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Communication: Finding destructive interference features in molecular transport junctions

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Associating molecular structure with quantum interference features in electrode-molecule-electrode transport junctions has been difficult because existing guidelines for understanding interferences only apply to conjugated hydrocarbons. Herein we use linear algebra and the Landauer-Büttiker theory for electron transport to derive a general rule for predicting the existence and locations of interference features. Our analysis illustrates that interferences can be directly determined from the molecular Hamiltonian and the molecule–electrode couplings, and we demonstrate its utility with several examples. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4901722>]

I. INTRODUCTION

The incorporation of molecular components into electrical circuits—perhaps organic semiconductors or molecular wires—has frequently been suggested as a route for future device miniaturization. Unlike conventional electronic circuit elements, molecules are inherently quantum mechanical, and consequently exhibit qualitatively different electronic behavior. For example, electrons traverse molecules via conduction channels,^{1–4} which are essentially open-system analogs of molecular orbitals. Each channel has a particular conductance (between 0 and $G_0 \equiv 2e^2/h$) and typically results in a non-Ohmic current-voltage relationship.

Numerous experimental and theoretical studies have further examined the generalization of other conventional electronic properties to molecules,^{5–23} including the conductance of multiple molecules connected in series or in parallel. Quantum mechanical effects, however, can also give rise to behaviors without classical equivalents. Among the most notable are destructive interference features,^{10–96} which can essentially block current and, therefore, may be alluring for the design of molecular insulators. Conceptually, interference features arise when the phase relations between multiple pathways through the molecule cause destructive interference. These effects are exemplified by transport through a *meta*-connected benzene molecule,^{18, 19, 46–53, 55–58, 62–65, 78, 84, 93, 97} as depicted in Fig. 1(a). Previous studies have established that interference depends on both the molecule and the molecule–electrode connections.^{15–19, 35–70}

Guidelines for predicting interference features are often restricted to conjugated hydrocarbons. Qualitatively, a conjugated hydrocarbon may exhibit interference when the molecule has a certain topology,^{40, 45–47, 65, 76–79, 95, 96} such as the presence of pendant groups,^{48, 55, 59, 68, 69, 75, 80–83, 87} cross-conjugation,^{22, 23, 38, 43, 55, 60, 74, 87–90} or (poly)cyclic structures.^{18, 19, 21, 40–42, 48, 55–57, 59, 66, 67, 92, 97, 98} Quantitatively, interferences are described by matrix cofactors if we only consider simple molecule–electrode connections and

transport through the molecule’s π network.^{39, 44–46, 49, 76, 77} Exceptions to these guidelines have nevertheless been reported,^{64, 70, 74, 94, 95} and, more generally, there are very few ideas for predicting interference features in molecules that are not conjugated hydrocarbons. The outstanding question is then, what chemistry leads to interference? We currently lack the chemical intuition to generally answer this question and instead resort to a Justice Potter Stewart-esque method⁹⁹ for finding interferences: *we know them when we see them*.

The goal of this communication is to develop a general rule for finding destructive interferences that makes no assumptions about the type of molecule, the couplings between the molecule and electrodes, or the basis set used in calculations. To this end, we use linear algebra to derive the condition for an interference feature in Sec. III. This condition, Eq. (5), is the main contribution of our work and only requires knowledge of the molecule and its connections to the electrodes. We subsequently demonstrate our theory with several examples in Sec. IV and conclude in Sec. V.

II. BACKGROUND

Before deriving the interference condition, we first review some pertinent linear algebra and the essentials of Landauer-Büttiker theory for electron transport.

A. Linear algebra

Let $\mathbf{A} : \mathcal{V}_1 \rightarrow \mathcal{V}_2$ be a linear operator with domain \mathcal{V}_1 and range \mathcal{V}_2 . The null and column spaces¹⁰⁰ of \mathbf{A} will be used heavily in the derivation. For reference, the null space of \mathbf{A} , denoted $\text{null}(\mathbf{A})$, is the set of all vectors $|x\rangle \in \mathcal{V}_1$ satisfying $\mathbf{A}|x\rangle = |0\rangle$. $\text{null}(\mathbf{A})$ forms a subspace; that is, any linear combination of two elements in $\text{null}(\mathbf{A})$ is also in $\text{null}(\mathbf{A})$. Similarly, the column space of \mathbf{A} , denoted $\text{im}(\mathbf{A})$, is the subspace containing all image vectors of \mathbf{A} . In other words, $|x_1\rangle \in \text{im}(\mathbf{A})$ if $|x_1\rangle = \mathbf{A}|x_2\rangle$ for some $|x_2\rangle \in \mathcal{V}_1$. Furthermore, if \mathbf{A} is Hermitian, then $\text{null}(\mathbf{A})$ and $\text{im}(\mathbf{A})$ are orthogonal complements,¹⁰⁰ meaning that $\text{null}(\mathbf{A})$ contains

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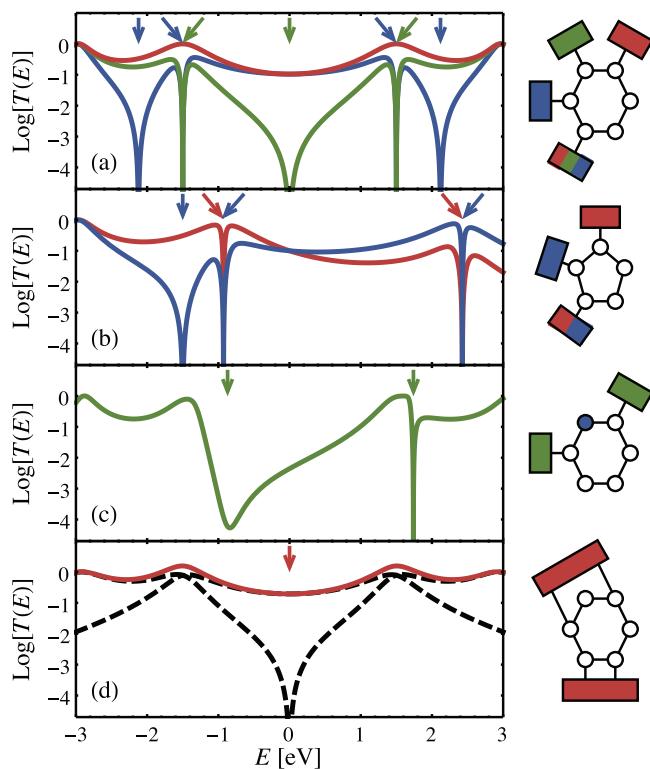


FIG. 1. Transmission functions (left) and schematics (right) for the model systems discussed in Sec. IV. The arrows near the top of each transmission plot signify interferences predicted by Eq. (5); in all cases, our theory accurately identifies interference features. (a) Transport through a benzene molecule connected to the electrodes in the *ortho* (blue), *meta* (green), and *para* (red) configurations. (b) Transport through a five-membered ring connected in the 1,2 (blue) and 1,3 (red) positions. (c) Transport through a pyridine-like molecule connected at the 2 and 6 positions. (d) Transport through a benzene molecule that couples to each electrode at two sites (red). The dashed black lines show the independent transmission through the channels.

every $|x_1\rangle \in \mathcal{V}_1$ that is orthogonal to any $|x_2\rangle \in \text{im}(\mathbf{A})$, and vice versa.

Our derivation will also employ the projections of operators to subdomains and subranges. Let \mathbf{P} (\mathbf{Q}) be an orthogonal projector onto a subspace of \mathcal{V}_1 (\mathcal{V}_2); that is, \mathbf{P} (\mathbf{Q}) is both Hermitian and idempotent. Then, the operator $\mathbf{A}_{\text{im}(\mathbf{P}) \rightarrow \text{im}(\mathbf{Q})} \equiv \mathbf{Q}\mathbf{A}\mathbf{P}$ is the projection of \mathbf{A} to the subdomain $\text{im}(\mathbf{P})$ and subrange $\text{im}(\mathbf{Q})$. Operator subscripts will denote the subdomain and subrange of a projected operator. Finally, if \mathbf{A} is invertible, then the nullity theorem¹⁰¹ relates the null spaces of complementary projections of \mathbf{A} and \mathbf{A}^{-1} . As needed for our purposes, if $\mathbf{A}_{\text{im}(\mathbf{P}) \rightarrow \text{im}(\mathbf{Q})}$ has a nontrivial null space, then the complementary projection of \mathbf{A}^{-1} , $(\mathbf{A}^{-1})_{\text{null}(\mathbf{Q}) \rightarrow \text{null}(\mathbf{P})} \equiv (\mathbf{I} - \mathbf{P})\mathbf{A}^{-1}(\mathbf{I} - \mathbf{Q})$, also has a nontrivial null space.

B. Landauer-Büttiker theory

The Landauer-Büttiker theory for electron transport^{1–3,102} uses coherent, elastic scattering to formulate the steady-state electrical properties of a molecule. Underlying this theory are the Hamiltonian of the isolated molecule (\mathbf{H}_0) and self-energy operators $\Sigma_{L/R}(E)$ that de-

scribe how the molecule couples to the left/right electrodes. As we will see later, these three operators [\mathbf{H}_0 , $\Sigma_L(E)$, and $\Sigma_R(E)$] are sufficient for finding interference features in a general system.

Several additional quantities that build on \mathbf{H}_0 , $\Sigma_L(E)$, and $\Sigma_R(E)$ help to formulate our theory for interferences. First is the (retarded) Green function¹⁰³ of the molecule, as modified by the electrode couplings,

$$\mathbf{G}(E) = [EI - \mathbf{H}_0 - \Sigma_L(E) - \Sigma_R(E)]^{-1}, \quad (1)$$

which describes electron dynamics in the molecule. Second are the spectral densities for coupling to the left/right electrodes, $\Gamma_{L/R}(E) \equiv i[\Sigma_{L/R}(E) - \Sigma_{L/R}^\dagger(E)]$. Note that $\Gamma_{L/R}(E)$ are Hermitian, positive semi-definite operators. Third is the transmission amplitude,

$$\mathbf{t}(E) \equiv \Gamma_L^{1/2}(E)\mathbf{G}(E)\Gamma_R^{1/2}(E), \quad (2)$$

which provides the probability amplitude for a conduction channel to transmit an electron with energy E between the electrodes. Finally, the transmission function,

$$T(E) = \text{Tr} [\mathbf{t}^\dagger(E)\mathbf{t}(E)],$$

gives the summed transmission probabilities through all channels. The transmission function is central to steady-state transport properties; e.g., the zero temperature, zero bias conductance through the molecule is proportional to $T(E)$ evaluated at the Fermi energy of the junction.¹ For notational brevity, we suppress the energy dependence of these quantities except for emphasis.

We end this overview of Landauer-Büttiker theory by commenting on bound (localized) states within the junction. Our analysis of interference features relies on the existence of $\mathbf{G}(E)$, which, mathematically, means E is not an eigenvalue of $\mathbf{H}_0 + \Sigma_L + \Sigma_R$. Because the self-energies are non-Hermitian, the eigenvalues of $\mathbf{H}_0 + \Sigma_L + \Sigma_R$ are generally complex; however, real eigenvalues are still possible and correspond to bound states within the junction.¹⁰⁴ Bound states do not contribute to steady-state transport,^{7,105–107} and, consequently, should be projected out of $\mathbf{H}_0 + \Sigma_L + \Sigma_R$ before beginning our analysis. Although beyond the scope of this communication, we note that bound states are more important in time-dependent transport.¹⁰⁸

III. FINDING INTERFERENCE FEATURES

To derive the condition for interference features, we first consider the definition of an interference feature and then use linear algebra to translate this definition to a condition on the molecular Hamiltonian \mathbf{H}_0 and the molecule-electrode connections $\Sigma_{L/R}$.

Many studies with simple systems use an intuitive definition of interference, $T(E) = 0$,^{43–49,57–60,75–78,83,84,109–113} where E is the energy (location) of the interference. More complicated systems subsequently show that this definition is too restrictive because the system may have multiple channels and $T(E) = 0$ requires *all* channels to have interferences at E .⁶⁰ For example, a conjugated hydrocarbon may still be weakly conductive through σ bonds even if an interference

appears in its π network.^{17,22,41,55,56,58,60,66,67,74,90–92} A more suitable definition for interference is

$$\langle \psi | \mathbf{t}^\dagger(E) \mathbf{t}(E) | \psi \rangle = 0, \quad (3)$$

where $|\psi\rangle \neq |0\rangle$ is a vector in the molecular space (i.e., conduction channel through the junction).

Equation (3) implies $|\psi\rangle \in \text{null}(\mathbf{t})$ because it requires $\mathbf{t}|\psi\rangle$ to have zero norm. The definition of \mathbf{t} in Eq. (2) indicates that there are three ways to satisfy this condition. Two possibilities are $|\psi\rangle \in \text{null}(\Gamma_R^{1/2}) = \text{null}(\Gamma_R)$ and $\mathbf{G}\Gamma_R^{1/2}|\psi\rangle \in \text{null}(\Gamma_L) \setminus \{|0\rangle\}$, which signify that the channel is decoupled from the right and left electrodes, respectively. These cases are not physically interesting and must be excluded from consideration. Accordingly, we could require $|\psi\rangle \notin \text{null}(\Gamma_R)$ and $\mathbf{G}\Gamma_R^{1/2}|\psi\rangle \notin \text{null}(\Gamma_L) \setminus \{|0\rangle\}$. However, because $\Gamma_{L/R}^{1/2}$ are Hermitian and because these operators both appear in \mathbf{t} , it suffices to impose $|\psi\rangle \in \text{im}(\Gamma_R)$ and $\mathbf{G}\Gamma_R^{1/2}|\psi\rangle \in \text{im}(\Gamma_L)$.

The third way to satisfy Eq. (3) is $\Gamma_R^{1/2}|\psi\rangle \in \text{null}(\mathbf{G})$, meaning that the channel fails to transmit electrons through the molecule. This condition seems more appropriate for interference, and must now be combined with the above restrictions that $|\psi\rangle \in \text{im}(\Gamma_R)$ and $\mathbf{G}\Gamma_R^{1/2}|\psi\rangle \in \text{im}(\Gamma_L)$. Denote by \mathbf{P}_L and \mathbf{P}_R the projectors onto $\text{null}(\Gamma_L)$ and $\text{null}(\Gamma_R)$, respectively. Because Γ_L is Hermitian, \mathbf{P}_L is an orthogonal projector, and $\mathbf{I} - \mathbf{P}_L$ is an orthogonal projector onto $\text{im}(\Gamma_L)$; likewise for \mathbf{P}_R . Our interference condition in Eq. (3) thus projects \mathbf{G} as

$$\mathbf{G}_{\text{im}(\Gamma_R) \rightarrow \text{im}(\Gamma_L)} \equiv (\mathbf{I} - \mathbf{P}_L)\mathbf{G}(\mathbf{I} - \mathbf{P}_R) \quad (4)$$

and specifies $\Gamma_R^{1/2}|\psi\rangle \in \text{null}(\mathbf{G}_{\text{im}(\Gamma_R) \rightarrow \text{im}(\Gamma_L)})$.

To summarize, interference features occur at energies where $\mathbf{G}_{\text{im}(\Gamma_R) \rightarrow \text{im}(\Gamma_L)}$ has a nontrivial null space. Although this may be a noteworthy result on its own, our interest is in determining interferences directly from \mathbf{H}_0 and $\Sigma_{L/R}$. When combined with Eq. (1), the nullity theorem accomplishes this goal. We first determine the complementary projection to that of Eq. (4): $\text{null}(\Gamma_L)$ is the subdomain and $\text{null}(\Gamma_R)$ is the subrange. Then, the nullity theorem tells us that $\mathbf{G}_{\text{im}(\Gamma_R) \rightarrow \text{im}(\Gamma_L)}$ has a nontrivial null space if and only if $(\mathbf{G}^{-1})_{\text{null}(\Gamma_L) \rightarrow \text{null}(\Gamma_R)} \equiv \mathbf{P}_R \mathbf{G}^{-1} \mathbf{P}_L$ also has a nontrivial null space. Finally, using Eq. (1), $(\mathbf{G}^{-1})_{\text{null}(\Gamma_L) \rightarrow \text{null}(\Gamma_R)}|\varphi\rangle = |0\rangle$ implies

$$\begin{aligned} & [\mathbf{H}_0 + \Sigma_L(E) + \Sigma_R(E)]_{\text{null}(\Gamma_L) \rightarrow \text{null}(\Gamma_R)} |\varphi\rangle \\ &= E \mathbf{I}_{\text{null}(\Gamma_L) \rightarrow \text{null}(\Gamma_R)} |\varphi\rangle. \end{aligned} \quad (5)$$

This equation generalizes the interference conditions for conjugated hydrocarbons based on matrix cofactors; its derivation does not require information on the type of molecule or the type of molecule-electrode coupling. Equation (5) is also formulated with operators such that the basis set is immaterial.¹¹⁴

IV. EXAMPLES

Interference features only appear at energies satisfying the nonlinear generalized eigenvalue problem in Eq. (5).

This is generally a difficult problem to solve, so we make several simplifications to facilitate our examples. First, we invoke the wide-band limit,^{1,71,115} which assumes that each electrode's density of states is constant (in E) near the Fermi energy. This results in energy-independent self-energies, thus linearizing Eq. (5). Second, for simplicity we use Hückel models to describe the molecule's electronic structure.^{16,20,21,37–55,71–82} Briefly, each atom contributes an orthonormal state (e.g., $|j\rangle$ for atom j) such that the Hamiltonian is

$$\mathbf{H}_0 = \sum_j \epsilon_j |j\rangle \langle j| + \sum_{j < k} (\beta_{j,k} |j\rangle \langle k| + \beta_{j,k}^* |k\rangle \langle j|).$$

$\{\epsilon_j\}$ are the site energies and $\{\beta_{j,k}\}$ are the inter-site coupling elements. Within the wide-band limit, the self-energies are

$$\Sigma_{L/R} = -i \sum_j \Gamma_j |j\rangle \langle j|,$$

where each $\Gamma_j \geq 0$ describes the spectral density between site j and the particular electrode. Unless specified otherwise, we take $\epsilon_j = \epsilon = 0$ eV, $\beta_{j,k}$ for neighboring sites as $\beta = -1.5$ eV, and the non-zero Γ_j as $\Gamma = 0.5$ eV. Finally, for mathematical reasons we require that $\text{null}(\Gamma_L)$ and $\text{null}(\Gamma_R)$ have the same dimensionality. These dimensionalities become the number of columns and rows, respectively, in the matrix representations of $[\mathbf{H}_0 + \Sigma_L + \Sigma_R]_{\text{null}(\Gamma_L) \rightarrow \text{null}(\Gamma_R)}$ and $\mathbf{I}_{\text{null}(\Gamma_L) \rightarrow \text{null}(\Gamma_R)}$, and solving generalized eigenvalue problems¹¹⁶ with non-square matrices is an open mathematical problem.¹¹⁷ Translated to our Hückel models, this means that Σ_L and Σ_R must have the same number of non-zero Γ_j elements. Note that a generalized eigenvalue problem with $n \times n$ matrices yields between 0 and n solutions (inclusive).¹¹⁶

We now examine interference features in several model systems by comparing solutions of Eq. (5) with each system's transmission function. From previous studies,^{17,22,54–61,73–76,83–87,111–113} a node and/or a deep well in the transmission function indicates an interference.

As the typical example of interference, we first consider a benzene molecule connected to the electrodes in the *ortho*, *meta*, or *para* configuration.^{45–58,62–65,78} In agreement with Ref. 49—which thoroughly discusses these systems—Eq. (5) predicts interferences through *ortho*-benzene at ± 2.12 eV and ± 1.5 eV and through *meta*-benzene at 0 eV and ± 1.5 eV. These interferences are easy to see in Fig. 1(a). Again in agreement with Ref. 49, Eq. (5) does not predict interferences through *para*-benzene. Note that if the two bound states in *para*-benzene are not projected out of $\mathbf{H}_0 + \Sigma_L + \Sigma_R$ before invoking Eq. (5), our theory incorrectly identifies the bound states as interferences.

Let us proceed to transport through several molecules that are not alternant hydrocarbons. As an example, we explicitly work through the five-membered ring (perhaps a cyclopentadienyl ion) displayed in Fig. 1(b). When the electrodes couple

to the 1 and 3 ring positions,

$$\mathbf{H}_0 \rightarrow \begin{bmatrix} \varepsilon & \beta & 0 & 0 & \beta \\ \beta & \varepsilon & \beta & 0 & 0 \\ 0 & \beta & \varepsilon & \beta & 0 \\ 0 & 0 & \beta & \varepsilon & \beta \\ \beta & 0 & 0 & \beta & \varepsilon \end{bmatrix},$$

$\Sigma_L \rightarrow \text{diag}(-i\Gamma, 0, 0, 0, 0)$, and $\Sigma_R \rightarrow \text{diag}(0, 0, -i\Gamma, 0, 0)$. Accordingly, the projectors \mathbf{P}_L and \mathbf{P}_R from Sec. III are $\text{diag}(0, 1, 1, 1, 1)$ and $\text{diag}(1, 1, 0, 1, 1)$, respectively, such that the projection in Eq. (5) eliminates the first column (due to \mathbf{P}_L) and the third row (\mathbf{P}_R) of the matrices. The generalized eigenvalue problem is then

$$\begin{bmatrix} \beta & 0 & 0 & \beta \\ \varepsilon & \beta & 0 & 0 \\ 0 & \beta & \varepsilon & \beta \\ 0 & 0 & \beta & \varepsilon \end{bmatrix} \vec{c} = E \begin{bmatrix} 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix} \vec{c},$$

which yields $E = \varepsilon - \beta(1 \pm \sqrt{5})/2 = \{-0.927, 2.43\}$ eV for the interference features. Figure 1(b) clearly shows interferences at these energies. Also displayed is the case where the electrodes couple to the 1 and 2 positions of the ring; Eq. (5) predicts interference features at both of the previous energies plus an additional feature at $E = \beta = -1.5$ eV.

Our next example introduces a heteroatom (akin to Ref. 76) to the *meta*-benzene system; a site with $\epsilon_j = 0.6$ eV is placed in the ring [see Fig. 1(c)]. This system is similar to a 2,6-connected pyridine. Using our theory, this system has interferences at $E = 1.74$ eV and also at $E = -0.870 \pm 0.140i$ eV. The real interference is visible in the figure. On the other hand, the complex interference energies only produce a deep well near $\text{Re}(E)$; the transmission does not drop to 0 because the interference energies are not on the real axis. Complex interference energies have been previously reported in transport through heterostructures,^{111,113} where they signify that two pathways through the system have opposite parity and are strongly coupled to the electrodes.

Finally we consider the system shown in Fig. 1(d). Because two sites of the benzene molecule couple to each electrode, this system has multiple channels. At first glance, the transmission function has neither nodes nor deep wells, and we might conclude that this system does not have interferences. However, Eq. (5) predicts an interference at $E = 0$ eV. To investigate this discrepancy, Fig. 1(d) also plots the transmission probabilities through both channels, which are the eigenvalues of $\mathbf{t}^\dagger \mathbf{t}$. We now see that one channel clearly has an interference at 0 eV, but its presence is masked by the other channel. Contrary to previous intuition, nodes and/or deep wells in $T(E)$ are perhaps sufficient but unnecessary indicators of interferences in molecular transport junctions.

V. CONCLUDING REMARKS

In this work, we developed a general theory for finding destructive interference features in molecular transport junctions that uses only the molecular Hamiltonian and the self-energies for coupling the molecule to the electrodes. Our

derivation indicates that the existence and locations of interference features are described by a nonlinear generalized eigenvalue problem, Eq. (5). We then demonstrated this theory with several example systems, some of which had been previously studied and others that confounded existing intuitions. In all examples, Eq. (5) accurately predicted the existence of interference features as well as their locations.

This theory has several future directions, both chemical and mathematical. Chemically, the proposed theory enables the prediction of interference features for a broad class of molecules, which should help us further associate molecular structure with transport properties. For one example, our theory already reveals that the electronic structure of the isolated molecule is the dominant factor in interference. Consider the projected domain and range in Eq. (5): the molecule-electrode couplings determine the projectors (and thus have a role in interference), but the projected portion of $\mathbf{H}_0 + \Sigma_L + \Sigma_R$ has no contribution from Γ_L or Γ_R . Additionally, our theory should help identify molecules and connections that might result in measurable interference effects, where the interference must be near the junction's Fermi energy.^{22,46,47,56,69,82,84,85} Finally, Eq. (5) facilitates generalization of the interference characterization schemes in Refs. 40 and 49 which may help us better understand interference effects.

Turning to mathematical applications, one development might address the relatively open issue of generalized eigenvalue problems with rectangular matrices.¹¹⁷ Additionally, our definition of interference in Eq. (3) raises an interesting geometric question: When is a vector orthogonal to its image under an operator? This question bears similarity to the antieigenvalue problem,¹¹⁸ in which one seeks to find the largest angle of rotation between a vector in the domain and its image.

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