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Comment on “Rethinking first-principles electron transport theories with projection operators: The problems caused by partitioning the basis set” [J. Chem. Phys. 139, 114104 (2013)]

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I. INTRODUCTION

Reuter and Harrison (RH)1 argue that a certain “decoupling condition” is required to be fulfilled in order to obtain correct results in transport calculations which employ an non-orthogonal basis (NOB) set, such as Ref. 2 and related in Ref. 1. The implicit assumption (decoupling condition) put forth by RH reads

$$\hat{N}_L \hat{H} \hat{N}_R = 0,$$  (1)

and violation is claimed to cause a “short circuit” problem. Here $\hat{N}_{L/R}$ are projection operators onto $L/R$ regions defined in real-space, and $\hat{H}$ is the Hamiltonian operator describing the full system coupled via region $C$ (see Fig. 1). RH state that their “short-circuit” problem resembles the ambiguity of assigning charge to atoms or regions in charge population analysis. Below we argue that this ambiguity problem does not carry over to calculations of charge flux.

We point out that Eq. (1) does not enter the NEGF derivations of current.3 It is clear for infinitely separated $L$ and $R$ regions, we should be able to partition the system into scattering regions, we should be able to partition the system into scattering regions, we should be able to partition the system into scattering regions, we should be able to partition the system into scattering regions. Below we argue that this ambiguity problem does not enter the NEGF derivations of current.3 It is clear for infinitely separated $L$ and $R$ regions, we should be able to partition the system into scattering regions, we should be able to partition the system into scattering regions, we should be able to partition the system into scattering regions. Below we argue that this ambiguity problem does not enter the NEGF derivations of current.

II. NONORTHOGONAL BASIS SET

We will argue that Eq. (2) can be violated while we obtain the exact transmission. First we consider a NOB chain-model with nearest neighbour hopping,7 and overlap (matrix elements $t$, $s$). It can be shown that the range of the effective hopping, $(|S^{-1}HS^{-1}|)_{ij} \propto ts^{ij} - \delta_{ij}$, is infinite, although rapidly decaying. This demonstrates how Eq. (2) is only possible as an asymptotic limit. On the other hand, the transmission can be calculated analytically exact7 for this model by the EK method using a 1-site region for $C$ thus explicitly violating Eq. (2).

Next, we consider an OB and an arbitrarily big central $C$ region (Fig. 1). The transmission in terms of quantities defined inside $C$, reads3,11

$$T = \text{Tr}[\Gamma_L \tilde{G} \Gamma_R \tilde{G}^\dagger].$$  (3)

All matrices are given in the OB (denoted by a bar). Now we rotate the basis set to introduce an overlap matrix between the orbitals inside $C$ using an “inverse” Löwdin transformation11 from the OB to the NOB,

$$T = \text{Tr}[S^{-1}_L \tilde{\Gamma}_L S^{-1}_R \tilde{S} \tilde{G} \tilde{S}^{-1}_R \tilde{S}^{-1}_L \tilde{\Gamma}_R \tilde{S} \tilde{S}^{-1}_L \tilde{S}^{-1}_R \tilde{G}^\dagger \tilde{S}^\dagger \tilde{S}^{-1}_L \tilde{S}^\dagger \tilde{S}^{-1}_R \tilde{G}^\dagger \tilde{S}^\dagger \tilde{S}^{-1}_L \tilde{S}^\dagger \tilde{S}^{-1}_R \tilde{G}^\dagger \tilde{S}^\dagger] \equiv \text{Tr}[\Gamma_L \tilde{G} \Gamma_R \tilde{G}^\dagger],$$  (4)

where $G \equiv S^{-1}_L \tilde{G} \tilde{S}^{-1}_R$, $H \equiv S^{-1}_L \tilde{H} \tilde{S}^{-1}_R$, and $\Sigma_{L/R} \equiv S^{-1}_L \tilde{\Sigma}_{L/R} S^{-1}_R$.

We now split region $C$ into $C_1$ and $C_2$. The range in the transport direction of the self-energies, $\Sigma$, in the NOB is that of $H$ and $S$. For a big enough $C$ and a NOB with infinite range, we have zero matrix elements between $L$, 2 and $R$, 1. Thus $\Sigma$ can be written as

$$\Sigma_L = \left( \begin{array}{cc} (\Sigma_{L})_{11} & 0 \\ 0 & 0 \end{array} \right) \text{ and } \Sigma_R = \left( \begin{array}{cc} 0 & 0 \\ 0 & (\Sigma_{R})_{22} \end{array} \right),$$  (5)

which is the typical case, and we have

$$T = \text{Tr}[\Gamma_L \tilde{G} \Gamma_R \tilde{G}^\dagger].$$  (6)

We can write the GF in the NOB,

$$G^{-1} = \left( \begin{array}{cc} g_{11}^{-1} & ES_{12} - H_{12} \\ ES_{21} - H_{21} & g_{22}^{-1} \end{array} \right),$$  (7)

where we introduce the inverse GF for region 1 without coupling to 2, $g_{11}^{-1} = ES_{11} - H_{11} - \Sigma_{11}$, and likewise $g_{22}$. It is
straightforward from (7) to obtain
\[ G_{11} = (g_{11}^{-1} - (ES_{12} - H_{12})g_{22}(ES_{21} - H_{21}))^{-1} \]
\[ = (g_{11}^{-1} - \overline{S}_R)_{11}^{-1} \] (8)

and
\[ G_{12} = -G_{11}(ES_{12} - H_{12})g_{22}, \] (9)
where we have introduced the right self-energy downfolded onto region 1,
\[ (\overline{S}_R)_{11} = (ES_{12} - H_{12})g_{22}(ES_{21} - H_{21}). \] (10)

Using \((\Gamma_R)_{22} = \ell (g_{22}^{-1}) - (g_{22})\), we rewrite Eq. (6) and get a transmission formula for region C = 1 (Fig. 1(b)),
\[ T = \text{Tr}[(\Gamma_L)_{11}G_{11}(\overline{\Gamma}_R)_{11}G_{11}]. \] (11)

Thus we get exactly the same T for the NOB as for the original OB if we treat the overlap in the self-energy as Eq. (10), as is done in the “standard” EK approach.4 We note that for the smaller region, \(C = 1\), we may have high values of \(|(S^{-1}HS^{-1})_{LR}|\) depending on S and H. But this is not relevant for the derivation.

In principle we can start by making a Löwdin transformation of the whole space. This leads to a long ranged H, but we may choose C big enough to ensure that \(H_{LR}\) is as small as we want. In actual calculations we make the C region small, as shown above, and need only to consider the range of H, S.

III. TRANSMISSION THROUGH A SURFACE DEFINED IN REAL-SPACE

The partition of space in terms of the orbitals for a given basis set yields the same result for T compared to a real-space division, when T is calculated with the same basis set. We sketch the proof and refer to Ref. 13 for details. The right flux normalized scattering states (label r) at energy, E, yield the current(T) through a surface, \(\sigma_{12}\), located inside C,
\[ T = \frac{\hbar}{m} \sum_r \int_{\sigma_{12}} d\tilde{r} \cdot (\Psi_r^*(\tilde{r})\tilde{V}\Psi_r(\tilde{r})) \] (12)
\[ = \frac{\hbar}{m} \sum_r \int_{\Omega_r} d\tilde{r} \Psi_r^*(\tilde{r})\tilde{V}^2\Psi_r(\tilde{r}) \] (13)

We have rewritten the surface integral as an integral over region 1. In region 1 \(\Psi_r\) fulfils
\[ \left[ -\frac{\hbar^2}{2m} \nabla^2 + V(\tilde{r}) + \int d\tilde{r}' \Sigma_L(\tilde{r}, \tilde{r}') \right] \Psi_r(\tilde{r}') = E\Psi_r(\tilde{r}), \] (14)
where the integral is over the support of \(\Sigma_L\). Note that \(\sigma_{12}\) is arbitrary as long as it is located within the freely chosen scattering region, and does not overlap with the support of \(\Sigma\). Using Eq. (13) in Eq. (14) we can obtain
\[ T = \frac{\hbar}{m} \int_{\Omega_r} d\tilde{r} \left( \int d\tilde{r}' \Sigma_r(\tilde{r}, \tilde{r}') \right) \] (15)
\[ = \frac{\hbar}{m} \sum_{\Omega_r} d\tilde{r} \left( \int d\tilde{r}' \Sigma_r(\tilde{r}, \tilde{r}') \right) \] (16)

This is similar to the expression found by “embedding.”14

The main point here is the partitioning in terms of a basis set, \(\{\phi_a\}\), which overlap in regions of real space. We write
\[ A_R(\tilde{r}, \tilde{r}') = \frac{1}{\hbar} \sum \Psi_r^*(\tilde{r})\Psi_r(\tilde{r}') = \sum_{\alpha} c_{\alpha r}^* c_{\alpha r} \phi_\alpha(\tilde{r})\phi_\beta(\tilde{r}'), \] (17)

and using the definition of \(A_R\) we immediately obtain,
\[ T = \text{Tr}[\Gamma_L A_R|_\Gamma_R]. \]