

Physical interpretation of orthogonal Hilbert space transformations in tight-binding systems with nonorthogonal bases

S. T. Rittenhouse and B. L. Johnson

Department of Physics, Western Washington University, Bellingham, Washington 98225-9064, USA
(Received 13 April 2004; revised manuscript received 8 September 2004; published 31 January 2005)

We study a recently introduced Hilbert space transformation from a nonorthogonal basis to an orthogonal basis, with an emphasis on the physical interpretation of the new Hilbert space. We find that the new Hilbert space may be interpreted as an orthogonal basis in the same *physical* space, wherein the basis overlap is formally transferred to the hopping matrix elements in the orthogonal system. The result is a standard tight-binding system in an orthogonal basis, with long-range hopping. The procedure is illustrated using an infinite one-dimensional hopping system with nearest-neighbor overlap. We also use the formal procedure to solve for the transmission characteristics of an impurity site coupled with semi-infinite leads, as an example of the interpretive power of the ordinary tight-binding formalism in the case of transport in the presence of basis-overlap effects: the antiresonances are produced, in the orthogonal space, by the presence of second-nearest-neighbor hopping.

DOI: 10.1103/PhysRevB.71.035118

PACS number(s): 03.65.-w, 73.61.Ph, 73.21.Hb

I. INTRODUCTION

The physics of quantum mechanical problems in which the natural physical basis is not orthogonal have proven to be remarkably rich. In order to solve problems using standard techniques and interpretations, many orthogonalization schemes and tensorial methods have been formulated,¹⁻⁵ and the effects of the overlap are diverse and in many cases surprising. Some examples where the overlap of basis states provides important physics include band structure calculations in a variety of solids,⁶⁻⁸ molecular electronic structure,⁹⁻¹¹ and transport problems in molecular and weakly-coupled nanoscale structures.^{5,12} Of particular interest for the present paper is the recent work of Emberly and Kirczenow (EK),⁵ in which the transport properties of molecular wire systems were investigated. In this case (and in many cases where tight-binding models are applicable), the natural basis consists of atomic orbitals localized to atomic sites. The basis is not orthogonal, and in this case, neglecting the orbital overlap causes the essential transport effects to be missed. The method adopted by EK is not an orthogonalization scheme per se, but rather a transformation to a new Hilbert space with an orthogonal basis. A brief review of the method will be given below. The keys to the Hilbert space transformation are (i) that the expansion coefficients of a general system state are the same as those in the original nonorthogonal basis, and (ii) the effective Hamiltonian in the new space has explicit dependence on the energy eigenvalues associated with the state. The equivalence of the expansion coefficients provides a bridge between the eigenstates of the new space and the scattering states in the physical basis, while the energy dependence of the Hamiltonian provides a natural mathematical connection between the basis function overlap and the physical phenomena in question, namely the transmission antiresonances in molecular wire systems.^{5,13} The anti-resonance effects have also been studied via more orthodox general tensorial methods.¹²

In this paper, we present an interpretation of the new orthogonal-basis Hilbert space which provides an explicit

context for ordinary tight-binding theory: we will show that the new basis can be interpreted via the usual orthogonal LCAO method treated via the standard Hamiltonian, wherein the overlap has been shifted to the hopping matrix elements. The notion of shifting the overlap to the hopping integrals has been alluded to previously in the context of one-dimensional chains,⁸ but in the current paper we will provide an exact derivation of the form of the hopping integrals, with an emphasis on the equivalence to the Hilbert space transformation of EK. We will derive explicit forms of the hopping terms for the infinite chain problem, in order to compare with analytical results for the energy dispersion in the presence of basis overlap, but the method is quite general and opens new possibilities for the treatment of systems in which the overlap of basis states is important. As an example of the power of the method, we will calculate the exact transmission characteristics of a sing-impurity wire: an impurity site coupled on each side to semi-infinite homogeneous leads. The transmission of the system is calculated via straightforward standard methods, once the proper transformation to the equivalent orthogonal space is performed. Many of the interesting aspects of the transmission antiresonance induced solely by the basis function overlap will be illuminated by examining the equivalent tight-binding problem, including the physical constraints on the occurrence of antiresonances. Most importantly, the overlap effects are explicitly transferred to the hopping terms, and the antiresonance effects become explicitly dependent upon second-nearest-neighbor hopping from the impurity site to the leads.

The rest of the paper is organized as follows. In the next section, we review the formalism introduced by EK, and outline the general procedure for transferring to a Hilbert space defined by an orthogonal basis with long-range hopping. In Sec. III we apply the general method to a specific example problem: the one-dimensional linear chain with nearest-neighbor overlap, and compare the solution to the analytical solution obtained directly in the nonorthogonal basis. In Sec. IV, we solve for the transmissivity of the single-

impurity molecular wire via the orthogonal tight-binding formalism. Finally, our results are summarized in Sec. V.

II. THEORY

In order to provide context for what follows, we will briefly review the Hilbert space transformation of EK. We start with the Schrödinger equation

$$H|\psi\rangle = E|\psi\rangle. \quad (1)$$

Expanding the state $|\psi\rangle$ in a nonorthogonal physical basis $|n\rangle$ representing a single-particle state localized on atom n , we find

$$|\psi\rangle = \sum_n a_n |n\rangle, \quad (2)$$

$$H \sum_n a_n |n\rangle = E \sum_n a_n |n\rangle. \quad (3)$$

The Schrödinger equation reduces to a difference equation by acting with $\langle m|$ on both sides of the equation:

$$\sum_n H_{mn} a_n = \sum_n E S_{mn} a_n, \quad (4)$$

where $H_{mn} = \langle m|H|n\rangle$, and $\langle m|n\rangle = S_{mn}$ is the overlap matrix. Adding the identity matrix (multiplied by E) to both sides and moving the matrix S to the left-hand side gives

$$\sum_n (H_{mn} - E(S_{mn} - \delta_{mn})) a_n = E a_m. \quad (5)$$

EK proposed that Eq. (5) is now in the form of an eigenvalue problem formulated in an *orthogonal basis* $\{|n'\rangle\}$. The goal now is to diagonalize a new energy dependent Hermitian operator H^E with

$$H_{m'n'}^E = H_{mn} - E(S_{mn} - \delta_{mn}). \quad (6)$$

Here we must emphasize that $H_{m'n'}^E$ are matrix elements in the new orthogonal basis, whereas the matrix elements on the right-hand side are written in terms of the nonorthogonal physical basis. This connection is made more formally below.

In the new basis, there exists a state $|\psi'\rangle$ which is an eigenvector of H^E with eigenvalue E , and which may be written in the orthogonal basis as $|\psi'\rangle = \sum_n a_n |n'\rangle$. Here the expansion coefficients a_n are the same as those in Eq. (3).

To formally prove that the new Hilbert space exists and that it has the desired properties, let us investigate a linear transformation T that maps an orthogonal basis from an arbitrary separable Hilbert space, A , to the basis of our physical Hilbert space, B .

$$T:A \rightarrow B,$$

$$T|n'\rangle = |n\rangle. \quad (7)$$

Thus we may rewrite (3) as

$$H \sum_n a_n T|n'\rangle = E \sum_n a_n T|n'\rangle. \quad (8)$$

Multiplying both sides by T^\dagger we find, with some manipulation, that Eq. (8) becomes

$$(T^\dagger H T - E T^\dagger T + E I) \sum_n a_n |n'\rangle = E \sum_n a_n |n'\rangle, \quad (9)$$

where I is the identity operator. By acting with an $\langle m'|$ on both sides of the equation and noting that

$$\langle m'|T^\dagger T|n'\rangle = \langle m|n\rangle = S_{mn},$$

$$\langle m'|T^\dagger H T|n'\rangle = \langle m|H|n\rangle = H_{mn},$$

and remembering the orthogonality of the new basis, $\langle m'|n'\rangle = \delta_{m'n'}$, we see that Eq. (9) is exactly the same as Eq. (5). The present formulation also makes explicit the space in which matrix elements are defined, i.e., S is defined only in the nonorthogonal physical basis (notation such as $S_{m'n'}$ is not valid), and likewise matrix elements of H^E above are only defined in the orthogonal basis. In addition, since throughout this process we did not change anything about the expansion coefficients a_n , i.e., when we modified Eq. (3) we replaced only the basis kets and not the amplitudes, we have the desired property that the expansion coefficients are exactly the same as in the nonorthogonal basis.

In general, since A was chosen as an arbitrary separable Hilbert space, we are free to choose any *physical* space corresponding to the new Hilbert space. Mathematically, we have established an orthogonal basis solely by choosing a T such that $(T^\dagger T)_{m'n'} = \langle m'|T^\dagger T|n'\rangle = \langle m|n\rangle = S_{mn}$. Therefore, we make the interpretation that the space A is the same *physical* space as B , but defined by the orthogonal basis $|n'\rangle$. The interpretation we use for this is that the overlap between two nonorthogonal basis elements in space B is spread over a number of orthogonal basis elements in A . Any general problem in the nonorthogonal space may then be reformulated in the orthogonal space, with the usual interpretations of the basis, etc. The effects of overlap are then formally transferred to the hopping integrals of a standard tight-binding Hamiltonian. The general procedure will be mapped out below, and an example system will be studied in detail.

Given an appropriate Hilbert space transformation T , the general (formal) procedure for transforming to the orthogonal space is to write out the Hamiltonian matrix elements in the new basis, using the well-known tight-binding Hamiltonian, and equate matrix elements from the orthogonal system to those of the nonorthogonal system. The result is a recursion relation between the hopping elements in the new system, with boundary conditions linking them to the hopping elements and on-site energies in the original system.

We consider a one-dimensional hopping chain and assume basis function overlap to extend N atoms, thus¹⁴

$$\langle n|n+j\rangle = S_{n(n+j)} = s_j \text{ for } 1 \leq j \leq N-1 \text{ otherwise.}$$

We then assume the existence of an appropriate transformation T , such that

$$\begin{aligned}
 s_j &= \langle n' | T^\dagger T | (n+j)' \rangle \\
 &= \sum_k T_{k'n'} \langle k' | \sum_m T_{m'(n+j)'} | m' \rangle \\
 &= \sum_m T_{m'n'} T_{m'(n+j)'}. \quad (10)
 \end{aligned}$$

Now, the matrix elements of the Hamiltonian in the original nonorthogonal basis may be written, for nearest-neighbor hopping, as

$$\langle n | H | n \rangle = \epsilon,$$

$$\langle n | H | n \pm 1 \rangle = t,$$

$$\langle n | H | n \pm j \rangle = 0 \quad \text{for } j \geq 2. \quad (11)$$

Using this Hamiltonian, a formal connection to the matrix elements of the Hamiltonian in the orthogonal basis is made term-by-term, as follows:

$$H_{n(n+j)} = \sum_k \sum_m T_{k'n'} T_{m'(n+j)'} \langle k' | H | m' \rangle. \quad (12)$$

The matrix elements on the right-hand side are in the orthogonal basis; we now interpret the new orthogonal basis as a chain of sites with *orthogonal* basis states which, as usual, represent the amplitude to be on a given site. With this interpretation the standard tight-binding (TB) Hamiltonian may used,

$$H_{\text{TB}} = \sum_j \epsilon_0 |j'\rangle \langle j'| + \sum_{ij} t_{ij} |j'\rangle \langle i'|, \quad (13)$$

where the t_{ij} are hopping energies, and the ϵ_0 is the on-site energy, all to be determined. To do so, the matrix elements in the nonorthogonal basis are written in terms of the tight-binding elements from Eq. (12) as

$$H_{n(n+j)} = \sum_k \sum_m T_{k'n'} T_{m'(n+j)'} (\epsilon_0 \delta_{k'm'} + t_{k'm'}). \quad (14)$$

Equation (14) produces, for $j \geq N+1$, a recursion relation for the $t_{k'm'}$, which together with the boundary conditions obtained by combining equations (11) and (14), fix the hopping and site energies in the orthogonal basis to the physical quantities ϵ and t from the nonorthogonal basis. In the next section, we will illustrate the procedure using a specific example. The resulting energy spectrum will be compared to the exact answer obtained in the original basis.

III. THE CASE OF NEAREST-NEIGHBOR OVERLAP

To make the general procedure clear, we will apply it to the simple problem of an infinite one-dimensional hopping chain with nearest-neighbor overlap. In this case, $S_{mm}=1$, $S_{n(n\pm 1)}=s$, and $S_{mm}=0$ otherwise. The first task is to find an appropriate T . We choose a T such that

$$|n\rangle = T|n'\rangle = \cos \theta |n'\rangle + \sin \theta |(n+1)\rangle$$

$$\text{with } \cos \theta \sin \theta = s. \quad (15)$$

It is a simple matter to demonstrate that this choice for T reproduces only nearest-neighbor overlap. It is also interesting that the magnitude of the overlap s is limited to $|s| \leq 1/2$. It should be noted that the restriction of s is consistent with the physical solution space for the problem. This problem is solvable in closed form in the original basis. It may be shown that the energy dispersion for the infinite chain with nearest-neighbor overlap is given by⁸

$$E = \frac{\epsilon + 2t \cos kl}{1 + 2s \cos kl}. \quad (16)$$

where l is the lattice spacing. Note that $|s| \geq 1/2$ produces singular behavior in the dispersion. In addition, it may be shown in general that for $|s| \geq 1/2$ the matrix S is noninvertible, which renders the problem insolvable. Therefore, the definition of T above is appropriate for the problem at hand.

To continue, because the system is translationally invariant, we may assume that the hopping energies appearing in Eq. (13) are given by $t_{ij}=t_{|i-j|}$ for all i and j . In other words, the hopping energy associated with moving from site i to site j only depends on the number of sites separating i and j . All that remains is to use the basis transformation to fix the $t_{|i-j|}$. Equating the matrix elements of H explicitly, i.e., using Eqs. (12) and (14), we find

$$\begin{aligned}
 \epsilon &= \langle n | H | n \rangle = \langle n' | T^\dagger H T | n' \rangle \\
 &= (\cos \theta \langle n' | + \sin \theta \langle (n+1)' |) H_{\text{TB}} \\
 &\quad \times (\cos \theta |n'\rangle + \sin \theta |(n+1)\rangle) \\
 &= \cos^2 \theta \epsilon_0 + \cos \theta \sin \theta t_1 + \cos \theta \sin \theta t_1 + \sin^2 \theta \epsilon_0 \\
 &= \epsilon_0 + 2st_1, \quad (17)
 \end{aligned}$$

$$\begin{aligned}
 t &= \langle n | H | n+1 \rangle = \langle n' | T^\dagger H T | (n+1)' \rangle \\
 &= (\cos \theta \langle n' | + \sin \theta \langle (n+1)' |) H_{\text{TB}} \\
 &\quad \times (\cos \theta |(n+1)\rangle + \sin \theta |(n+2)\rangle) \\
 &= \cos^2 \theta t_1 + \cos \theta \sin \theta \epsilon_0 + \cos \theta \sin \theta t_2 + \sin^2 \theta t_1 \\
 &= t_1 + s(\epsilon_0 + t_1), \quad (18)
 \end{aligned}$$

$$\begin{aligned}
 0 &= \langle n | H | (n+j) \rangle = \langle n' | T^\dagger H T | (n+j)' \rangle \\
 &= (\cos \theta \langle n' | + \sin \theta \langle (n+1)' |) H_{\text{TB}} \\
 &\quad \times (\cos \theta |(n+j)\rangle + \sin \theta |(n+j+1)\rangle) \\
 &= \cos^2 \theta \epsilon_0 + \cos \theta \sin \theta t_1 + \cos \theta \sin \theta t_1 + \sin^2 \theta \\
 &= t_j + s(t_{j-1} + t_{j+1}) \quad \text{for } j \geq 2. \quad (19)
 \end{aligned}$$

We now have a second order difference equation for the hopping elements in the orthogonal system. As stated above, the first two equations combine to give us one boundary condition on t_1 . In addition, we require $\lim_{n \rightarrow \infty} t_n = 0$ for the system to be physically meaningful. The solution to the difference equation, subject to the boundary conditions, is

$$t_n = A\gamma^n,$$

$$\epsilon_0 = \epsilon - 2A\gamma, \quad (20)$$

where

$$A = \frac{t - s\epsilon}{\gamma + s\gamma^2 - 2s^2\gamma}$$

and

$$\gamma = \left(\frac{\sqrt{1 - 4s^2} - 1}{2s} \right).$$

So we have an infinite sequence of hopping energies corresponding to the fact that each orthogonal basis element contains all of the nonorthogonal vectors. Recalling that the $n = |i - j|$ we note that γ^n decays rapidly with increasing site separation. Therefore, for many circumstances, it may be sufficient to approximate the overlap problem by a tight binding system with next-nearest-neighbor hopping.¹⁵

To demonstrate the equivalence of the current treatment to the original problem in the nonorthogonal basis, we replace the hopping elements into the original Hamiltonian (13), and write the Schrödinger equation for a general state,

$$\left(\sum_j (\epsilon - 2A\gamma) |j'\rangle \langle j'| + \sum_{i,j} A\gamma^j |(i+j)'\rangle \langle i'| \right) \sum_n a_n |n'\rangle = E \sum_n a_n |n'\rangle.$$

Taking the inner product of both sides of this equation with an arbitrary orthogonal element $\langle m'|$ generates the difference equation

$$(\epsilon - 2A\gamma)a_m + \sum_{j=1}^{\infty} (A\gamma^j a_{m+j} + A\gamma^j a_{m-j}) = E a_m. \quad (21)$$

Assuming solutions of the form $a_n = e^{inl}$ leads immediately to the energy eigenvalues

$$E = (\epsilon - 2A\gamma) + \sum_{n=1}^{\infty} 2A\gamma^n \cos(nkl). \quad (22)$$

The second term in the energy is a Fourier series. The convergence of the Fourier series is guaranteed, note that for $|s| < 1/2$ we have $|\gamma| < 1$. Replacing A and γ with their appropriate values, we see that the Fourier series converges to

$$E = \frac{\epsilon + 2t \cos kl}{1 + 2s \cos kl} \quad (23)$$

which is exactly the solution we get from solving via the original difference equation formulated from the nonorthogonal basis. We also note that the Fourier coefficients are in fact twice the hopping energies in the orthogonal chain. As noted earlier, previous authors have noted the existence of a Fourier series result for the infinite homogeneous one-dimensional system with nearest-neighbor overlap.¹² The analytical result for the hopping energies as the Fourier coefficients, and the overall general procedure, are new results

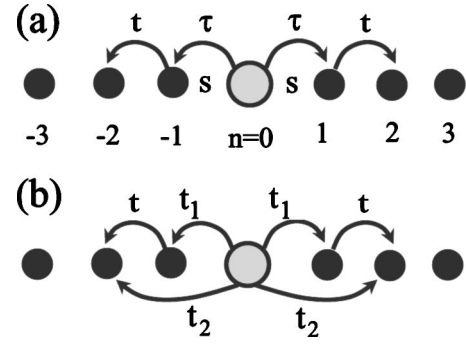


FIG. 1. (a) The geometry of the physical space, with an impurity at site $n=0$, coupled to homogeneous leads via hopping (τ) and basis overlap (s). The hopping elements are shown schematically. (b) The geometry in the orthogonal space, where the overlap has been replaced with effective nearest- and second-nearest-neighbor hopping (t_1 and t_2 , respectively).

from the current work, that provide a general procedure for problems involving basis function overlap.

IV. TRANSMISSION ANTIRESONANCE

In this section, we will again utilize the general methods described above, but we will focus on the problem of transmission through an impurity site in an otherwise homogeneous linear chain. We will study the transmission antiresonance which gives rise to the transmission antiresonance due solely to basis function overlap,⁵ a single impurity at site $n=0$ which is coupled to semi-infinite leads. The hopping elements to and from the impurity site, τ , are different from the hopping energies in the leads t , and we assume that the basis function overlap exists *only* between the leads and the impurity.¹⁶ The overlap matrix in this case is given by

$$S_{0,\pm 1} = \langle 0 | \pm 1 \rangle = s,$$

$$S_{m,n} = \langle n | m \rangle = \delta_{m,n}, \quad \text{otherwise,} \quad (24)$$

The site energy of the impurity is the same as that of the leads (an assumption that is not necessary, but it simplifies the description). A schematic of the geometry is shown in Fig. 1(a). We will proceed by demonstrating that the transformation of GK will produce an antiresonance at a specific energy; we then find the appropriate T for the model system and connect the nonorthogonal physical space with the orthogonal space, wherein we show that the current model system is equivalent to an ordinary (orthogonal) tight-binding chain with both nearest- and next-nearest-neighbor hopping elements from the impurity site to the leads. We show that the transmission antiresonance in the orthogonal space is controlled by the ratio of the nearest- and next-nearest-neighbor hopping energies.

Using the transformation of GK, we find that the matrix $H_{m,n}^E$ has energy-dependent off-diagonal hopping terms due to the impurity given by $H_{0,\pm 1}^E = \tau - sE$. The great utility of the transformation is then apparent, since the hopping is clearly *cut off* at $E = \tau/s$. Any calculation of the transmission of waves incident on the impurity from one of the leads will

consequently show an antiresonance at this energy, due entirely to the existence of the overlap s .^{5,12} The drawback is in the interpretation of the physical effects of the overlap, as viewed in a physical basis where the usual interpretations cannot apply.

The same situation may be studied using the methods described above, with the advantage that the problem may be cast in an ordinary tight-binding framework where the essential physics may be illuminated via standard approaches. To proceed, we first find a transformation which satisfies the relation $\langle m'|T^\dagger T|n'\rangle = S_{mn}$ with the matrix S given above. An appropriate T is given by

$$T|0'\rangle = s(|-1'\rangle + |1'\rangle) + \sqrt{1-2s^2}|0'\rangle,$$

$$T|n'\rangle = |n'\rangle, \quad \text{otherwise.} \quad (25)$$

The form of T given in Eq. (25) is not unique, but provides a simple framework on which to proceed. The next task is to once again utilize Eqs. (12) and (14) to equate matrix elements of the Hamiltonian explicitly. The connections thus obtained are

$$\epsilon = \langle 0|H|0\rangle = 2s^2\epsilon + 4s\sqrt{1-2s^2}t_1 + (1-2s^2)\epsilon_0,$$

$$\tau = \langle 1|H|0\rangle = s\epsilon + \sqrt{1-2s^2}t_1,$$

$$0 = \langle 2|H|0\rangle = st + \sqrt{1-2s^2}t_2. \quad (26)$$

Where t_1 and t_2 are the hopping elements from the impurity to the first and second near neighbors, respectively, and ϵ_0 is the site energy at $n=0$ in the orthogonal basis (i.e., $\langle 0'|H_{\text{TB}}|0'\rangle$). We note that further relationships simply reproduce the result that the remaining hopping elements are all equivalent between the bases, i.e., $t_{n,n+1}=t$ for $n \geq 1$. The formal connections between the bases are thus given by

$$\epsilon_0 = \frac{4s\tau - \epsilon - 2s^2\epsilon}{2s^2 - 1},$$

$$t_1 = \frac{\tau - s\epsilon}{\sqrt{1-2s^2}},$$

$$t_2 = \frac{-st}{\sqrt{1-2s^2}}. \quad (27)$$

We note that in the limit $s \rightarrow 0$ these behave as expected, $\epsilon_0 \rightarrow \epsilon$, $t_1 \rightarrow \tau$, and $t_2 \rightarrow 0$.

Given the connections (27), we may study the (equivalent) case of a tight-binding system with a single impurity coupled to the leads via nearest- and next-nearest-neighbor hopping. We note that this is the simplest *orthogonal* scheme which gives rise to an antiresonance. The geometry for this case is sketched in Fig. 1(b).

Recalling the Schrödinger equation for a general state in the orthogonal system, $\sum_n H_{mn} a_n = E a_m$, we find, for second-nearest-neighbor hopping at $n=0$,

$$t_2(a_{-2} + a_2) + t_1(a_{-1} + a_1) + \epsilon_0 a_0 = E a_0,$$

$$t_1 a_0 + \epsilon a_1 + t a_2 = E a_1,$$

$$t a_{-2} + \epsilon a_{-1} + t_1 a_0 = E a_{-1}. \quad (28)$$

We then make the usual substitution for waves incident from the left-hand side, vis.

$$e^{inkl} + \alpha e^{-inkl} \quad \text{for } n < 0,$$

$$a_n = a_0 \quad \text{for } n = 0,$$

$$\beta e^{inkl} \quad \text{for } n > 0 \quad \text{for } n < 0, \quad (29)$$

By inserting Eq. (29) into Eq. (28) to produce three equations in the unknowns α , β , and a_0 , we find, after lengthy algebra, that the transmission coefficient is given by

$$\beta = \frac{2it_1 t_2 \left(\frac{t_1 t}{t_2} + E - \epsilon \right) \sin(kl)}{e^{2ikl} (E - t e^{ikl} - \epsilon) A} \quad (30)$$

with $A = E(\epsilon_0 + \epsilon + t e^{ikl} - E) + (2t_1 t_2 - t \epsilon_0) e^{ikl} + 2t_1^2 - \epsilon \epsilon_0$. So we see the transmission coefficient will vanish at the energy $E_A = \epsilon - (t_1 t / t_2)$, note that substitution of the connections (27) into this expression for the energy immediately reproduces the result for the antiresonance energy in the nonorthogonal basis, $E_A = \tau / s$.

It is quite instructive to study the total transmission in the orthogonal basis, where standard interpretation of the basis states simplifies the description. In the leads, far from the impurity, the energy dispersion is given by the usual single-band result $E = \epsilon + 2t \cos(kl)$. Using this, we can find the point in the band where the antiresonance occurs. Equating this energy with the antiresonance energy, we find that, for k in the Brillouin zone, antiresonance occurs for $k_A l = \pi - \cos^{-1}(t_1 / 2t_2)$. Therefore, the ratio t_1 / t_2 must satisfy $-2 \leq t_1 / t_2 \leq 2$ for antiresonance to occur. In the original physical basis, this corresponds to $-2 \leq (s\epsilon - \tau) / st \leq 2$. As an example of the restrictiveness of the constraint, consider the case $\epsilon = 0$ (a simplifying assumption which does not influence the outcome) and look at the range of τ (in units of the lead hopping t). In this case, $|\tau| \leq 2s$. Since s is restricted to $|s| < 0.5$ (see above), then $|\tau| < 1$, and antiresonance in the band is only possible for coupling of the impurity to the leads that is *weaker than that within the leads*. This important result follows directly from the utility of the transformation to the orthogonal space, where the usual methodology applies.

The energy dispersion may be substituted into the transmission coefficient (30), and the total transmission is found via $T = |\beta|^2$. Numerical examples for the transmission under different parameters will be examined next.

In Fig. 2 we show the transmission as a function of the wave vector for the case where $\epsilon = 0$, $s = 0.15$, and $\tau = 0.25$. In all cases, $t = 1$ (the other hopping elements are in units of t). We note that the current choice represents weak overlap, which forces a relatively weak coupling of the impurity to the leads. The corresponding parameters in the orthogonal basis are $\epsilon_0 = -0.6283$, $t_1 = 0.2558$, and $t_2 = -0.1535$. We note that in the new basis, the direct coupling is weak, with the

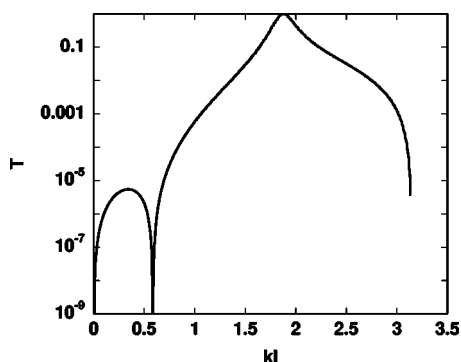


FIG. 2. The transmission as a function of kl for the case $\epsilon=0$, $\tau=0.25$, and $s=0.15$. Note the antiresonance at $kl=0.584$.

second-nearest-neighbor hopping weaker still. The transmission antiresonance is prominent in the graph, at the value $kl = \pi - \cos^{-1}(t_1/2t_2) = 0.584$. A transmission resonance occurs near the center of the band, and is independent of overlap in all cases where the overlap is small and the coupling to the leads is stronger, $\tau > s$.

In contrast, Fig. 3 depicts the transmission as a function of kl for the case of strong overlap, $s=0.45$, and very weak coupling, $\tau=0.15$. In this case, the corresponding orthogonal-

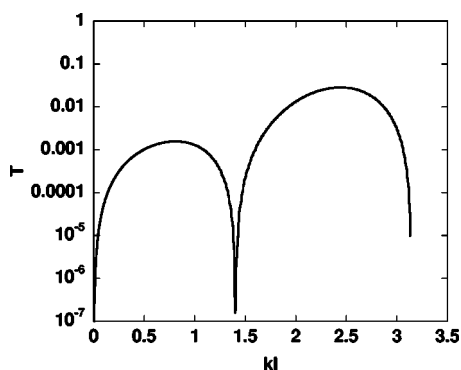


FIG. 3. The transmission as a function of kl for the case $\epsilon=0$, $\tau=0.15$, and $s=0.45$. This case represents weak coupling and strong overlap; the antiresonance here requires strong second-nearest-neighbor hopping from the impurity, as discussed in the text.

space parameters are $\epsilon_0 = -3.025$, $t_1 = 0.1945$, and $t_2 = -0.5834$. (Note that the effective on-site energy of the impurity represents a relatively deep well.) So we see that, in this case, the second-nearest-neighbor hopping dominates, and the antiresonance occurs near the center of the band at $kl = 1.402$. The transmission characteristics of the weakly coupled case are strongly influenced by the overlap, the analogue of which in the orthogonal tight-binding scheme is domination by long range hopping.

V. SUMMARY

We have studied a Hilbert space transformation introduced in conjunction with the investigation of electronic transport in molecular wires. The purpose of the transformation is to solve for eigenvalues and eigenvectors of a system (for which the physical basis is not orthogonal) in terms of a system with an orthogonal basis and which preserves the expansion coefficients for a general wave function. We demonstrate that in general the transformation matrix may be defined in terms of the general overlap matrix. Once the transformation matrix is defined, we interpret the new Hilbert space as being in the same physical space as the original problem, but described by an orthogonal basis. The problem may then be treated via the usual tight-binding formalism, where the effects of overlap have been formally transferred to the hopping matrix elements. The effects of overlap are then studied in the context of long-range hopping. We have demonstrated the formal equivalence of the orthogonal basis/long-range hopping system and the original system via the example of a one-dimensional hopping system with nearest-neighbor overlap. The analytic forms of the energy eigenvalues calculated via the different bases are shown to be equivalent. We have further demonstrated that the transmission properties of molecular wire systems may be calculated more easily via the orthogonal tight-binding interpretation. The transmission of a single-impurity system was solved exactly, and the antiresonance effect that is induced by basis function overlap occurs in the orthogonal system via the presence of a second-nearest-neighbor hopping term.

ACKNOWLEDGMENTS

The authors are grateful to George Kirczenow for many helpful discussions. This work was supported by an award from Research Corporation.

¹P. O. Löwdin, *J. Chem. Phys.* **18**, 365 (1950).

²P. C. P. Andrade and J. A. Frieire, *J. Chem. Phys.* **118**, 6733 (2003).

³M. Head-Gordon, P. E. Maslen, and C. A. White, *J. Chem. Phys.* **108**, 616 (1998).

⁴E. Artacho and L. M. del Bosch, *Phys. Rev. A* **43**, 5770 (1991).

⁵E. Emberly and G. Kirczenow, *Phys. Rev. Lett.* **81**, 5205 (1998); *J. Phys.: Condens. Matter* **11**, 6911 (1999).

⁶J. Tejeda and N. J. Shevchick, *Phys. Rev. B* **13**, 2548 (1976).

⁷B. A. McKinnon and T. C. Choy, *Phys. Rev. B* **52**, 14 531 (1995).

⁸D. A. Mirabella, C. M. Aldao, and R. R. Deza, *Am. J. Phys.* **62**,

162 (1994).

⁹R. M. McWeeney, *Methods of Molecular Quantum Mechanics* (Academic, London, 1989).

¹⁰A. A. Stuchebrukhov, *J. Chem. Phys.* **104**, 8424 (1996).

¹¹I. A. Balabin and J. N. Onuchic, *J. Phys. Chem.* **100**, 11573 (1996).

¹²K. W. Sulston and S. G. Davison, *Phys. Rev. B* **67**, 195326 (2003).

¹³M. A. Ratner, *J. Phys. Chem.* **94**, 4877 (1990).

¹⁴This assumption is based on the fact that the individual basis states $|n\rangle$ must be square-integrable (centered on site n), and therefore the overlap integrals must decay at least exponentially.

The assumption in the text implies a cutoff imposed on the decay.

¹⁵In addition, for many cases of experimental interest, the value of s itself is very small, and the decay of the hopping terms is quite rapid. For example, if $s=0.1$, and for typical values of t and ϵ , (i.e., t in the range 2 to 5 eV, and ϵ of order 10 eV) the hopping energies will drop off by a factor of 10 from $n=1$ to $n=2$, and by a factor of 100 from $n=1$ to $n=3$.

¹⁶This assumption reduces the problem to the most fundamental level where basis overlap influences the physics. In addition, it is reasonable from the point of view of metallic leads coupling molecular systems, since an orthogonal tight-binding scheme is reasonable for leads. The molecular orbital structures can reasonably be modelled via the assumption of overlap (even in the case of weak coupling), since the bonding is via a different mechanism.