Electron transport through an interacting region: The case of a nonorthogonal basis set

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The formula derived by Meir and Wingreen [Phys. Rev. Lett. **68**, 2512 (1992)] for the electron current through a confined, central region containing interactions is generalized to the case of a nonorthogonal basis set. As the original work, the present derivation is based on the nonequilibrium Keldysh formalism. By replacing the basis functions of the central region by the corresponding elements of the dual basis the lead and central region subspaces become mutually orthogonal. The current formula is then derived in this new basis, using a generalized version of second quantization and Green's function theory to handle the nonorthogonality within each of the regions. Finally, the appropriate nonorthogonal form of the perturbation series for the Green's function is established for the case of electron-electron and electron-phonon interactions in the central region.

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I. INTRODUCTION

Electron transport in nanoscale contacts is a highly active research area. During the past decade it has become possible to create two-terminal junctions where atomic-sized conductors are contacted by macroscopic metal electrodes using scanning tunnelling microscopes,[1,2] mechanically controlled break junctions,[3,4] or electromigration techniques.[5] In this way *I-V* characteristics have been obtained for a variety of different nano-contacts including carbon nanotubes,[6] metallic point contacts,[7] atomic wires,[8] as well as individual molecules ranging from large organic compounds[1,4] down to a single hydrogen molecule.[9]

The quantitative modeling of the electrical properties of a nanoscale contact represents a great theoretical challenge involving a detailed description of both the atomic- and electronic structure of a current-carrying system out of equilibrium. At present, the most popular approach to the problem combines a nonequilibrium Green's function (NEGF) formalism with *ab initio* electronic structure theory. A cornerstone of this approach is a formula giving the current through the system in terms of the Green's function of a spatial region containing the contact (the central region). When interactions are limited to the central region, the current formula is an exact result, however, in practice some approximation for the full interacting Green's function must be invoked. For example, in the commonly used NEGF-DFT approximation the exact Green's function is replaced by the noninteracting Kohn-Sham Green's function defined within density functional theory.[10,11]

Application of the NEGF theory to electronic transport in quantum wires was introduced as an alternative to the Landauer-Büttiker formalism to treat electronic interactions. In 1991 Hershfield and co-workers[12] derived an expression for the current through a single interacting level (an Anderson impurity), and the following year Meir and Wingreen[13] generalized the current formula to the case of an arbitrary number of states in the central region [Eq. (6) of Ref. 13]. In these studies the system, i.e., the conductor, was partitioned into three parts (the leads plus the central region), and the basis of the single-particle Hilbert space was taken as an orthonormal set of functions each belonging to one of the three regions. In practical *ab initio* calculations, however, the requirement of localized basis functions, which is essential for the partitioning, is difficult to combine with orthogonality.[14,15] It is therefore of great practical importance to generalize the current formula to nonorthogonal basis sets.

In this paper, a rigorous operational framework for applying second quantization and Green's function methods in a nonorthogonal basis is presented and used derive a generalized current formula which is valid for nonorthogonal basis sets. The main problem in deriving the current formula in the general case is the lack of orthogonality between basis functions in the central region and basis functions in the leads (due to the assumption of localized basis functions, we can take basis functions belonging to different leads to be nonoverlapping and thus orthogonal). We solve this problem by replacing the basis functions of the central region by the so-called dual basis functions which, by construction, are orthogonal to the basis functions of the leads. The nonorthogonality of the basis within each of the three regions is handled by applying a generalized version of second quantization and Green's function theory.

For noninteracting electrons, the NEGF current formula takes a particularly simple form [Eq. (7) of Ref. 13]. This version of the formula, which is equivalent to the well-known Landauer-Büttiker formula, has been applied extensively over the past years and forms the basis of most numerical schemes addressing phase-coherent transport in nano-scale structures. In the special case of no interactions, Xue *et al.* have derived the form of the current formula in a nonorthogonal basis.[10] Xue *et al.* take a route which is less direct than the one by Meir and Wingreen as it involves transformations between the basis and real space representations. In contrast, the derivation given here follows the original work closely and is formulated entirely within the basis set representation. More importantly, the derivation of Xue *et al.* cannot be extended to the interacting case since it relies on a spectral representation of the Green's function in terms of single-particle eigenstates. Emberly and Kirczenow[16] have addressed the problem of nonorthogonality within the Landauer-Büttiker formalism. Here the current due to nonin-

teracting electrons is obtained directly from the single-particle scattering states which are evaluated in a Hilbert space with an energy-dependent inner product. Finally, Fransson *et al.* have studied the effects of nonorthogonality within the tunnelling formalism.[17,18] Using the Kadanoff-Baym approach and the Hubbard operator technique, they derived an expression for the current through a single interacting level (Anderson model) in the weak coupling limit, taking the finite overlap of the tunnelling wave functions into account.[18] In contrast, the derivation presented here makes no assumptions about the type of interactions and is not limited to the case of weak coupling between the leads and the central region. Moreover, the use of the dual basis in the central region simplifies the formalism significantly and avoids many technical problems otherwise arising from the nonorthogonality between the lead and central region states.

The paper is organized as follows: In Sec. II the general theory of second quantization and Green's functions in a nonorthogonal basis is reviewed, and the concept of the dual basis is introduced. In Sec. III these results are used to derive the current formula in a nonorthogonal basis, both in the interacting and the noninteracting case.

II. NONORTHOGONAL BASIS SETS

In this section we generalize the second quantization formalism and elements of the Green's function theory to the case of nonorthogonal basis sets. To avoid mathematical problems with convergence, we assume that our single-particle Hilbert space, $\mathcal{H}$, is finite dimensional. While this assumption might seem unsatisfactory from a fundamental point of view, it will always be satisfied in practical applications.

A. Second quantization of one- and two-body operators

Throughout this section let $\{\phi_i\}$ denote a—not necessarily orthonormal—basis of the single-particle Hilbert space, $\mathcal{H}$. The corresponding creation and annihilation operators,[19] $c_i^\dagger$ and c_i, acting on the fermionic Fock space fulfill the canonical anticommutation relations[20]

$$\{c_i^\dagger, c_j^\dagger\} = 0, \tag{1}$$

$$\{c_i, c_j\} = 0, \tag{2}$$

$$\{c_i, c_j^\dagger\} = S_{ij}, \tag{3}$$

where $S_{ij} = \langle \phi_i | \phi_j \rangle$ is the overlap matrix.

To any one-body operator, $\hat{A}^{(1)}$, acting on $\mathcal{H}$, we associate the matrix $A_{ij} = \langle \phi_i | \hat{A}^{(1)} | \phi_j \rangle$. We have the following representation of $\hat{A}^{(1)}$ in terms of the basis vectors $\{\phi_i\}$,

$$\hat{A}^{(1)} = \sum_{ij} \mathfrak{A}_{ij} |\phi_i\rangle\langle\phi_j|, \tag{4}$$

where we have used Dirac's bra-ket notation and introduced the matrix $\mathfrak{A} = S^{-1}AS^{-1}$. This matrix transform will appear often throughout the text, and we shall reserve the Gothic font for matrices that results from such a transformation. The validity of the representation (4) is easily checked by evaluating the inner products $\langle \phi_n | \hat{A}^{(1)} | \phi_m \rangle$ on both sides of the equation. The second quantized form of $\hat{A}^{(1)}$, which we denote by $\hat{A}$, is

$$\hat{A} = \sum_{ij} \mathfrak{A}_{ij} c_i^\dagger c_j. \tag{5}$$

The easiest way to derive this expression is to start from the well known form of $\hat{A}$ in terms of some orthonormal basis, $\{\psi_n\}$, and corresponding creation and annihilation operators $d_n^\dagger, d_n$ and then expand these in terms of the original $c_i^\dagger, c_i$. The explicit form of this expansion reads $\psi_n = \Sigma_{ij} (S^{-1})_{ij} \langle \phi_j | \psi_n \rangle | \phi_i \rangle$, which follows from Eq. (4) applied to the identity operator.

We now turn to a general two-body operator, $\hat{B}^{(2)}$, defined on the two-particle Hilbert space $\mathcal{H}^{(2)} = \mathcal{H} \otimes \mathcal{H}$. A basis for $\mathcal{H}^{(2)}$ is provided by the tensor products $\{\phi_i \otimes \phi_j\}$. We define the corresponding overlap matrix $S^{(2)}_{ij,kl} = \langle \phi_i \otimes \phi_j | \phi_k \otimes \phi_l \rangle = S_{ik} S_{jl}$, as well as the matrix $B_{ij,kl} = \langle \phi_i \otimes \phi_j | \hat{B}^{(2)} | \phi_k \otimes \phi_l \rangle$. As for the one-body operators we have the first quantized representation

$$\hat{B}^{(2)} = \sum_{i,j,k,l} \mathfrak{B}_{ij,kl} |\phi_i \otimes \phi_j\rangle\langle \phi_k \otimes \phi_l|, \tag{6}$$

where the matrix $\mathfrak{B}$ is defined by $\mathfrak{B} = (S^{(2)})^{-1} B (S^{(2)})^{-1}$. For later use we note that

$$(S^{(2)})^{-1}_{ij,kl} = (S^{-1})_{ik} (S^{-1})_{jl}, \tag{7}$$

which can be directly verified by multiplication with $S^{(2)}$. Finally, the following expression for the second quantized version of $\hat{B}^{(2)}$ can be derived using the same technique as for the one-body operator,

$$\hat{B} = \frac{1}{2} \sum_{i,j,k,l} \mathfrak{B}_{ij,kl} c_i^\dagger c_j^\dagger c_l c_k. \tag{8}$$

B. Single-particle Green's functions

In order to fix notation we start with some well known definitions. Given two single-particle orbitals ϕ_i and ϕ_j (not necessarily normalized or orthogonal) the retarded and advanced single-particle Green's functions (GFs) are defined by

$$G^r_{ij}(t,t') = -i\theta(t-t') \langle \{c_i(t), c_j^\dagger(t')\} \rangle, \tag{9}$$

$$G^a_{ij}(t,t') = i\theta(t'-t) \langle \{c_i(t), c_j^\dagger(t')\} \rangle. \tag{10}$$

Here the brackets $\langle\ \rangle$ denote an expectation value with respect to the equilibrium state of the system. The greater and lesser GFs are defined by

$$G^<_{ij}(t,t') = i \langle c_j^\dagger(t') c_i(t) \rangle \tag{11}$$

$$G^>_{ij}(t,t') = -i \langle c_i(t) c_j^\dagger(t') \rangle. \tag{12}$$

In fact all of these GFs can be derived from the contour-ordered GF which is defined by

$$G_{ij}(\tau,\tau') = -i\langle T_C[c_i(\tau)c_j^\dagger(\tau')]\rangle. \quad (13)$$

Here $\tau=(t,\sigma)$ is a collection of the time variable t and a branch index, σ, and T_C is the contour-ordering operator. Note that $c_i(\tau)\equiv c_i(t)$ and $c_j^\dagger(\tau')\equiv c_j^\dagger(t')$, while the branch indices merely serve to determine the ordering of the operators. For more comprehensive introductions to the general GF theory the reader is referred to Refs. 21–23.

We consider first the case where both the expectation value and the time-evolution of the creation and annihilation operators entering the GF is governed by a time-independent, quadratic Hamiltonian, $\hat{h}$. Expressing $\hat{h}$ as in Eq. (5), using that $\partial_t c_i(t)=i[\hat{h},c_i](t)$, and Fourier transforming with respect to the time difference $t-t'$, we obtain the equation of motion for the retarded GF matrix in the basis $\{\phi_i\}$:

$$(S^{-1}\omega^+ - S^{-1}hS^{-1})G^r(\omega) = I. \quad (14)$$

Here $h_{ij}=\langle\phi_i|\hat{h}^{(1)}|\phi_j\rangle$ where $\hat{h}^{(1)}$ is the first-quantized version of $\hat{h}$, and $\omega^+=(\omega+i\eta)$ with η a small positive number ensuring proper convergence of the Fourier integral. The same equation holds for $G^a(\omega)$ when $\eta\to-\eta$. It is useful to introduce another matrix quantity related to the GF and defined by

$$\mathfrak{G}^x = S^{-1}G^xS^{-1}. \quad (15)$$

As indicated by the superscript x the definition applies to any of the GFs introduced above. To have a name we shall refer to $\mathfrak{G}$ as the overlap GF. Its retarded variant clearly fulfills the following matrix equation:

$$(S\omega^+ - h)\mathfrak{G}^r(\omega) = I. \quad (16)$$

Next, we ask about the form of the perturbation series of the GF in a nonorthogonal basis. We thus consider a quantum system with a Hamiltonian $\hat{H}=\hat{h}_0+\hat{V}$, where $\hat{h}_0$ is a simple quadratic Hamiltonian, while $\hat{V}$ is a complicated one- or two-body perturbation. In the perturbation expansion of the contour-ordered Green's function, $G_{ij}(\tau,\tau')$, we encounter the usual terms (generating diagrams with two external vertices):

$$\int d\tau_1\cdots d\tau_n\langle T_C[\hat{c}_{i,h_0}(\tau)\hat{c}_{j,h_0}^\dagger(\tau')\hat{V}_{h_0}(\tau_1)\cdots\hat{V}_{h_0}(\tau_n)]\rangle_0. \quad (17)$$

In this expression both the average and the time evolution is governed by $\hat{h}_0$, i.e., $\hat{X}_{h_0}(\tau)=\exp(it\hat{h}_0)\hat{X}\exp(-it\hat{h}_0)$ and $\langle\hat{X}\rangle_0=\mathrm{Tr}[\hat{X}\exp(-\beta\hat{h}_0)]/\mathrm{Tr}[\exp(-\beta\hat{h}_0)]$, with $\beta=1/kT$. When $\hat{V}$ is represented in terms of a nonorthogonal basis as in Eqs. (5) or (8), the term (17) will generate unperturbed $(n+1)$-particle GFs (or $(2n+1)$-particle GFs if $\hat{V}$ is a two-body operator) involving creation and annihilation operators of the nonorthogonal orbitals ϕ_i. As usual this $(n+1)$-or $(2n+1)$-particle GF can be broken down into unperturbed single-particle GFs using Wick's theorem.[21,22] Although Wick's theorem is normally proved for orthonormal states, its validity for nonorthogonal states can be readily verified by expanding each creation or annihilation operator entering the $(n+1)$-or $(2n+1)$-particle GF in terms of a fixed orthonormal basis. Wick's theorem can then be applied to each term in this expansion, which now involves only orthonormal states, and finally the original basis functions can be reintroduced. The perturbation series for the matrix $G_{ij}(\tau,\tau')$ in terms of the nonorthogonal basis, $\{\phi_i\}$, should therefore be constructed according the usual Feynman rules, using $G_{ij}^0(\tau,\tau')$ as free propagator and $\mathfrak{V}_{ij}$ (or $\mathfrak{V}_{ij,kl}$) as the coupling strengths entering at the vertices. Equivalently, the perturbation series for the overlap GF, $\mathfrak{G}_{ij}(\tau,\tau')$, is obtained by evaluating each diagram using $\mathfrak{G}_{ij}^0(\tau,\tau')$ as free propagator and V_{ij} (or $V_{ij,kl}$) as coupling. In the case where $\hat{V}$ is a two-body operator the latter statement follows from Eq. (7).

C. Dual basis

Below we introduce the concept of a dual basis. The dual basis will be used in the next section for orthogonalizing the central region to the leads in the derivation of the current formula. Given a general basis set, $\{\phi_i\}$, (which we refer to as the direct basis) for the finite dimensional Hilbert space, $\mathcal{H}$, there exists a dual basis, $\{\phi_{\bar{i}}\}$, with the property

$$\langle\phi_i|\phi_{\bar{j}}\rangle = \delta_{ij}. \quad (18)$$

The vectors of the dual basis can be represented explicitly in terms of the direct basis,

$$\phi_{\bar{i}} = \sum_j (S^{-1})_{ji}\phi_j. \quad (19)$$

We shall make the general convention that indices marked with a bar refer to the dual basis. From the expansion (19) it follows that the overlap matrix of the dual basis is simply the inverse of S, i.e.,

$$S_{\bar{i}\bar{j}} = \langle\phi_{\bar{i}}|\phi_{\bar{j}}\rangle = (S^{-1})_{ij}. \quad (20)$$

Here it is natural to make a connection with the work of Fransson *et al.*, who introduce a set of creation or annihilation operators fulfilling the anti-commutation relations $\{c_i,c_j^\dagger\}=(S^{-1})_{ij}$ [this should be contrasted with Eq. (3)]. However, as can be seen from Eq. (1) of Ref. 18 these are simply the creation/annihilation operators of the dual basis, and thus the formalism of Fransson *et al.* is consistent with the one presented here.

As a final observation we note that the following relation holds for any of the single-particle GFs

$$G_{\bar{i}\bar{j}}^x = \mathfrak{G}_{ij}^x. \quad (21)$$

That is, the GF matrix in the dual basis equals the overlap GF in the direct basis.

III. CURRENT FORMULA

In this section we derive a formula for the electron current through a spatially confined region possibly containing interactions. The derivation follows the original work of Meir and Wingreen,[13] but is here extended to the case of a nonorthogo-

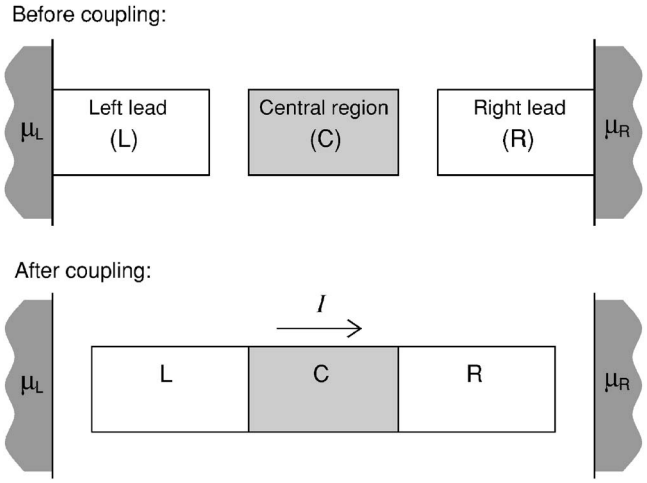

FIG. 1. Schematic diagram of the system used to derive the current formula. Before the coupling between the three regions is established, the leads are in equilibrium with chemical potentials μ_L and μ_R, respectively. Upon coupling a current, I, starts to flow as the system approaches a common equilibrium. Interactions are allowed inside the central region (C).

nal basis set. Atomic units will be used throughout.

We consider the transport of electrons through a system which can be divided into three regions (see Fig. 1): A left lead (L), a right lead (R), and a central region (C). For times $t<t_0$ the three regions are uncoupled, and the leads are in thermal equilibrium with chemical potentials μ_L and μ_R, respectively. When the leads, which we assume to be macroscopic yet finite in size, are coupled to the central region a current will start to flow as the system approaches a common equilibrium. The macroscopic size of the leads ensures that a steady state with a constant dc current will exist for a considerable time before the system reaches equilibrium and the current dies out. It is the determination of this steady state current that we address in the following.

As a basis of the single-particle Hilbert space, we take a set of localized functions each of which can be assigned to exactly one of the three regions, e.g., by the center position. We denote the elements of this basis by $\phi_{\alpha i}$, where $\alpha \in \{L,C,R\}$ specifies the region and i enumerates the basis function within the region. Since the $\phi_{\alpha i}$ are all localized, we can safely assume that there is no overlap between two basis functions belonging to different leads. Indeed, the central region can always be enlarged by part of the leads until this condition is fulfilled. We thus have $S_{Li,Rj}=0$ and $S_{Ri,Lj}=0$ for all i,j, which we write compactly as $S_{LR}=S_{RL}=0$.

The main difficulty in the derivation of the current formula is caused by the nonorthogonality of the basis functions in the central region and those in the leads. To overcome this problem, we replace the basis functions in the central region by the corresponding functions of the dual basis, i.e., $\phi_{Ci} \rightarrow \phi_{\overline{Ci}}$. The original basis functions are maintained in the leads. We shall refer to the resulting basis, $\{(\phi_{Li}),(\phi_{\overline{Ci}}),(\phi_{Ri})\}$, simply as the new basis. The introduction of the new basis amounts to a redefinition of the subspace associated with the central region, such that all three subspaces become orthogonal. It should be stressed that this is merely a basis change, and thus the full Hilbert space as well as any calculated physical quantity remains unaffected. The nonorthogonality of basis functions within a given region presents no serious problem, and can be handled by the techniques of the previous section. In the following all matrix quantities referring to the new basis will be denoted by a tilde.

The electronic Hamiltonian, $\hat{H}$, consists of a noninteracting part, $\hat{h}$, and a part containing interactions, $\hat{V}_{int}$. The physical nature of the interactions is not important, however, we assume that $\hat{V}_{int}$ only affects electrons located in the central region. In terms of the new basis, the matrix associated with the noninteracting part of the Hamiltonian has the generic shape:

$$\tilde{h}=\begin{pmatrix} h_{LL} & h_{L\bar{C}} & 0 \\ h_{\bar{C}L} & h_{\bar{C}\bar{C}} & h_{\bar{C}R} \\ 0 & h_{R\bar{C}} & h_{RR} \end{pmatrix}. \tag{22}$$

Here, for example, the matrix element $\tilde{h}_{Ci,Lj}=(h_{\bar{C}L})_{ij}$ is given by (in the coordinate representation),

$$\tilde{h}_{Ci,Lj}=\int d\mathbf{r}\ \phi^*_{\overline{Ci}}(\mathbf{r})\left[-\frac{1}{2}\Delta_{\mathbf{r}}+v(\mathbf{r})\right]\phi_{Lj}(\mathbf{r}), \tag{23}$$

where $v(\mathbf{r})$ is the sum of all external potentials acting on the electron system. We shall not be concerned about the specific form of $v(\mathbf{r})$, as this has no importance for the general treatment presented here. The noninteracting $\hat{h}$ is further divided into the two terms, $\hat{h}_0$ and $\hat{h}_{coup}$:

$$\hat{H}=\hat{h}_0+\hat{h}_{coup}+\hat{V}_{int}, \tag{24}$$

where

$$\hat{h}_0=\hat{h}_0^L+\hat{h}_0^R+\hat{h}_0^C \tag{25}$$

$$=\sum_{\alpha\in\{L,R\},i,j}\tilde{\mathfrak{h}}_{\alpha i,\alpha j}c^\dagger_{\alpha i}c_{\alpha j}+\sum_{i,j}\tilde{\mathfrak{h}}_{Ci,Cj}c^\dagger_{\overline{Ci}}c_{\overline{Cj}}, \tag{26}$$

describes each of the regions separately, and

$$\hat{h}_{coup}=\sum_{\alpha\in\{L,R\},i,j}\tilde{\mathfrak{h}}_{Ci,\alpha j}c^\dagger_{\overline{Ci}}c_{\alpha j}+\text{H.c.} \tag{27}$$

provides the coupling. As described in Sec. II A, the matrix $\tilde{\mathfrak{h}}$ is given by $\tilde{\mathfrak{h}}=\tilde{S}^{-1}\tilde{h}\tilde{S}^{-1}$, where $\tilde{S}$ is the overlap matrix in the new basis,

$$\tilde{S}=\begin{pmatrix} S_{LL} & 0 & 0 \\ 0 & (S^{-1})_{CC} & 0 \\ 0 & 0 & S_{RR} \end{pmatrix}. \tag{28}$$

The form of $\tilde{S}$ within the central region follows from Eq. (20). Note that in the new basis there is no overlap between basis functions belonging to different regions of the system, i.e., the three subspaces are orthogonal. As a consequence, all creation or annihilation operators of a given region commute with all creation or annihilation operators of the other re-

gions. This property of the new basis is crucial for what follows.

For times $t<t_0$ the three regions are decoupled and the state of the system is described by the density operator

$$\rho_0 = \frac{1}{Z_0}\rho_0^L\rho_0^C\rho_0^R \otimes \rho_{ext}, \tag{29}$$

where $\rho_0^\alpha = e^{-\beta(\hat{h}_0^\alpha - \mu_\alpha \hat{N}_\alpha)}$ and $Z_0 = \mathrm{Tr}[\rho_L^0\rho_C^0\rho_R^0 \otimes \rho_{ext}]$, while ρ_{ext} describes the state of possible external degrees of freedom such as phonons or magnetic impurities. Notice that the order of the density operators in Eq. (29) plays no role since they all commute due to the properties of the new basis.

After the coupling has been switched on at time t_0, the state ρ_0 will evolve according to the full Hamiltonian of Eq. (24). At the later time t_1 the system has reached equilibrium and the current has died out. We assume that there is a time interval $[t_0+\Delta t; t_1-\Delta t]$ during which the current through the system stays constant, i.e., the system is in a steady state. In the following we consider times t for which the system is in the steady state.

The particle current from the left region into the central region at time t is given by the time derivative of the particle number in lead L[21]

$$I_L(t) = \frac{d}{dt}\langle \hat{N}_L(t)\rangle = i\langle[\hat{H}, \hat{N}_L](t)\rangle. \tag{30}$$

The second quantized form of $\hat{N}_L$ follows from Eqs. (4) and (5) when $\hat{A}^{(1)}$ is the orthogonal projection onto the subspace spanned by the basis functions of lead L,

$$\hat{N}_L = \sum_{ij} (S_{LL}^{-1})_{ij} c_{Li}^\dagger c_{Lj}. \tag{31}$$

Note that only basis functions of the left lead occur in the expression for $\hat{N}_L$. If we had used the original basis, the expression would also contain creation or annihilation operators of the regions C and R. Since the interaction, $\hat{V}_{int}$, by assumption contains creation or annihilation operators of the central region only, the commutator in Eq. (30) vanishes for all terms in $\hat{H}$ except those coupling L and C, i.e.,

$$\begin{aligned} I_L &= i\sum_{i,j}[\tilde{\mathfrak{h}}_{Li,Cj}\langle c_{Li}^\dagger(t)c_{\overline{Cj}}(t)\rangle - \tilde{\mathfrak{h}}_{Ci,Lj}\langle c_{\overline{Ci}}^\dagger(t)c_{Lj}(t)\rangle] \\ &= \frac{1}{2\pi}\int \mathrm{Tr}[\tilde{\mathfrak{h}}_{LC}\tilde{G}_{CL}^<(\omega) - \tilde{G}_{LC}^<(\omega)\tilde{\mathfrak{h}}_{CL}]d\omega, \end{aligned} \tag{32}$$

where the commutation relations Eqs. (1)–(3) have been used and the lesser GF defined in Eq. (11) has been introduced. In the second line we have assumed that in the steady state the GFs depend only on the time difference $t-t'$, and moreover that the steady state exists for sufficiently long that boundary effects associated with the switching on of the coupling and leveling out of the current can be neglected when performing the Fourier transform. These conditions can always be fulfilled by increasing the size of the leads. In the following, explicit reference to the ω dependence will sometimes be omitted to simplify the notation.

The lesser GF can be obtained from its contour-ordered counter parts via analytic continuation as described in Ref. 21. Treating $\hat{h}_{coup}$ and $\hat{V}_{int}$ perturbatively, the rules for perturbation theory in a nonorthogonal basis (see Sec. II B) lead to the following Dyson equations for the lesser GF matrix

$$\tilde{G}_{CL}^< = \tilde{G}_{CC}^r\tilde{\mathfrak{h}}_{CL}\tilde{g}_{LL}^{0,<} + \tilde{G}_{CC}^<\tilde{\mathfrak{h}}_{CL}\tilde{g}_{LL}^{0,a}, \tag{33}$$

$$\tilde{G}_{LC}^< = \tilde{g}_{LL}^{0,r}\tilde{\mathfrak{h}}_{LC}\tilde{G}_{CC}^< + \tilde{g}_{LL}^{0,<}\tilde{\mathfrak{h}}_{LC}\tilde{G}_{CC}^a, \tag{34}$$

where $\tilde{g}_{LL}^0$ is the GF of the uncoupled left lead, i.e., the GF defined by $\hat{h}_0$ and ρ_0. Here it is important to realize that this is *not* an equilibrium GF, since ρ_0 involves different chemical potentials and therefore is not an equilibrium state. However, since the $c_{Li}, c_{Li}^\dagger$ commute with the corresponding operators of region C and R (due to the properties of the new basis), $\tilde{g}_{LL}^0$ is in fact equal to the GF defined by $\hat{h}_0^L$ and ρ_0^L. Since the latter describes a system in equilibrium the fluctuation-dissipation theorem provides the relation

$$\tilde{g}_{LL}^{0,<}(\omega) = -f_L(\omega)[\tilde{g}_{LL}^{0,r}(\omega) - \tilde{g}_{LL}^{0,a}(\omega)], \tag{35}$$

where $f_L(\omega)$ is the Fermi distribution function of the left lead. The relation (35) introduces the equilibrium distribution of the lead into the current formula. Since the strict validity of this relation, as explained above, relies on the orthogonality of the three regions, we again see the importance of working in new basis.

For the contour-ordered GF matrix of the central region we have the Dyson equation

$$\tilde{G}_{CC} = \tilde{G}_{CC}^0 + \tilde{G}_{CC}^0[\tilde{\Sigma}_L + \tilde{\Sigma}_R + \tilde{\Sigma}_{int}]\tilde{G}_{CC}, \tag{36}$$

where $\tilde{\Sigma}_{int}$ and $\tilde{\Sigma}_\alpha$ are self-energies due to the interactions and the coupling to lead α, respectively. Note that the former also contains contributions from the coupling since a complete separation of the diagrams related to the two perturbations is not possible. The contour-ordered self-energy matrix due to the coupling to lead α is given by

$$\tilde{\Sigma}_\alpha = \tilde{\mathfrak{h}}_{C\alpha}\tilde{g}_{\alpha\alpha}^0\tilde{\mathfrak{h}}_{\alpha C}. \tag{37}$$

It is useful to introduce the coupling strength due to lead α,

$$\tilde{\Gamma}_\alpha(\omega) = i[\tilde{\Sigma}_\alpha^r(\omega) - \tilde{\Sigma}_\alpha^a(\omega)]. \tag{38}$$

Inserting $\tilde{G}_{CL}^<$ and $\tilde{G}_{LC}^<$ from Eqs. (33) and (34) into the expression for the current, Eq. (32), and symmetrizing, $I=(I_L - I_R)/2$, we arrive, after some algebra, to the desired current formula

$$\begin{aligned} I = \frac{i}{4\pi}\int \mathrm{Tr}[&(\tilde{\Gamma}_L - \tilde{\Gamma}_R)\tilde{G}_{CC}^< + (f_L(\omega)\tilde{\Gamma}_L - f_R(\omega)\tilde{\Gamma}_R)(\tilde{G}_{CC}^r \\ &- \tilde{G}_{CC}^a)]d\omega. \end{aligned} \tag{39}$$

Equation (39) is formally equivalent to the corresponding formula valid in an orthonormal basis,[13] and indeed it reduces to it when the basis is orthonormal. However, it should be remembered that all quantities entering Eq. (39) refer to the new basis (as indicated by the tildes), and that the cou-

pling strengths, $\tilde{\Gamma}_L$ and $\tilde{\Gamma}_R$, involve $\tilde{\mathfrak{h}}$ instead of $\tilde{h}$.

As the dual basis in most cases is not explicitly known it is desirable to reexpress Eq. (39) in terms of the original basis, that is, in terms of untilted quantities. For the GFs of the central region we have the simple relation

$$\tilde{G}^x_{CC}(\omega) \equiv G^x_{\bar{C}\bar{C}}(\omega) = \mathfrak{G}^x_{CC}(\omega), \tag{40}$$

where the second equality follows directly from Eq. (21). As for the Γs we note that this relation holds in particular when $\hat{V}_{int}=0$. In this case Eq. (16) establishes that $\mathfrak{G}^r_{CC}=[(\omega^+ S - h)^{-1}]_{CC}$. On the other hand $\tilde{G}^r_{CC}$ can be obtained from the Dyson equation (36) using that $\tilde{G}^{0,r}_{CC}=[\omega^+\tilde{S}^{-1}_{CC} - \tilde{S}^{-1}_{CC}\tilde{h}_{CC}\tilde{S}^{-1}_{CC}]^{-1}$ which in turn follows from Eq. (14). In terms of self-energies we thus have

$$\mathfrak{G}^r_{CC} = [\omega^+ S_{CC} - h_{CC} - \Sigma^r_L - \Sigma^r_R]^{-1}, \tag{41}$$

$$\tilde{G}^r_{CC} = [\omega^+\tilde{S}^{-1}_{CC} - \tilde{S}^{-1}_{CC}\tilde{h}_{CC}\tilde{S}^{-1}_{CC} - \tilde{\Sigma}^r_L - \tilde{\Sigma}^r_R]^{-1}, \tag{42}$$

where[24]

$$\Sigma^r_\alpha = (\omega^+ S_{C\alpha} - h_{C\alpha})[\omega^+ S_{\alpha\alpha} - h_{\alpha\alpha}]^{-1}(\omega^+ S_{\alpha C} - h_{\alpha C}). \tag{43}$$

By equating Eqs. (41) and (42), it follows after some matrix algebra, that

$$\tilde{\Gamma}_\alpha = i[\Sigma^r_\alpha - \Sigma^a_\alpha] - 2i\eta S_{C\alpha}S^{-1}_{\alpha\alpha}S_{\alpha C} \to \Gamma_\alpha \text{ as } \eta \to 0, \tag{44}$$

where $\Gamma_\alpha = i[\Sigma^r_\alpha - \Sigma^a_\alpha]$ and $i\eta$ is the imaginary part of ω^+. Equation (44) holds, of course, also when interactions are present.

With Eqs. (40) and (44) we can state our main result, namely an expression for the current in terms of quantities which are all evaluated in terms of the original nonorthogonal basis:

$$I = \frac{i}{4\pi}\int \mathrm{Tr}[(\Gamma_L - \Gamma_R)\mathfrak{G}^<_{CC} + [f_L(\omega)\Gamma_L - f_R(\omega)\Gamma_R](\mathfrak{G}^r_{CC} - \mathfrak{G}^a_{CC})]d\omega. \tag{45}$$

A. Noninteracting electrons

In the special case of noninteracting electrons the Keldysh equation[21] for the lesser GF of the central region in combination with Eqs. (35), (37), and (38) yields

$$\tilde{G}^<_{CC} = \tilde{G}^r_{CC}(\tilde{\Sigma}^<_L + \tilde{\Sigma}^<_R)\tilde{G}^a_{CC} \tag{46}$$

$$= \tilde{G}^r_{CC}[f_L(\omega)\tilde{\Gamma}_L + f_R(\omega)\tilde{\Gamma}_R]\tilde{G}^a_{CC}. \tag{47}$$

(The Keldysh equation relies only on the temporal properties of the various GFs and is therefore valid in any single-particle basis.) Substituting this relation into Eq. (39) and using the general result $G^r - G^a = G^> - G^<$, we obtain the following Landauer-type formula for the current,

$$I = \frac{1}{2\pi}\int [f_L(\omega) - f_R(\omega)]\mathrm{Tr}[\tilde{G}^r_{CC}\tilde{\Gamma}_L\tilde{G}^a_{CC}\tilde{\Gamma}_R]d\omega. \tag{48}$$

By virtue of the identities (40) and (44) we can again reexpress Eq. (48) in terms of quantities of the original basis:

$$I = \frac{1}{2\pi}\int [f_L(\omega) - f_R(\omega)]\mathrm{Tr}[\mathfrak{G}^r_{CC}\Gamma_L\mathfrak{G}^a_{CC}\Gamma_R]d\omega. \tag{49}$$

This is the celebrated "trace-formula" which has been widely used for numerical calculations of coherent transport. The same formula has previously been derived by Xue *et al.* using a somewhat different approach involving transformations to a real space representation.

B. Interactions

In the presence of interactions in the central region, the current formulas (39) and (45) are exact provided the full interacting Green's function, $\tilde{G}_{CC}(=\mathfrak{G}_{CC})$, is known. In this section we address the evaluation of the interacting GF within perturbation theory given a nonorthogonal basis. To avoid any confusion we denote the GFs evaluated in the presence of the coupling to the leads, but without the interaction, by the superscript "*ni*." In the following we use the idea of the "new basis" introduced in the beginning of Sec. III without further explanations.

1. Electron-electron interactions

Assume that the electrons located in the central region can interact through a two-body potential, $\hat{V}^{(2)}$. The direct basis of $\mathcal{H}^{(2)}$ consists of the tensor products $\{\phi_{\alpha i}\otimes\phi_{\beta j}\}$, where $\alpha,\beta\in\{L,C,R\}$, while the new basis is obtained by replacing ϕ_{Ci} by its dual $\phi_{\bar{Ci}}$. The limitation of interactions to the central region means mathematically that the matrix element $V_{\alpha i\beta j,\gamma k\delta l}=\langle\phi_{\alpha i}\otimes\phi_{\beta j}|\hat{V}^{(2)}|\phi_{\gamma k}\otimes\phi_{\delta l}\rangle$ is nonzero only when all $\alpha,\beta,\gamma,\delta=S$. Since the single-particle basis functions used in the lead regions are the same in the new and the original basis, the same holds for the matrix $\tilde{V}$, as well as for the matrix $\tilde{\mathfrak{V}}=(\tilde{S}^{(2)})^{-1}\tilde{V}(\tilde{S}^{(2)})^{-1}$. The first claim can be verified by expanding $\phi_{\bar{Ci}}$ in terms of the direct basis $\{(\phi_{Li}),(\phi_{Ci}),(\phi_{Ri})\}$ according to Eq. (19), and the second then follows from direct calculation using Eqs. (7) and (28).

As described in Sec. II A, the second quantized version of $\hat{V}^{(2)}$ in the new basis reads

$$\hat{V}_{int} = \frac{1}{2}\sum_{ijkl}\tilde{\mathfrak{V}}_{CiCj,CkCl}c^\dagger_{\bar{Ci}}c^\dagger_{\bar{Cj}}c_{\bar{Cl}}c_{\bar{Ck}}. \tag{50}$$

By direct calculation it can be shown that $\tilde{\mathfrak{V}}=V$, and thus

$$\hat{V}_{int} = \frac{1}{2}\sum_{ijkl}V_{CiCj,CkCl}c^\dagger_{\bar{Ci}}c^\dagger_{\bar{Cj}}c_{\bar{Cl}}c_{\bar{Ck}}. \tag{51}$$

Treating $\hat{V}_{int}$ as a perturbation to the noninteracting Hamiltonian, $\hat{h}=\hat{h}_0+\hat{h}_{coup}$, the corrections (diagrams) to the noninteracting GF of the central region should thus be evaluated according to the usual Feynman rules using V as the coupling

matrix and $\tilde{G}^{ni}_{CC}$ as the free propagator, see last paragraph of Sec. II B. From Eq. (40) we get that $\tilde{G}^{ni}_{CC}=\mathfrak{G}^{ni}_{CC}$, and consequently we have established the perturbation series for the central object of the current formula, $\tilde{G}_{CC}$, in terms of V and $\mathfrak{G}^{ni}_{CC}$, i.e., quantities referring to the original basis.

2. Electron-phonon interactions

The interaction between the electron system and a single vibrational mode is, to first order in the ion displacements, described by an operator of the generic form:

$$\hat{V}_{int}=v^{(1)}(\mathbf{r})[b+b^{\dagger}]. \tag{52}$$

Here $b^{\dagger},b$ are creation and annihilation operators acting on the phonon system, and $v^{(1)}(\mathbf{r})$ is a one-body potential acting on the electrons. $v^{(1)}$ is obtained by differentiating the electron-ion potential, $V_{el\text{-}ion}(\mathbf{r},\mathbf{R})$, with respect to the ion coordinates in the direction of the vibration under consideration; see, e.g., Ref. 22. The restriction of interactions to the central region implies that $v_{\alpha i,\beta j}=\langle\phi_{\alpha i}|v^{(1)}|\phi_{\beta j}\rangle$ is nonzero only when $\alpha,\beta=C$. Physically this means that the vibration does not distort the potential felt by an electron outside the central region. According to Eq. (5), the matrix that is relevant for the second quantized form of $v^{(1)}$ in the new basis, is $\mathfrak{v}=\tilde{S}^{-1}\tilde{v}\tilde{S}^{-1}$. Using the expansion (19) and the block diagonal form of $\tilde{S}$ [see Eq. (28)], it is straightforward to establish that $\mathfrak{v}=v$. The second quantized version of Eq. (52) thus reads

$$\hat{V}_{int}=\sum_{ij} v_{Ci,Cj}c^{\dagger}_{\overline{Ci}}c_{\overline{Cj}}[b+b^{\dagger}]. \tag{53}$$

Considering $\hat{V}_{int}$ as a perturbation to the noninteracting Hamiltonian, $\hat{h}=\hat{h}_0+\hat{h}_{coup}$, the diagrams generated by the interaction should thus be evaluated using v as the coupling matrix and $\tilde{G}^{ni}_{CC}(=\mathfrak{G}^{ni}_{CC})$ as the free propagator; see the last paragraph of Sec. II B.

IV. SUMMARY

The use of localized basis sets in electronic structure calculations calls for general formulations of applied physical theories taking the nonorthogonality of the basis into account. In this paper, I have presented a general form of the second quantization formalism and Green's function theory which is valid in a nonorthogonal basis, and used it to obtain a nonorthogonal version of Eqs. (6) and (7) in Ref. 13 for the current through an interacting electron region. The main problem in deriving the generalized current formula, namely that the lead subspaces are not orthogonal to the central region subspace, was solved by replacing the basis functions of the central region by the corresponding elements of the dual basis. This simply amounts to a basis change, under which the central region subspace becomes orthogonal to the leads. The nonorthogonality of the basis functions within each of the regions was handled by applying the generalized form of the second quantization and Green's function formalisms. Finally, the appropriate nonorthogonal form of the perturbation expansion for the Green's function was established for the case of electron-electron and electron-phonon interactions in the central region.

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