Comment on "Critical analysis of a variational method used to describe molecular electron transport"

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Bâldea and Köppel [Phys. Rev. B **80**, 165301 (2009)] have generalized our correlated transport formalism [P. Delaney and J. C. Greer, Phys. Rev. Lett. **93**, 036805 (2004)] to constrain the occupancies of single-electron orbitals, and then claimed that zero conductivity $G = 0$ in linear response follows and that our method is invalid. We show here that it was their incorrect choice to constrain the occupancies of real orbitals that resulted in $G = 0$. In a scattering state incident to a barrier with values at $\pm\infty$ differing by eV, only the incoming plane wave component has the bias-independent amplitude of 1, while the outgoing has r which depends on the voltage V and the barrier geometry. Thus, if occupancies are to be constrained to bias-independent values in transport, those of complex orbitals such as an incoming plane wave on each side are suitable, while real orbitals such as sines are not. This is true whether constant current constraints are additionally imposed or not.

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In a recent paper [1] Bâldea and Köppel have analysed the linear response of our correlated transport formalism,[2] which involves a minimization of an energy functional subject to constraints. Doubting the validity of using the Wigner function constraints to apply open-system boundary conditions, these authors seek to test the variational approach to transport by changing the Wigner constraints to another form. The steps in their argument are as follows:

(1) Generalize our formalism from Wigner constraints F_k to a class $\mathcal{C}$ of Hermitian constraints Q_k.

(2) Analyze the current I predicted in linear response to the voltage V imposed.

(3) Make a particular choice $Q_k^{BK} = \alpha_k^{\dagger \mathrm{BK}} \alpha_k^{\mathrm{BK}} \in \mathcal{C}$.

(4) Show that the linear-response matrix elements $\langle \Psi_n | Q_k^{BK} | \Psi_0 \rangle$ are real.

(5) Deduce that I is zero within linear response.

(6) Conclude that our formalism's minimization of an energy functional is inappropriate, for any boundary conditions.

The key step is (3), for we agree that *if this choice of* Q_k^{BK} *in step (3) is made*, then the matrix elements of step (4) are real, and agree that (4) $\Rightarrow$ (5): in fact, I is zero even beyond linear response. This Comment shows that the particular Q_k^{BK} chosen in step (3) are not a physically correct choice as they fail to break time-reversal symmetry. Hence, the conclusion in step (6) is unjustified.

The deduction (4) $\Rightarrow$ (5) is simply understood mathematically as a consequence of time-reversal symmetry T. Expanding the wave function Ψ in the real basis of Slater determinants Φ_i built from the real molecular orbitals of the junction, we find that our Hamiltonian H is a real matrix in this basis, as are the constraint matrices $\langle \Phi_i | Q_k^{BK} | \Phi_j \rangle$ by the same logic as step (4) and the constraint $\langle \Psi | 1 | \Psi \rangle = 1$ on the norm. Therefore, if Ψ' minimizes $\langle \Psi' | H | \Psi' \rangle$ subject to these constraints, so does Ψ'^*. The variational approach assumes a unique solution Ψ up to an overall phase, so we must have $\Psi'^* = e^{i\theta}\Psi'$ for some real θ. Therefore $\Psi = e^{i\theta/2}\Psi'$ is purely real and carries no current [giving step (5)]. In fact, the current will be zero even beyond linear response: time-reversal symmetry has not been broken. This deduction remains true if we introduce constraints $\langle \Psi | I_i | \Psi \rangle = \langle \Psi | I_{i+1} | \Psi \rangle, i = 1,2,3\ldots$, to ensure the current operators I_i at grid points x_i have the same (unconstrained) expectation value; if Ψ has constant current I at the x_i, then Ψ^* will also have constant current $-I$ there; again, if Ψ is a solution, so is Ψ^*.

Bâldea and Köppel accept that our Wigner constraints $F_k \in \mathcal{C}$ as previously applied have complex matrix elements $\langle \Psi_n | F_k | \Psi_0 \rangle$ and nonzero linear-response current. Thus, choices for constraints having complex matrix elements and nonzero current are very possible, so it is puzzling that Bâldea and Köppel select from their generalized set $\mathcal{C}$ of constraints in step (3) creation and destruction operators α_k^{BK} and $\alpha_k^{\dagger \mathrm{BK}}$ for states $|\alpha_k^{\mathrm{BK}}\rangle$, which give the nonphysical result of zero linear-response current.

Let us examine the $|\alpha_k^{\mathrm{BK}}\rangle$ that Bâldea and Köppel choose in step (3) to get more physical insight into why their current is zero. In their paper,[1] $\alpha_k^{\dagger\,\mathrm{BK}}$ and α_k^{BK} are creation and destruction operators for single-electron states $|\alpha_k^{\mathrm{BK}}\rangle$ in the left electrode, which are obtained by diagonalizing their equation (6),

$$H_L = \mu_L \sum_{l \leqslant q_L, \sigma} a_{l,\sigma}^\dagger a_{l,\sigma} - \sum_{l \leqslant q_L, \sigma} t_{l,\sigma} (a_{l,\sigma}^\dagger a_{l-1,\sigma} + a_{l-1,\sigma}^\dagger a_{l,\sigma}) ,$$

a standard Hamiltonian for a one-dimensional chain with nearest-neighbor hopping. Here, q_L is the index of the right end of this left electrode, μ_L is the on-site energy, $t_{l,\sigma}$ is the hopping matrix element, and σ sums over spin. Their equation (21) again shows that the $\alpha_k^{\dagger \mathrm{BK}}$ and α_k^{BK} create and destroy the eigenstates of H_L; they write

$$H_L = \sum_k \epsilon_k \alpha_k^\dagger \alpha_k,$$

where k runs over the eigenstates of H_L, with eigenvalues ϵ_k. A similar argument applies to the right electrode Hamiltonian H_R, with the replacements $l \to r, \mu_L \to \mu_R$ and $l \leqslant q_L \longrightarrow r \geqslant q_R$. The full Hamiltonian of their paper also has a central region where the electron-electron interaction may be present, and hopping terms between these three regions.

Our discussion will confine itself to the $|\alpha_k^{\rm BK}\rangle$ of the left electrode for simplicity, as the extension to both electrodes is straightforward.

The eigenvalues of such a Hamiltonian H_L, either semi-infinite or finite, as in our calculations and those of Bâldea and Köppel, are singly degenerate and the eigenvectors can be chosen to be purely real. For the finite chain that Bâldea and Köppel consider, the discrete eigenstates go to the form $\alpha_k^{\rm BK}(x) = \sin\frac{k\pi}{L}x$, $k = 1,2,\cdots$, when the density of sites approaches infinity over a left electrode covering $[0,L]$. Real wave functions carry no current, and their choice may raise some warning bells in a transport scheme.

The action of $Q_k^{BK} = \alpha_k^{\dagger \rm BK}\alpha_k^{\rm BK}$ on a one-electron wave function $\psi(x)$ is straightforward:

$$\left[Q_k^{BK}\psi\right](x) = \alpha_k^{\rm BK}(x)\int \alpha_k^{\rm BK*}(x')\psi(x')\,dx' \,. \tag{1}$$

The formula for action on an m-electron wave function $\Psi(x_1,\ldots,x_m)$ is a simple extension:

$$\left[Q_k^{BK}\Psi\right](x_1,\ldots,x_m) = \sum_{i=1,m}\alpha_k^{\rm BK}(x_i)\int dx_i'\,\alpha_k^{\rm BK*}(x_i')\Psi(x_1,\ldots,x_i',\ldots,x_m), \tag{2}$$

that is,

$$Q_k^{BK} = \alpha_k^{\dagger \rm BK}\alpha_k^{\rm BK} = \sum_{i=1,m}\left|\alpha_k^{\rm BK}\right\rangle_i\left\langle\alpha_k^{\rm BK}\right|_i, \tag{3}$$

where each projector $|\alpha_k^{\rm BK}\rangle_i\langle\alpha_k^{\rm BK}|_i$ acts on the ith coordinate. The Q_k^{BK} operators simply count the occupation of these real states $|\alpha_k^{\rm BK}\rangle$. Bâldea and Köppel constrain this occupation number under application of a voltage: another real operator.

The matrix element of these counting operators $Q_k^{BK} = |\alpha_k^{\rm BK}\rangle\langle\alpha_k^{\rm BK}|$ needed in linear response is simply

$$\langle\Psi_n|Q_k^{BK}|\Psi_0\rangle = m\left\langle\Psi_n\left|\alpha_k^{\rm BK}\right\rangle_1\left\langle\alpha_k^{\rm BK}\right|_1\Psi_0\right\rangle \tag{4}$$

$$= m\int dx_1dx_2\cdots dx_m\,\Psi_n^*(x_1,x_2,\ldots,x_m) \times\alpha_k^{\rm BK}(x_1)\int dx_1'\,\alpha_k^{\rm BK*}(x_1')\Psi_0(x_1',\ldots,x_m), \tag{5}$$

where in the first line we use the antisymmetry of the wave functions, and in the next lines the definition of $|\alpha_k^{\rm BK}\rangle_1\langle\alpha_k^{\rm BK}|_1$.

Here Ψ_0 and the Ψ_n are the ground and excited states of the full system of left electrode, centre, and right electrode, and may be sums of many determinants Φ_i if there is electron correlation. Bâldea and Köppel choose Ψ_0 and the Ψ_n to be real functions, as is standard, but then all quantities in Eq. (5) are real and we see clearly why step (4) of their argument is then true: *the orbitals whose occupations they constrain are real*.

The reason why Bâldea and Köppel's choice of $|\alpha_k^{\rm BK}\rangle$ gives zero current I [their step (5)] is now made physically clear. They have decided to constrain the occupations of *real* states of the left electrode of approximate form $\sin\frac{k\pi}{L}x$, which gives real matrix elements $\langle\Psi_n|\alpha_k^{\rm BK}\rangle_1\langle\alpha_k^{\rm BK}|_1\Psi_0\rangle$. However, in transport only the occupations of the *incoming states* are known beforehand, i.e. on the left, states of the form $e^{i\kappa x}$ with $\kappa > 0$. The occupations of the outgoing states $e^{i\kappa x}$ with $\kappa < 0$ are what are to be worked out by the transport calculation and will generally be different. In fact, it is the imbalance between these two sets of occupations that gives the net current, as Fig. 1 (bottom) of Ref. 2 makes clear.

This is why we were careful in our transport formalism to only constrain the Wigner function of the incoming states, i.e. $f(q_L,p>0)$ on the left and $f(q_R,p<0)$ on the right. The Wigner distributions allow us to select between the incoming and outgoing states and it is only the incoming, propagating states that are constrained. Notice that under time reversal $T:\Psi\longrightarrow\Psi^*$, we have $f_\Psi(q_L,p) = \langle\Psi|F(q_L,p)|\Psi\rangle \longrightarrow \langle\Psi^*|F(q_L,p)|\Psi^*\rangle = \langle\Psi|F(q_L,-p)|\Psi\rangle = f_\Psi(q_L,-p)$, where $F(q,p)$ is the operator for which $\langle\Psi|F(q_L,p)|\Psi\rangle$ gives the Wigner function $f_\Psi(q,p)$; that is, time-reversal reflects velocities. Thus, a contraint on only the incoming electrons explicitly breaks time-reversal symmetry T and is necessary to deduce nonzero current in an open quantum system [see Fig. 7(c) of Ref. 3]. In constraining the occupations of states of the form $\sin\kappa x = (e^{+i\kappa x} - e^{-i\kappa x})/2i$, Bâldea and Köppel have constrained both incoming and outgoing electrons symmetrically. This does not allow an imbalance of incoming and outgoing electrons (a net current) to build up. Their inappropriate boundary conditions correspond to Figs. 7(a) and 7(b) of Ref. 3.

Bâldea and Köppel seem to have realized some of this inconsistency in an Erratum to their article, where they state[4] "Here and whenever related to boundary conditions $\cdots$, the label κ obviously refers to electrons flowing from electrodes into the device."

However, it is impossible to constrain only the electrons flowing into the device with the real states $|\alpha_k^{\rm BK}\rangle$ chosen by the authors. Instead, states more like $|\alpha_\kappa^{\rm DG}\rangle = e^{+i\kappa x}$ for $\kappa > 0$ must be constrained. The key point is that the matrix elements are now

$$\langle\Psi_n|Q_\kappa^{\rm DG}|\Psi_0\rangle = m\left\langle\Psi_n\left|\alpha_\kappa^{\rm DG}\right\rangle_1\left\langle\alpha_\kappa^{\rm DG}\right|_1\Psi_0\right\rangle = m\int dx_1\ldots dx_m\,\Psi_n^*(x_1,\ldots,x_m) \times e^{i\kappa x_1}\int dx_1 e^{-i\kappa x_1'}\Psi_0(x_1',x_2,\ldots,x_m), \tag{6}$$

which are generally complex. In summary, having generalized our formalism to a much larger set $\mathcal{C}$ of possible Hermitian constraints Q_k, Bâldea and Köppel have not realized that not all the elements of the set are physically reasonable constraints. It is because they make the unsuitable choice in step (3) of Q_k^{BK}, which count the occupation of real orbitals, that steps (4) and (5) follow. Physically reasonable constraints $Q_k^{\rm DG}$ can be picked from $\mathcal{C}$, but, when one does so, the matrix elements in step (4) become complex, and so the rest of their argument becomes invalid: their deduction in step (5) that I is zero within linear response is incorrect and their conclusion in step (6) that our formalism's energy minimization is inappropriate does not follow.

While we think that Bâldea and Köppel's idea to constrain populations $|\alpha_k\rangle\langle\alpha_k|$ is an interesting alternative to the Wigner

function, our analysis makes clear that it is essential to choose complex states $\alpha_k(x)$. Otherwise, time-reversal symmetry is not broken by the imposition of the constraints, as is necessary to open the system.[3]

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