Highly parallelizable electronic transport calculations in periodic rhodium and copper nanostructures

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Abstract
We extend the highly-parallelizable open-source electronic transport code TRANSEC (Feldman et al 2014 Phys. Rev. B 90 035445; https://gitlab.com/computational-physics2/transec/) to perform real-space atomic-scale electronic transport calculations with periodic boundary conditions in the lateral dimensions. We demonstrate the use of TRANSEC in periodic Cu and Rh bulk structures and in large periodic Rh point contacts, in preparation to perform calculations of reflection probability across Rh grain boundaries.

Keywords: conductance, electronic transport, first principles calculations, density functional theory, copper, rhodium, nanotechnology

1. Introduction

In order for semiconductor technology to continue scaling, the most local level of metal interconnects must scale with the minimum feature size (5–7 nm in current technology nodes) to form logical circuits among the billions of individual transistor devices in an integrated circuit. However, in metal wires with ~10 nm line width, conductivity can degrade by as much as 90% compared to the bulk metal [1]. Thus, interconnects may in fact be the limiting factor in integrated circuit delay times and power consumption [2].

Key causes of this conductivity degradation, also known as the size effect, include increased scattering from grain boundaries, surface roughness, and wire-liner interfaces. Since these size-dependent scattering processes tend to scale inversely with the wire dimensions, resistivity $\rho$ is augmented over its bulk value $\rho_0$ by an amount proportional to the product of $\rho_0\lambda$ and the bulk mean free path (MFP) $\lambda$ divided by line width $L$ [1, 3–5]:

$$\rho(L) = \rho_0 \sim \frac{\rho_0\lambda}{L}.$$ 

The product $\rho_0\lambda$ has therefore been used to indicate which materials are promising candidates to replace copper in future nanoscale interconnects. Previously, rhodium was identified as one of the most promising such materials [1, 6, 7], so we use it as an example of an alternative interconnect metal.

In this article, we extend the highly-parallelizable open-source electronic transport code TRANSEC, based on the density functional theory (DFT) code PARSEC [8–13], to perform real-space atomic-scale electronic transport calculations with periodic boundary conditions (PBC) in the lateral dimensions (section 2). We then describe a mode counting method we use to validate our calculations (section 3), and demonstrate the use of TRANSEC in periodic Rh and Cu structures (section 4). In a subsequent work, we will present TRANSEC calculations of reflection probability across Rh grain boundaries, using the absorbing boundary condition (ABC) parameters developed here to represent bulk Rh electrodes.

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TRANSEC and PARSEC use a real-space grid to represent the Kohn–Sham (KS) DFT orbitals. The advantages of real-space calculations include an extremely sparse Hamiltonian, leading the computation to parallelize very efficiently. As described previously [8, 10], this allows real-space calculations to take better advantage of parallel computing resources in order to solve large, computationally intensive problems such as the ones studied here. For example, in section 4.4, we present calculations with 350,000 to 500,000 basis orbitals. In addition, real-space calculations allow straightforward convergence of the DFT ‘basis’ set. Finally, real-space calculations naturally handle periodic, non-periodic, or mixed boundary conditions, as demonstrated in this work.

TRANSEC uses complex absorbing potentials (CAPs; also referred to as ABCs) to represent semi-infinite electrodes at the two edges of the transport simulation cell. The use of CAPs in the ‘wide-band limit approximation’ avoids the computational burden of independent self-energy calculations for each energy \( E \), making it possible to compute a dense transmission curve \( T(E) \) in constant time [8].

2. Method: real-space electronic transport calculations in periodic structures

2.1. Preliminaries and notation

Let the KS effective potential, \( V_{KS} (x, y, z) \), be periodic in the \( xy \)-plane with lattice vectors \( \vec{a} \) and \( \vec{b} \), and let \( z \) be the transport direction. In this section, we describe the formalism for two-dimensional periodicity, or ‘slab’ geometry, but the extension to the case of one-dimensional periodicity is straightforward. Note that since \( \vec{a} \) and \( \vec{b} \) span the \( xy \)-plane, \( V_{KS} (x, y, z) \) is also at least approximately periodic in the \( x \) and \( y \) directions.

Then Bloch’s theorem tells us that the KS eigenstates \( \phi \) can be chosen to have the Bloch form

\[
\phi \left( \vec{x} \right) = \phi \left( x, y, z \right) = u \left( \vec{x} \right) e^{i \left( \vec{k} \cdot \vec{x} \right)} = u \left( x_a, x_b, z \right) e^{i \left( k_a x_a + k_b x_b \right)}, \tag{1}
\]

where \( \vec{k} \perp \vec{z} \), \( x_a, b \), and \( k_a, b \) are the components of \( \vec{k} \) and \( \vec{k} \), respectively, along the two lattice vectors, and \( u \) is the periodic part of \( \phi \), with periodicity \( L_a = |\vec{a}| \) and \( L_b = |\vec{b}| \) in \( x_a \) and \( x_b \), respectively.

As always in TRANSEC [8], we seek to evaluate the transmission function

\[
T(E) = \text{Tr} \{ G(E) \Gamma_R G^* (E) \Gamma_L \},
\]

with \( \Gamma_L \) and \( \Gamma_R \) the CAPs in the left and right electrodes, respectively, which we take to have Gaussian form:

\[
\Gamma_{L,R} (x, y, z) = \Gamma_0 e^{-\left( z - z_L, z \right) / 2 \sigma^2}.
\]

Here \( \Gamma_0 \) and \( \sigma \) are the CAP strength and standard deviation, respectively, \( \Gamma \equiv \Gamma_L + \Gamma_R \),

\[
G(E) = \left[ E \mathbb{1} - H_{KS} + i \Gamma \right]^{-1}
\]
is the retarded Green’s function, \( G^* \) is the complex conjugate of \( G \), \( \mathbb{1} \) is the identity operator, and \( H_{KS} \) is the KS Hamiltonian. \( H_{KS} \) can be chosen real thanks to its time-reversal symmetry, and \( i \Gamma \) and \( E \mathbb{1} \) are diagonal matrices. Therefore \( G \) is complex symmetric, and \( G^* = G^T = G^\dagger = G^\ast \), where \( G^\ast \) is the transpose of \( G \), \( G^\dagger \) is the Hermitian conjugate of \( G \), and \( G^\ast \) is the advanced Green’s function.

Following [8], we wish to carry out the trace in the diagonal basis of \( G^{-1} \), i.e., the basis of right eigenvectors \( U \) of \( \left( H_{KS} - i \Gamma \right) \). The eigenvectors \( U \) can be chosen with the Bloch form (1), and therefore each individual eigenvector \( U_{n, \vec{k}} \) can be identified by a band index \( n \) and Bloch wavevector \( \vec{k} \). Accordingly, the formula for transmission becomes:

\[
T(E) = \text{Tr} \left\{ \hat{G}(E) \hat{\Gamma}_R \hat{G}^* (E) \hat{\Gamma}_L \right\}, \tag{3}
\]

where

\[
\hat{\Gamma}_L \equiv U^\dagger \Gamma_L U, \tag{4}
\]

\[
\hat{\Gamma}_R \equiv U^\dagger \Gamma_R U^\ast, \tag{5}
\]

\[
\hat{G}(E) \equiv U^T G(E) U = \text{diag} \left\{ 1 / \left( E - \epsilon_{n, \vec{k}} \right) \right\},
\]

and \( \epsilon_{n, \vec{k}} \) is an eigenvalue of \( \left( H_{KS} - i \Gamma \right) \). Note that \( H_{KS} \) is complex symmetric, so \( U \) is complex orthogonal, \( U^{-1} = U^\dagger \), and the individual vectors \( U_{n, \vec{k}} \) are biorthogonal [8].

The CAPs (2) decay and are therefore clearly non-periodic in the \( z \)-direction, but they are in fact constant in the \( xy \)-plane. Therefore, the transformed CAPs \( \hat{\Gamma} \) will be diagonal in the subspaces of \( U \) with constant \( \vec{k} \), while \( G \) remains fully diagonal as in equation (5) even with PBCs. So we need not consider the possibility that \( \vec{k} \) complicates equation (3), and the formalism of [8] can be adapted directly to the case with PBCs.

Evidently, the main adaptation required to introduce PBCs is carrying out the basis change (4) of the CAPs with an eigenbasis \( U \) having Bloch form (1). Formally, this transformation can be expressed as:

\[
\langle n, \vec{k} | \hat{\Gamma} | m, \vec{k}' \rangle = \int \cdots \int u^*_{n, \vec{k}} (\vec{x}) u_{m, \vec{k}'} (\vec{x}) e^{i (\vec{k} - \vec{k}') \cdot \vec{x}} \Gamma (\vec{x}) d^3 \vec{x}
\]

\[
= \sum_{j, \ell} e^{i \left( (k_j - k'_j) t_{\ell a} + (k_b - k'_b) t_{\ell b} \right)} \hat{u}_a \times \hat{b} \int_{-\infty}^{L_a} \int_{-\infty}^{L_b} \hat{u}^*_m (\vec{x}) \hat{u}_{m, \vec{k}'} (\vec{x}) e^{i (\vec{k} - \vec{k}') \cdot \vec{x}} \Gamma (\vec{x}) d\vec{x},
\]

where \( n \) and \( m \) are band indices, \( A \) is the Born-von Karman cross-sectional area, and \( \hat{u} \) is the restriction of \( u \) to the periodic cell,

\[
0 < x_a < L_a, \quad 0 < x_b < L_b.
\]
The key observation is that we can transform $\Gamma_{L,R}$ using only the periodic portions $\hat{u}$ of the eigenbasis restricted to the periodic cell, and in fact do not need to keep track of the $k$-dependent complex exponentials.

As in [8], after basis change, the CAPs (6) are no longer expected to be diagonal between different bands $n$ and $m$, so in equation (3) we must multiply the blocks of $\hat{\Gamma}_{L,R}$ for each subspace of fixed $\vec{k}$. But each matrix inside the trace in equation (3) is at least diagonal over $\vec{k}$, so the trace over $\vec{k}$ merely entails performing an independent multiplication and subspace trace for each sampled value of $\vec{k}$. As a result, $k$-space integration can be performed by computing the transmission $T_{\vec{k}}(E)$ for each sampled $k$-point, and averaging $T_{\vec{k}}(E)$ over the sampled $k$-points to estimate $T(E)$, as is generally the case for $k$-averaged quantities [14].

We therefore express the Bloch state (1) as a tensor product
\[ |U_{n,\vec{k}}\rangle = |u_{n,\vec{k}}\rangle \otimes |\vec{k}\rangle. \tag{7} \]
Here the tensor product is understood as connecting two disjoint parts of Hilbert space, in the sense that $|\vec{k}\rangle$ has $\vec{k}$ lying within the first Brillouin zone (FBZ), whereas the periodic function $u_{n,\vec{k}}$ can be Fourier expanded into reciprocal lattice vectors outside the FBZ [15]. We likewise decompose $H_{KS}$ into a sum of tensor products of parts $H_{\vec{k}}$ that operate only on $|u_{n,\vec{k}}\rangle$, and projection operators that select the $|\vec{k}\rangle$ component:
\[ H_{KS} = \frac{A}{(2\pi)^2} \int_{\vec{k} \in FBZ} H_{\vec{k}} \otimes |\vec{k}\rangle \langle \vec{k}| \ d^2\vec{k}, \tag{8} \]
where
\[ H_{\vec{k}} = V_{KS}(\vec{x}) + \frac{\hbar^2}{2m} \left( \nabla^2 + \vec{k}^2 - 2i\vec{k} \cdot \nabla \right), \tag{9} \]
within the periodic cell [15].

2.2. Transmission within a subspace of constant $\vec{k}$
We wish to substitute equation (6) into (3), so as to express $T(E)$ in terms of $|u_{n,\vec{k}}\rangle$. As in [8], our main computational problem is partial diagonalization of $G^{-1}$ in the neighborhood of the Fermi energy, $E_F$. In the present problem, this model is modified by restricting $H_{KS}$ to each respective sampled $\vec{k}$-point, as in (9) and the discussion above.

However, note that the transmission formulas of [8], and its orthonormalization convention for the eigenvectors $U$, assume $G^{-1}$ to be complex symmetric. By contrast, equation (9) is Hermitian but not real (not time-reversible), so $H_{\vec{k}}$ is not symmetric, $H_{\vec{k}} - i\Gamma$ is not complex symmetric, and the $|u_{n,\vec{k}}\rangle$ are not biorthogonal. We seek to restore complex symmetry by rearranging equation (8):
\[ H_{KS} = \frac{A}{(2\pi)^2} \int_{FBZ} H_{\vec{k}} \otimes |\vec{k}\rangle \langle \vec{k}| + H_{-\vec{k}} \otimes |\vec{k}\rangle \langle -\vec{k}| \ d^2\vec{k} \]
\[ = \frac{A}{(2\pi)^2} \int_{FBZ} 2 \Re \left\{ H_{\vec{k}} \otimes |\vec{k}\rangle \langle \vec{k}| \right\} \ d^2\vec{k}. \tag{10} \]
Here the integration domain is half the FBZ:
\[ \text{FBZ}_+ \equiv \vec{k} \in \{ \text{FBZ} | k_n \geq 0 \}, \]
but we have suppressed special treatment of points like $\vec{k} = 0$ for simplicity of presentation. Therefore, we consider
\[ G_{\vec{k}}^{-1} = EE_1 - 2 \Re \left\{ H_{\vec{k}} \otimes |\vec{k}\rangle \langle \vec{k}| \right\} + i\Gamma, \tag{11} \]
which acts on both $|u_{\pm,\vec{k}}\rangle$ for each sampled value of $\vec{k}$ in the integration domain of (10), and by construction is complex symmetric.

With the rearrangement (10) and the definition (11), we can obtain a biorthogonal basis of eigenvectors for $G_{\vec{k}}^{-1}$, as in [8]. By inspection, we propose these to have the form
\[ |v_{\gamma\vec{k}}\rangle_+ = \frac{1}{\sqrt{2}} \left( |u_{\vec{k}}\rangle \otimes |\vec{k}\rangle + |u_{\vec{k}}\rangle \otimes |\vec{k}\rangle \right), \]
\[ i|v_{\gamma\vec{k}}\rangle_- = \frac{1}{\sqrt{2}} \left( |u_{\vec{k}}\rangle \otimes |\vec{k}\rangle - |u_{\vec{k}}\rangle \otimes |\vec{k}\rangle \right). \tag{12} \]
Note that $|v_{\gamma\vec{k}}\rangle_-$ is undefined for the $\Gamma$ point, $\vec{k} = 0$, since here $\vec{k} = -\vec{k}$.

To validate the form of (12) as eigenvectors, we must confirm that $|u_{\pm,\vec{k}}\rangle$ lie in the same eigenspace, i.e. share the same eigenvalue. We start by considering the eigenvectors $|u_{\pm,\vec{k}}\rangle$ and eigenvalues $\epsilon_{\pm,\vec{k}}$ of $H_{\vec{k}}$ without $\Gamma$. These are, of course, the KS-DFT eigenpairs of the one- or two-dimensional periodic DFT calculation without CAPs. Because $H_{\vec{k}}$ is Hermitian and $H_{-\vec{k}} = H_{\vec{k}}^\dagger$ in the real-space basis employed by TRANSEC, time-reversal symmetry or complex conjugation of the eigenvalue equation show that $|u_{\vec{k}}\rangle \propto |u_{\vec{k}}\rangle$ and $\epsilon_{\vec{k}} = \epsilon_{\vec{k}}^*$. Thus, both $H_{\vec{k}}$ have the same eigenvalue $\epsilon_{\vec{k}}$, albeit different eigenvectors, and the linear combinations $|v_{\gamma\vec{k}}\rangle_{\pm}$ remain eigenvectors of $\Re \{H_{\vec{k}} \otimes |\vec{k}\rangle \langle \vec{k}|\}$.

2.3. With $R_{\pi,\pi}$ symmetry
The time-reversal symmetry we have used to relate $|u_{\vec{k}}\rangle$ to $|u_{\vec{k}}\rangle^*$ is present in equilibrium KS-DFT, but broken in the electronic transport problem. However, although the addition of the CAPs $i\Gamma$ breaks time-reversal symmetry of the Hamiltonian, $\epsilon_{\vec{k}}$ remain equal. This is manifestly true when $V_{KS}$ respects $C_2$ symmetry about the transport axis, i.e. when $V_{KS}$ is symmetric under rotation by $\pi$ about $z$, or equivalently 2D inversion in the $xy$-plane, which maps between $\pm \vec{k}$. For clarity, we will refer to this as the $R_{\pi,\pi}$ symmetry operation, rather than by the usual point-group symbol $C_2$. With $R_{\pi,\pi}$ symmetry, $|u_{\vec{k}}\rangle$ and $|u_{\vec{k}}\rangle^*$ are both eigenvectors of $H_{\vec{k}} + i\Gamma$ with the same eigenvalue $\epsilon_{\vec{k}}$, so $|v_{\gamma\vec{k}}\rangle_{\pm}$ continue to be eigenvectors of equation (11).

Now that we have validated the form of the vectors $|v_{\gamma\vec{k}}\rangle_{\pm}$ for the case with $R_{\pi,\pi}$ symmetry, we wish to check their normalization in preparation to apply the transformations (4). Different
valid, as we now show by treating the decaying CAPs in the form (16) above. So normalizing (12):

\[ |v^\gamma_\pm\rangle = \frac{|u^\gamma_\pm\rangle \cdot (|u^\gamma_-\rangle + |u^\gamma_+\rangle |u^\gamma_-\rangle}{2} \]

while \(|v^\gamma_\pm\rangle \cdot |v^\gamma_\mp\rangle = 0\). Here we use notation where a dot product represents the biorthogonal scalar product of two KS states: \(|a\cdot b\rangle \equiv \int a(x) \overline{b(x)} \, dx\), while the bracket represents the standard inner product: \langle a|b \rangle = \langle a^*|b \rangle. Thus, if \(|u^\gamma_{+}\rangle \) is normalized against \(|u^\gamma_-\rangle \) via the biorthogonal scalar product, the \(|v^\gamma_\pm\rangle\) are properly normalized also.

By contrast, transforming \(\Gamma\) to \(\tilde{\Gamma}\) proceeds according to equation (4), and can mix different bands \(n\) and \(m\):

\[
\tilde{\Gamma}_{\lambda,n\bar{k}_\pm,m\bar{k}_\pm} = \pm (v^\lambda_{n\bar{k}} \Gamma_{\lambda} v^\lambda_{m\bar{k}}) \pm \frac{\delta^2 \left( \tilde{k} - \tilde{k}' \right)}{2A} \left\{ |u^\lambda_{n\bar{k}}\rangle \Gamma_{\lambda} |u^\lambda_{m\bar{k}}\rangle + \langle u^\lambda_{m\bar{k}}| \Gamma_{\lambda} |u^\lambda_{n\bar{k}}\rangle \right\} \\
= \frac{\delta^2 \left( \tilde{k} - \tilde{k}' \right)}{A} \langle u^\lambda_{n\bar{k}}| \Gamma_{\lambda} |u^\lambda_{m\bar{k}}\rangle.
\]

Here we have reduced each \(\Gamma_{\lambda,R}\) expression to a single term by making use of \(|u^\lambda_{n\bar{k}}\rangle \propto R_{\pi} |u^\lambda_{m\bar{k}}\rangle\), which is valid only when \(R_{\pi}\) symmetry is present, and of \([R_{\pi}, \Gamma_{\lambda,R}] = 0\), which is always true. Substituting these expressions into (3), and following [8], we see that

\[
T_\xi(E) = \sum_{n,m}^{N} \tilde{\Gamma}_{L,n\bar{k},m\bar{k}} \tilde{\Gamma}_{R,n\bar{k},m\bar{k}} \frac{1}{(E - \epsilon_{n\bar{k}}^r) (E - \epsilon_{m\bar{k}}^r)}.
\]

In practice, the summation can be restricted to a small fraction \(p\) of the total of \(N\) bands (where \(N\) is the dimension of the simulation), having \(\epsilon_{m\bar{k}}^r\) and \(\epsilon_{n\bar{k}}^r\) in the neighborhood of \(E_F\) [8].

### 2.4. Lacking \(R_{2\pi}\) symmetry

\(R_{2\pi}\) symmetry is absent from many important atomic systems, for example most non-twin grain boundaries we wish to study, and even some bulk orientations. Without \(R_{2\pi}\) symmetry, we have no definite relationship between \(|u^\lambda_{i\bar{k}}\rangle\), and consequently, our method must expend additional computing time to solve for both \(|u^\lambda_{i\bar{k}}\rangle\), as described in the appendix. Still, the form (12) of the biorthogonal eigenvectors of \(G_{\xi}^{-1}\) remains small perturbation [8] in equation (11). Moreover, the explicit computations presented in section 4 below serve to demonstrate that \(\epsilon_{1\bar{k}}^r\) are equal in practice.

We argue schematically that the eigenvalue corrections \(\epsilon_{M,n\bar{k}}^r\) are equal to all orders \(M\) in perturbation theory (PT) in \(i\Gamma\), and explicitly confirm this for the first- and second-order corrections. All perturbative corrections to both the eigenvalues and vectors are proportional to products and powers of

\[
\langle U_{n\bar{k}}^0 | i\Gamma | U_{m\bar{k}}^0 \rangle = \frac{\delta^2 \left( \tilde{k} - \tilde{k}' \right)}{A} \langle u^0_{n\bar{k}} | i\Gamma | u^0_{m\bar{k}} \rangle,
\]

since \(\Gamma\) is uniform in the \(xy\)-plane, as shown in equation (6). Thus the perturbation \(i\Gamma\) could cause the un-perturbed bands to mix, but not different \(k\)-points, and so should not affect the form of (12). Note that these brackets, and the PT expressions they represent, should be well-defined since the states inside the brackets are un-perturbed, i.e. eigenvectors of the Hermitian operators \(H_{\pm\tilde{k}}\).

Moreover, the perturbation \(i\Gamma\) is anti-Hermitian (since it is purely imaginary and diagonal in the real-space basis):

\[
\langle u^0_{n\bar{k}} | i\Gamma | u^0_{m\bar{k}} \rangle = -\langle u^0_{m\bar{k}} | i\Gamma | u^0_{n\bar{k}} \rangle^* = \langle u^0_{m\bar{k}} - \tilde{k} | i\Gamma | u^0_{n\bar{k}} - \tilde{k} \rangle, 
\]

as can also be seen explicitly from complex conjugation of equation (6). Here the last equality follows from \(|u^0_{\tilde{k}}\rangle \propto |\bar{u}^0_{\tilde{k}}\rangle\), which is true for the un-perturbed states, and from \(-i\Gamma^* = +i\Gamma\).

In particular, the \(M\)-th-order PT eigenvalue correction \(\epsilon_{M,n\bar{k}}^r\) depends on a sum of fractions like

\[
\sum_{m_1, \ldots, m_{M-1}}^{n_{M-1} = n} \left( \langle u^0_{n\bar{k}} | i\Gamma | u^0_{m_1\bar{k}} \rangle \ldots \langle u^0_{m_{M-2}\bar{k}} | i\Gamma | u^0_{m_{M-1}\bar{k}} \rangle \right),
\]

where there are \(M\) brackets in the numerator and \((M-1)\) factors in the denominator. Equation (17) implies that motion reversal \(\tilde{k} \rightarrow -\tilde{k}\) transposes each bracket in the numerator, which rearranges the summation indices \(m_1, \ldots, m_{M-1}\), but leaves the sum overall unchanged. Hence, we argue that to each order \(M\) in PT, \(\epsilon_{M,n\bar{k}} = \epsilon_{n\bar{k}}^r\). For example, the first-order eigenvalue correction is equal for \(\pm\tilde{k}\):

\[
\epsilon_{n\bar{k}}^r = \langle u^0_{n\bar{k}} | i\Gamma | u^0_{n\bar{k}} \rangle = \langle u^0_{n\bar{k}} | i\Gamma | u^0_{n\bar{k}} \rangle = \epsilon_{n\bar{k}}^r.
\]

Likewise, the second-order eigenvalue correction \(\epsilon_{n\bar{k}}^r\) is a sum over \(m \neq n\) of terms proportional to \(|\langle u^0_{n\bar{k}} | i\Gamma | u^0_{m\bar{k}} \rangle|^2\), so equation (17) shows that \(\epsilon_{n\bar{k}}^r = \epsilon_{n\bar{k}}^r\). As a result, \(|u^0_{\pm\tilde{k}}\rangle\) continue to be degenerate, and the linear combinations (12) remain eigenvectors of (11).

We also note that the un-perturbed states \(|u^0_{\pm\tilde{k}}\rangle\) are complex conjugates of each other, but have the same real eigenvalue \(\epsilon_{n\bar{k}}^r\) due to time-reversal symmetry. However, the perturbed states are not complex conjugates since the \(i\Gamma\) term
in (11) retains its sign when $\vec{k}$ is reversed. Evidently the perturbed $|v_{n,\vec{k}}\rangle$ and $|v_{m,\vec{k}}\rangle^* \propto \hat{R} \vec{k}$ would instead be eigenvectors of $G_{\vec{k}}^{-1}$ and $G_{\vec{k}}^{-1*}$, respectively (corresponding to the retarded and advanced Green’s functions), with conjugate eigenvalues.

When $R_{c,\pi}$ symmetry is absent, the trace formula (16) must be modified to include cross terms between $|v_{n,\vec{k}}\rangle$ and $|v_{m,\vec{k}}\rangle^*$ having the schematic form $\pm (v|G|v)^\pi$, which are antisymmetric under interchange of $+$ and $-$. To this end, we consider a formula for such cross contributions in the CAP basis change:

$$\tilde{\Gamma}_{L,m\vec{k}\pm, m\vec{k}\pm} = \pm (v_{n,\vec{k}}|\Gamma_L|v_{m,\vec{k}})^\pi$$

$$= \pm \frac{\delta^2}{2\delta \vec{k}} \left\{ (u_{n,\vec{k}}^*|\Gamma_L|u_{m,\vec{k}}) - (u_{m,\vec{k}}^*|\Gamma_L|u_{n,\vec{k}}) \right\},$$

$$\tilde{\Gamma}_{R,n\vec{k}\pm, n\vec{k}\pm} = \pm (v_{n,\vec{k}}|\Gamma_R|v_{m,\vec{k}})^\pi$$

$$= \pm \frac{\delta^2}{2\delta \vec{k}} \left\{ (u_{n,\vec{k}}^*|\Gamma_R|u_{n,\vec{k}}) - (u_{n,\vec{k}}^*|\Gamma_R|u_{n,\vec{k}}) \right\}.\quad (19)$$

With $R_{c,\pi}$ symmetry, $|u_{n,\vec{k}}\rangle \propto R_{c,\pi}|u_{n,\vec{k}}\rangle$, so equations (18) and (19) manifestly vanish, but without $R_{c,\pi}$ symmetry, we must generalize equation (16) to include cross terms:

$$T_{\vec{k}}(E) = \sum_{m,n} \sum_{\alpha,\beta = \pm 1} \Gamma_{L,m\vec{k}\alpha n\vec{k}\beta} \Gamma_{R,n\vec{k}\beta n\vec{k}\alpha} \delta(E - \epsilon_{n,\vec{k} \alpha}),\quad (20)$$

In TRANSEC, we explicitly compute $\tilde{\Gamma}_{m\vec{k}}$ for $m \leq n$, and then require $\tilde{\Gamma}_{m\vec{k}} = \tilde{\Gamma}_{n\vec{k}}^*$. We remark that the summand of (20) is symmetric under transposition of $\alpha$ and $\beta$. In particular, the signs and factors of $i$ in $\Gamma_{\vec{k}}$ cancel those in $\tilde{\Gamma}_{\vec{k}}$, and thus it is unnecessary to keep detailed track of whether these correspond to $\Gamma_{L}$ or $\Gamma_{R}$. Some other details of the implementation in TRANSEC of the methods described in this section are provided in the appendix.

3. Method: mode counting

To validate the method of section 2, we also make use of a mode-counting method to compute the ballistic conductance of bulk materials. The ballistic conductance $G_B$ of a bulk sample of cross-section $A$ is proportional to the number of current-carrying modes in the sample [16]:

$$G_B = \frac{T_B(E_F)}{2eA} = \frac{M(E_F)}{A} = \frac{1}{(2\pi)^2} \int \hat{n}_{\perp} \cdot \vec{z} d^2k_{||},\quad (21)$$

where $G_B$ is the ballistic conductance, $T_B(E)$ is the ballistic transmission at energy $E$, $\hat{n}_{\perp} \propto \nabla_{\vec{k}}E$ is a unit vector normal to the Fermi surface, $\vec{z}$ is a unit vector in the transmission direction, $M(E)$ is the number of forward-moving modes with energy $E$, and the integration domain is the set of points on the Fermi surface with $n_{\perp} \cdot \vec{z} > 0$. Note our convention that $T_B(E)$ and $M(E)$ are per-spin quantities, which explains the factor of 2 in the denominator of the left-hand side of equation (21).

Our mode-counting method computes a discrete approximation to equation (21) based on a Fermi surface constructed from DFT. Our approach is to discretize the Brillouin Zone into tetrahedra, and find the differential element $\Delta k_{||} \approx d^2k_{||}$ of the Fermi surface in each tetrahedron [6, 7]. The integration in equation (21) is thus transformed into a sum of $(\hat{n}_{\perp} \cdot \vec{z}) \Delta k_{||}$ inside the tetrahedra.

Our electronic structure calculation is performed with the Vienna Ab-initio Simulation Package (VASP) [17, 18] DFT code using the local density approximation (LDA). For calculations of the bulk Cu and Rh conductances, we considered the primitive cell of the face-centered cubic (FCC) lattice, and employed a $48 \times 48 \times 48$ Monkhorst-Pack $k$-point grid. When testing for convergence of the $k$-point sampling, we also confirmed that the surface integral equation (21) was converged.

We used VASP to compute the KS energy levels on the Monkhorst-Pack grid in the irreducible Brillouin zone (IBZ). We considered tetrahedra formed from sets of four neighboring $k$-points covering the IBZ, and built the full FBZ by applying symmetry operations on the IBZ. To find the Fermi surface within each tetrahedron, we interpolated the energy $E_n$ of each band $n$ linearly between the four vertices. The Fermi surface is then the surface of constant energy $\{E_n(k) \equiv E_F, \forall n\}$ within the tetrahedron, iterating over bands $n$ to find the bands with energy nearest $E_F$. The resulting Fermi surface projections for Rh in the (110) and (111) planes are shown in figure 1.

The Fermi velocity for band $n$ is given by

$$\vec{v}_{F,n} = \frac{1}{\hbar} \frac{\partial E_n}{\partial k}.\quad (21)$$

We set $\vec{n}_{\perp} = \vec{v}_{F,n}/|\vec{v}_{F,n}|$ as the normal direction of the Fermi surface, for the band $n$ with energy closest to $E_F$, as described above. This method is described in greater detail in [7].
4. Results

We now turn to demonstrating the methods of section 2 with bulk transmission calculations in transition metals, along the (100) and (111) transmission directions of the FCC lattice. Since Cu is computationally amenable and well-understood, we study it in sections 4.1 and 4.2 to validate the PBC method described in section 2, as well as the mode counting method in section 3. In sections 4.3 and 4.4, we turn to tuning the CAPs for Rh, in preparation to study its potential as an alternative interconnect material. Note that the PARSEC and TRANSEC source codes implementing our methods, and example input and output from the simulations we performed, are available online [9, 13].

As pointed out above, we study Cu as a validation of our method, since it is a well-understood material, whereas we study Rh for its technological potential as an alternative interconnect in integrated circuits. We note that, while both materials are transition metals with FCC lattices, Rh has a more complicated Fermi surface (see figure 1), while the Fermi surface of Cu is largely spherical. In addition, Rh differs from Cu because Rh has a higher density of states (DOS) near the Fermi level $E_F$, which helps to compensate for its shorter electron MFP. Rh has been significantly less studied previously, but is now of technological interest, as discussed in the Introduction.

As seen in figures 2 and 4 below, the $T(E)$ curves for bulk Cu and Rh resemble each other, but display a drop at different energies relative to $E_F$. We note that $T(E)$ is related to the material’s DOS and band structure. In particular, as shown by equation (21), a bulk material with ballistic conductance has $T(E)$ governed by the number of bands $M(E)$, i.e. by its DOS. Thus, both figures display a drop in $T(E)$ at energies $E_p$ where the respective materials’ band structures reduce from having multiple bands to having just one. For Cu, this occurs at energies well below $E_F$, whereas for Rh, it occurs at approximately $E_p + 0.5\, \text{eV}$.

The (100) bulk calculations presented in sections 4.1 and 4.3 possess $R_{\pi,\pi}$ symmetry, whereas the (111) bulk, disorder, and point contact calculations presented in sections 4.2–4.4 do not. We also performed other validation tests with $R_{\pi,\pi}$ symmetry intentionally broken, and make extensive use of section 2.4 in our forthcoming work on Rh grain boundaries.

4.1. Bulk FCC Cu

To validate the PBC method described in section 2, we first computed ballistic conductance in bulk FCC Cu in the (100) orientation. For the (100) calculations here and in section 4.3 below, we used a tetragonal periodic simulation cell. Specifically, the lattice vectors for the lateral PBCs are the primitive cell for the two-dimensional lattice of a (100) monolayer, pointing from the vertices of the cubic lattice to the face-centers of two adjacent cubic cells. Thus, the two lateral cell axes are rotated so the basic repeating unit contains only two atoms, compared to four in the cubic unit cell. Meanwhile, the transmission dimension aligns with the (001) direction of the usual FCC unit cell. We chose this geometry because it is analytically simpler than the 3D primitive cell, having orthogonal lattice vectors, but has a smaller cross-section than the cubic unit cell so as to reduce the computational burden. Of course, this choice of simulation cell orientation is not expected to affect any physical results of the calculation.

The Cu lattice constant was chosen as $a_{Cu} = 6.77\, \text{a}_0$, the result of a lattice constant optimization of the bulk primitive cell. Thus, the tetragonal simulation cell used 2D PBCs with orthogonal lattice vectors of length $a_{Cu}/\sqrt{2} = 4.79\, \text{a}_0$ pointing towards two adjacent face centers. The calculation used 18 monolayers along the transport dimension, for a total length of $17\, a_{Cu}/2 = 57.5\, \text{a}_0$ between the first and last layer. In the transport dimension, we padded the cell length with an additional $8.8\, \text{a}_0$ of vacuum on each end to allow the outermost orbitals to decay, resulting in a total cell length of $75\, \text{a}_0$.

Our DFT calculation in PARSEC used LDA and $11 \times 11 \times 11$ $k$-point sampling. We used a norm-conserving Troullier-Martins pseudopotential for Cu with electronic configuration of $3d^{10}4s^24p^0$ and $s/p/d$ cutoff radii of $2.05/2.30/2.05\, \text{a}_0$. We used a grid spacing of $h = 0.37\, \text{a}_0$, after checking for convergence in the bulk primitive cell, so the simulation cell contained a total of $N = 29\, 100$ grid points.

For the transmission calculation, the results presented here used Gaussian CAPs, as in equation (2), centered on the outermost Cu monolayers, with strength $\Gamma_0 = 100\, \text{mRy}$ and standard deviation $\sigma = 8.5\, \text{a}_0$, providing contact regions of approximately $57.5\, \text{a}_0/(2 \times 8.5\, \text{a}_0) = 3.4$ standard deviations for each CAP to decay before the central region. We also tested for convergence of the contact length. In addition, we performed calculations using $\Gamma_0 = 77\, \text{mRy}$, $\sigma = 7.6\, \text{a}_0$ and $\Gamma_0 = 120\, \text{mRy}$, $\sigma = 9.2\, \text{a}_0$, and found the $T(E)$ results were very insensitive to these different choices, an indication that the CAP parameters are valid [8]. We computed a fraction $p = 2\%$ of total complex eigenpairs [8], and tested this fraction for convergence. Both DFT and transmission used an $11 \times 11 \times 11$ Monkhorst-Pack grid, for a total of 61 $k$-points after application of $R_{\pi,\pi}$ symmetry.

Figure 2(a) shows the computed transmission $T(E)$ for bulk FCC Cu in the (100) orientation. Also shown for comparison are results from OpenMX [19, 20]; PWCOND [21] using electronic structure from Quantum Espresso [22]; TranSiesta [23] using double-zeta polarized orbitals; and our mode-counting method (see section 3) using electronic structure from VASP. Note that we performed the TranSiesta calculation for the (111) orientation, but $T(E)$ for this orientation is similar to $T(E)$ for (100). The other (100) calculations shown used the same tetragonal lattice vectors as the TRANSEC calculation. Also note that PWCOND uses boundary value matching, TranSiesta uses self-energies to represent the electrodes, and OpenMX implements a mode-counting method similar to the one described in section 3 for ballistic calculations. Therefore, none of these calculations used CAPs, so all used shorter simulation cells in the transmission dimension than our TRANSEC calculations. As shown, these calculations agree with the TRANSEC calculation.

We find a ballistic conductance per unit cross-sectional area of $T_B / A = T(E_F) / A = 0.93$ / (4.79 $\text{a}_0)^2 = 0.041 \text{a}_0^{-2}$. This finding is also in agreement with the findings of Xu et al [24], as well as with a simple Sommerfeld model [15] under the
assumption that the Cu Fermi surface is modeled by a spherical shell with a radius equal to the length of the Fermi wavevector $k_F$, and that Cu has one conductance electron per atom. Thus, in this model, the conduction electron density is $n = 4 / a_{Cu}^2 = k_F^3 / 3\pi^2$, and $M(E_F) / A$ is given by the cross-section of the Fermi sphere (see section 3 above). Applying Gauss’ Theorem in equation (21), we derive

$$\frac{M(E_F)}{A} = \frac{\pi k_F^2}{4\pi^2} = \frac{(12^{2/3}\cdot\pi)^{1/3}}{4 a_{Cu}^2} = 0.042 a_0^{-2},$$

in good agreement with the $T(E_F)/A$ results in figure 2(a).

Figure 2(b) shows the density of states (DOS) as a function of energy $E$ (blue curves). Also shown are results from OpenMX (red), OpenMX, PWCOND, and TranSiesta, respectively. We computed each DOS by preparing a histogram of the KS eigenvalues from the corresponding electronic structure calculation. The total number of KS eigenvalues (and therefore the integral of the DOS over all energies) equals the product of the number of bands and $k$-points computed. However, because comparison of these numbers is complicated by the various simulation cell volumes, $k$-point sampling grids, energy ranges, and valence configurations in the different calculations, we normalized each DOS curve to a peak height of 1 in arbitrary units near $E_F - 1.8$ eV. As expected, any quantitative variation among the ballistic $T(E)$ curves in figure 2(a) evidently corresponds to variation among the computed electronic structures reflected in the DOS. For example, the drops in $T(E)$ occur at roughly the same energies as the drops in the DOS.

4.2. Periodic Cu structures with disordered layers or vacancy scatterers

We have also repeated transmission calculations in bulk (100) Cu structures with disordered layers or vacancies, using the same scattering region geometries as used previously in [4]. In particular, the disordered structures had 3 or 6 central monolayers with added random disorder of root mean square (RMS) deviation 0.45 $a_0$, and the vacancy structures had one vacancy per 68.8 $a_0^2$ of the cross-sectional area. Figure 3 shows the structures. For these calculations, we continued to use CAPs with $\Gamma_0 = 100$ mRy and $\sigma = 8.5 a_0$, as in section 4.1. Because of slight variations in the geometry or lattice constants, we repeated the ballistic calculations for the electrodes.

We found reflection probabilities $R = 1 - T(E_F) / M(E_F) = 7\%$ for 3 disordered layers and $R = 13\%$ for six disordered layers, in fair agreement with [4], which reported $R = 3\%$ and
12%, respectively. For the vacancy, we found $R = 14\%$, in good agreement with [4], which reported $R = 16\%$.

We consider these successful ballistic and scattering results in Cu to be a validation of the PBC method described in section 2. In the remainder of this article, we determine and validate CAPs for use with bulk Rh electrodes. In our forthcoming work, we will use these validated CAPs to calculate reflection probability across Rh grain boundaries.

### 4.3. Bulk FCC Rh

Next, we performed simulations of ballistic conductance in bulk FCC Rh in the (100) and (111) orientations. For the Rh electrodes in (100) orientation, we used the same geometry as in the Cu bulk calculations of section 4.1, but scaled the lattice constant to $a_{Rh} = 7.26\, a_0$ as optimized in a bulk primitive cell, and scaled all lengths and atomic coordinates accordingly. Thus, the cell had a cross-section of $5.13\, a_0 \times 5.13\, a_0$ and was $61.7\, a_0$ long from the first to the last monolayer, with a total cell length of $87\, a_0$ including vacuum. We continued to use a $0.37\, a_0$ grid spacing and $11 \times 11$ $k$-point sampling, resulting in $N = 33\, 700$ grid points.

For DFT, we used the LDA. We used a norm-conserving Troullier–Martins pseudopotential for Rh with an electronic configuration of $4d^{10}5s^15p^6$ and $s/p/d$ cutoff radii of $2.38 / 2.57$ / $2.38\, a_0$. For transmission, we used CAPs centered on the outermost monolayers, with strength $\Gamma_0$ in the range of 90 to 100 mRy and standard deviation $\sigma$ of 6.3 to 8.5 $a_0$, providing contact regions of at least 3.6 standard deviations for each CAP to decay before the central region. To explore the stability of our chosen CAP parameters, we also present $T(E)$ results using strength $\Gamma_0$ in the range of 50 to 120 mRy and standard deviation $\sigma$ of 4.8 to 12.0 $a_0$. We computed a fraction $p = 2\%$ of total complex eigenpairs, and tested this for convergence.

Figure 4(a) shows transmission for bulk FCC Rh in the (100) orientation using $\Gamma_0 = 90$ mRy, $\sigma = 6.3\, a_0$. Also shown for comparison are results from PWCOND, OpenMX, and our mode-counting method.

Figure 4(b) shows several $T(E)$ curves we generated with various CAP parameters. One way we validate our choice of CAPs is by determining a region of stability where $T(E)$ is relatively insensitive to the CAP parameters [8]. As shown in figure 4(b), $T(E)$ is stable for CAPs in the region $\Gamma_0 = 90$ mRy to 120 mRy, and $\sigma = 6.3\, a_0$ to 9.2 $a_0$. However, unlike the nanowire calculations reported in [8], here $T(E)$ displays insensitivity to $\Gamma_0$, yet scales monotonically over a range of $\sigma$ values. For example, the three curves with $\Gamma_0 = 120$ mRy (the dotted orange curve with $\Gamma_0 = 120$ mRy, $\sigma = 12\, a_0$), the violet curve with $\sigma = 9.2\, a_0$, and the brown curve with $\sigma = 6.3\, a_0$ are quite different from each other, despite having the same CAP strength. By contrast, the curve with $\Gamma_0 = 120$ mRy, $\sigma = 9.2\, a_0$ is very similar to the dotted black curve with $\Gamma_0 = 150$ mRy, $\sigma = 9.2\, a_0$, and the curve with $\Gamma_0 = 120$ mRy, $\sigma = 6.3\, a_0$ is very similar to the dark blue curve with $\Gamma_0 = 90$ mRy, $\sigma = 6.3\, a_0$. For the remaining Rh calculations in this work, we use $\Gamma_0 = 90$ mRy, $\sigma = 6.3\, a_0$.

A second way we validate our choice of CAPs is by comparing $T(E)$ to accepted values and to calculations we performed using the mode counting method, as described in section 3 above. Figure 4(a) shows results from OpenMX; PWCOND using an electronic structure from Quantum Espresso; and our mode-counting method using an electronic structure from VASP, which are in good agreement with TRANSEC.

We also obtained $T(E)$ for the (111) orientation using TRANSEC, as well as TranSiesta, and our mode-counting method based on electronic structure from VASP. The TRANSEC calculation used an orthogonal $9.7\, a_0 \times 8.4\, a_0$ unit cell, with a total of 134,000 grid points, and used the same CAP parameters as for the (100) orientation, $\Gamma_0 = 90$ mRy and $\sigma = 6.3\, a_0$. We performed the TranSiesta calculation with triple-zeta polarized orbitals. As shown in figure 5, these bulk calculations also agree.
We find a ballistic conductance per unit cross-sectional area of $T(E_F)/A = 0.087 \alpha_0^{-2}$, over twice that of Cu. While this result agrees with our independent calculations presented in figures 4(a) and 5, note that it disagrees with results by Lanzillo, who found that Rh nanowires have only 14% more ballistic conductance per unit cross-sectional area than Cu ones, even in a bulk-like regime where conductance scales linearly with wire cross-sectional area [25]. However, we performed multiple other validation checks of our results, as described here and in the next section [26]. A possible explanation for this discrepancy is the precipitous drop from $T(E_F) = 0.087 \alpha_0^{-2}$ to $T(E_F + 1.1 \text{ eV}) = 0.028 \alpha_0^{-2}$. Because linear-response conductance is governed by $T(E_F)$, a relatively small shift in the $T(E)$ curve along the energy axis could result in a significantly lower predicted conductance. For our PWCOND bulk Rh calculation, we found the $T(E)$ curve shown in figure 4(a) shifted to the left when the plane-wave cutoff energy was not converged, such that $T(E_F)/A \approx 0.06 \alpha_0^{-2}$. In addition, surface or other size effects in the Rh nanowire Lanzillo considers might contribute to this discrepancy, even though Lanzillo reports conductance scaling approximately linearly with cross-section.

Finally, in view of the disagreement with results in [25] and the uncertainties mentioned above regarding the CAP region of stability, we wish to validate our CAPs further. As a more strenuous validation of our CAPs, we have computed transmission in a large Rh point contact with periodic BCs and bulk electrodes, as described in the next section.

### 4.4. Periodic Rh point contact with H as central atom

As further validation of the CAP parameters we identified for Rh (100) bulk electrodes, we computed $T(E)$ in a periodic Rh point contact having Rh (100) electrodes and H as a central ‘device’ atom. This calculation also serves as a demonstration of the real-space PBC method in a large, periodic transition metal nanostructure without $R_{c,\pi}$ symmetry.

As in [8], we rely on analytical understanding of the point contact transmission to validate results from TRANSEC. In particular, we choose H for the central atom since it has only a single electron, and so must have unit transmission at the Fermi level, provided it is distant from the two electrodes and from its own periodic image. In choosing a central H atom, we thus circumvent any uncertainty in the value of $M(E_F)$ of the Rh electrodes.

The geometry of this system is shown in figure 6. For sufficiently large gaps between the electrodes and device atom, the central device atom’s KS orbitals approach those of an isolated H atom. As a result, transmission near $E_F$ is dominated by the H atom’s hybridized $1s$ orbital, with a Lorentzian-shaped peak of height 1, and a width depending on the electrode-device gap. As shown, the central H atom is positioned slightly off-center, thereby breaking $R_{c,\pi}$ symmetry. Because we continued to use a ‘slab’ geometry with periodic BCs in the lateral dimensions, the electrodes comprised of bulk (100) Rh far from the central region, identical to those in section 4.3. Thus, we continued to use our previously-tuned CAP parameters.

Despite using bulk electrodes, in the limit of large lateral cross-section, we expect the transmission peak not to be modified by communication among the device atom and its periodic images—a point we now address in greater depth. We find that when performing this calculation with a smaller cross-section of $10.26 \alpha_0 \times 10.26 \alpha_0$, the $k$-point-averaged peak $T(E \approx E_F)$ is about 20% lower than expected, even though each individual $k$-point resolved transmission curve $T_k(E)$ correctly displays a peak of unit height and approximately Lorentzian shape. Since the individual peaks do have height of 1, the low average is attributed to poor peak location alignment. We attribute this misalignment, in turn, to communication between the central H atom and its periodic images. In the limit of large cross-section, we anticipate that any electronic-structure band formed from different $k$-points should flatten and the individual $T_k(E)$ curves become identical, resulting in an averaged peak height of 1.

Therefore, we present a calculation of the point contact structure shown in figure 6. For this calculation, the simulation cell was $3 \times 3 \times 3$ larger than the tetragonal cells described in sections 4.1–4.3, giving lateral dimensions of $\frac{15.40}{\alpha_0} \times \frac{15.40}{\alpha_0} \times \frac{15.40}{\alpha_0} = 15.40 \alpha_0 \times 15.40 \alpha_0$ and a total cross-section of $237.2 \alpha_0^2$. Along the transport dimension, we used seven mono-layers, comprising of 63 Rh atoms, for each electrode and...
electrode gaps of 8.3 $a_0$ and 8.8 $a_0$. As expected, the peak height is nearly 1, the peak location is approximately $E_F$, and the peak width narrows as the H atom-Rh electrode gap increases from 8.3 $a_0$ to 8.8 $a_0$. Figure 7(b) shows the k-point resolved transmission $T(E)$ for the calculation with electrode-central atom gap of 8.8 $a_0$. As expected, the peak alignment of $T(E)$ is good, resulting in a peak height of nearly 1 in the average $T(E)$.

In some large point contact calculations, we also encountered difficulties converging $T(E)$ with respect to the number $pN$ of complex eigenpairs solved. We attributed these difficulties to a loss of bioorthogonality among separate eigenspaces, similar to the loss of orthogonality in Lanczos-like algorithms described by Paige’s Theorem [28, 29]. Specifically, we observed that the bioorthogonal scalar product did not vanish between eigenvectors with relatively large eigenvalue separations, as it is expected to do. We found we could fix this issue by explicitly bioorthogonalizing vectors in different eigenspaces. In response to this explicit bioorthogonalization, the $T(E)$ curve converged much more reliably with $pN$. The results shown in figure 7 used $pN = 2085$ complex eigenpairs, and we tested this number for convergence.

We also performed an even larger point contact calculation using a rectangular cross-section of $3 \times 2$ cubic cells, for a total cross-sectional area of 316.2 $a_0^2$, and a total of 500,000 grid points. This structure contained 84 Rh atoms in each electrode, and used a $2 \times 3$ Monkhorst-Pack grid. This calculation also displayed good alignment of the k-point resolved peaks $T(E)$, an averaged $T(E)$ peak of approximately 1, and a peak width depending on the electrode-central atom gap, as expected analytically.

5. Conclusions

As discussed above, a real-space approach to electronic transport has advantages [8, 10], including straightforward basis set convergence and efficient parallel scaling capable of treating extended structures. Because of the real-space approach’s large basis set and unambiguous convergence, it can serve as a benchmark against which other transport methods’ accuracy can be tested, as long as any additional approximations specific to this approach are controlled (e.g. the fraction of eigenpairs computed $p$, the grid spacing $h$, and the CAP contact length, which we converged in the calculations presented in section 4).

In addition, our use of CAPs subject to the wide-band limit approximation enables us to compute $T(E)$ at multiple energies $E$ in essentially constant time once the CAPs have been tuned.

It is desirable to extend the real-space method to include PBCs, so as to extend the method’s usefulness to scattering systems with 1- or 2-dimensional periodicity, such as grain boundaries, other interfaces, or bulk materials. In this work, we have described and validated a method to include PBCs in real-space calculations of electronic conductance. We demonstrated this method in bulk Cu and Rh as well as large Rh point contacts with H as the central atom. We developed CAP parameters for bulk Rh electrodes, to be used for Rh grain
boundary simulations in subsequent work. Although the resulting bulk Rh $T(E)$ disagrees with results in [25], we have validated our CAP parameters against numerous calculations with other conductance packages, as well as analytical expectations for the point contact structure.

The calculations presented in section 4.4, with 1100 to 1500 valence electrons and basis sets including 350 000 to 500 000 orbitals, are among the largest we have performed to date with TRANSEC. The calculations were performed on 32 to 40 computing cores, exhibiting good parallel speedup. Thus, the efficient parallel scaling previously demonstrated in cluster structures [8, 10] has also been demonstrated for periodic systems in this work. Indeed, in the PBC calculations, $k$-point sampling provides an additional dimension of ideal parallelization, as discussed in the appendix.

Data availability statement

The data that support the findings of this study are openly available at the following URLs: https://gitlab.com/computational-physics2/TRANSEC/ and https://gitlab.com/computational-physics2/TRANSEC/-/tree/main/Tests/Periodic_BCs_JPCM.

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Appendix. Notes on implementation and parallelization

We have implemented the PBC methods of section 2 in TRANSEC by performing each $k$-point calculation independently. In addition, we have implemented collinear spin polarization, which performs the calculation for each spin independently (but in this work we present only unpolarized calculations of non-magnetic materials). Because the $k$-points and spins are independent (see equations (6) and (7)), the individual $T_{k,s}(E)$ calculations for spin $s$ and lateral Bloch vector $k$ can be performed on separate computing nodes with distributed memory. Hence, the $T_{k,s}(E)$ calculations can be naturally parallelized over $k$ and $s$, or can be performed in serial on the same nodes.

However, a drawback to parallelization is that each $T_{k,s}(E)$ calculation requires its own independent memory, driving up the total memory requirement. The number of parallelization groups should therefore be chosen to balance the available memory and computing time resources. Alternatively, the total memory and/or computing time requirements can be reduced by partitioning the eigenspectrum of individual $T_{k,s}(E)$ calculations, as described in [10].

For the case with $R_{s,s}$ symmetry, the eigenvectors for $+k$ and $-k$ points are closely related, so our calculations are restricted to those $k$-points with non-negative $k_x$, reducing the computational burden by about half. For the case without $R_{s,s}$ symmetry, separate eigensolutions must be performed for both $+k$ and $-k$ points. But as equations (18)–(20) show, the eigenpairs for both $+k$ and $-k$ points must be combined to determine $T_{k}(E)$. As a result, we prefer to perform $+k$ and $-k$ eigensolutions in serial in the same parallelization group, so as to avoid additional communication and load-balancing issues when combining the eigenpairs. However, we have implemented automated parallelization of the $+k$ and $-k$ eigensolutions in the relatively rare cases when the calculation as a whole can be performed in less elapsed time this way.

The computed eigenpairs for $+k$ are then matched to those for $-k$ by determining the best agreement between respective eigenvalues in these two sets, while discarding or otherwise resolving spurious or missing eigenpairs that have no sufficiently close match. We find that the matching eigenvalues generally agree to about $10^{-5}$ of the next-best match. For the $\Gamma$-point, i.e. $k = 0$, even without $R_{s,s}$ symmetry it is only necessary to perform the eigensolution once, since $k = -k$, so if practical we balance the computing load by assigning a greater share of $k$–points to the group with the $\Gamma$-point.

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