Comment on "Spin-orbit interaction and spin selectivity for tunneling electron transfer in DNA"

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The observation of chiral-induced spin selectivity (CISS) in biological molecules still awaits a full theoretical explanation. In a recent Rapid Communication, Varela *et al.* [Phys. Rev. B **101**, 241410(R) (2020)] presented a model for electron transport in biological molecules by tunneling in the presence of spin-orbit interactions. They then claimed that their model produces a strong spin asymmetry due to the intrinsic atomic spin-orbit strength. As their Hamiltonian is time-reversal symmetric, this result contradicts a theorem by Bardarson [J. Phys. A: Math. Theor. **41**, 405203 (2008)], which states that such a Hamiltonian cannot generate a spin asymmetry for tunneling between two terminals (in which there are only a spin-up and a spin-down channel). Here we solve the model proposed by Varela *et al.* and show that it does not yield any spin asymmetry, and therefore cannot explain the observed CISS effect.

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In spite of many theoretical papers, the observation of a large spin filtering in chiral molecules [1], termed "chiral induced spin selectivity (CISS)" still awaits a full explanation, which is accepted by everyone. In a recent Rapid Communication, Varela *et al.* [2] followed a series of their earlier papers, and mapped the detailed tunneling electron transfer through the molecule onto an effective one-dimensional continuum model, which mimics the molecule by a region with a barrier potential and a Rashba spin-orbit interaction (SOI). Using a scattering solution of this model, they concluded that the molecule causes spin splitting of the scattered electrons, thus explaining the CISS experiments.

Since the Rashba SOI obeys time-reversal symmetry, the above result contradicts a general theorem by Bardarson [3], which states that a time-reversal symmetric Hamiltonian cannot generate a spin asymmetry for tunneling between two terminals (in which there are only a spin-up and a spin-down channel) [4]. Indeed, this led several groups to propose models which effectively break time-reversal symmetry without a magnetic field for two-terminal systems [6], or to increase the number of channels [7]. Below we solve the model of Ref. [2] explicitly, and show that indeed it does not generate any spin splitting, thus obeying the Bardarson theorem.

After several mappings, Ref. [2] ends up with a one-dimensional Hamiltonian for the electronic spinors on the molecule, Eq. (5) in that paper,

$$\mathcal{H} = \left[\frac{p_x^2}{2m} + V_0\right]\mathbf{1} + \alpha\sigma_y p_x \quad \text{for } 0 < x < a, \tag{1}$$

where a is the molecule's length, σ_y is the Pauli spin matrix, $\mathbf{1}$ is the 2×2 unit matrix, α represents the strength of the spin-orbit interaction, and V_0 represents an energy barrier on the molecule. For $x < 0$ and $a < x$ Ref. [2] has $V_0 = 0$ and $\alpha = 0$, and therefore the Hamiltonian in those regions is that of free electrons $p_x^2/(2m)$, with arbitrary spinors, with a spatial wave function $e^{\pm ikx}$, and energy $E = \hbar^2k^2/(2m)$.

It is convenient to choose as a basis of the spin Hilbert space the eigenspinors of σ_y, $\sigma_y|\mu\rangle = \mu|\mu\rangle$, with $\mu = \pm 1$, and write the solutions as $|\Psi_\mu(x)\rangle = \psi_\mu(x)|\mu\rangle$. Applying $\mathcal{H}$ to each of these states yields

$$\mathcal{H}|\Psi_\mu(x)\rangle = \left[\frac{p_x^2}{2m} + V_0 + \alpha\mu p_x\right]|\Psi_\mu(x)\rangle. \tag{2}$$

In the chosen basis, the Hamiltonian is diagonal, and this equation separates into two scalar equations. In the range $0 < x < a$ these are

$$\left[\frac{p_x^2}{2m} + V_0 + \alpha\mu p_x\right]\psi_\mu(x) = E\psi_\mu(x). \tag{3}$$

Assuming a solution of the form $\psi_\mu(x) \propto e^{iQ_\mu x}$, we find that Q_μ must obey the quadratic equation

$$E = \frac{\hbar^2[(Q_\mu + k_{\rm SO}\mu)^2 - k_{\rm so}^2]}{2m} + V_0, \tag{4}$$

where $m\alpha/\hbar = k_{\rm so}$ is the strength of the SOI in units of inverse length. This equation has two solutions,

$$Q_\mu^\pm = -k_{\rm so}\mu \pm q\,, \quad \text{with } q = \sqrt{k^2 + k_{\rm SO}^2 - q_0^2}, \tag{5}$$

where $q_0^2 = 2mV_0/\hbar^2$.

Our Eq. (5) differs from Eq. (7) of Ref. [2], which in our notation would be

$$Q_\mu^\pm(\text{Varela}) = \pm(k_{\rm SO}\mu + q). \tag{6}$$

Clearly, these values do not obey Eq. (5) of Ref. [2] [and our Eq. (4)]. We suspect that this discrepancy led to the spin splitting found there. Explicitly, one faces a simple scattering problem [8]

$$\begin{aligned}
\psi_\mu &= [e^{ikx} + r_\mu e^{-ikx}], \quad x < 0\\
\psi_\mu &= e^{-ik_{\rm so}\mu x}[C_\mu e^{iqx} + D_\mu e^{-iqx}], \quad 0 < x < a\\
\psi_\mu &= t_\mu e^{ikx}, \quad a < x.
\end{aligned} \tag{7}$$

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The prefactor in the middle region is nothing but the Aharonov-Casher phase factor [9] due to the spin-orbit interaction. The SOI adds opposite phases to the two spin states.

Generally, the conjugate velocity is given by $v = \partial\mathcal{H}/(\partial p_x)$. For each of the four solutions in Eq. (5), the corresponding gauge-covariant velocities inside the molecule are $v_\mu^\pm = \hbar(Q_\mu^\pm + k_{\rm SO}\mu)/m = \pm\hbar q/m$. For $E > V_0 - (\hbar k_{\rm SO})^2/(2m)$, q is real, and the solution on the molecule has waves propagating to the right and to the left. For $E < V_0 - (\hbar k_{\rm SO})^2/(2m)$, q is imaginary, and the waves become evanescent. The continuity conditions at $x = 0$ and a yield four equations for the four unknowns $C_\mu,\ D_\mu,\ r_\mu$, and t_μ:

$$\begin{aligned} 1 + r_\mu &= C_\mu + D_\mu, \\ k(1 - r_\mu) &= q[C_\mu - D_\mu], \\ t_\mu e^{ika} &= e^{-ik_{\rm so}\mu a}[C_\mu e^{iqa} + D_\mu e^{-iqa}], \\ kt_\mu e^{ika} &= qe^{-ik_{\rm so}\mu a}[C_\mu e^{iqa} - D_\mu e^{-iqa}]. \end{aligned} \tag{8}$$

Replacing t_μ by $\tilde{t}_\mu = t_\mu e^{ik_{\rm SO}\mu a}$ yields equations which are independent of μ, and therefore the solutions for r_μ and $\tilde{t}_\mu$ are independent of μ. Since the transmission and reflection probabilities are $T_\mu = |t_\mu|^2 = |\tilde{t}_\mu|^2$ and $R = |r_\mu|^2$, it is clear that the reflection and transmission matrices R and T are proportional to the 2×2 unit matrix, and therefore there is no spin selection, in accordance with the Bardarson theorem [3]. The model of Ref. [2] does not generate any asymmetry in the outgoing spin currents.

Specifically, the solutions are

$$\begin{aligned} r_\mu &= \frac{k^2 - q^2}{q^2 + k^2 + 2ikq\ \cot(qa)}, \\ t_\mu &= \frac{2e^{-ia(k_{\rm SO}\mu + k)}kq}{2kq\ \cos(qa) - i(k^2 + q^2)\sin(qa)} \end{aligned} \tag{9}$$

and thus

$$T_\mu = |t_\mu|^2 = \frac{4k^2q^2}{4k^2q^2 + (k^2 - q^2)^2\sin^2(qa)}, \tag{10}$$

independent of μ! It is also straightforward to check unitarity, $R_\mu + T_\mu = 1$. This result also holds when q is purely imaginary. Solving the same equations with the Q's used in Ref. [2], Eq. (6), indeed yields different velocities for the two spins, ending up with spin-dependent reflection and transmission.

An alternative way to derive the scattering amplitude is to first apply a gauge transformation (related to the Aharonov-Casher phase factor [9])

$$|\Psi(x)\rangle = U(x)|\widetilde{\Psi}(x)\rangle, \quad U(x) = e^{-ik_{\rm SO}x\sigma_y}, \tag{11}$$

so that

$$\widetilde{\mathcal{H}} = U(x)^\dagger\mathcal{H}U(x) = \frac{p_x^2 - (\hbar k_{\rm SO})^2}{2m} + V_0. \tag{12}$$

This is a spin-independent Hermitian Hamiltonian, whose eigenstate in the "molecule" region has the form

$$\widetilde{\psi}(x) = \widetilde{C}e^{iqx}|+\rangle + \widetilde{D}e^{-iqx}|-\rangle, \tag{13}$$

with the same $q = \sqrt{k^2 + k_{\rm SO}^2 - q_0^2}$ given in Eq. (5). The boundary conditions for $\widetilde{\psi}$ are the same as for spinless particles, hence, the transmission amplitude is

$$\widetilde{t} = \frac{2e^{-iak}kq}{2kq\ \cos(qa) - i(k^2 + q^2)\sin(qa)}. \tag{14}$$

From Eq. (11), $|\Psi(a)\rangle = U^\dagger(a)|\widetilde{\Psi}(a)\rangle$. Noting that $U(x)|\pm\rangle = e^{\mp ik_{\rm SO}x}|\pm\rangle$, it follows that $t_\mu = e^{-iak_{\rm SO}\mu}\widetilde{t}_\mu$, reproducing Eq. (9) and the spin independence of the transmission probability. In fact, the gauge transformation simply shifts the covariant momentum $\tilde{p}_x = p_x + \hbar k_{\rm SO}\mu$ onto the momentum p_x, which is also seen directly from Eq. (4). This results in a simple Aharonov-Casher phase shift in the transmission amplitude, and does not affect the transmission probability. The reflection and transmission probabilities are invariant under the gauge transformation, and therefore remain spin independent.

In conclusion, one cannot generate spin splitting with only spin-orbit interactions, as done in Eq. (5) of Ref. [2], and the chiral-induced spin selectivity effect still awaits a full theoretical explanation.

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