels are well-defined scattering states calculated without approximations on the full device subspace.

It is interesting to note that the eigenchannels [Eq. (31)] are eigenvectors to $G_{\Gamma_1} G_{\Gamma_2}$ (can be shown using the formalism presented above). This provides a simple method to obtain an idea about the eigenchannels. However, it is important to realize that the eigenchannel wave functions calculated from Eq. (31) are energy normalized; i.e., the amplitudes are well defined and can be compared between different eigenchannels. In contrast, the eigenvectors to $G_{\Gamma_1} G_{\Gamma_2}$ may have any normalization and it is, therefore, not possible to compare amplitudes between different channels. Moreover, the energy-normalized scattering states Eq. (31) yield amplitudes which correspond to local density of states and are useful to plot, as will be shown in the next section.

### III. EIGENCHANNELS FOR ATOMIC AND MOLECULAR WIRES

To exemplify the method developed in the previous section, we will use three different examples of atomic and molecular wires connected to gold electrodes. Using the TRANSIESTA (Ref. 12) extension of the SIESTA (Ref. 28) density functional theory (DFT) code, we have previously studied elastic and inelastic transport properties for the systems under consideration here: (i) atomic gold wires, (ii) conjugated organic molecules, and (iii) oligo-phenylene ethynylene (OPE). The TRANSIESTA calculations on these systems were performed using DFT in the generalized gradient approximation using the Perdew-Burke-Ernzerhof functional. The semi-infinite leads connecting the device region was modeled using self-energies in the NEGF method. A more detailed description of the calculational method may be found in Ref. 29.

Gold atomic wires have been realized and studied experimentally by several different techniques. The low bias elastic and inelastic (phonon scattering) transport are well characterized and understood; see Ref. 29, and references therein. The first eigenchannel (from left) at the Fermi energy is shown in Fig. 3 for a seven-atom gold chain. Not surprisingly, the majority of the transmission is carried by the first eigenchannel ($T_1=0.994$), with only a small transmission for the other eigenchannels ($<10^{-5}$). In addition, it is clear that the current through the wire is carried by the $6s$ electrons forming a half-filled one-dimensional band, where the sign of the wave function changes by a factor of $i$ (right moving) along the wire. The only difference with the corresponding eigenchannel from the right (not shown) is the phase factor, which corresponds to a left-moving wave.
which is situated approximately at half filling of the 6s}

sections of the channels, therefore, show the exponentially decaying solu-

tions of the wave function.

The eigenchannels are found from quantities normally available

in transport calculations using the NEGF technique. In addi-

tion, we show three brief examples of elastic scattering states

calculated for molecular and atomic wires connected to

three-dimensional contacts. The eigenchannels for these sys-


tems can be understood from the band structure of the infi-

nite wires, providing an intuitive understanding.

The eigenchannels are useful in interpreting elastic elec-
	ron transport through junctions. We believe that they will be

especially useful in investigating the effect of the contacts

between device and leads, e.g., binding site of the thiol bond

on Au surfaces. In addition, the method gives a useful basis

to understand the effects of phonon scattering on the conduc-
tance and their propensity rules.25,26

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APPENDIX: ORTHOGONALITY OF SCATTERING

STATES

Viewing the Bloch states in the infinite, periodic leads,

\[ |\tilde{u}_i\rangle \]

as a starting point for perturbation theory, we can obtain the
totally reflected solutions \( \tilde{u}_i \) of a semi-infinite lead. In

this case, the perturbation is the removal of the coupling

between the periodic cells at the surface. Furthermore, the
totally reflected solutions may again be used as the starting point
in a perturbation calculation to obtain the full scattering

states \( |\Psi_{l,i}\rangle \). In this case, the perturbation is the device region

and its coupling to the leads. Here, we will show that the
perturbation expansion gives solutions that are orthogonal

and normalized. To do this, we focus on the perturbation

expansion of \( |\Psi_{l,i}\rangle \) from \( |\tilde{u}_i\rangle \) and note that the same derivation

may be used to obtain the \( |\tilde{u}_i\rangle \) from \( |\tilde{u}_i\rangle \).
Starting with a set of orthogonal and energy-normalized eigenfunctions $|\tilde{u}_n(E)\rangle$ of the isolated leads ($n \in \mathbb{I}, \mathbb{R}$), we generate the full scattering states $|\Psi_n(E)\rangle$,

$$|\Psi_n(E)\rangle = G(E)|\tilde{u}_n(E)\rangle + |u_n(E)\rangle,$$ (A1)

where $V = V_L + V_R$. The response given by the retarded Green’s function only contains waves traveling outward from the device region. To show that the solutions generated in this way are normalized, we use the Lippmann-Schwinger equation

$$|\Psi_n(E)\rangle = G_0(E)|\Psi_n(E)\rangle + |u_n(E)\rangle,$$ (A2)

where the unperturbed Green’s function is $G_0(E) = (E - H_L - H_R - \delta)/\Delta^{-1}$. Together with Eq. (A1), we obtain

$$\langle \Psi_n(E)|\Psi_n'(E')\rangle = \langle \tilde{u}_n(E)|\tilde{u}_n'(E')\rangle + \langle \tilde{u}_n(E)|V|\Psi_n'(E')\rangle$$ (A3a)

$$= \langle \tilde{u}_n(E)|\tilde{u}_n'(E')\rangle + \langle \tilde{u}_n(E)|G_0(E')V|\Psi_n'(E')\rangle + \langle \tilde{u}_n(E)|V|G_0(E')|\Psi_n'(E')\rangle$$ (A3b)

$$= \delta_{n,n'} \delta(E - E') + \langle \tilde{u}_n(E)|V|\Psi_n'(E')\rangle \times \left( \frac{1}{E' - E + i\delta} + \frac{1}{E' - E - i\delta} \right)$$ (A3c)

$$= \delta_{n,n'} \delta(E - E'),$$ (A3d)

which show that the final scattering states $|\Psi_n\rangle$ are orthogonal and normalized.