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

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Delaney and Greer [DG incorrectly assert that in Phys. Rev. B **80**, 165301 (2009)] (denoted as I) we have "generalized" a transport approach proposed by them. In reality, we have *criticized* and demonstrated the complete failure of that approach. The Comment is based on the false supposition that real orbitals are constrained in I. We show that the complex orbitals suggested by DG as a way-out solution merely represent a particular case of the general case considered in I, which do not in the least affect our conclusion. The scattering states mentioned in their abstract in a sentence that is not substantiated by the main text of the Comment pertain to the correct Landauer approach. They have nothing in common with the incorrect DG variational approach. In conjunction with the issues raised by DG, we show that, astonishingly, by uncritically imposing the Wigner constraints in their original work [Phys. Rev. Lett. **93**, 036805 (2004)], DG actually constrained the *outgoing* and not incoming charge carriers, which makes absolutely no sense for transport.

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I. INTRODUCTION

Delaney and Greer (DG) claimed[1] that the current J in a two-terminal setup can be determined by a constrained energy minimization of a finite cluster consisting of the molecule of interest and (small) parts of electrodes (Au_{13}-clusters[1]) subjected to a bias V, completely *decoupled* from an infinite environment. According to DG, one should constrain the current to be position independent, and the distributions of incoming electrons at the left and right boundaries ($q_{L,R}$) for $V \neq 0$ to coincide with those for $V = 0$ of the same finite isolated cluster. By arguing that the single-particle momentum Fermi distributions (FDs) $f_\kappa^{\rm FD}$ can not be employed for correlated systems, they constrained the Wigner function (WF) of incoming electrons $f(q_{L,R}, p \lessgtr 0)$.[1] In our previous works,[2,3] we demonstrated the lamentable failure of this WF approach for the simplest typical models used in nanotransport. Reference 4 (hereafter, I) emerged from our efforts to rescue the DG method by replacing the WF constraints criticized in Ref. 2 with physically justified boundary constraints, first and foremost in terms of FDs. The predicted current within the linear-response limit was again completely unphysical ($J = 0$), so we had to ineluctably conclude that this modified DG approach is also incorrect.

In the Comment,[5] DG claim (i) that our constraints prevent a broken time-reversal symmetry and, therefore, the result $J = 0$ holds even beyond the linear response, and (ii) that we used real orbitals, which concomitantly constrain incoming and outgoing electrons. (iii) Although DG *accept that our idea to constrain populations* "is an interesting alternative to the Wigner function," they argue that, to get $J \neq 0$, it is essential to use the complex orbitals obtained by applying periodic boundary conditions for electrodes. (iv) Further, DG assert that, in their work, they "were careful. . . to only constrain the Wigner function $f(q_L, p)$ for $p > 0$ on the left and $f(q_R, p)$ for $p < 0$ on the right" such that "it is only the incoming, *propagating* states that are constrained."

Responding briefly, claim (i) is incorrect, claim (ii) misses any real basis, claim (iii) does not remedy their approach because the complex orbitals discussed by them solely represent a particular case of the general case of I, and claim (iv) demonstrates that, even if the WF were a true momentum distribution, amazingly, in their work,[1] DG did not constrain the incoming but rather the *outgoing* majority charge carriers.

II. POPULATION CONSTRAINTS DO NOT PREVENT A BROKEN TIME-REVERSAL SYMMETRY

As already noted, the demonstration of I refers to linear response. DG argue that the result $J = 0$ also holds even beyond the linear response and is the consequence of constraining *real* particle number operators $Q_\kappa \equiv \alpha_\kappa^\dagger \alpha_\kappa$, which yields a real many-body wave function Ψ incompatible with a broken time inversion. Unless otherwise specified, we use throughout the notations and definitions of I and ignore the spin for simplicity.

Let us show that this claim is incorrect. Let $|\Psi\rangle = \sum_n A_n |\Psi_n\rangle$ be a general many-body state exactly expanded in terms of the complete set of the real eigenstates of the Hamiltonian H of the cluster at $V = 0$, $H|\Psi_n\rangle = E_n|\Psi_n\rangle$. The coefficients A_n are *allowed* to be complex. Accepting the DG challenge, we generalize in this section our analysis of I beyond the linear-response limit considered there. We do not single out the ground state $|\Psi_0\rangle$, unlike e.g., Eq. (10) of I, and we consider the general matrix elements of the relevant operators [external bias Hamiltonian W and current operator at site q, $j_q = iet_q(a_q^\dagger a_{q+1} - a_{q+1}^\dagger a_q)$]

$$\mathcal{W}_{nm} \equiv \langle\Psi_n|W|\Psi_m\rangle = \mathcal{W}_{mn}; \quad \mathcal{Q}_{nm}^\kappa \equiv \langle\Psi_n|\alpha_\kappa^\dagger\alpha_\kappa|\Psi_m\rangle = \mathcal{Q}_{mn}^\kappa, \tag{1}$$

$$\mathcal{J}_{nm}^q \equiv -i\langle\Psi_n|\left(j_q - j_{q_0}\right)|\Psi_m\rangle \equiv \mathcal{I}_{nm}^q - \mathcal{I}_{nm}^{q_0} = -\mathcal{J}_{mn}^q, \tag{2}$$

where q_0 is an arbitrary fixed site. Notice that all the above calligraphic symbols denote real quantities. The DG

constrained energy minimization yields

$$\sum_{n,m} A_n^* A_m \Bigg[(E_n - \omega)\,\delta_{nm} + \mathcal{W}_{nm} - \sum_{\kappa} \lambda_\kappa \mathcal{Q}^\kappa_{nm} - i \sum_{q \neq q_0} \chi_q \mathcal{J}^q_{nm} \Bigg] = \min , \tag{3}$$

where ω, λ_κ, and χ_q are real Lagrange multipliers. The constraints are (see I)

$$\sum_{n,m} A_n^* A_m \mathcal{Q}^\kappa_{nm} = \mathcal{Q}^\kappa_{00}, \tag{4}$$

$$\sum_{n,m} A_n^* A_m \mathcal{J}^q_{nm} = 0, \tag{5}$$

$$\sum_{n,m} A_n^* A_m = 1. \tag{6}$$

The minimization with respect to A_n and A_n^* of Eq. (3) yields

$$\sum_{m} A_m \Bigg[(E_n - \omega)\,\delta_{nm} + \mathcal{W}_{nm} - \sum_{\kappa} \lambda_\kappa \mathcal{Q}^\kappa_{nm} - i \sum_{q \neq q_0} \chi_q \mathcal{J}^q_{nm} \Bigg] = 0, \tag{7}$$

$$\sum_{m} A_m^* \Bigg[(E_n - \omega)\,\delta_{nm} + \mathcal{W}_{nm} - \sum_{\kappa} \lambda_\kappa \mathcal{Q}^\kappa_{nm} + i \sum_{q \neq q_0} \chi_q \mathcal{J}^q_{nm} \Bigg] = 0. \tag{8}$$

Notice the reversed sign of the last term in the square brackets of Eqs. (7) and (8). It is due to the antisymmetry expressed in Eq. (5), which is related to the fact that the matrix elements in the Hermitian current operator are purely imaginary, i.e., $\mathcal{I}^q_{nm}$ are real. By rephrasing, this reflects the fact that, if the state $|\Psi\rangle = \sum_n A_n |\Psi_n\rangle$ corresponds to a current $J[\Psi] \equiv +J$, the state $|\Psi^*\rangle = \sum_n A_n^* |\Psi_n\rangle$ corresponds to a current $J[\Psi^*] = -J$. To determine the expansion coefficients (and the Lagrange multipliers), one must solve Eqs. (4)–(8), and then the position-independent current can be computed as

$$J \equiv J_q = i \sum_{n,m} A_n^* A_m \mathcal{I}^q_{nm} = \frac{i}{2} \sum_{n,m} (A_n^* A_m - A_n A_m^*) \mathcal{I}^q_{nm}. \tag{9}$$

As visible in Eqs. (7) and (8), A_n and A_n^* obey *different* equations: the A_n's are *allowed* to be complex, hence, $|\Psi\rangle$ is also *allowed* to be complex. The phase factors $A_n^*/A_n = \exp(-2i\phi_n)$ are *allowed* to depend on n, and Eq. (9) *allows* a nonvanishing current within or beyond linear response. To conclude, the constraint of populations, Eq. (4), *allows* an irreversible flow (broken "time"-reversal symmetry) $J \neq 0$.

The DG argumentation of the Comment that Ψ is necessarily real is incorrect because (a) on one hand, it eliminates an important aspect and (b) on the other hand, it introduces an unjustified assumption:

(a) DG seem to have realized that current conservation is a serious inconsistency of their argumentation; noteworthy, the steps (1)–(6) listed in the Comment *omit* the current conservation. DG first discuss the minimization *ignoring* the current conservation. This amounts to *illegitimately* excluding the last term of Eqs. (3), (7), and (8) above.

(b) Even with this impermissible omission of the imaginary terms, Eqs. (4)–(8) do not automatically imply real coefficients A_n. The unknown A_n can be complex even if all the other quantities entering these equations are real (remember $x^2 + 1 = 0$). Then, to more "convincingly" argue that our constraints do not break the time-reversal symmetry, DG make an *unjustified* supposition: they simply *postulate* that "the variational approach assumes a unique solution Ψ ...." The DG variational approach is a well-defined mathematical problem. Whether a solution *exists* and is furthermore *unique* can not be "assumed" in any mathematical problem. This should be *demonstrated* an imperious requirement particularly in the case of such an approach, whose shortcomings are so amply documented.[2–4]

In fact, it is just the opposite sign of the last term in the square brackets of Eqs. (7) and (8) that is related to the broken "time" inversion expressed by the transformation $\Psi \to \Psi^*$, $J \to -J$ mentioned by DG. So, an irreversible flow (broken "time" inversion) with constrained particle occupations is very possible, and the DG claim is incorrect.

To see whether the A_n's *are* indeed complex [thence whether a current J, Eq. (9), *can* indeed flow], one has to solve Eqs. (4)–(8). Beyond linear response, these are coupled nonlinear equations, and the solution is *not* necessarily unique. In I, we do *solve* this problem for linear response, show that the solution *is* unique, and the unphysical result $J = 0$ is the *outcome* of these calculations. Throughout our analysis of the DG approach,[2–4] to be on the safe side, we confined ourselves to the linear response, wherein the solution is *unique* and its lamentable failure can be unambiguously stated. It *is* possible that the DG current vanishes beyond the linear-response limit,[6] but we can not *safely* state this. But, *if* this were the case, it would have nothing to do with the DG claim; as seen above, constraining populations does not prevent a broken "time" inversion. Whether the solution of the nonlinear problem corresponds to $J = 0$ or not did not and does not represent our concern once the linear-response limit is incorrect. This would be yet another unphysical DG prediction, as we already stated *explicitly* in the next-to-last paragraph of Sec. VI in Ref. 2.

III. COMPLEX ORBITALS DO NOT RESCUE THE DG APPROACH

DG incorrectly claim that we can not constrain only incoming electrons because our single-particle wave functions (orbitals) are real, and outgoing electrons become concomitantly constrained. The demonstration of I is general, and (as in Sec. II) specifying orbitals explicitly is not needed. The DG claim that we used real orbitals in I is not founded. Let us still note that, if the orbitals were real, this would be a *physical* fact, *whatever* the quantity to be constrained. The objection that incoming and outgoing states are entangled would apply when constraining the WF as well.

DG accept our idea of constraining populations, but claim that it is essential to choose complex orbitals associated to periodic boundary conditions in electrodes. To demonstrate that the DG criticism is invalid, let us explicitly work out just this case,

which is merely a particular case of that considered in I: By inspecting the second and third lines of Eq. (6) of I, one can immediately realize that our electrodes are described by *general* boundary conditions; we wrote, e.g., $l \leqslant q_L$ and *not* $-M_L + q_L < l \leqslant q_L$. It is puzzling that, although DG even reproduce our expression of H_L, they completely overlook this fact.

Assuming periodic electrodes ($a_{q_L - M_L} \equiv a_{q_L}$ and $a_{q_R + M_R} \equiv a_{q_R}$) and homogeneous hopping integrals $\mathcal{T}_{L,R}$ in electrodes, Eq. (22) of I can be written explicitly as

$$a_{q_L + l} = M_L^{-1/2} \sum_k \alpha_k e^{2\pi i k l / M_L},$$
$$a_{q_R + r} = M_R^{-1/2} \sum_p \alpha_p e^{2\pi i p r / M_R}. \quad (10)$$

Throughout, we use $l = -M_L, \ldots, -2, -1$; $r = 1,2, \ldots, M_R$; $-M_L/2 \leqslant k < M_L/2$; and $-M_R/2 \leqslant p < M_R/2$. With Eq. (10), the Hamiltonians H_L, H_R, and $H_{D,e}$ of Eq. (6) of I become ($\tau_{L,R} \equiv t_{q_{L,R}}$, $\varepsilon_F = \mu_L = \mu_R$)

$$H_L = \sum_k [\varepsilon_F - 2\mathcal{T}_L \cos(2\pi k / M_L)]\, \alpha_k^\dagger \alpha_k,$$
$$H_R = \sum_p [\varepsilon_F - 2\mathcal{T}_R \cos(2\pi p / M_R)]\, \alpha_p^\dagger \alpha_p,$$
$$H_{D,e} = -\tau_L M_L^{-1/2} \sum_k (\alpha_k^\dagger a_{q_L} + a_{q_L}^\dagger \alpha_k) - \tau_R M_R^{-1/2} \sum_p (\alpha_p^\dagger a_{q_R} + a_{q_R}^\dagger \alpha_p). \quad (11)$$

Further operators affected by the transformation (10) entering the relevant equations are

$$W = \frac{eV}{2} \sum_k \alpha_k^\dagger \alpha_k + \sum_q e V_q a_q^\dagger a_q - \frac{eV}{2} \sum_p \alpha_p^\dagger \alpha_p, \quad (12)$$
$$j_L = i \frac{e}{\hbar} \tau_L M_L^{-1/2} \sum_k (\alpha_k^\dagger a_{q_L} - a_{q_L}^\dagger \alpha_k), \quad (13)$$
$$j_R = i \frac{e}{\hbar} \tau_R M_R^{-1/2} \sum_p (a_{q_R}^\dagger \alpha_p - \alpha_p^\dagger a_{q_R}), \quad (14)$$

representing the Hamiltonian of the external bias W and the current operators $j_{L,R}$ at the contacts, respectively. The sites within the device $q = q_L + 1, \ldots, q_R - 1$ are not affected by Eq. (10), and the corresponding operators (device's Hamiltonian H_D and the current within the device j_q) can be found in I.

By inspecting Eq. (11), one can immediately see that, in spite of the fact that the single-particle wave functions

$$\phi_k(x_l) = e^{2\pi i k l / M_L} \quad \text{and} \quad \phi_p(x_r) = e^{2\pi i p r / M_R} \quad (15)$$

of Eq. (10) are complex, *all* the parameters of the Hamiltonian $H = H_L + H_R + H_{D,e} + H_D$ are real. Consequently, *all* its many-body eigenstates $|\Psi_n\rangle$ are real. All the parameters entering W are real, so the matrix elements $\langle \Psi_n | W | \Psi_0 \rangle \equiv \mathcal{W}_n$ [Eq. (13) of I] are again real. In accord with the general case of I, the matrix elements of the current operator are purely imaginary (i.e, real $\mathcal{J}_{q,n}$). All the matrix elements of the particle number operators $\alpha_\kappa^\dagger \alpha_\kappa$ ($\kappa = p,k$) remain real $\langle \Psi_n | \alpha_\kappa^\dagger \alpha_\kappa | \Psi_0 \rangle = \mathcal{Q}_\kappa$ ($\mathcal{Y}_\kappa \equiv 0$). Equations (24) and (25) of I remain unaltered. So, the completely unphysical result ($J = 0$) follows as the ineluctable conclusion of applying the DG method. The labels of the single-particle states of incoming *electrons* can be explicitly given (for *hole* conduction, see Sec. V): $\alpha_\kappa \to \alpha_{k_{\rm in}}$ with $0 < k_{\rm in} < M_L/2$ and $\alpha_\kappa \to \alpha_{p_{\rm in}}$ with $-M_R/2 < p_{\rm in} < 0$. One can *explicitly* see that only these incoming electrons can, and are to be, constrained in Eqs. (12) and (23) of I or in the present Eq. (4). They do differ from the outgoing electrons, the labels of which are $-M_L/2 < k_{\rm out} < 0$ and $0 < p_{\rm out} < M_R/2$, and one can convince oneself *explicitly* that outgoing electrons (can) remain *un*constrained. So, these constraints correspond to Fig. 7(c) of Ref. 7 and not to Figs. 7(a) and (7b), contrary to what the Comment claims.

To summarize, the constraints used by us within the calculations based on the DG approach *allowed* a broken symmetry between incoming and outgoing electrons. Whether this symmetry is broken or not remained an *open* result, which emerged from the DG transport calculations. The *result* is that this symmetry is not broken, $J = 0$, demonstrating the *incorrectness* of the DG variational approach, and this also holds true for the complex orbitals and the associated electrodes' periodic boundary conditions, contrary to what the Comment argues.

Like in the situation encountered in a closely related issue (see Ref. 3), DG attempt to discuss aspects of the correct Landauer approach conveying the false impression that they belong to their incorrect variational approach. In a part that is not at all substantiated by the main body of the Comment, in their abstract DG refer to the asymptotic scattering states and assert that the amplitude of incoming waves is $1 (\equiv r_i)$ (i.e., bias independent), while the amplitude r of the outgoing waves is bias (and barrier) dependent. To this, we comment as follows. The fact that $r_i = 1$ is constant is nothing but the trivial consequence of a comfortable normalization. What is important for a nonvanishing current (broken "time" inversion) is that $r_i \neq r$, and this emerges from valid Landauer's transport calcuations. The fact that the DG calculations fail to yield a broken "time"-reversal symmetry is just the stumbling block of their variational approach based on a constrained energy minimization.

IV. WIGNER FUNCTION CONSTRAINTS VERSUS POPULATION CONSTRAINTS

DG mention that, by constraining the WF, a nonzero current is possible. In Refs. 2–4, we discussed that, although, *luckily*, mathematically this may be possible, the result is completely unphysical. The inappropriateness of the Wigner constraints could not be immediately recognized only because, luckily, the matrix elements of the Fano operator are generally complex.[2,3] They are generally complex no matter whether the orbitals are real or complex (see Refs. 2 and 3); this is not the result of any "careful" choice of certain complex functions, as incorrectly claimed by DG. Let us show that this is also the case when the Comment's continuous space description is used instead of the discrete one of Refs. 2 and 4. The Fano operator reads as

$$F(x,p) \equiv \frac{1}{N} \int dr\, e^{-ipr}\, \hat{\psi}^\dagger(x - r/2) \hat{\psi}(x + r/2), \quad (16)$$

where $\hat{\psi}^\dagger(x)$ and $\hat{\psi}(x)$ are the electron field creation and destruction operators. Its general matrix element for

two arbitrary N-body states $|\Psi\rangle$ and $|\Phi\rangle$ corresponding to the multielectronic wave functions $\Psi(x_1,\ldots,x_N) \equiv \langle x_1,\ldots,x_N|\Psi\rangle \equiv \langle 0|\hat{\psi}(x_1),\ldots,\hat{\psi}(x_N)|\Psi\rangle/\sqrt{N!}$ ($|0\rangle$ is the vacuum) and $\Phi(x_1,\ldots,x_N) \equiv \langle x_1,\ldots,x_N|\Phi\rangle$ can be easily expressed as ($\mathbf{X}_{N-1} \equiv \{x_1,\ldots,x_{N-1}\}$)

$$\langle\Phi|F(x,p)|\Psi\rangle = \int e^{-ipr}\Phi^*\left(\mathbf{X}_{N-1},x-\frac{r}{2}\right)\Psi\left(X_{N-1},x+\frac{r}{2}\right)d\,\mathbf{X}_{N-1}d\,r. \tag{17}$$

This matrix element is generally complex irrespective of whether the wave functions $\Psi(\mathbf{X}_N)$ and $\Phi(\mathbf{X}_N)$ entering Eq. (17) are real or complex. Equation (17) is general and holds whatever the employed single-particle wave functions (real or complex, which need *not* be specified). The exponential entering Eq. (17) belongs to the definition of the Fano operator [Eq. (16)] and has nothing to do with the employed orbitals. Whatever the latter, it can be artificially split as $\exp(-ipr) = \exp[ip(x-r/2)] \times \exp[-ip(x+r/2)]$. This is a trivial splitting, and the superscript of the Comment's notation α_k^{DG} for these factors is misleading: DG did *not* employ periodic boundary conditions for the small Au_{13} clusters, which mimic their electrodes of Ref. 1. For this, it suffices to inspect, e.g., Eqs. (1) and (2) of Ref. 1.

Let us express the population constraints for the incoming electrons ($p<0$) for the right electrode ($\mathcal{R}$) [Eq. (23) of I] making use of the Fano operator[4] and Eqs. (10):

$$\sum_{x\in\mathcal{R}}\int\langle\Psi|F(x,p)|\Psi\rangle = \langle\Psi|\alpha_p^\dagger\alpha_p|\Psi\rangle = \langle\Psi_0|\alpha_p^\dagger\alpha_p|\Psi_0\rangle = \sum_{x\in\mathcal{R}}\int\langle\Psi_0|F(x,p)|\Psi_0\rangle. \tag{18}$$

Instead of constraining the above sums over x of the Fano operators (which do represent particle momentum distributions), DG constrain a single term thereof in either electrode (namely, $x = q_{L,R}$),[1] which is a quantity that does not represent a physical momentum distribution. Emerging from an *ad hoc mathematical* constraint, it is not at all surprising that the currents predicted by the DG approach,[1] whether they vanish or not, are completely unphysical, as demonstrated in Refs. 2 and 3. Still, *mathematically*, the WF constraints used by the DG approach (can) yield a nonvanishing J even when using real orbitals, in spite of the "warning bells" that "real wave functions carry no current" mentioned in the Comment.[5]

V. CONSTRAINTS FOR *n*- AND *p*-TYPE CONDUCTION

In Sec. III, to specify the incoming (outgoing) electrons, we have naively *assumed* that the single-particle states with positive (negative) wave numbers k and p correspond to right (left) motion. However, they are related via Eqs. (10) to *quasi* momenta, which are not necessarily physical momenta. Especially for later purposes, it is important to *demonstrate* that the sign of k and p is related to the direction of the motion in the *real* world.

Let us consider the isolated left electrode. Its ground state is the Fermi sea $|F\rangle \equiv (\prod_{|k|\leqslant k_F}\alpha_k^\dagger)|0\rangle$, where the Fermi wave vector k_F is determined by the number of electrons. By using Eq. (10), one can straightforwardly demonstrate that, at any position q_L+l within the (left) electrode, the average of the electron number current $\bar{j}_{q_L+l} = i(a^\dagger_{q_L+l+1}a_{q_L+l} - \mathrm{H.c.})$ vanishes, $\langle F|\bar{j}_{q_L+l}|F\rangle = 0$. (Notice the opposite signs of $\bar{j}$ and the *electric* current j of Sec. II for electrons.) Let us also consider the states ($M_L/2 > |K| > k_F, |K'| \leqslant k_F < M_L/2$)

$$\left|\Phi_K^{el}\right\rangle \equiv \alpha_K^\dagger|F\rangle, \quad \left|\Phi_{K'}^{h}\right\rangle \equiv \alpha_{K'}|F\rangle. \tag{19}$$

They represent states with one extra electron (el) and hole (h) in the Fermi sea, respectively. Straightforward calculations using Eqs. (19) and (10) yield

$$\left\langle\Phi_K^{el}\left|\bar{j}_{q_L+l}\right|\Phi_K^{el}\right\rangle = +2\frac{\mathcal{T}_L}{M_L}\sin\frac{2\pi K}{M_L}, \tag{20}$$

$$\left\langle\Phi_{K'}^{h}\left|\bar{j}_{q_L+l}\right|\Phi_{K'}^{h}\right\rangle = -2\frac{\mathcal{T}_L}{M_L}\sin\frac{2\pi K'}{M_L}. \tag{21}$$

The sign of the $\bar{j}$ average does *express* the real direction of electron quantum-mechanical motion. So, Eqs. (20) and (21) demonstrate that the sign of the wave vectors belonging to the Brillouin zones of Sec. III (symmetric around zero) specifies the direction of electron motion, and that electrons and holes with a given wave vector move in opposite directions. The latter result can also be seen by performing the general particle-hole transformation $e \to -e$ (charge conjugation) and $\{\hat{\psi}^\dagger(x),\hat{\psi}(x)\} \to \{\hat{\psi}_h^\dagger(x) \equiv \hat{\psi}(x), \hat{\psi}_h(x) \equiv \hat{\psi}^\dagger(x)\}$ ($\{a_x^\dagger, a_x\} \to \{a_x^{h\,\dagger} \equiv a_x, a_x^h \equiv a_x^\dagger\}$, $\{\alpha_\kappa^\dagger,\alpha_\kappa\} \to \{\alpha_\kappa^{h\,\dagger} \equiv \alpha_{-\kappa}, a_\kappa^h \equiv \alpha_{-\kappa}^\dagger\}$). By using Eq. (16), one easily gets

$$\bar{j}_x^h = -\bar{j}_x; \quad j_x^h = +j_x, \tag{22}$$

$$F_h(x,-P) \equiv \frac{1}{N}\int dr\, e^{iPr}\hat{\psi}_h^\dagger(x-r/2)\hat{\psi}_h(x+r/2) = -F(x,P) + \mathrm{const.} \tag{23}$$

In view of the aforementioned, one can conclude that incoming and outgoing *electrons* correspond to the wave vectors

$$0 < k_{\mathrm{in}} < M_L/2; \quad -M_R/2 < p_{\mathrm{in}} < 0, \tag{24}$$

$$-M_L/2 < k_{\mathrm{out}} < 0; \quad 0 < p_{\mathrm{out}} < M_R/2, \tag{25}$$

(for electrons)

while for incoming and outgoing *holes*

$$-M_L/2 < k_{\mathrm{in}} < 0; \quad 0 < p_{\mathrm{in}} < M_R/2, \tag{26}$$

$$0 < k_{\mathrm{out}} < M_L/2; \quad -M_R/2 < p_{\mathrm{out}} < 0. \tag{27}$$

(for holes)

The fact that the above electron and hole descriptions are equivalent is trivial in general, but not in the context of transport approaches aiming at constraining incoming *charge carriers*.[7] If the charge carriers are *electrons* (n-type conduction), the constraints should be imposed to incoming electrons [Eq. (24)]. In this case, the naive assumption of Sec. III is justified. However, if the charge carriers are *holes* (p-type conduction), one should constrain the incoming holes [Eq. (26)]; that is, the labels κ in the above Eq. (4), and in Eqs. (12) and (23) of I, are those given by Eq. (26) and not by Eq. (24).

The analysis of this section and of Sec. III makes it now clear why we preferred to consider the general case in I and not to enter in unnecessary involved details: they are absolutely not necessary to understand the unphysical prediction $J=0$

of the DG approach, and hence its lamentable failure. Just to avoid any possible misunderstanding, in Ref. 8 (which DG misinterpret), we have stated what we already noted at step (ii) in Sec. II of I, namely, that incoming carriers are constrained. But, because the incorrect DG claims in the Comment brought us to enter such details, we can show another shortcoming of the original DG approach[1] related to them, one of many other aspects,[6] which we did not present so far.

In their work,[1] DG did not discuss at all whether the molecule they considered, BDT (benzenedithiolate), exhibits an n- or a p-type conduction. Uncritically (as also repeated in the Comment), they merely impose constraints on $f(q_L, P > 0)$ and $f(q_R, P < 0)$. Even if these WFs were true momentum distributions, these constraints would be appropriate only if the charge carriers were electrons [conduction mediated by lowest unoccupied molecular orbital (LUMO)]. In reality, in BDT, the majority charge carriers are holes (p-type conduction), as clearly demonstrated by the recent reliable experiment of Ref. 9. By inspecting now Eqs. (23) (noting the reversed sign of P in the left- and right-hand sides), (24), and (27), one is amazed to see that what DG constrained in Ref. 1 are in fact the *outgoing* majority carriers, and *not* the incoming ones; what sense does such a constraint make for transport? It is certainly too simplistic to describe the conduction through BDT merely as a process mediated by highest occupied molecular orbital [(HOMO); p-type conduction] instead of accounting for several or numerous ionization and electroaffinity levels, but the fact that the constraints of majority carriers (holes) are unphysical in Ref. 1 is a clear demonstration that uncritically using Wigner boundaries is completely unjustified. To conclude, even if all the other DG ingredients were correct (which is obviously not the case[2,3]), this very reason irrefutably demonstrates that the results of Refs. 1 have absolutely no physical meaning.

In our first work[2] that challenged the DG approach with Wigner constraints,[1] we considered uncorrelated and correlated quantum dots modeled by a single level whose energy offset from the electrodes' Fermi level $\varepsilon_F = 0$ is ε_g. The results of the DG calculations presented there (e.g., in Figs. 2–5 and 7) are for $\varepsilon_g \geqslant 0$, that is, the dot's level plays the role of a LUMO (n-type conduction). The charge carriers are electrons, and our constraints [corresponding to the above Eq. (24)] refer to incoming electrons.

Both the uncorrelated and the correlated models of Ref. 2 are described by Hamiltonians $H(\varepsilon_g)$ possessing a particle-hole (or charge-conjugation) symmetry (see e.g., Ref. 10 and citations therein) around $\varepsilon_g = 0$: $H_h(\varepsilon_g) = H(-\varepsilon_g)$. Hence, the zero-bias conductance $g(+\varepsilon_g) = g(-\varepsilon_g)$ should be identical irrespective of whether the level is located above $(+\varepsilon_g)$ or below $(-\varepsilon_g)$ the electrodes' Fermi level $\varepsilon_F = 0$. It is noteworthy that the charge carriers are electrons for positive ε_g and holes for negative ε_g. As a test for numerical calculations, we checked that DG calculations for the LUMO case ($\varepsilon_g > 0$) constraining the incoming electrons [Eq. (24)] and for the HOMO case ($\varepsilon_g < 0$) constraining the incoming holes [Eq. (26)] yield the same, albeit completely unphysical linear conductance. [The electric current operator has the same sign both in the electron and the hole representation, cf. Eq. (22).] As clearly demonstrated,[2] the DG conductance computed in this way is completely unphysical, but... it is still positive, $g_{\rm DG}(\varepsilon_g) \geqslant 0$, both for positive and negative ε_g. That is, with Wigner constraints of incoming *carriers*, the DG approach can still "predict" that electrons flow from the lower potential to the higher potential, and holes flow from the higher potential to the lower potential.

If we drew the curves of Figs. 3, 5, and 7 of Ref. 2 also for $\varepsilon_g < 0$,[6] by blindly computing the DG conductance using *exactly* the DG prescribed constraints[1] [i.e., Eq. (24)], we could have shown another unphysical "prediction" of the DG approach,[1] namely, that the *linear* conductance can be negative, $g_{\rm DG}(\varepsilon_g < 0) < 0$! That is, to comply with the DG calculations, holes should have to flow... from the lower potential to the higher potential. This results from the fact that the blind constraints of $f(q_L, P > 0)$ and $f(q_R, P < 0)$ erroneously constrain, in fact, the outgoing carriers; this situation corresponds to Fig. 7(d), and not to Fig. 7(c) of Ref. 7. Indeed, these Wigner-DG constraints yield a complex wave function Ψ and a nonvanishing current, but... what is the physical relevance of this broken "time" inversion? As a matter of fact, it is just such an unphysical imbalance, which is shown in Fig. 1 (bottom) of Ref. 1 [the counterpart of Fig. (7d) of Ref. 7 and not of Fig. 7(c), as incorrectly claimed in the Comment], that breaks the "time" inversion in Ref. 1. In Ref. 2, we did not show this conductance $g(\varepsilon_g < 0) < 0$ because the demonstration of the severe failure of the DG approach with Wigner constraints was sufficiently convincing, even without mentioning this "prediction." However, we have to note it here since, in spite of the clear evidence of Refs. 2 and 3, DG still continue to uncritically refer to their work[1] in the Comment.

VI. DISCUSSION AND CONCLUSION

In Ref. 1, DG constrained the WF only because they claimed that the FD can not be used for correlated transport. As explained in I, the electrodes inject uncorrelated electrons even in correlated devices, and constraints can and should be imposed to the momentum distribution of incoming carriers: this is precisely the FD $f_\kappa^{\rm FD} \equiv \langle Q_\kappa \rangle$ and not the WF $f(x,P) \equiv \langle F(x,P) \rangle$, which is not a true momentum distribution. In Ref. 11, we present an example demonstrating that using the sign of the Wigner "momentum" P to specify the direction of motion in real world is physically inadequate. This example demonstrates that, although DG "were careful... to only constrain the Wigner function $f(q_L, p)$ for $p > 0$ on the left and $f(q_R, p)$ for $p < 0$ on the right," it is not necessarily true that"it is only the incoming, *propagating* states that are constrained" (quotation from the Comment). Fortunately, using the FDs obviates the need for this equivocal ingredient. By using the orbital quantum indices (quasimomenta $\{\kappa\} \equiv \{k, p\}$), one can unambiguously distinguish between incoming and outgoing charge carriers and constrain only the FD of the former [cf. Sec. III and Eqs. (24)–(27)]. The fact that the results obtained by constraining the FD and the WF are qualitatively different [$J = 0$ (Ref. 4) versus $J \neq 0$ (Ref. 2)] merely demonstrates the limited physical content of the WF, which is well known from standard textbooks.[12] Within the Comment's argumentation, a current flow is possible only to the extent to which the WF does differ from the FD.

There are certainly *many* possibilities to obtain nonvanishing currents by constraining *ad hoc* complex Hermitian operators, since all these generally yield $J \neq 0$ [see Eqs. (18)–(20) of I]; one needs not be too "careful" for this. It is essential to choose Hermitian operators, which are associated to observables able to express the physical reality at the boundaries. And, according to the present community's wisdom, a choice better justifiable physically than the electronic momentum distributions is not known; DG themselves have to admit that they represent "an interesting alternative to the" WF. Most well-established approaches for transport successfully employ FDs to express open boundary conditions. Examples include time-dependent approaches [Boltzmann's equations, nonequilibrium Green's functions (NEGF), master equations, time-evolved wave packets introducing complex absorbing potentials at boundaries, etc.], which successfully employ Fermi distributions (FDs). Strictly speaking, a broken time inversion only exists in such time-dependent approaches. The irreversible stationary flow $J \neq 0$ results only by taking the infinite time limit $t \to \infty$ after that of infinite volume $L \to \infty$; otherwise, the (effective) Hamiltonian remains Hermitian (no imaginary contributions to self-energies and $J = 0$). FDs for carriers flowing from electrodes into a device are also employed in time-independent treatments, e.g., the uncorrelated scattering Landauer approach. There, an irreversible flow (broken "time" inversion) is possible (only) because, from transport calculations (i.e., solving the Schrödinger equation) for $V \neq 0$, one *deduces* complex wave functions and different single-particle states (orbitals) of incoming and outgoing carriers, which are *allowed* and are *obtained* to be different.

Because the DG approach is also time independent, the comparison with Landauer's approach is most illuminating. At $V \neq 0$, a current through a device coupled to two electrodes implies (i) an asymmetry between the incoming and outgoing carriers at either contact and (ii) a left-right asymmetry. Within the Landauer approach, the asymmetry (i) is *deduced* by solving the Schrödinger equation, which yields a nonvanishing transmission; the asymmetry (ii) follows from the fact that the electron distributions (FDs) ensure an asymmetric filling of the incoming states at either contact [$f^{\mathrm{FD}}_{k_{\mathrm{in}}} = \theta(\varepsilon_F + eV/2 - \varepsilon_{k_{\mathrm{in}}})$ and $f^{\mathrm{FD}}_{p_{\mathrm{in}}} = \theta(\varepsilon_F - eV/2 - \varepsilon_{p_{\mathrm{in}}})$].

As explicitly shown above, it is possible to distinguish between incoming and outgoing states within the DG framework. In Sec. III, the orbitals of Eq. (15) describing electrons in isolated electrodes are *identical* to those used in the Landauer approach, and the asymmetry (ii) has been accounted for exactly in the same way as in Landauer's approach. The essential difference between the two approaches is the transport ansatz employed in the calculations. If the DG transport ansatz (constrained energy minimization) were correct, the *result* would be a broken incoming-outgoing symmetry [condition (i)] and a nonvanishing stationary (and also position-independent[2,3]) current. For uncorrelated systems, as an alternative to our many-body second quantization approach, cumbersome DG calculations could also be done by using Slater determinants built from single-electron states $\varphi_k(x)$ for the coupled source-device-drain system at $V \neq 0$. If the DG transport ansatz were equivalent to the Schrödinger equation, the solutions would recover the standard expressions, e.g., $\varphi_{k_{\mathrm{in}}}(x_l) = \exp(2\pi i k_{\mathrm{in}} l/M_L)$ and $\varphi_{k_{\mathrm{out}}}(x_l) = R(k_{\mathrm{out}}) \exp(2\pi i k_{\mathrm{out}} l/M_L)$ [$|R(k_{\mathrm{out}})| < 1$], with k_{in} and k_{out} given by Eqs. (24)–(27). Conversely, if the Schrödinger equation were a wrong framework, it would yield the incorrect DG result $R(k_{\mathrm{out}}) = 1$ (and hence $J = 0$).

Above, we preferred to respond to and rebut in detail all the issues raised by the Comment. Still, we note that this analysis of all the concrete aspects is actually not necessary. In Sec. VII of Ref. 3, we pointed out more serious reasons as to why the DG approach fails. This criticism comprises fundamental aspects not restricted to specific boundary constraints. Our criticism was presented in Ref. 3 in sufficient detail and will not be repeated here.

The lamentable failure of the DG approach was demonstrated for the simplest uncorrelated and correlated, discrete, and continuous models.[2,3] It contradicts well-established experimental and theoretical results, and it would make little sense to more amply document the incorrectness in *many* other cases.[6]

Based on ingredients unfounded physically, it is not at all surprising that the currents predicted by the DG approach are completely unphysical and agree much more poorly with experiment than more common approaches, contrary to the seemingly original success claimed in Ref. 1. In Sec. VIII of Ref. 3, we clearly showed that a standard NEGF-DFT calculation yields currents slightly larger by a factor ∼1.5–3, while DG's currents[1] represent ∼2%–5% of the experimental currents of the recent accurate experiment of Ref. 9.

Let us summarize the whole debate. The basic DG idea[1] was to minimize the energy and appropriately constrain the electrons coming from electrodes at the contacts. So, what is important is to constrain the distributions of incoming charge carriers correctly. To do this, DG used the WF as if it were a true momentum distribution. In Refs. 2 and 3, we demonstrated that constraining the WF yields unphysical results. But, just within the DG framework, it is illogical to constrain the WF, which is not a true momentum distribution since the true momentum distribution (FD) can be used. Our work[4] demonstrated that, by constraining the incoming carriers using FDs, the DG method again yields wrong results. DG accept our idea of constraining populations but claim that we constrained populations of real orbitals, and therefore incoming and outgoing electrons are concomitantly constrained, and suggest to use complex orbitals. Above, we show that, by using just the complex orbitals suggested by DG (in fact, merely a particular case of I), our demonstration of I is untouched.

To conclude, we reaffirm the conclusion presented earlier in Refs. 2–4 on the real issue: the variational method proposed by DG to study the transport based on a finite cluster decoupled from environment and constraining incoming carriers at the contacts is *conceptually* inadequate.

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