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An Antisymmetric Berry Frictional Force At Equilibrium in the Presence of Spin-Orbit Coupling

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We analytically calculate the electronic friction tensor for a molecule near a metal surface in the case that the electronic Hamiltonian is complex-valued, e.g. the case that there is spin-orbit coupling and/or an external magnetic field. In such a case, *even at equilibrium*, we show that the friction tensor is not symmetric. Instead, the tensor is the real-valued sum of one positive definite tensor (corresponding to dissipation) plus one antisymmetric tensor (corresponding to a Berry pseudomagnetic force). Moreover, we find that this Berry force can be much larger than the dissipational force, suggesting the possibility of strongly spin-polarized chemicurrents or strongly spin-dependent rate constants for systems with spin-orbit coupling.

I. INTRODUCTION

When nuclear degrees of freedom (DoF) are allowed to fluctuate in the presence of a continuum of electronic DoFs, not only will the electronic wave function change at different nuclear positions (in accordance with the Born-Oppenheimer picture) — the nuclear wave packet will also change as it receives feedback from the electronic DoF. In the adiabatic limit, the electronic feedback on the nuclei is composed of three parts: the adiabatic force F_μ, the random force operator ζ_μ, and the frictional damping force. The friction tensor $\gamma_{\mu\nu}$ captures the strength of the nuclear damping force in the μ-direction as caused by nuclear motion in the ν direction and reflects how fast electronic transitions inevitably interfere with simple nuclear (Newtonian) motion. Mathematically, the nuclei follow a stochastic Langevin equation[1, 2] of the form,

$$M_\mu \ddot{R}_\mu = F_\mu - \sum_\nu \gamma_{\mu\nu}\dot{R}_\nu + \zeta_\mu, \tag{1}$$

where M_μ is the mass of a nuclei and R_μ is the nuclear position in the μ direction.

Several important general properties (and proofs) about $\gamma_{\mu\nu}$, including the positive definiteness and the fluctuation-dissipation theorem, are provided in SM **??**-**??**[3]. Historically, electronic friction was first considered as a first-order correction to the Born-Oppenheimer approximation for dynamics near a metal surface, and though there have been many separate approaches for calculating the electronic friction tensor[2, 4–21], all agree in the Markovian limit[2]. $\gamma_{\mu\nu}$ can be divided into a symmetric part $\gamma^{\mathrm{S}}_{\mu\nu}$ and an antisymmetric part $\gamma^{\mathrm{A}}_{\mu\nu}$. For a system at equilibrium, $\gamma^{\mathrm{S}}_{\mu\nu}$ is positive definite; this term can only dissipate energy to the surroundings (and avoid unstable dynamics). Such relaxation processes have been reported as important for molecule-metal interface dynamics (scattering, adsorption etc.)[22–25], electron transfer within electronic devices[26], and heating due to the phonon motion[27, 28]. The diagonal component ($\mu = \nu$) can significantly change the electron-hole pair induced vibrational lifetime[29, 30], and the off-diagonal elements of a symmetric friction tensor ($\mu \neq \nu$) can also be crucial[31, 32].

We have far less experience with the antisymmetric component of the friction tensor, $\gamma^{\mathrm{A}}_{\mu\nu}$, which contributes a Lorentz-like force. Within the chemical physics condensed matter community, the usual assumption is that $\gamma^{\mathrm{A}}_{\mu\nu} = 0$ at equilibrium. That being said, for a strictly real-valued Hamiltonian describing a typical molecule on a typical metal, von Oppen and others[16, 17] have demonstrated that $\gamma^{\mathrm{A}}_{\mu\nu} \neq 0$ only when molecules are in contact with two metals that are *out of* equilibrium (i.e. with a current).

Now, within the description above[16, 17], there has been the assumption of a strictly real-valued Hamiltonian. However, for molecule-metal interfaces or for surface heterostructures, due to the short electron screening length of a metal, the effective electric field gradient on the surface should lead to strong Rashba spin-orbit coupling[33]. Furthermore, a built-in molecular spin-orbit coupling can be enhanced due to molecular geometry, i.e. molecules with large curvature or torsion in geometry are believed to have larger spin-orbit

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coupling[34, 35]. For these reasons, *a complex-valued Hamiltonian may be quite relevant.* Moreover, Robbins and Berry have demonstrated that antisymmetric (Berry) forces may appear if the Hamiltonian is complex-valued[36]. Exact scattering calculations have shown that, for a closed model complex-valued Hamiltonian, the resulting Berry force effects can be large and strongly affect electron transfer processes[37].

Where does this leave us as far as understanding molecular dynamics near a metal surface? For the most part, a molecule on a metal surface is occupied by a fractional number of electrons; as electrons are shared between molecule and metal, the molecular nuclei will feel different forces depending on the fluctuating electronic charge state. While such fluctuations are known to lead to fast vibrational relaxation of a diatomic on a metal surface[23] through the symmetric tensor, one can ask: Does a significant nonzero antisymmetric friction tensor (i.e. a pseudomagnetic field) also appear when we consider a complex-valued Hamiltonian describing a molecule near a metal surface in equilibrium? Note that, except for a few analogous examples in the realm of spintronics[38], to date, the effect of a magnetic field or spin-orbit coupling has been ignored in friction tensor calculations (even though $\gamma_{\mu\nu}$ is general). Note also that Ref. 39 predicts that a huge Berry force can be generated for an isolated molecular system near a sharp avoided crossing in the presence of spin-orbit coupling. One must wonder whether such a huge Berry force will still exist when one considers a molecule strongly coupled to a metal surface.

Below, we will address these questions. In particular, we will show that: (i) Like the case of an isolated molecular system, a Berry force exists whenever a molecular system with a complex-valued Hamiltonian is coupled to a bath (no matter whether or not the total system is in *equilibrium*). (ii) Unlike the case of an isolated molecular system, the strength of the Berry force does not require a tiny energy gap (i.e. a sharp avoided crossing) to achieve a large Berry force (in fact an energy gap is necessary). (iii) $\gamma^{\mathrm{A}}_{\alpha\nu}$ is comparable or can even be one order of magnitude larger than $\gamma^{\mathrm{S}}_{\mu\nu}$ and thus affects the experimental observable. These facts suggest that nuclear motion at surfaces should promote certain flavor of electronic spin selectivity, e.g. perhaps spin selectivity in transport with chiral molecules.

II. MODEL SYSTEM

We consider a model in which a two-level system is coupled to two leads and the two-level system depends on two dimensional nuclear DoF. While there is an immense amount known about the (symmetric) friction tensor that arises for a resonant level model[17, 40], no such results or intuition have been derived for the antisymmetric friction tensor even in the case of a two-level model at equilibrium.

Here we will derive the friction tensor analytically. The total electronic Hamiltonian $\hat{H}$ is divided into three components, the system $\hat{H}_{\mathrm{s}}$, the bath $\hat{H}_{\mathrm{b}}$ and the system-bath coupling $\hat{H}_{\mathrm{c}}$:

$$\begin{aligned}\hat{H} =&\hat{H}_{\mathrm{s}}+\hat{H}_{\mathrm{b}}+\hat{H}_{\mathrm{sb}},\\ \hat{H}_{\mathrm{s}} =&\sum_{mn} h^{\mathrm{s}}_{mn}(\mathbf{R})\hat{b}^{\dagger}_{m}\hat{b}_{n}+U(\mathbf{R}),\\ \hat{H}_{\mathrm{b}} =&\sum_{k\alpha}\epsilon_{k\alpha}\hat{c}^{\dagger}_{k\alpha}\hat{c}_{k\alpha},\\ \hat{H}_{\mathrm{c}} =&\sum_{m,k\alpha} V_{m,k\alpha}\hat{b}^{\dagger}_{m}\hat{c}_{k\alpha}+\mathrm{H.c.}\end{aligned}$$

Above, m, n label system orbitals, and $\hat{b}^{\dagger}_{m}$ ($\hat{b}_{m}$) creates (annihilates) an electron in the system orbital m. $\hat{c}^{\dagger}_{k\alpha}$ ($\hat{c}_{k\alpha}$) creates (annihilates) an electron in the k-th orbital of a lead α. Note that, for the sake of generality, all expressions below will be derived for the case of two electronic leads; $\alpha = \mathrm{L},\mathrm{R}$ indicates left and right leads. If we set the fermi levels μ_α of both leads to be equal, $\mu_{\mathrm{L}} = \mu_{\mathrm{R}}$, there is no difference between having one lead (with $2N$ orbitals) or two leads (with N orbitals). h^{s}_{mn} is the molecular electronic Hamiltonian that depends explicitly on $\mathbf{R}$, the molecular nuclear DoFs, and we know that this dependence on $\mathbf{R}$ leads to a symmetric friction tensor[2]. $U(\mathbf{R})$ is a purely nuclear potential energy. $V_{m,k\alpha}$ represents the tunneling element between the system orbital m and the lead orbital $k\alpha$, which we assume independent of $\mathbf{R}$ (the so-called Condon approximation). Within this model, the most general system Hamiltonian can be written in Pauli matrices representation (σ_i[41]) as:

$$\mathbf{h}^{\mathrm{s}} = \mathbf{h}(x,y)\cdot\boldsymbol{\sigma} = \sum_{i=1,2,3} h_i(x,y)\sigma_i,$$

where $\{h_i\}$ is real. Note that the inclusion of h_2 makes the Hamiltonian possibly complex-valued, as might arise from an external magnetic field or spin-orbit coupling.

If we now evaluate $\gamma_{\mu\nu}$ for the case of non-interacting electrons (following Ref. 42; $\hbar = 1$), we find that the (exact) final results is (see SM **??**[3]):

$$\gamma_{\mu\nu} = \int \frac{d\epsilon}{2\pi}\mathrm{Tr}\{\partial_\mu h^{\mathrm{s}}\partial_\epsilon G^{\mathrm{R}}\partial_\nu h^{\mathrm{s}} G^{<}\} + \mathrm{H.c.}, \qquad (2)$$

where $G^{\mathrm{R}} = (\epsilon - h^{\mathrm{s}} - \Sigma^{\mathrm{R}})^{-1}$ is the (two-level) system retarded Green's function, $\Sigma^{\mathrm{R}}_{mn} = \sum_{k\alpha} V_{m,k\alpha} g^{\mathrm{R}}_{k\alpha} V^{*}_{n,k\alpha}$ is the system self energy, and $g^{\mathrm{R}}_{k\alpha} = (\epsilon - \epsilon_{k\alpha} + i\eta)^{-1}$ is the lead retarded self energy ($\eta \to 0^{+}$). $G^{<}$ is the system lesser Green's function and, provided that an imaginary surrounding is quadratic[42] or the system spectral broadening due to the leads is finite[43], $G^{<}$ can be calculated by the Keldysh equation, $G^{<} = G^{\mathrm{R}}\Sigma^{<}G^{\mathrm{A}}$. Here $\Sigma^{<}_{mn} = \sum_{k\alpha} V_{m,k\alpha} g^{<}_{k\alpha} V^{*}_{n,k\alpha}$ is the system lesser self energy, and $g^{<}_{k\alpha}(\epsilon) = i2\pi f_\alpha(\epsilon)\delta(\epsilon - \epsilon_{k\alpha})$ is the lead lesser Green's function. ($f(\epsilon) = 1/[\exp(\beta(\epsilon-\mu))+1]$ is the Fermi-Dirac distribution with the inverse temperature β and the chemical potential μ.)

We further make the following standard assumptions[44]: (i) the tunneling-width matrix $\Gamma_{mn} = 2\pi \sum_{k\alpha} V_{m,k\alpha} V^*_{n,k\alpha} \delta(\epsilon - \epsilon_{k\alpha})$ is independent of ϵ (i.e. the wide band limit approximation), (ii) $\Gamma_{mn} = \tilde{\Gamma}$ is a constant, (iii) the tunneling elements $V_{m,k\alpha}$ are independent of k, and (iv) the left lead couples only to orbital 1 and the right lead couples only to orbital 2, with the two coupling constants the same real value. Therefore, $\Sigma^{\rm R} = -\frac{i}{2}\tilde{\Gamma}$, and $\Sigma^{<} = i\tilde{\Gamma}\,(f_{\rm L}\,0;\,0\,f_{\rm R})$ where $f_{\rm L}$ and $f_{\rm R}$ are Fermi-Dirac distribution of the left and right leads respectively. Please see SM **??** for a schematic picture (equilibrium case)[3].

A calculation (see SM **??**[3]) shows that the friction tensor (from Eq. (2)) is,

$$\gamma_{\mu\nu} = \gamma^{\rm S}_{\mu\nu} + \gamma^{\rm A}_{\mu\nu}, \tag{3}$$

$$\begin{aligned}\gamma^{\rm S}_{\mu\nu} =& \frac{2}{\pi}\int_{-\infty}^{\infty} d\epsilon \Big\{ -2\mathfrak{Re}\left\{C\tilde{\epsilon}\right\}(\partial_\mu \mathbf{h}\cdot\partial_\nu\mathbf{h})(\mathbf{h}\cdot\boldsymbol{\kappa}) \\ &+ 2\mathfrak{Re}\left\{C\tilde{\epsilon}\right\}(\partial_\mu\mathbf{h}\cdot\mathbf{h})(\partial_\nu\mathbf{h}\cdot\boldsymbol{\kappa}) \\ &+ 2\mathfrak{Re}\left\{C\tilde{\epsilon}\right\}(\partial_\nu\mathbf{h}\cdot\mathbf{h})(\partial_\mu\mathbf{h}\cdot\boldsymbol{\kappa}) \\ &+ \kappa_0\mathfrak{Re}\left\{C\left(\tilde{\epsilon}^2+h^2\right)\right\}\partial_\mu\mathbf{h}\cdot\partial_\nu\mathbf{h}\Big\}\end{aligned} \tag{4}$$

$$\begin{aligned}\gamma^{\rm A}_{\mu\nu} =& \frac{2}{\pi}\int_{-\infty}^{\infty} d\epsilon \Big\{ -\mathfrak{Im}\left\{C\left(\tilde{\epsilon}^2+h^2\right)\right\}\boldsymbol{\kappa}\cdot(\partial_\mu\mathbf{h}\times\partial_\nu\mathbf{h}) \\ &+ 2\kappa_0\mathfrak{Im}\left\{C\tilde{\epsilon}\right\}\mathbf{h}\cdot(\partial_\mu\mathbf{h}\times\partial_\nu\mathbf{h})\Big\},\end{aligned} \tag{5}$$

Here

$$C \equiv -\left(\frac{1}{\tilde{\epsilon}^2-h^2}\right)^2 i\tilde{\Gamma}\left|\frac{1}{\tilde{\epsilon}^2-h^2}\right|^2,$$

where $\tilde{\epsilon} = \epsilon + i\tilde{\Gamma}/2$ is a complex number, and $h^2 = \mathbf{h}\cdot\mathbf{h}$. The κ's are defined as

$$\begin{aligned}\kappa_0 =& \frac{1}{2}\left[(f_{\rm L}+f_{\rm R})\left(h_1^2+h_2^2\right) + f_{\rm L}|\tilde{\epsilon}+h_3|^2 + f_{\rm R}|\tilde{\epsilon}-h_3|^2\right], \\ \kappa_1 =& \mathfrak{Re}\left\{\left[f_{\rm L}\left(\tilde{\epsilon}^*+h_3\right)+f_{\rm R}\left(\tilde{\epsilon}-h_3\right)\right](h_1+ih_2)\right\}, \\ \kappa_2 =& \mathfrak{Im}\left\{\left[f_{\rm L}\left(\tilde{\epsilon}^*+h_3\right)+f_{\rm R}\left(\tilde{\epsilon}-h_3\right)\right](h_1+ih_2)\right\}, \\ \kappa_3 =& \frac{1}{2}\left[(f_{\rm R}-f_{\rm L})\left(h_1^2+h_2^2\right) + f_{\rm L}|\tilde{\epsilon}+h_3|^2 - f_{\rm R}|\tilde{\epsilon}-h_3|^2\right].\end{aligned}$$

Note that κ_0 and $\boldsymbol{\kappa} = (\kappa_1,\kappa_2,\kappa_3)$ are real functions. When the total system is in equilibrium, namely $f_{\rm L} = f_{\rm R} = f$,

$$\kappa_0 = f\left(\epsilon^2 + h^2 + \frac{\Gamma^2}{4}\right), \tag{6}$$

$$\boldsymbol{\kappa} = 2f\epsilon\mathbf{h}. \tag{7}$$

Equations (3)-(5) represent a very general electronic friction tensor for a minimal model of a molecule near metal surfaces in the presence of spin-orbit coupling.

III. RESULTS AND DISCUSSIONS

According to Eq. (3) we can make two important and general conclusions regarding Berry forces of equilibrium near a metal surface. First, according to Eqs (5)-(6), $\gamma^{\rm A}_{\mu\nu}$ is proportional to $\mathbf{h}\cdot(\partial_\mu\mathbf{h}\times\partial_\nu\mathbf{h})$. Therefore, $\gamma^{\rm A}_{\mu\nu}$ will vanish when at least one element of $\mathbf{h}$ is zero, or when two elements of $\mathbf{h}$ are the same. These facts demonstrate not only that an imaginary off-diagonal coupling (h_2) is required for a nonzero $\gamma^{\rm A}_{\mu\nu}$, but also that the key source of a nonzero $\gamma^{\rm A}_{\mu\nu}$ is the spatial dependence of the phase of the off-diagonal coupling, $\tan^{-1}(h_2/h_1)$. After all, if $h_1 = 0$ or $h_1(x,y) = h_2(x,y)$, we can find a constant change of basis transformation that guarantees a globally real-valued Hamiltonian and therefore $\gamma^{\rm A}_{\mu\nu} = 0$. In other words, in such a case, there is no Lorentz-like force.

Second, according to Eqs. (3)-(7), one can construct several nonequivalent Hamiltonians that generate equivalent friction tensors. To see this, note that, when the system is in equilibrium, the symmetric terms in Eq. (3) all have dot product dependence on $\mathbf{h}$, namely h^2, $\sum_i \partial_\mu h_i \partial_\nu h_i$ and $\sum_i \partial_\mu h_i h_i$. Thus, the symmetric terms are invariant to any permutation of $\mathbf{h} = \{h_1,h_2,h_3\}$. Moreover, the two terms comprising $\gamma^{\rm A}_{\mu\nu}$ depend on $\mathbf{h}\cdot(\partial_\mu\mathbf{h}\times\partial_\nu\mathbf{h})$, which are also invariant under cyclic permutation of the $\mathbf{h}$ elements. Thus, different Hamiltonians can generate the same friction tensor and, as a practical matter, this must have experimental consequences as some Hamiltonians are undoubtedly easier to realize than others. For example, in Eq. (8) we will consider a model Hamiltonian with diagonal coupling $h_3 = x + \Delta$; here, as in standard Marcus theory, Δ is a driving force that will be shown to play an important role in generating a large antisymmetric friction tensor. Nevertheless, if ones imagines permuting the $\mathbf{h}$ elements by substituting $h_1 \to h_3 \to h_2$, then the parameter Δ will enter on the off-diagonal of the Hamiltonian and can be realized, e.g., by tuning an external magnetic field.

These are the only direct, general conclusions we can make from Eqs. (3)-(7). Next, let us focus on a model problem which can yield further insight using numerical analysis. We imagine the standard case of two shifted parabolas, expressed in a nuclear space with two dimensions and with a driving force of 2Δ. Mathematically, the system Hamiltonian is taken to be of the form:

$$\mathbf{h}^{\rm s} = \begin{pmatrix} x+\Delta & Ax - iBy \\ Ax + iBy & -x-\Delta \end{pmatrix}, \tag{8}$$

and $U = x^2/2 + y^2/2 + 1/2$. We calculate the electronic friction tensor by using Eq. (3). Note that the purely nuclear potential U does not contribute to the friction tensor. Recall that $\gamma^{\rm A}_{\mu\nu} \propto \mathbf{h}^{\rm s}\cdot(\partial_\mu\mathbf{h}^{\rm s}\times\partial_\nu\mathbf{h}^{\rm s}) = AB\Delta$. Thus, as argued above, if there is no change in the phase of the off-diagonal coupling ($A = 0$ or $B = 0$) in the nuclear space, we will find that $\gamma^{\rm A}_{xy} = 0$. Also notice that when the driving force $\Delta = 0$, again $\gamma^{\rm A}_{\mu\nu} = 0$. Beyond these two extreme cases, we will find both symmetric and antisymmetric components of the friction tensor.

In Fig. 1, we show contour plots for the friction tensor with $\beta = 2$, $A = B = 1$. Here, $A = B$ corresponds to a strong change of phase in the off-diagonal coupling.

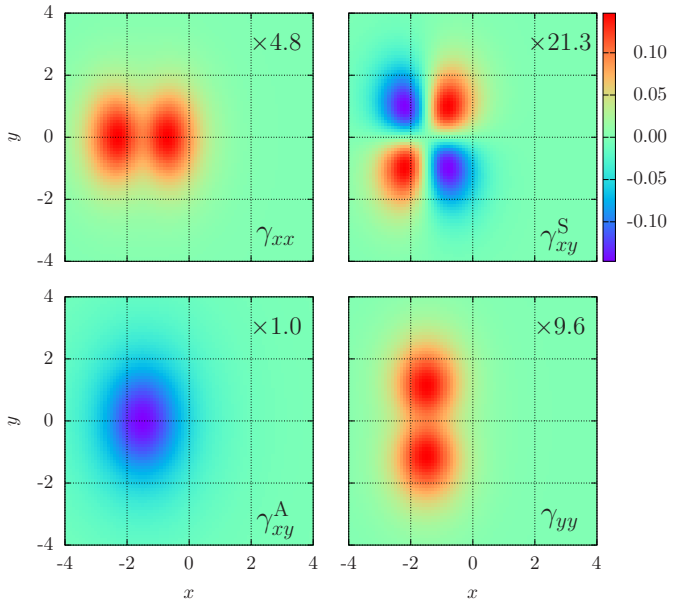


FIG. 1. Friction tensor calculation results: γ_{xx} (top left), γ^{S}_{xy} (top right), γ^{A}_{xy} (bottom left) and γ_{yy} (bottom right). Parameters: $\tilde{\Gamma} = 1$, $\mu_{\mathrm{R}} = \mu_{\mathrm{L}} = 0$, $\beta = 2$, $A = 1$, $B = 1$, $\Delta = 3$. Notice that all the results in Figs. **??** and 1 have mirror symmetry about $x = -1.5 = -\Delta/(A^2+1)$ and $y = 0$, because all six terms in Eq. (4) and Eq. (5) are functions of $[x+\Delta/(A^2+1)]^2$ and B^2y^2 when the system is in equilibrium.

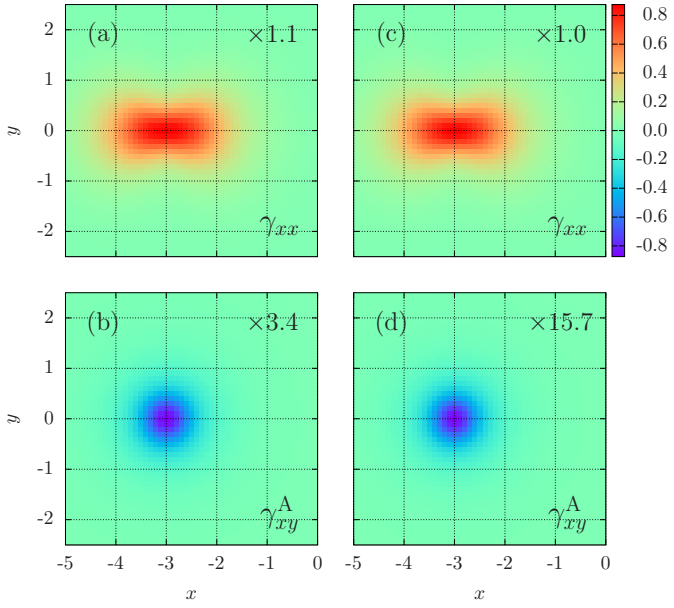


FIG. 2. Friction tensor calculation results (only γ_{xx} and γ^{A}_{xy} are shown). Parameters for (a) and (b) are $\tilde{\Gamma} = 1$, $\mu_{\mathrm{R}} = \mu_{\mathrm{L}} = 0$, $\beta = 2$, $A = 0.05$, $B = 1$, $\Delta = 3$; (c) and (d) have the same parameters as (a) and (b), except that $A = 0.01$.

Several features are clear from the contour plot. First, the antisymmetric friction tensor γ^{A}_{xy} is one order larger than all other symmetric friction tensors. Thus, clearly Lorentz-like motion can be as important as any dissipative process. Second, the magnitude of γ^{A}_{xy} is maximized around the avoided crossing at $(-1.5, 0)$, but for each component of the symmetric friction tensor, the magnitude is maximized far from the avoided crossing. Therefore, depending on the preparation of the initial nuclear wave packet, one might imagine that slow nuclei will equilibrate before feeling any Lorentz like force. That being said, the exact details for any calculation must be evaluated on a case-by-case basis.

In Fig. 2, we further investigate how the relative strength of the antisymmetric friction tensor changes as a function of how the off-diagonal coupling changes phase. Here we keep the same parameters as in Fig. 1, except we change A. In subplots (a)(b), the antisymmetric friction tensor γ^{A}_{xy} has the same order of magnitude as the symmetric friction tensors. In subplots (c)(d), we reduce A so that $A = 0.01$; we find the antisymmetric friction tensor approaches zero rapidly. We conclude that in *any* theoretical or experimental works which consider an external magnetic field or/and spin-orbit coupling with reasonable changes for the phase (here larger than 5%) in the nuclear space, we cannot ignore the effect of the antisymmetric friction tensor. We have also performed several *ab initio* calculations so as to extract parameters for a real system — a diphenylmethane junction (See SM **??**[3]). The results are consistent with the conclusion above — even when spin-orbit coupling is small, γ^{A}_{xy} can still be dominant.

Lastly, before concluding, we summarize a few results that are addressed in the SM. First, we investigate the dependence of γ^{S} and γ_{A} on β and $\tilde{\Gamma}$ in SM **??** and SM **??** respectively[3]. We find that the relative strength of γ^{A}_{xy} grows stronger for lower temperatures. Also, when the system-bath coupling strength $\tilde{\Gamma}$ grows very large, both the symmetric and antisymmetric friction tensors become smaller and these tensors are nonzero over an effectively smaller portion of nuclear configuration space. Second, while we have considered an avoided crossing above, in SM **??** we investigate true complex-valued conical intersections[3]. There, we show that the dynamical effect of a pseudomagnetic field in the direct vicinity of a true conical intersection is likely not very large. Third, and most importantly, throughout this letter, we have focused mostly on the magnitude of the antisymmetric friction tensor. Note that, in a basis of spin orbitals, switching spin up and spin down orbital will swap h_2 and $-h_2$ and lead to different signs of $\gamma^{\mathrm{A}}_{\mu\nu}$. Thus, different spins will feel different directions of the Lorentz force and the present formalism may underlie spin selectivity for molecular processes near metal surfaces[45–47]. As a practical matter if we were to construct an overall electronic friction tensor for the case of a system with multiple spin degrees of freedom, such a tensor would be meaningful only when the spin degrees of freedom interconvert rapidly, so that nuclear motion remains the slowest process of interest; alternatively, one would re-

quire separate friction tensors (one for up spin, and one for down spin) as in the present letter.

IV. CONCLUSIONS AND OUTLOOK

We have demonstrated that a large Lorentz force can operate on nuclei *in equilibrium* for systems with *complex-valued* Hamiltonians. For a simple model of two shifted parabolas, with spin-orbit coupling, according to an analytic expression for the friction tensor, the magnitudes of the relevant frictional components ($\gamma^{\mathrm{S}}_{\mu\nu}$ and $\gamma^{\mathrm{A}}_{\mu\nu}$) can be controlled by tuning the driving force Δ and the inverse temperature β. The antisymmetric part can be one order larger than the symmetric part for low temperatures. Moreover, $\gamma^{\mathrm{A}}_{\mu\nu}$ and $\gamma^{\mathrm{S}}_{\mu\nu}$ can be of comparable magnitude even when the phase change of the off-diagonal coupling is very small. All of these results show that, for any relaxation processes with an external magnetic field or/and spin-orbit coupling, careful consideration of a Lorentz force due to the nuclear Berry curvature is necessary. We have also provided *ab initio* calculations of a diphenylmethane junction, showing the same conclusions as above.

Looking forward, one can imagine two scenarios whereby the antisymmetric nature of $\gamma_{\mu\nu}$ will be paramount. First, if one scatters a molecule off a surface in the presence of spin-orbit coupling , there is the real possibility that the presence of $\gamma^{\mathrm{A}}_{\mu\nu}$ will contribute meaningfully to a spin-polarized chemicurrent. Second, there is a deep question about whether the Lorentz force described here can help explain spin-selectivity as found in chiral-induced spin selectivity (CISS) experiments[45–47]. In other words, if nuclear wave packets attached to different spins feel different forces, might not one consequence of such a difference be spin-polarized of a current through a system where nuclei and electrons interact? Such a claim might be verified experimentally by the presence of an isotopic CISS effect. Finally, from a theoretical point of view, note that a recent paper has argued empirically that, for a molecule in the gas phase, the Lorentz force is accentuated dynamically when the molecule passes near a conical intersection that is slightly modified by spin-orbit coupling[39]. For our part, we find a similar result near a metal surface, i.e. the effect of the Lorentz force is maximized if $\hat{H}_{\mathrm{s}}$ admits an energy gap rather than displaying a true conical intersection. In fact, according to Eq. (5), the antisymmetric part of the friction tensor is zero if one considers a gapless two-dimensional linear vibronic complex-valued Hamiltonian (See SM **??**[3])[48].

Finally, in this letter we have analyzed the antisymmetric friction tensor that appears at equilibrium (with spin-orbit coupling). At the same time, a set of recent calculations has shown that a Berry force also appears when a molecule is placed between two leads out of equilibrium (without spin-orbit coupling)[16, 17]. To that end, the question remains as to what is the relationship between the equilibrium Lorentz force analyzed here (derived in the case of a complex-valued Hamiltonian) and the previously published nonequilibrium Lorentz forces (derived in the case of real-valued Hamiltonian)[8, 17]. One can ask: Can the two Lorentz forces add to each other constructively? Can the forces be controlled individually by the properties of two leads? The present approach opens up the door to merge spintronics and nonadiabatic dynamics for an accurate description of spin-dependent current induced forces.

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[3] See Supplemental Material at [URL will be inserted by publisher] for proofs of several properties of the friction tensor (SM **??**-**??**), a schematic picture of the molecular junction model (SM **??**), details of the derivations of Eqs. (3)-(5) (SM **??**), an examination of the friction tensors that arise for a variety of different Hamiltonians (**??**-**??**), and an analysis of friction tensors for one *ab initio* molecule in a junction (**??**). SM includes Refs. [Ref. 49-Ref. 56].
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