# Symmetry breaking in the Stark Control of Electrons at Interfaces (SCELI)

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## ABSTRACT

Ultrafast control of electron dynamics is essential for future innovations in nanoelectronics, catalysis, and molecular imaging. Recently, we developed a general scheme (Stark Control of Electrons at Interfaces or SCELI) to control electron dynamics at interfaces [A. J. Garzón-Ramírez and I. Franco, Phys. Rev. B **98**, 121305 (2018)] that is based on using few-cycle lasers to open quantum tunneling channels for interfacial electron transfer. SCELI uses the Stark effect induced by non-resonant light to create transient resonances between a donor level in material B and an acceptor level in material A, resulting in B  $\rightarrow$  A electron transfer. Here, we show how SCELI can be employed to generate net charge transport in ABA heterojunctions without applying a bias voltage, a phenomenon known as laser-induced symmetry breaking. The magnitude and sign of such transport can be controlled by simply varying the time asymmetry of the laser pulse through manipulation of laser phases. In particular, we contrast symmetry breaking effects introduced by manipulation of the carrier envelope phase with those introduced by relative phase control in  $\omega + 2\omega$  laser pulses. The  $\omega + 2\omega$  pulse is seen to be far superior as such pulses exhibit a larger difference in field intensity for positive and negative amplitudes. The results exemplify the power of Stark-based strategies for controlling electrons using lasers.

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# I. INTRODUCTION

Controlling electron dynamics using lasers is a central goal of science and technology.<sup>1-4</sup> This is because electrons and their interactions determine many physical properties of matter, and lasers open up opportunities to manipulate them on an ultrafast timescale.<sup>5–28</sup> This opens new ways to control the ability of matter to chemically react,<sup>29–36</sup> conduct charge,<sup>6–10,16,21,24,26,28,37–43</sup> and absorb light<sup>44–48</sup> or other properties in a femto to attosecond timescale, something that is unachievable by conventional means such as chemical/thermodynamic control or through applied voltages.

A major challenge in the laser control of electrons in matter is to overcome the deleterious effects of decoherence. The fact that such decoherence is ultrafast (typically in ~10 s fs)<sup>49-52</sup> has traditionally limited the applicability of coherent control scenarios as they are based on quantum interference and thus are fragile to such decoherence.<sup>53</sup>

As an alternative, Stark-based strategies  $^{11,26,34-36,54-56}$  can be used to control electrons even in the presence of strong

decoherence.<sup>11,26,57</sup> The Stark effect refers to the shifts of energy levels in matter due to the application of an electric field. In lasermatter interactions, such an effect becomes dominant when the laser frequency is chosen to be far detuned from any transition in the system such that near-resonance photon absorption is suppressed. This route for control employs non-resonant lasers of intermediate intensity (non-perturbative but non-ionizing) to dramatically distort the electronic structure of the material, and as such, it is a Hamiltonian type of control.<sup>11,26,56</sup> The reason why this control route is robust to decoherence is because it does not rely on creating electronic superposition states with fragile coherence properties. Instead, the control is based on pushing energy levels around; on modifying the Hamiltonian.

Recently, we introduced a Stark-based Control scenario that is able to induce ELectron transfer across Interfaces (SCELI) in heterojunctions.<sup>26</sup> The scenario uses few-cycle non-resonant laser pulses to induce transient resonances among the electronic energy levels of the different semiconductors that compose the heterojunction. When the transient resonances involve valence band (VB) levels of one semiconductor and conduction band (CB) levels of the second semiconductor, quantum tunneling channels for electron transfer between the two adjacent semiconductors are opened. SCELI can be used to control electron dynamics at interfaces and turn insulating heterojunctions into conducting ones on a femtosecond timescale.

In this paper, we demonstrate how SCELI<sup>26</sup> can be extended to induce phase-controllable currents in spatially symmetric heterojunctions even in the absence of bias voltage, a phenomenon known as laser-induced symmetry breaking.<sup>8–10,16,58–60</sup> We focus on symmetry-breaking effects that can be generated by few-cycle laser pulses as such pulses enable the use of intense electric fields of  $10^{11}$  W/cm<sup>2</sup>- $10^{13}$  W/cm<sup>2</sup> before the onset of dielectric breakdown.<sup>10,27,61</sup> Using them, the electronic dynamics can be controlled by the instantaneous value of the electric field of light,<sup>5–10,14–19,21–24,26,28</sup> as opposed to dynamic Stark effects that depend on the laser envelope.<sup>34–36,54,55</sup>

Laser-induced symmetry breaking arises because of the nonlinear response of matter to fields of low temporal symmetry. <sup>1,59</sup> In its most basic form, laser pulses  $E(t) = \epsilon_{\omega} \cos(\omega t + \phi_{\omega}) + \epsilon_{2\omega} \cos(2\omega t + \phi_{2\omega})$  with frequency components  $\omega$  and  $2\omega$  are used to photoexcite a spatially symmetric system from a bound state to a given energy in the continuum by means of a near-resonance one-photon and two-photon excitation. Since odd-photon processes connect states with opposite parity, while even-photon processes connect states with the same parity, simultaneous photoexcitation via a one- and a two-photon process creates a state in the continuum of no definitive parity. This breaks the spatial symmetry of the system and generates a net phase-controllable current  $I \sim \overline{E(t)}^3 = \frac{3}{4} \epsilon_{2\omega} \epsilon_{\omega}^2 \cos(2\phi_{\omega} - \phi_{2\omega})$ , where the overline denotes time-averaging.

More generally, the effect emerges in the odd-order nonlinear response of matter to resonant or non-resonant laser fields that violate the following temporal symmetries:<sup>59</sup> (i) E(t + T/2) = -E(t), (ii) E(t - t') = + E(-(t - t')), and (iii) E(t - t') = -E(-(t - t')), where *T* is the period of the field and *t'* is some reference time. If the field changes sign every half a period [symmetry (i)], no net dipoles/currents that survive time-averaging can be photogenerated. In turn, if the field violates (i) but is symmetric with respect to time inversion [symmetry (ii)], no net currents can be produced. Finally, if the field violates (i) but is antisymmetric with respect to time inversion [symmetry (iii)], no net dipoles can be produced. If all three conditions are violated, net dipoles and currents are expected.

Few-cycle laser pulses are of low temporal symmetry, and the degree of time asymmetry can be manipulated by varying the carrier envelope phase (CEP)  $\phi$ .<sup>8–11,16,53,58–60,62–64</sup> Gaussian few-cycle pulses with  $\phi = 0, \pm \pi$  violate symmetry condition (i) but satisfy (ii) and can induce net dipoles. Those with  $\phi = \pm \pi/2$  violate (i) but satisfy (iii) and can induce net momenta when an energy continuum is accessible to photoexcitation.<sup>59</sup> Such lasers allow generating ultrafast electronic currents<sup>6–10,16,24,26,28</sup> that can be employed to design photoelectronic actuators,<sup>7</sup> imaging techniques,<sup>56</sup> and routes to catalysis that operates on a femto to attosecond timescale.

Here, we contrast the symmetry breaking effects in SCELI introduced by few-cycle laser pulses with a Gaussian spectrum to



FIG. 1. Laser-induced transient resonances among the single-particle electronic energy levels of the ABA heterojunction. (a) Insulating ABA heterojuntion composed of two semiconductors A and B (tight-binding parameters  $h_{\text{odd}}^{\text{A}} = 1.0$ eV,  $h_{\text{even}}^{\text{A}} = 7.0$ ,  $h_{\text{odd}}^{\text{B}} = -3.0$  eV,  $h_{\text{even}}^{\text{B}}$ = 3.0 eV, and  $t_{odd}^i = t_{even}^i = 3.0 eV$ , *i* = A, B) with no spectral overlap. (b) Eigenenergies for different electric field amplitudes  $E_0$ . Under the influence of a non-resonant laser field, the laser-dressed eigenenergies of the ABA heterojunction fan out as the laser field amplitude  $E_0$  changes, resulting in multiple trivial and avoided crossings. Avoided crossings between VB levels of B and CB levels of A, such as those signaled by the colored lines (red: CB level of AR; green: CB level of AL; and blue: VB levels of B), open tunneling pathways for  $B \rightarrow A$  electron transfer. For  $E_0 > 0$  (or  $E_0 < 0$ ) B  $\rightarrow A^L$  (or B  $\rightarrow A^R$ ), electron transfer dominates. Panel (c) [or (d)] details the most effective avoided crossing (with the average energy offset for clarity) between CB of A<sup>L</sup> (or A<sup>R</sup>) and VB of B [colored lines in (b)]. [(e) and (f)] Wavefunctions of the associated diabatic states. Their overlap at the interface leads to the anticrossings in [(c) and (d)].

J. Chem. Phys. **153**, 044704 (2020); doi: 10.1063/5.0013190 Published under license by AIP Publishing that introduced by  $\omega + 2\omega$  few-cycle laser pulses. As discussed below, to maximize the symmetry breaking effect, it is desirable to design pulses with a large difference in intensity for positive and negative field amplitudes. This makes the  $\omega + 2\omega$  fields superior for symmetry breaking purposes.

We demonstrate this phenomenology in the context of spatially symmetric heterojunctions composed of a semiconductor B sandwiched in between two semiconductors A [see Fig. 1(a)]. The heterojunction is chosen to be insulating to both resonant photoexcitation and an applied voltage. The few-cycle laser pulse is employed to open tunneling channels for interfacial electron transfer. By varying the CEP, one can selectively control the direction of the electron transport across the ABA heterojunction.

This paper is organized as follows: Section II describes the tightbinding Hamiltonian model for the ABA heterojunction and the method employed to solve the time-dependent Schrödinger equation during and after photoexcitation. Section III details the symmetry breaking effect and contrasts the effectiveness of pulses with a Gaussian spectrum around frequency  $\omega$ , with those with two central frequencies centered around  $\omega$  and  $2\omega$ . Our main results are summarized in Sec. IV.

#### **II. MODEL AND METHODS**

#### A. Hamiltonian

We consider a neutral insulating ABA heterojunction, where a slab of semiconductor B is sandwiched in between slabs of semiconductor A [Fig. 1(a)]. The heterojunction is modeled as a onedimensional chain, where each of the materials that form it is described by a tight-binding Hamiltonian. The Hamiltonian for the whole system is given by

$$\hat{H}(t) = \hat{H}_{A}^{(L)}(t) + \hat{H}_{B}(t) + \hat{H}_{A}^{(R)}(t) + \hat{H}_{AB} + \hat{H}_{BA},$$
(1)

where  $\hat{H}_{\rm B}$  is the Hamiltonian for semiconductor B and  $\hat{H}_{\rm A}^{\alpha}$  is the Hamiltonian for semiconductor A to the left ( $\alpha = L$ ) or to the right ( $\alpha = R$ ) of B. The term  $\hat{H}_{\rm AB}/\hat{H}_{\rm BA}$  refers to the interfacial coupling. Each material is modeled as a two-band tight-binding semiconductor with  $N_j = 50$  unit cells (j = A or B) in dipole interaction with a laser field E(t),

$$\hat{H}_{j}(t) = \sum_{n=1}^{2N_{j}} (h_{n,n}^{j} + |e|E(t)x_{n})\hat{a}_{n}^{\dagger}\hat{a}_{n} + \sum_{\langle n,m \rangle}^{2N_{j}-1} h_{n,m}^{j}(\hat{a}_{n}^{\dagger}\hat{a}_{m} + \text{H.c.}).$$
(2)

Here,  $\hat{a}_n(\hat{a}_n^{\dagger})$  annihilates (creates) a fermion in site or Wannier function n,  $\hat{a}_n^{\dagger}|0\rangle = |n\rangle$ , where  $|0\rangle$  is the vacuum state, and satisfies the usual fermionic anti-commutation relations. Each unit cell is composed of two Wannier functions with alternating on-site energies  $(h_{n,n}^j = h_{\text{even}}^j \delta_{n,\text{even}} + h_{\text{odd}}^j \delta_{n,\text{odd}})$  and tight-binding coupling among them  $[h_{n,n+1}^j = -(t_{\text{even}}^j \delta_{n,\text{even}} + t_{\text{odd}}^j \delta_{n,\text{odd}})]$ . Here,  $x_n$  is the position of each Wannier function  $|n\rangle$  along the junction, |e| is the electron charge,  $\langle n, m \rangle$  denotes nearest neighbors, and H.c. is the Hermitian conjugate. The interaction of the semiconductors at the interface is taken to be

$$\hat{H}_{AB} = -t_{AB} (\hat{a}_{2N_{B}}^{\dagger} \hat{a}_{2N_{B}+1} + \text{H.c.}),$$
 (3a)

$$\hat{H}_{BA} = -t_{AB} (\hat{a}_{2N_{B}+2N_{A}}^{\dagger} \hat{a}_{2N_{B}+2N_{A}+1} + H.c.),$$
 (3b)

where  $t_{AB}$  is the interfacial tight-binding coupling. As a representative lattice constant for a semiconductor, we use a = 5.0 Å and a distance between sites in each cell of 1.7 Å for both materials. As an interfacial distance, we employ  $a_{AB} = 7.7$  Å and coupling  $t_{AB} = 0.2$  eV. The remaining tight-binding parameters are defined in Fig. 1. The parameters were chosen to yield semiconductors with a 6 eV bandgap and 3.7 eV bandwidths. The energetic alignment between the semiconductors were chosen such that there is no spectral overlap among the bands (the case of partial overlap was considered previously<sup>26</sup>). This ensures that the heterojunction is insulating to both an applied voltage and resonant photo-excitation and that all electron transfer events are due to SCELI.<sup>26</sup> This choice enables us to cleanly assess the ability of SCELI to be employed in laser-induced symmetry breaking.

#### **B.** Laser pulse

Unless noted otherwise, the laser pulse employed in the simulations is a few-cycle laser of central frequency  $\hbar\omega = 0.5$  eV, width  $\tau = 5.85$  fs, centered around  $t_c = 50$  fs, and carrier envelope phase (CEP)  $\phi$ . A few-cycle laser is chosen to suppress the onset of dielectric breakdown<sup>10,27,61</sup> even for moderately strong fields. Such a laser pulse is far detuned from electronic transitions in the system such that Stark effects dominate the photoresponse. The vector potential associated with the laser pulse is of the form

$$A(t) = \frac{E_0}{\omega} e^{-(t-t_c)^2/2\tau^2} \sin(\omega(t-t_c) + \phi).$$
(4)

The associated electric field  $E(t) = -\frac{dA(t)}{dt}$  is given by

$$E(t) = \frac{E_0}{\omega} e^{-(t-t_c)^2/2\tau^2} \times \left[\frac{(t-t_c)}{\tau^2}\sin(\omega(t-t_c)+\phi) - \omega\cos(\omega(t-t_c)+\phi)\right].$$
(5)

This form guarantees that E(t) remains as an ac source even for fewcycle lasers as  $\int_{-\infty}^{\infty} E(t)dt = A(-\infty) - A(\infty) = 0$ .

#### C. Equation of motion

Since the Hamiltonian in Eq. (1) is a single-particle operator, all the electronic properties are determined by the single-particle electronic reduced density matrix,

$$\rho_{nm}(t) = \langle \Psi(t) | \hat{a}_n^{\dagger} \hat{a}_m | \Psi(t) \rangle, \tag{6}$$

where  $|\Psi(t)\rangle$  is the many-body wavefunction. The dynamics of  $\rho_{nm}(t)$  is governed by the Liouville–von Neumann equation

$$i\hbar\frac{d}{dt}\rho_{nm}(t) = \langle [\hat{a}_n^{\dagger}\hat{a}_m, \hat{H}] \rangle, \tag{7}$$

with initial condition  $\rho_{nm}(0) = \langle \Psi(0) | \hat{a}_n^{\dagger} \hat{a}_m | \Psi(0) \rangle$ .

To integrate Eq. (7), it is useful to employ an orbital decomposition for  $\rho_{nm}(t)$ . Taking  $|\varepsilon\rangle$  as the eigenorbitals of the system at initial time, defined by the relation  $\hat{H}(t = 0)|\varepsilon\rangle = \varepsilon|\varepsilon\rangle$ , the initial single-particle electronic reduced density matrix can be expressed as

$$\rho_{nm}(0) = \sum_{\varepsilon=1}^{N} \langle \varepsilon | n \rangle \langle m | \varepsilon \rangle f(\varepsilon), \qquad (8)$$

J. Chem. Phys. **153**, 044704 (2020); doi: 10.1063/5.0013190 Published under license by AIP Publishing where *N* is the total number of eigenorbitals,  $\hat{a}_{\varepsilon}^{\dagger}$  creates a fermion in the orbital with energy  $\varepsilon$ , and  $f(\varepsilon) = \langle \Psi(0) | \hat{a}_{\varepsilon}^{\dagger} \hat{a}_{\varepsilon} | \Psi(0) \rangle = 0, 1$  is the initial electronic distribution among the single-particle states. Here, we have used the basis transformation

$$\hat{a}_{n}^{\dagger} = \sum_{\varepsilon=1}^{N} \langle \varepsilon | n \rangle \hat{a}_{\varepsilon}^{\dagger}.$$
<sup>(9)</sup>

Upon time evolution, we adopt the ansatz that  $\rho_{nm}(t)$  maintains the form in Eq. (8). That is,

$$\rho_{nm}(t) = \sum_{\varepsilon=1}^{N} \langle \varepsilon(t) | n \rangle \langle m | \varepsilon(t) \rangle f(\varepsilon).$$
(10)

The utility of this ansatz is that if the time-dependent orbitals  $|\varepsilon(t)\rangle$  satisfy the single-particle Schrödinger equation,

$$i\hbar \frac{d}{dt}|\varepsilon(t)\rangle = \hat{H}(t)|\varepsilon(t)\rangle,$$
 (11)

with initial condition  $|\varepsilon(t = 0)\rangle = |\varepsilon\rangle$ , the single-particle electronic reduced density matrix automatically satisfies the correct equation of motion [Eq. (7)].

Equation (11) is numerically integrated for 110 fs using the predictor-corrector Adams–Moulton method with an adaptive time step in the SUNDIALS package.<sup>65</sup> The heterojunction is taken to be neutral such that the number of electrons  $N = 6N_j = 300$ . Snapshots of selected observables are recorded every  $\Delta t_{obs} = 0.01$  fs.

## D. Main observables

The electron transfer dynamics is monitored through changes in the total charge  $\Delta Q_i$  of each material. Specifically, we focus on

$$\Delta Q_{\mathrm{A}^{\alpha}}(t) = \sum_{n \in \mathrm{A}^{\alpha}} (\rho_{nn}(t) - \rho_{nn}(0)), \qquad (12a)$$

$$\Delta Q_{\rm B}(t) = \sum_{n \in {\rm B}} (\rho_{nn}(t) - \rho_{nn}(0)). \tag{12b}$$

Any symmetry breaking in the charge transfer processes leads to a charge imbalance between  $A^L$  and  $A^R$ . This is quantified by monitoring

$$Q_{\rm SB}(t) = \Delta Q_{\rm A^{\rm L}}(t) - \Delta Q_{\rm A^{\rm R}}(t).$$
(13)

## **III. RESULTS AND DISCUSSION**

## A. Symmetry breaking with few-cycle laser pulses

Throughout, we study the charge transfer across ABA heterojunctions induced by few-cycle non-resonant laser pulses of intermediate intensity via Stark shifts. The ABA heterojunction is modeled as a 1D tight-binding chain, as described in Eq. (2). The model parameters are chosen to create a perfectly insulating material with no spectral overlap between the bands of semiconductor B and semiconductor A [Fig. 1(a)]. This prevents the emergence of charge transfer across the heterojunction upon resonant photoexcitation or due to the application of an external voltage.

#### 1. Basic electron transfer mechanism behind SCELI

When the ABA heterojunction interacts with an electric field, its electronic structure is distorted through Stark shifts. This distortion destroys the periodicity of the potential of the semiconductors that compose the heterojunction.<sup>66–68</sup> As a consequence, the energy spectrum shows equally spaced resonances known as the Wannier– Stark ladder (WSL), and the wavefunctions become localized. This is best appreciated in a tight-binding one-band model<sup>66–68</sup> where the energy of the Wannier–Stark states are given by

$$\varepsilon_m = \varepsilon_0 + |e| maE, \tag{14}$$

where  $\varepsilon_0$  denotes the center of the energy band for the field-free model,  $m = \ldots, -2, -1, 0, 1, 2, \ldots$  denotes the site, *a* denotes the lattice constant, and *E* denotes the electric field. That is, the energy levels of each band of the semiconductor fan out due to the Stark shifts. Additionally, because the electric field introduces a linear potential, with a |e|aE drop between consecutive sites, the wavefunctions become localized. In fact, for the one-band model, the wavefunction of the Wannier–Stark state with energy  $\varepsilon_m$  is given by

$$|\Psi_m\rangle = \sum_n J_{n-m}(t_0/2|e|aE)|n\rangle, \qquad (15)$$

where  $J_{n-m}(t_0/2|e|aE)$  is a Bessel function and  $t_0$  is the tight-binding coupling between sites. In the presence of an electric field, the wave-functions become localized around site m. The degree of localization increases as the electric field, and thus the potential drop between consecutive sites, increases.

In the ABA heterojunction, the formation of Wannier–Stark states leads to transient resonances among the electronic energy levels of the semiconductors that compose it [Fig. 1(b)]. As the magnitude of the electric field of light increases, the first set of levels that cross are the VB levels of B and the CB levels of A as they are the closest in energy. Two representative pairs are signaled by colored lines in Fig. 1(b), where the color indicates the material associated with them (blue represents B, red  $A^{R}$  and green  $A^{L}$ ). At these transient resonances, quantum tunneling channels for  $B \rightarrow A$  electron transfer are opened. These tunneling events are particularly effective when the wavefunction of the Wannier–Stark states involved overlap at the interface between the two materials, as those shown in Figs. 1(e) and 1(f). This strong overlap leads to large hybridization between them, enhanced tunneling, and large avoided crossings in the adiabatic energies [Figs. 1(c) and 1(d)].

More explicitly, for a given electric field E(t), the Wannier–Stark diabatic basis is defined by

$$\hat{H}_{j}|\Psi_{m}^{j}\rangle = \varepsilon_{m}^{j}|\Psi_{m}^{j}\rangle, \qquad (16)$$

where  $\hat{H}_j$  is the Hamiltonian for material *j* in the presence of such an electric field [Eq. (2)]. In this basis, during a  $B \to A^{\alpha}$  electron transfer event, the Hamiltonian of the two levels involved in a given crossing is

$$\hat{H} = \begin{pmatrix} \varepsilon_m^{A^{\alpha}} & \Delta/2\\ \Delta/2 & \varepsilon_n^{B} \end{pmatrix}, \tag{17}$$

where  $\Delta/2 = \langle \Psi_m^{A^{\alpha}} | \hat{H}_{AB} | \Psi_n^B \rangle = \langle \Psi_n^B | \hat{H}_{AB} | \Psi_m^{A^{\alpha}} \rangle$  is the coupling between the diabatic states. The adiabatic states  $|\psi_{\pm}\rangle$  are obtained by diagonalizing this Hamiltonian,

$$|\psi_{-}\rangle = \cos\xi |\Psi_{n}^{B}\rangle + \sin\xi |\Psi_{m}^{A^{\alpha}}\rangle,$$
 (18a)

$$|\psi_{+}\rangle = -\sin\xi |\Psi_{n}^{B}\rangle + \sin\xi |\Psi_{m}^{A^{\circ}}\rangle, \qquad (18b)$$

with  $\sin 2\xi = \Delta/\sqrt{\Delta^2 + (\epsilon_m^{A^\alpha} - \epsilon_n^B)^2}$ . The adiabatic energies  $\epsilon_{\pm} = \frac{(\epsilon_m^{A^\alpha} + \epsilon_n^B)}{2} \pm \sqrt{\frac{\Delta^2 + (\epsilon_n^{A^\alpha} - \epsilon_n^B)^2}{4}}$  are those shown in Figs. 1(c) and 1(d). The energy gap at the crossing  $\Delta$  and the effectiveness of the B  $\rightarrow$  A<sup> $\alpha$ </sup> electron transfer increase with the overlap of the diabatic states at the interface.

Importantly, transient resonances between the VB levels of B and CB levels of  $A^L$  are induced when the sign of the electric field  $E_0$  is positive, which leads to  $B \rightarrow A^L$  electron transfer. By contrast, negative field amplitudes lead to  $B \rightarrow A^R$  electron transfer. This suggests that the direction of the electron transfer can be controlled by using laser pulses that have a difference in intensity for negative and positive field amplitudes, as those offered by few-cycle laser pulses.

To demonstrate that this idea can be realized through actual laser photoexcitation, we follow the dynamics of the ABA heterojunction under the influence of few-cycle laser pulses in Eq. (5) by directly solving the time-dependent Schrödinger equation. Figure 2(a) shows the electron transfer dynamics induced by the laser pulse ( $\hbar \omega = 0.5$  eV,  $\phi = 0$ , and  $E_0 = 0.24$  V/Å) detailed in the upper panel of the figure. The dynamics is characterized by following charge flow into the two A semiconductors through  $\Delta Q_{A^{\alpha}}$ ,  $\alpha = L$ , R. As can be seen, electron transfer is onset by the laser pulse through the Stark mechanism described above.



**FIG. 2.** Femtosecond charge transfer dynamics across the ABA heterojunction induced by non-resonant few-cycle laser pulses. (a) As the laser pulse with  $\phi = 0$  and  $E_0 = 0.24$  V/Å is turned on (upper panel), it opens quantum tunneling channels for interfacial electron transfer from B to A through Stark shifts (lower panel). (b) Net charge transfer after the pulse  $\Delta Q_{A^{\alpha}}(\infty)$  to the left ( $\alpha = L$ ) and right ( $\alpha = R$ ) of B and the degree of spatial symmetry breaking  $Q_{SB}(\infty)$  as a function of laser amplitude  $E_0$ .

Notice that the electron transfer consists of alternating bursts of charge transfer from  $B \to A^L$  and then from  $B \to A^R$  as is reflected in the dynamics of  $\Delta Q_{A^{\alpha}}$ . In agreement with the picture in Fig. 1, the bursts of charge transferred from  $B \to A^L$  arise when the amplitude of the electric field of the laser pulse is positive. This is because for these amplitudes, the induced transient resonances are between the VB levels of B and the CB levels of  $A^L$ . In turn, for negative field amplitudes, we observe bursts of charge being transferred from  $B \to A^R$ .

Additionally, note that once the laser pulse is turned off, the transferred charge  $\Delta Q_{A^{\alpha}}$  does not change. This is because the heterojunction is an insulating material, and electron transfer can only occur during the interaction with the laser field.

Figure 2(b) shows the asymptotic charge in  $A^R$  and  $A^L$  $[\Delta Q_{A^{\alpha}}(\infty)]$  as a function of the laser amplitude  $E_0$  ( $\phi = 0, \hbar \omega$ = 0.5 eV) and the net degree of symmetry breaking  $Q_{SB}(\infty)$ . Both  $\Delta Q_{A^R}$  and  $\Delta Q_{A^L}$  show similar behavior as a function of  $E_0$ . Their response can be divided into three regions<sup>26</sup> labeled I, II, and III in Fig. 2(b). In region I (0 <  $E_0 \leq 0.076$  V/Å), the amplitude of the electric field induces several transient resonances between VB levels of B and CB levels of A. However, these are trivial crossings that do not lead to electron transfer as the wavefunction of the diabatic levels involved do not spatially overlap (see Fig. 3). By contrast, in region II (0.076 <  $E_0 \leq 0.5$  V/Å), the induced transient resonances between VB levels of B and CB levels of A lead to avoided crossings because the diabatic wavefunction overlap along the interface, as seen in Figs. 1(e) and 1(f). Therefore, quantum tunneling channels for interfacial electron transfer are opened. Increasing the magnitude of the electric field  $E_0$  opens more of these channels, which leads to an increase in charge transfer  $\Delta Q_{A^{\alpha}}(\infty)$ . In region III  $(E_0 > 0.5 \text{ V/Å})$ , the amplitude of the electric field is strong enough to induce avoided crossings between the VB levels of A and the CB levels of B that lead to  $A \rightarrow B$  charge transfer events and between the VB and CB of each material that lead to large Zener interband tunneling.<sup>69</sup> The competition of these processes leads to a complicated dependence of the effect on the laser amplitude in this region.

# 2. Spatial symmetry breaking

Because of the spatial symmetry of the ABA heterojunction, as the field develops from zero to a given positive or negative amplitude  $\pm |E_0|$ , the number and the effectiveness of the level crossings that induce  $B \to A^R$  (for  $-|E_0|$ ) and  $B \to A^L$  (for  $+|E_0|$ ) electron transfer are identical. Symmetry breaking is achieved by using a pulse that has a difference in intensity for positive and negative field amplitudes. For such pulses, the number of induced transient resonances that lead to interfacial electron transfer for  $B \rightarrow A^L$  and  $B \rightarrow A^R$  differs, leading to a net transferred charge  $Q_{SB}(\infty) \neq 0$ . For few-cycle laser pulses, this difference in intensity for positive and negative field amplitudes, and thus the direction and magnitude of  $Q_{SB}(\infty)$ , can be manipulated by changing the CEP. Figure 4 shows the dependence of the shape of the laser and  $Q_{SB}(\infty)$  on the CEP. The maximum  $Q_{SB}(\infty)$  is obtained for  $\phi = 0$ ,  $\pi$  as those phases maximize the difference in intensity of the field for positive and negative amplitudes. In turn, for  $\phi = \pi/2$ ,  $Q_{SB}(\infty) = 0$  because such laser pulses have equal intensity for positive and negative field amplitudes as E(t - t') = -E(-(t - t')) in this case. By changing the CEP by  $\pi$ ,



**FIG. 3.** Trivial crossings in the Stark control of electrons at interfaces. (a) Electric fields in region I in Fig. 2(b) induce multiple crossings among the levels of B and those of A. As an example, the colored lines highlight a particular crossing between a VB level of B (in blue) and a CB level of A (in green). (b) Trivial energetic crossing between the levels (with the average energy offset for clarity) and (c) associated wavefunctions. There is no avoided crossing because the wavefunctions do not appreciably spatially overlap and the levels do not hybridize. These crossings do not open channels for interfacial electron transfer.

it is possible to change the direction of the symmetry breaking as  $E(\phi + \pi) = -E(\phi)$ .

Figure 2(b) shows the dependence of  $Q_{SB}(\infty)$  for  $\phi = 0$  as a function of laser amplitude  $E_0$ . The symmetry breaking effect is



**FIG. 4**. Asymptotic laser-induced symmetry breaking  $Q_{SB}(\infty)$  in a ABA heterojunction induced by few-cycle laser pulses of varying CEP ( $\hbar \omega = 0.5$  eV and  $E_0 = 0.24$  eV/Å). The CEP controls the shape of the laser field (insets) and thus the direction and magnitude of the symmetry breaking.

robust to changes in field amplitude. However, the direction of the symmetry breaking  $Q_{SB}$  is very sensitive to  $E_0$ . This effect arises because for this pulse, the ratio of positive and negative peak amplitudes ( $\Gamma \approx 1.2$ ) is not large enough to guarantee that the number of  $B \rightarrow A^L$  quantum tunneling channels sampled during the pulse is larger than those for  $B \rightarrow A^R$  for all values of  $E_0$ , which could lead to  $Q_{SB}(\infty) < 0$ .

## B. Enhancing the symmetry breaking

Clearly, to enhance the ability of a laser pulse to induce symmetry breaking, it is desirable to make  $\Gamma \gg 1$  or  $\Gamma \ll 1$ . This quantity is defined as  $\Gamma = \frac{E_0^+}{E_0^+}$ , where  $E_0^{+/-}$  is the global maximum/minimum of the electric field of light. One path to do so is to change the time width  $\tau$  of the laser pulse. The quantity  $\Gamma$  increases by decreasing  $\tau$  [Fig. 5(a)]. By selecting a  $\tau$  with a bigger  $\Gamma$ , the direction of  $Q_{SB}$  becomes robust to changes in  $E_0$ . For example, Fig. 5(b) compares the behavior of  $Q_{SB}(\infty)$  as a function of  $E_0$  for laser pulses with  $\tau = 1.0$  fs (black line,  $\Gamma = 1.97$ ) and 5.85 fs (red line,  $\Gamma = 1.2$ ). Notice that for  $\tau = 1.0$  fs, the direction of  $Q_{SB}(\infty)$  becomes robust to changes of  $E_0$  in region II. However, creating such ultrafast laser pulses demands increasingly more frequency bandwidth.

An alternative is to use  $\omega + 2\omega$  few-cycle laser pulses with the vector potential

$$A(t) = e^{-(t-t_c)^2/2\tau^2} \left(\frac{\epsilon_{\omega}}{\omega} \sin(\omega(t-t_c) + \phi_{\omega}) + \frac{\epsilon_{2\omega}}{2\omega} \sin(2\omega(t-t_c) + \phi_{2\omega})\right),$$
(19)



**FIG. 5.** Effect of the laser pulse time width  $\tau$  on the symmetry breaking. (a) Ratio  $\Gamma$  between the maximum positive and negative values of the electric field of light as a function of  $\tau$  for  $\phi = 0$ . (b) Total photoinduced charge transfer as a function of the laser amplitude for  $\tau = 1.0$  fs and  $\tau = 5.85$  fs. The direction of the effect becomes robust to changes in  $E_0$  when  $\Gamma$  is increased.



**FIG. 6.** Optimizing  $\Gamma$  for  $\omega + 2\omega$  laser pulses. The figure shows the effect of laser parameters on  $\Gamma$ , which quantifies the difference in laser intensity for positive and negative field amplitudes for  $\hbar\omega = 0.5$  eV. (a) Dependence on  $\epsilon_{\omega}/\epsilon_{2\omega}$  for  $\tau = 5.85$  fs and  $\phi_{\omega} = \phi_{2\omega} = 0$ . (b) Dependence on  $\phi_{2\omega}$  for  $\tau = 5.85$  fs and  $\epsilon_{\omega} = 2\epsilon_{2\omega}$ . Each curve corresponds to different values of  $\phi_{\omega}$ . (c) Dependence on the laser pulse time width  $\tau$  for  $\epsilon_{\omega} = 2\epsilon_{2\omega}$  and  $\phi_{\omega} = \phi_{2\omega} = 0$ .

where the peak electric field amplitude is given by  $E_0 = \epsilon_{\omega} + \epsilon_{2\omega}$ . The presence of the second harmonic leads to fields with different intensities for positive and negative field amplitudes even for pulses with many cycles in the laser envelope. The  $\omega$  + 2 $\omega$  few-cycle laser pulses have four parameters that control  $\Gamma: \epsilon_{\omega}/\epsilon_{2\omega}, \tau, \phi_{\omega}$ , and  $\phi_{2\omega}$ . To determine how to maximize  $\Gamma$ , we explore its behavior as a function of these parameters. Figure 6(a) shows  $\Gamma$  as a function of  $\epsilon_{\omega}/\epsilon_{2\omega}$ . The maximum  $\Gamma$  is found for  $\epsilon_{\omega} = 2\epsilon_{2\omega}$ . With this relation for the laser amplitude, Fig. 6(b) explores how  $\Gamma$  changes with laser phases. Here, several combinations of  $\phi_{2\omega}$  and  $\phi_{\omega}$  show the same maximum value of  $\Gamma$ . For definitiveness, we choose  $\phi_{2\omega} = \phi_{\omega} = 0$ . Finally, Fig. 6(c) shows  $\Gamma$  vs  $\tau$  for  $\hbar\omega = 0.5$  eV,  $\epsilon_{\omega} = 2\epsilon_{2\omega}$ , and  $\phi_{\omega} = \phi_{2\omega} = 0$ . The ratio  $\Gamma$  decreases as the pulse includes more cycles, as observed for Gaussian pulses [Fig. 5(a)]. However, contrary to Gaussian pulses, the asymptotic value of  $\Gamma$  as  $\tau$  increases for this type of pulses is 2. This means that even for long pulses, the  $\omega + 2\omega$  laser breaks the spatial symmetry of the system.<sup>1</sup>

Figure 7 compares the shape of the regular few-cycle laser pulse (red line) with the  $\omega + 2\omega$  laser pulse (black line) and their effectiveness for symmetry breaking for fixed  $\tau = 5.85$  fs. Notice that the  $\omega + 2\omega$  laser has a larger difference in intensity for positive and negative field amplitudes than the laser pulse in Eq. (5) ( $\Gamma = 2.01$  vs 1.2, respectively). We observe that the larger  $\Gamma$  for  $\omega + 2\omega$  lasers guarantees that in region II, the number of effective  $B \rightarrow A^L$  quantum tunneling channels that are opened is greater than those for  $B \rightarrow A^R$ for  $\phi = 0$ . As a result,  $Q_{SB}(\infty) \neq 0$ , and its direction is robust to changes in  $E_0$  in region II [see in Fig. 7(b)]. These results show that laser pulses with high  $\Gamma$  optimize the control over the symmetry breaking. The  $\omega + 2\omega$  laser pulses are far superior than Gaussian few-cycle pulses because they maintain a large  $\Gamma$  even as the number of cycles in the pulses is increased.

By varying the shape of the  $\omega + 2\omega$  laser pulses through  $\phi_{\omega}$ and  $\phi_{2\omega}$ , the direction and magnitude of the symmetry breaking  $Q_{\text{SB}}(\infty)$  can be controlled. Figure 8 shows the behavior of  $Q_{\text{SB}}(\infty)$  as a function of  $\phi_{2\omega}$  for  $\phi_{\omega} = 0$ . The maximum  $Q_{\text{SB}}(\infty)$  is obtained for  $\phi_{2\omega} = 0$ ,  $\pi$  as those maximize the difference in intensity of the field for positive and negative amplitudes (see Fig. 6(b). In turn, for  $\phi_{2\omega}$ = 0.48 $\pi$ , Q<sub>SB</sub>( $\infty$ )  $\approx$  0 because for this pulse,  $\Gamma$  = 1.1, and its shape is approximately antisymmetric (see inset Fig. 8). Notice, that the  $\omega$  +  $2\omega$  laser pulses does not satisfy the condition  $E(\phi_{2\omega} + \pi) = -E(\phi_{2\omega})$ .



**FIG. 7**. Control of charge transfer using few-cycle  $\omega + 2\omega$  pulses in the ABA heterojunction. (a) Comparison of a few-cycle  $\omega$  (red) pulse with CEP of zero and  $\omega + 2\omega$  (black) pulse with phase  $\phi_{\omega} = \phi_{2\omega} = 0$ . (b) Total photoinduced charge transfer as a function of the laser amplitude. The direction of the effect induced by the  $\omega + 2\omega$  is robust to changes in the laser amplitude  $E_0$ .



**FIG. 8**. Phase dependence of photoinduced charge transfer using few-cycle  $\omega$  +  $2\omega$  laser pulses. The largest symmetry breaking effect is observed for  $\phi_{2\omega}$  that maximizes the difference in laser intensity for negative and positive field amplitudes.

Therefore, changing  $\phi_{2\omega}$  by  $\pi$  does not completely reverse the symmetry breaking.

#### C. Evidence for quantum tunneling

To demonstrate that the main mechanism of the electron transfer in SCELI is quantum tunneling, the numerical simulations are contrasted with the results obtained from a rate equation with transition probabilities determined by Landau–Zener (LZ) theory.<sup>70,71</sup> We focus on region II [see Fig. 2(b)] where only the single-particle states in the VB of B and the CB of A play a prominent role in the photoinduced process. Therefore, we consider a minimal model in which only those single-particle states are allowed to exchange charge.<sup>26</sup> The charge change from time *t* to time  $t + \Delta t$  is determined by

$$\eta_l^{A^{\alpha}}(t+\Delta t) = \eta_l^{A^{\alpha}}(t) + (\eta_k^{B}(t) - \eta_l^{A^{\alpha}}(t))P_{kB\to lA^{\alpha}}(t), \quad (20)$$

where  $\eta_l^{A^{\alpha}}$  is the population of the *l*th diabatic level of material A to the left ( $\alpha = L$ ) or right ( $\alpha = R$ ) of B and  $\eta_k^B$  is the *k*th diabatic level population of material B. In turn,  $P_{lA^{\alpha} \to kB}(t) = P_{kB \to lA^{\alpha}}(t)$  is the LZ tunneling probability,

$$P_{kB \to lA^{\alpha}}(t) = 1 - e^{-\beta_{lA^{\alpha}}^{\kappa B}}, \qquad (21)$$

with

$$\beta_{lA^{\alpha}}^{kB} = \frac{2\pi (\Delta_{lA^{\alpha}}^{kB})^2}{\hbar \left| \frac{d}{dt} \left( \varepsilon_k^{B} [E(t)] - \varepsilon_l^{A^{\alpha}} [E(t)] \right) \right|_{t=t_{\text{crossing}}}},$$
(22)

at the time ( $t_{crossing}$ ) where the *k*th VB level of B and the *l*th CB level of A become degenerate and zero otherwise. Here,  $\Delta_{lA^{\alpha}}^{kB}$  is the gap between the associated adiabatic levels at the avoided crossing, while  $\varepsilon_l^i$  are the energies of the diabatic states. For strong laser fields, the Stark shifted energies vary linearly with the electric field such that  $\frac{d\varepsilon_l^i}{dt} = M_l^i \frac{dE(t)}{dt}$  [see Eq. (14)]. To calculate the population dynamics in Eq. (20), the slopes  $M_l^i$  are obtained by fitting the diabatic energy states  $\varepsilon_l^i$  to a linear function around the avoided crossing. In this case, the symmetry breaking in the charge transfer processes is tracked by monitoring

$$Q_{SB}(t) = \sum_{l=1}^{N} (\eta_l^{A^{L}}(t) - \eta_l^{A^{R}}(t)), \qquad (23)$$

where N is the total number of CB energy levels in A.

Figure 9 compares the net charge transfer dynamics obtained with the LZ rate equation with that obtained by solving the timedependent Schrödinger equation for a few-cycle  $\omega + 2\omega$  laser pulse of  $E_0 = 0.24$  V/Å and  $\hbar\omega = 0.5$  eV. The results obtained with the LZ rate equation reproduce qualitatively well the features of the charge transfer dynamics. Note that the LZ rate equation reproduces well the dynamics until  $t\omega/2\pi \approx 0.97$ , where it overestimates the charge transferred. This overestimation arises because LZ theory was developed for diabatic energies that change linearly with time<sup>72</sup> in the crossing region, and this condition is not satisfied around  $t\omega/2\pi \approx 0.97$  where the electric field of light is near a maximum. These results indicate that quantum tunneling induced by Stark shifts is the main mechanism of the charge transfer.

#### D. Decoherence effects

To demonstrate that the SCELI is robust to decoherence, we repeated the LZ rate computations but using a modified version of Eq. (21), which takes into account the effect of strong decoherence.<sup>73-75</sup> In this case, the transition probability is given as

$$P_{kB \to lA^{\alpha}}^{\text{incoh}}(t) = \frac{1 - e^{-2\beta_{lA^{\alpha}}^{\text{co}}}}{2}.$$
(24)

Figure 9 compares the electron transfer dynamics for the LZ rate equation with (black dashed line) and without (red dashed line)



**FIG. 9**. Comparison of Landau–Zener rate theory (red dashed line) with the full quantum dynamics (red solid line) and effect of decoherence (black dashed line). The plot shows the net charge transfer induced by a few-cycle  $\omega + 2\omega$  laser pulse (upper panel:  $E_0 = 0.24$  V/Å,  $\hbar\omega = 0.5$  eV). Note the LZ rate equations qualitatively reproduce the basic features of the quantum dynamics, indicating that the effect is due to quantum tunneling processes induced by Stark shifts.



**FIG. 10.** Comparison of Landau–Zener rate theory with (black dashed line) and without (black line) decoherence effects. The plot shows the symmetry breaking  $Q_{SB}(\infty)$  as function of the photon energy  $\hbar\omega$  of few-cycle  $\omega + 2\omega$  laser pulses ( $E_0 = 0.32 \text{ V/Å}$ ). The ratio between the Landau–Zener rate theory without and with decoherence effects (red line) shows that these effects are quite mild on the electron transfer.

decoherence effects. Notice the electron transfer dynamics in both cases is essentially identical, which indicates that decoherence has a minor effect on the scheme of control. This is because in the regime in which the control takes place,  $\beta_{lA^{\alpha}}^{kB}$  is small for most crossings, leading to  $P_{kB \rightarrow lA^{\alpha}}^{incoh}(t) \approx P_{kB \rightarrow lA^{\alpha}}(t)$ .

Figure 10 quantifies the effect of decoherence for different laser frequencies. Even for small frequencies for which  $\beta_{lA^{\alpha}}^{kB}$  is sizable, the effect remains robust to decoherence. Decoherence is seen to decrease the effect in 3.5%–8% in the range studied. Reducing the laser frequency increases the magnitude of the symmetry breaking as there is more time for electrons to tunnel at the relevant energy crossing.

# **IV. CONCLUSIONS**

In conclusion, we have demonstrated that the Stark Control of Electrons at Interfaces (SCELI) can be extended to induce laserinduced symmetry breaking on an ultrafast timescale. The scheme can be used to induce directional charge transfer in spatially symmetric systems whose magnitude and sign can be controlled by varying laser phases, without exciting carriers through near-resonance photon absorption. Instead, the scheme is based on using the Stark effect introduced by non-resonant lasers to distort the electronic structure of interfaces and open opportunities for interfacial charge transfer. This is done by using the instantaneous electric field of light to create transient resonances between the VB and CB of two adjacent materials. This contrasts with Zener tunneling effects that create transient resonances between the VB and CB of the same material. The scheme requires lasers with a difference in intensity for positive and negative field amplitudes, such as those offered by fewcycle laser sources. A major advantage of SCELI is that the effect is robust to decoherence since it does not rely on creating fragile electronic superposition states. In this sense, SCELI is a superior route for exerting laser control of electrons in matter with respect to traditional interference-based laser control strategies as the latter are fragile to decoherence.

The phenomenon was exemplified in a two-band tight-binding model of an ABA heterojunction driven by few-cycle lasers with the well-defined carrier envelope phase (CEP). Few-cycle lasers exhibit a difference in intensity for positive and negative field amplitudes and have the advantage that strong electric fields  $(10^{13} \text{ W/cm}^2-10^{14} \text{ W/cm}^2)$  can be applied before inducing dielectric breakdown. For definitiveness, we have focused on model atomistically sharp interfaces and have not taken into account additional effects that may arise due to screening and band bending. These effects are expected to influence the magnitude of SCELI but to leave the basics of the rectification mechanism intact.

There are a growing number of reports<sup>5–10,15,16,18,19,24,28</sup> using few-cycle laser pulses for laser-induced symmetry breaking and other effects that rely on radiation with different intensity for positive and negative field amplitudes. Such effects are controllable by varying the CEP since this quantity determines the ratio  $\Gamma$  between the maximum positive and negative values of the electric field. Most studies use fields with one central frequency  $\omega$  for which decreasing the number of cycles contained in the laser envelope increases  $\Gamma$ and thus the magnitude of the CEP-controllable effect. We have contrasted the effectiveness of such fields for symmetry breaking against fields with two central frequencies  $\omega$  and  $2\omega$ . Except in the limit of impulsive pulses (of time width  $\tau \rightarrow 0$ ) with the infinitely broad frequency spectrum, the  $\omega + 2\omega$  laser fields were found to be superior for symmetry breaking purposes because they have a larger difference in intensity for positive and negative field amplitudes that is largely insensitive to  $\tau$ .

The control of interfacial charge transfer in a semiconductorsemiconductor interface is seen to be the largest for the CEP of 0,  $\pi$ when the fields exhibits the largest difference in intensity for positive and negative field amplitudes. Such a CEP dependence was also observed in experiments inducing currents in gold–silica–gold junctions<sup>9,10</sup> as both effects depend on controlling interfacial charge transfer through Stark shifts.<sup>16</sup>

The simulations exemplify the power of Stark-based strategies for the laser control of electrons at interfaces. Future prospects include quantifying the role of band bending and screening in the effectiveness of this general control route.

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## DATA AVAILABILITY

The data that support the findings of this study are available within the article.

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