Topological Superconductivity in Ferromagnetic Metal Chains

Jian Li*,1 Hua Chen*,2 Ilya K. Drozdov,1 A. Yazdani,1 B. Andrei Bernevig,1 and A.H. MacDonald2

1Department of Physics, Princeton University, Princeton, NJ 08544, USA
2Department of Physics, University of Texas at Austin, Austin, TX 78712, USA

Recent experiments have provided evidence that a possible platform for one-dimensional (1D) topological superconductivity, transition metal atom chains formed on a superconducting substrate, can be realized experimentally. We address the properties of this type of system by using a Slater-Koster tight-binding model to account for important features of transition metal electronic structure. We predict that topological superconductivity is nearly universal when ferromagnetic transition metal chains form straight lines on superconducting substrates and that it is possible for more complex chain structures. The proximity induced gap is \( \sim \Delta E_{so}/J \) where \( \Delta \) is the \( s \)-wave pairing potential on the chain, \( E_{so} \) is the spin-orbit splitting energy induced in the normal chain state bands by hybridization with the superconducting substrate, and \( J \) is the exchange-splitting of the ferromagnetic chain \( d \)-bands. Because of the topological character of the 1D superconducting state, Majorana end modes appear within the gaps of finite length chains. Pb is a particularly favorable substrate material for ferromagnetic chain topological superconductivity because it provides both strong \( s \)-wave pairing and strong Rashba spin-orbit coupling, but there seems to be considerable freedom to optimize the 1D topological superconductivity by varying the atomic composition and structure of the chain. We note that in the absence of disorder a new chain magnetic symmetry, one that is also present in the crystalline topological insulators, can stabilize multiple Majorana modes at the end of a single chain.

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I. INTRODUCTION

Recent interest in exploiting the exchange properties of Majorana states in \( p \)-wave superconductors has motivated interest in a variety of different strategies for engineering topological superconductivity. One-dimensional topological superconductivity can be achieved by engineering effective \( p \)-wave superconductivity by combining spin-orbit coupling with broken time reversal symmetry in a variety of different ways. Ideas have been proposed in involving semiconductor quantum wires, half-metallic ferromagnets, metallic chains, strongly spin-orbit coupled superconductors, and helical magnetic chain. Indeed there is strong, but at present still inconclusive, evidence that Majorana states can be realized by following the semi-conductor nanowire strategy. The present work is motivated by the appearance of zero-bias anomalies in experimental work that was originally motivated by the helical magnetic chain strategy, but finally interpreted in terms of the properties of ferromagnetic states. Ref. reports strong evidence that Fe chains on Pb are ferromagnetic, and that they are one-dimensional topological superconductors with Majorana end states that are responsible for zero-bias anomalies in the local density of states measured near the ends of finite length chains. In this article we explain why topological states are not only possible, but for some structures overwhelmingly likely, when atom chains formed from the late 3\( d \) transition elements (or other strong magnetic materials) are placed on the surface of a superconductor. The ubiquity of topological states is related to features in the electronic structure of straight transition metal chains detailed below. In order to bring out the essential physics in a transparent fashion we first study a simplified but still realistic chain model with proximity-induced \( s \)-wave pairing and \( d \)-orbital Slater-Koster tight-binding bands. We then model the experimental situation of the one-dimensional chain embedded near the \((110)\) surface of bulk Pb. We provide quantitative results for substrate induced spin-orbit coupling on the chain, the superconducting gap of the chain, the structure of Shiba states in this system, and for Majorana state decay away from the chain ends. Finally, we also point out that in the absence of disorder, a combined magnetic symmetry (mirror times time-reversal) first identified in Ref. can stabilize multiple Majoranas at the end of a single Fe chain.

Under most circumstances ferromagnetism and superconductivity are antagonistic. Superconductivity is however able to survive on a ferromagnetic chain because a single row of aligned spins does not generate significant magnetic flux density, obviating damaging orbital effects, and because the substrate provides a non-magnetic Cooper pair reservoir. The mean-field Hamiltonian of the ferromagnetic chain contains two spin-dependent terms, a very large spin-splitting term produced by magnetic order which is odd under time reversal, and a much smaller spin-orbit coupling term that is even under time reversal. When only the large term is retained, quasiparticle wave functions are unperturbed and spin \( \uparrow \) and \( \downarrow \) quasiparticle energies are shifted in opposite directions by half the

*These authors contributed equally to this work
We discuss the properties of band Hamiltonians $H_0$ with $d$-orbital Slater-Koster approximation tight-binding ($H_{SK}$), Stoner-theory spin-splitting ($H_J$), and atomic-

**FIG. 1:** Bogoliubov quasiparticle bands of a system with a strong exchange splitting $J$, and a pair potential $\Delta$ and spin-orbit coupling strength $E_{so}$ that are by comparison weaker. This illustration assumes that the majority-spin $d$-bands (red) are full and the minority-spin $d$-bands (blue) are partially filled, the usual case for transition metal ferromagnets. The minority-spin electron (solid) and hole (dashed) bands which cross at the Fermi level are coupled via a virtual process in which the pair potential $\Delta$ couples minority spin electrons (holes) to majority spin holes (electrons) and $E_{so}$ couples minority spin holes (electrons) to majority spin holes (electrons). It follows that the quasiparticle gap at the Fermi energy indicated in the inset is $\sim \Delta E_{so}/J$. 

exchange splitting $J$. When the Fermi level lies in the minority bands (see Fig. 1) the electron and hole Bogoliubov bands which cross at the Fermi level have the same spin, the pair potential $\Delta$ couples quasiparticles with different bare energies, and the pair amplitude on the chain is small. The reservoir of Cooper pairs in the substrate effectively allows superconductivity to survive in the chain when it would be suppressed in a bulk system. Spin-orbit interactions produce a gap at the Fermi level because like-spin electrons and holes are coupled by a virtual process in which the pair potential reverses both spin and charge (i.e., electron/hole character) whereas spin-orbit reverses spin without reversing charge. It follows that the gap at the Fermi energy is $\sim \Delta E_{so}/J$ where $E_{so}$ is the spin-orbit coupling strength. The effective spin-orbit interaction matrix elements responsible for the gap are closely related to the pair creation and annihilation terms which were already carefully analyzed in the original BCS paper Pb substrates are rather unique in providing both relatively strong $s$–wave pairing and strong spin-orbit coupling. Because $E_{so}$ is not as small compared to $J$ as $\Delta$, at least in systems with a Pb substrate, sizable Fermi level gaps are possible even though the Clogston limit is exceeded enormously, i.e. $J \gg \Delta$. The main focus of this paper is on explaining why this gapped superconducting state is topological much more often than not. The system-parameter regime over which topological superconductivity can appear is much wider than in previously studied mechanism for effective $p$-wave superconductivity. The material in this paper expands on theoretical ideas that were partially presented in Ref. 27.

The paper is organized as follows: In Section II we address the electronic structure of isolated transition metal chains and discuss how it is altered by proximity induced superconductivity. We explain why straight ferromagnetic transition metal chains almost always exhibit topological superconductivity and show why Rashba spin-orbit interactions, allowed in systems with broken inversion symmetry, are necessary to open a superconducting gap in the system. In Section III we look at more realistic chain geometric configurations similar to the ones appearing in the experiment Ref. 27 and calculate their phase diagram when they are suspended and influenced by a singlet pair-potential whose strength is treated as a phenomenological parameter. In Section IV we consider the experimental situation of one dimensional Fe chains on the surface of a three-dimensional Pb superconductor modeled by a realistic tight-binding Hamiltonian with parameter values obtained from ab-initio calculations. We introduce a new magnetic symmetry that can protect more than one Majorana at the edge of the chain, and construct a phase diagram for the number of Majorana modes at the edge. We also calculate the spatial extent of the Majorana state and show that the hybrid situation induces strong power-law deviations from the simple exponential decay of a suspended one-dimensional chain. In Section V we present our conclusions.

II. SUPERCONDUCTIVITY IN FERROMAGNETIC CHAINS

A. Slater-Koster model of a superconducting ferromagnetic chain

Our discussion of topological superconductivity in ferromagnetic metal chains is informed by realistic electronic structure considerations. Since metallic ferromagnetism is most often associated with Fermi level $d$-electrons, we focus our attention here on chains formed by transition metal atoms. Chains formed by rare earth atoms like Gd could however also be of interest. We first discuss the properties of band Hamiltonians $H_0$ with $d$-orbital Slater-Koster approximation tight-binding ($H_{SK}$), Stoner-theory spin-splitting ($H_J$), and atomic-
like spin-orbit coupling coupling \( (H_{so}) \) contributions:

\[
H_0 = H_{SK} + H_J + H_{so}.
\]

Of the three terms in the band Hamiltonian, only the hopping term \( H_{SK} \) is spin-independent:

\[
H_{SK} = \sum_{\langle ij \rangle \alpha' \alpha} t_{\alpha' \alpha} c_{i \alpha}\dagger c_{j \alpha}.
\]

Here \( i \) and \( j \) label sites, \( \langle ij \rangle \) implies a restriction to nearest-neighbor sites, \( \alpha \) labels spin, and \( \alpha' \alpha \) label the five \( d \)-orbitals on each site. As will become clear later neither the inclusion of \( s \)-orbitals, which are not strongly spin-polarized according to \textit{ab initio} calculations\(^{27}\), nor the inclusion of longer-range hopping processes would our main conclusions. The \( t_{\alpha' \alpha} \) hopping parameters are real Slater-Koster integrals that depend for each orbital pair on the direction cosines of the vector connecting nearest neighbors, and on the three parameters \( V_{dd\sigma} \), \( V_{dd\pi} \), and \( V_{dd\delta} \). We focus our attention first on straight chains, using this geometry to identify important trends. Real chains need not be straight\(^{27}\) because of incommensurability between isolated chain and substrate lattice constants even periodic. However we expect that straight chain features in the electronic structure will sometimes be reflected in actual geometries. For concrete calculations we use the Slater-Koster parameter values proposed for bulk Fe in Ref.\(^{44}\) which are listed in Table I for completeness. These parameters exhibit the generic metal-like band property \( |V_{dd\sigma}| > |V_{dd\pi}| > |V_{dd\delta}| \) which we will see is key to the ubiquity of topological states in straight chains.

### Table I: Slater-Koster tight-binding model parameters for Fe (in eV).

The hopping integral values are for the nearest-neighbor distance of bulk Fe(bcc), \( r_0 = 2.383 \text{ Å} \).

| Parameters | Value (eV) |
|------------|------------|
| \( V_{dd\sigma} \) | -0.6702 |
| \( V_{dd\pi} \) | 0.5760 |
| \( V_{dd\delta} \) | -0.1445 |

We first consider models in which both spin-dependent terms \( H_J \) and \( H_{so} \) are diagonal in site:

\[
H_J = -J \hat{m} \cdot \mathbf{s},
\]

\[
H_{so} = \lambda_{so} \mathbf{L} \cdot \mathbf{s},
\]

where \( J \) is the ferromagnetic state quasiparticle spin-splitting energy, \( \hat{m} \) is the magnetization direction on the chain, \( \lambda_{so} \) is the spin-orbit coupling parameter, and \( \mathbf{L} \) and \( \mathbf{s} \) are respectively the atomic angular momentum and electron spin operators. It will be important in what follows that \( H_J \) changes sign under time reversal whereas \( H_{so} \) is time-reversal invariant. For Fe \( J \sim 2.5 \text{ eV} \) and \( \lambda_{so} \sim 0.06 \text{ eV} \). By comparing with \textit{ab initio} electronic structure calculations one can confirm that this simple model accounts accurately for the electronic structure and magnetic anisotropy of isolated Fe chains. We will see later that in straight chains atomic spin-orbit coupling does not provide the \( E_{so} \) coupling required in Fig.1. This property will elevate the importance of spin-orbit coupling inherited the superconducting substrate through orbital hybridization.

Figure 2(a) shows the band structure of a straight Fe chain without atomic spin-orbit coupling. Due to rotational symmetry around the chain direction (\( \hat{x} \)), there are two pairs of spin-degenerate bands, \( dd\pi \) (\( xz \) and \( xy \) orbitals) with band minima at \( ka = \pi \) and and narrower \( dd\delta \) (\( yz \) and \( y^2 - z^2 \) orbitals) with band minima at \( ka = 0 \). The broadest \( dd\sigma \) band is not orbitally degenerate and also has its minimum at the zone center. Because the spin-splitting exceeds the chain band width, which is smaller than the bulk band width because of the reduced coordination number in a 1D system, the minority and majority spin \( d \)-bands do not overlap. When spin-orbit coupling \( (H_{so}) \) is added (Figure 2(b)), with \( \hat{m} \cdot \hat{x} = 0 \), corresponding to an easy magnetization direction perpendicular to the chain, states near the Fermi level of a late transition metal system are still nearly pure minority spin in character and the two-fold degeneracy of the \( dd\delta \) and \( dd\pi \) bands is only weakly lifted. Neglecting this small splitting, the number of minority spin bands which cross the Fermi level is always odd. This property will be responsible for superconductivity that is always topological, provided that spin-orbit coupling mixes the superconducting quasiparticle states which cross at the exchange-shifted Fermi energy. Straight transition metal chains are therefore favorable for topological states. Since the the Fe chains in the initial experimental studies\(^{22}\) were not straight, this observation suggests one strategy to follow in an effort to optimize this Majorana platform.

We now add a pair-potential term to the Hamiltonian, assuming that it is dominated by a local, orbital-independent, spin-singlet contribution:

\[
H_{pair} = \Delta \sum_{\alpha} \left( c_{\alpha\uparrow}\dagger c_{\alpha\downarrow} + c_{\alpha\downarrow}\dagger c_{\alpha\uparrow} \right),
\]

where we have chosen a real Slater-Koster basis for the \( d \)-orbitals. Although outside the scope of the present work, it will also be interesting to consider spin-triplet contributions to the pair potential. Triplet pairing is inevitably present, and should be smaller than the singlet pairing by a factor \( \sim E_{so}/W \) where \( W \) is the chain band width. We neglect it in the same spirit as we neglect longer range hopping on the chain, \textit{i.e.} as an expedient to reduce the number of parameters in our model calculations. We have not identified a mechanism by which weak triplet pairing would alter our main conclusions. Fully realistic calculations of pair-potentials would have to account for modifications of phonons and electron-phonon coupling near the surface of the superconducting substrate. Although these calculations are feasible, we judge that it would be premature to undertake this effort at present.
In its doubled particle-hole Nambu space the $20N \times 20N$ Bogoliubov-de Gennes (BdG) mean-field Hamiltonian $H_{BdG}$ for a chain with singlet-pairing and $N$ sites is

$$H_{BdG} = \begin{pmatrix} H_{\text{chain}} & \Delta I_{5N \times 5N} \otimes i\sigma_y \\ -\Delta I_{5N \times 5N} \otimes i\sigma_y & -H^*_{\text{chain}} \end{pmatrix}$$

(5)

where $\sigma_y$ is a Pauli matrix acting on spin labels.

The BdG spectrum obtained by diagonalizing $H_{BdG}$ is illustrated in Figs. 2 (c). Interestingly no gap is opened at the Fermi level, indicating that the singlet-pairing induced virtual coupling between minority spin electrons and holes vanishes. This property can be traced to the charge conjugation symmetry of the BdG equations combined with the inversion-symmetry of the model described thus far, as explained in detail in Subsection II B below. Spin-orbit coupling within the chain, which usually provides the largest spin-orbit coupling scale, does support the formation of a gapped topological state unless the chain structure breaks inversion symmetry. We conclude that chain structures that break inversion symmetry can potentially be favorable for topological state formation. Fortunately, inversion symmetry is always broken for chains which lie on the surface of a substrate. At a surface hopping processes in which the spin-component perpendicular to the surface is flipped are always allowed to depend on hopping direction, leading to band Hamiltonian terms that are odd in momentum. This effect is generically referred to as Rashba spin-orbit coupling. We therefore add an band-independent term of the form,

$$H_R = it_R \sum_{\langle ij \rangle \gamma \tau} c^\dagger_{ij\gamma} c_{j\gamma\tau} (\hat{d}_{ij} \times \sigma_{\gamma\tau}) \cdot \hat{z}$$

(6)

to the model Hamiltonian. Here $\hat{d}_{ij}$ is a unit vector pointing from site $i$ to site $j$, and $\gamma$, $\tau$ are spin indices. As shown in Fig. 2 (d), as soon as $t_R$ becomes nonzero a gap opens at the Fermi level. We conclude that chains on the surface of a superconductor should generally have more robust topological states than submerged chains, because have stronger inversion symmetry breaking and should have stronger Rashba spin-orbit interactions. The Rashba process is discussed in more detail in Subsection II C below.

B. Inversion-Symmetry and Finite Gaps

In this section we explain the observation made in the previous subsection that inversion symmetry protects gapless points in one dimensional spinful charge conjugation symmetric systems. We will show that when inversion and spinful charge conjugation symmetry are both present, one-dimensional gapless points are stable. Adding inversion symmetry to the BdG equation leads to an analog of Weyl fermions in 3D, which however do not need symmetry to be protected, and of the 2-D fermions in graphene, which need combined inversion and time reversal symmetry to be protected from gapping. In all these cases, the issue of whether or not gapped points are allowed can be addressed by considering an effective Hamiltonian including only the bands involved at the gapless crossing point, counting the number of symmetry allowed parameters in this reduced Hamiltonian, and checking to see whether or not it is larger than the space dimension of the system. When the number of allowed Hamiltonian parameters is equal to (or smaller)
than the space dimension, momentum tuning parameters can be adjusted to points (or surfaces) at which the reduced Hamiltonian vanishes. In this case level crossings are generally allowed and do not require fine-tuning of the Hamiltonian.

Generically, since the BdG Hamiltonian of a ferromagnetic chain breaks time reversal symmetry, bands are singly degenerate at points in the 1D Brillouin zone. In order to analyze a gap-closing transition, we have to consider a 1D $k$-dependent reduced Hamiltonian describing two Bogoliubov bands that are about to touch at zero energy due to charge conjugation. To examine whether or not spin-orbit coupling is almost certain to open a gap we expand the 2 $\times$ 2 reduced BdG Hamiltonian in terms of Pauli matrices:

$$H(k) = \sum_{i=1,2,3} d_i(k)\sigma_i.$$  \hfill (7)

Inversion $P$ and charge conjugation $C$ operations transform the Hamiltonian as follows:

$$PH(k) = H(-k); \quad CH(k)C^{-1} = -H^*(-k).$$  \hfill (8)

Hence the little group of the Hamiltonian at $k$ is

$$(PC)H(k)(PC)^{-1} = -H^*(k)$$ \hfill (9)

For spinful fermions the matrix $C$ has the property $(CK)^2 = 1$ where $K$ is complex conjugation. For spinless fermions or for the case of SU(2) symmetry (no spin orbit coupling), a basis rotation can be made in spin space to make $(CK)^2 = -1$, but this is not a physical situation.

For the spinful fermions case we can choose from several representations of the inversion and charge conjugation operators on the two crossing bands described by the reduced Hamiltonian in Eq. 7. The only restrictions is that these operators satisfy the squaring relations discussed above, and the commutation relation $[P,C,K] = 0$.

Suppose the inversion operator is the identity operator $I$. Then for the $C$ operator we can choose $C = \sigma_z$ or $\sigma_z$. In the first case imposing the little group symmetry requires that $d_x(k) = d_y(k) = 0$, \forall $k$, while in the second case it requires $d_x(k) = d_y(k) = 0$, \forall $k$. The Hamiltonian therefore has codimension zero. For example, the Hamiltonian for the first case is $d_z(k)\sigma_z$. A gapless point at some point $K_0$ has $d_z(k) \sim \lambda - K_0$. Adding a small $d_z$ term can only move the 1D Dirac point, and cannot produce a gap. One can pick other representations of inversion and convince oneself that the Hamiltonian still has codimension zero. For example $P = \sigma_z$, $C = I$ is just a shuffling of the representation above.

The situation is different for spinless fermions. The representation of $C$ is $i\sigma_y$. Taking $P = I$ we have $\sigma_y H(k)\sigma_y = -H^*(k)$ which does not impose any constraints on the Hamiltonian. The codimension in this case is 2, and the system is almost certainly gapped.

### C. Rashba Spin-Orbit Coupling

As explained above, inversion-symmetry breaking Rashba spin-orbit coupling is crucial to realize topological superconductivity in ferromagnetic chains with 1D inversion symmetry. Rashba spin-orbit coupling is always present in the supported chain system because inversion symmetry is inevitably broken by the position of the chain on top of a substrate. Previous proposals for Majorana end modes in 1D chains have mainly focused on inversion symmetry breaking within the chains. For a 3d ferromagnetic chain on Pb however, hybridization with the strongly spin-orbit coupled orbitals of the substrate likely plays the dominant role.

In this section we discuss the physical processes leading to Rashba spin-orbit coupling in a ferromagnetic chain coupled to a substrate that has strong atomic spin-orbit coupling. We start from the heuristic example of two atoms with a single $s$-orbital, linked by an atom with only $p$-orbitals only, and assume that there is no direct hopping between the two $s$ atoms (Fig. 6). The choices of $s$- and $p$-orbitals are not essential and the argument below can be easily applied to other types of orbitals. The angle $\theta$ between the line defined by the two $s$-atoms and one $sp$ bond determines the extent of inversion symmetry breaking in this simple three-atom system. Choosing the zero of energy at the $s$-orbital cite energy and assuming that the $s-p$ hybridization is weak, the Hamiltonian for virtual hopping between the two $s$ atoms from right to left via the $p$ atom is

$$T_{ss} = T_{sp}^\dagger H_p^{-1} T_{sp},$$ \hfill (10)

where $T_{sp}$ is the spin-independent but orbital-dependent hopping matrix between $s$ and $p$ orbitals proportional to the $V_{sp\sigma}$ Slater-Koster parameter, and $H_p$ is the local Hamiltonian of the $p$ atom including both a site energy $E_p$ and atomic spin-orbit coupling:

$$H_p = E_p + \lambda \mathbf{L} \cdot \mathbf{S}.$$ \hfill (11)

$T_{ss}$ is a $2 \times 2$ matrix in which the first label is the $s$-orbital spin on the left site and the second label is the $s$-orbital spin on the right site. Because the overall Hamiltonian is Hermitian, the left to right hopping Hamiltonian can be obtained by reversing spin labels and taking a complex conjugate. Because the system lacks 3D inversion symmetry we expect a Rashba contribution to the effective hopping Hamiltonian, and characterize its strength by the coupling constant

$$t_R = \frac{1}{2}(T_{s\uparrow, s\downarrow} - T_{s\downarrow, s\uparrow})^\ast.$$ \hfill (12)

Assuming $E_p$ to be much larger than $V_{sp\sigma}$ and $\lambda$, we arrive at the following expression for the Rashba coupling constant of this illustrative toy model:

$$t_R = \frac{V_{sp\sigma}^2}{E_p^2} \frac{\lambda}{2E_p} \sin(2\theta).$$ \hfill (13)
Although this simplified model does not apply directly to realistic transition metal chains on Pb substrates, there are several general remarks we can make based on Eq. (13) (i): Rashba spin-orbit coupling is due to both atomic spin-orbit coupling and structural inversion symmetry breaking. Note, however, that even in this simple model $t_R$ is not a monotonic function of $\theta$. The Rashba spin-orbit coupling strength on a chain will always depend sensitively on the chain structure and on its coordination with the structure of the substrate. If these are known, it is a conceptually straightforward to calculate Rashba interactions quantitatively. (ii): $t_R$ should be roughly proportional to $t^2/\delta E$, where $t$ is a typical hopping parameter between the system of interest (e.g., an atomic chain) and the environment (e.g., a substrate), and $\delta E$ is the energy difference between the system and the environment. This is easy to understand from a perturbation theory point of view. In general both $t$ and $\delta E$ can be matrices due to the presence of many orbitals. Specially, if the band structure of the system is diagonal in some localized Wannier orbital basis (such as in the straight Fe chain), different bands will in general acquire different Rashba spin-orbit coupling by interacting differently with the environment, in addition to possible orbital off-diagonal hopping. The largest Rashba spin-orbit coupling will be in the bands whose orbitals have strongest hybridization with the spin-orbit coupled environmental states. (iii): The Rashba spin-orbit coupling strength will be proportional to the ratio of atomic spin-orbit coupling $\lambda$ to spin-independent hybridization terms. Because of the strong $p-d$ hybridization of transition metals on Pb this ratio will normally be smaller than one. (iv): The calculation described here includes only the lowest order process leading to Rashba spin-orbit coupling. In general an electron in the system of interest can be scattered into the environment, travel a long distance, and then be scattered back to the system. Contributions from higher-order processes are important especially when the states of the system and that of the environment have similar energy, i.e., when $\delta E$ is small. This is likely the main qualitative consideration influencing effective Rashba spin-orbit coupling strengths trends across materials, and can therefore play a role in formulating strategies to optimize ferromagnetic chain topological superconductivity.

The heuristic analysis explained above suggests that a Green’s function (or the scattering) method might often be convenient in studying realistic systems. In this approach, the whole substrate is viewed as a scatterer and its influence on the electronic states of the chain it supports can be captured by a self-energy term $\Sigma_S$. In this approach the single-particle retarded Green’s function of the chain is

$G^r_{\text{chain}}(\omega) = [\omega + i\eta - H_{\text{chain}} - \Sigma_S(\omega)]^{-1},$  

where $\eta$ is an infinitesimal real number. For example if we assume an infinite chain is along the $\hat{x}$ direction and a surface normal $\hat{z}$,

$\Sigma_S(\omega, k_x) = h^\dag_S g_S h_t$  

where $h_t$ is the hopping matrix between the chain and the substrate, and $g_S$ is the surface Green’s function of the substrate which can be conveniently calculated using an iterative approach when a tight-binding model of the substrate can be constructed. Note that we have used the convention that lower case letters stand for matrices of infinite dimension, while upper case letter refer to the finite matrices obtained after diagonalizing the surface Greens function in a momentum representation.

If the substrate is metallic, $\Sigma_S$ will in general have a large non-hermitian contribution representing decay from the atomic chain into the substrate. Nonetheless, one can still crudely define the effective chain Hamiltonian including the substrate contribution as

$H_{\text{eff}} \equiv H_{\text{chain}} + \frac{1}{2} \left[ \Sigma_S(\omega = 0) + \Sigma_S(\omega = 0) \right].$  

If one is especially interested in the size of the induced Rashba spin-orbit coupling, it can be extracted from $\Sigma_S(\omega = 0)$ as the net spin-flip hopping contribution that is odd in $k_x$, similar to our definition of $t_R$ in Eq. (12) 

However, the Rashba spin-orbit coupling will now be a matrix, have a nontrivial dependence on $k_x$, and sensitively depend on the relative positions of the chain and the lattice of the substrate. For model calculation purposes different approximations can be further made to obtain a manageable form of the Rashba spin-orbit coupling. One example following this approach is described in Ref. [27]
III. MAJORANA STATES ON A TRANSITION METAL FERROMAGNETIC CHAIN

Fig. 4 illustrates where topological superconductivity occurs as a function of band filling and exchange splitting $J$ in straight transition metal chains. Note that in the physically realistic part of this phase diagram, where $J$ is comparable to or larger than the band width, the superconducting state is almost always topological for the reasons explained previously. This phase diagram has been determined by evaluating the Majorana number of an infinite chain, but is of course in agreement with the simple heuristic requirement that superconducting states are topological when the number of bands crossing the Fermi level in the absence of pairing is odd.

When placed on a superconducting substrate, transition metal atoms do not in general form straight chain structures. For example, the structure formed by iron atoms in the chains studied in Ref. 27 consists of several rows of atoms. The structure in general will depend on the details of the chemical bonding between transition metal and substrate atoms. Within single row structures, the straight chain can be generalized to consider zig-zag chains in which the metal-metal-metal bonding angles alternate around 180°. Angular momentum along the chain axis is no longer a good quantum number in zig-zag chains, and higher energy minority spin bands are no longer populated in pairs. As a result the topologically nontrivial regions in the phase diagram will in general shrink when the bonding angles deviate from 180°. This trend is illustrated in Fig. 5, where we have fixed the exchange splitting at $J = 2.65$ eV, but varied the bond angle along a zigzag chain between 180° (corresponding to a straight chain) and 120°.

To confirm that zero energy Majorana modes exist in topologically nontrivial chains, we have also solved the BdG equations for finite length chains. For example, when parameters are chosen so that the energy gap is $\sim 0.1$ eV in the infinite chain, we find two BdG eigenstates with $|E| \approx 2 \times 10^{-6}$ eV. Fig. 6 demonstrates that these eigenstates are localized at the chain ends. Majorana states in systems with more realistic gap values are discussed later.

FIG. 4: Topological phase diagram for the 3d straight ferromagnetic chain model. Blue regions in chemical-potential vs. exchange coupling strength phase diagram have Majorana number $M = 1$ while white regions have $M = -1$. This figure was constructed using the hopping parameters listed in Table I. When the exchange splitting is larger than the band width, the realistic case for transition metal chains, the gapped superconducting state is almost always topological.

FIG. 5: (Color online) Majorana phase diagram of a zigzag chain with nearest neighbor hopping vs. chemical potential and bond angle at fixed exchange coupling $J = 2.65$ eV.

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FIG. 6: Spatial distribution of one of the two Majorana states ($E \approx \pm 2 \times 10^{-6}$ eV) for a finite chain with 200 atoms. $\Delta = 0.9$ eV, $t_R = 0.1$ eV, so that the zero energy gap is $\sim 0.1$ eV in the infinite chain.

Given a model Hamiltonian, the local density of states, which is closely related to STM $dI/dV$ data, can be conveniently calculated for infinite or semi-infinite chains using an iterative Green’s function method. In Fig. 7,
(a) we compare the local density of states at the end of a semi-infinite chain and in the middle of an infinite chain. Although both chains are topologically nontrivial and have the same parameter values, a zero-energy peak corresponding to the Majorana mode appears only at the end of the semi-infinite chain.

![Graph](Image)

**FIG. 7:** (a) Local density of states at the end of a semi-infinite chain (blue) and in the middle of an infinite chain (red). Both calculations were performed for chains with $M = -1$, $\Delta = 1.5$ meV, $t_R = 0.1$ eV, $J = 2.65$ eV, and $\mu = 1.3$ eV. (b) and (c), Non-monotonic dependence of the height of the zero energy peak with the parameters (b) $t_R$ and (c) $\Delta$. The left panel in each figure is the spectral function of the end Green’s function in an energy window around zero energy, and the right panel is the zero energy value of the spectral function. In (b) $\Delta$ is fixed at 0.1 eV and in (c) $t_R$ is fixed at 0.1 eV. Values of the other parameters in (b) and (c) are the same as those in (a).

The decay length of the Majorana states towards the center of the chain is, roughly speaking, inversely proportional to the superconducting gap. However, for multi-orbital systems such a simple proportionality may not hold. To see this we point out that in our isolated chain model the decay length of the end states is proportional to the height of the local density of states peak. In Figs. 7 (b) and (c) we plot the local density of states or spectral function at the end of a semi-infinite chain with changing $s$-wave pairing $\Delta$ and Rashba spin-orbit coupling $t_R$, respectively. One can see that the height of the local density of states is neither monotonically proportional to these parameters, nor to the apparent superconducting gap of the chain. This behavior originates from the multi-orbital nature of the chain model, in which different bands may have different zero-energy splitting due to the same pairing potential, and all of them influence the decay length of the Majorana end modes to varying extents.

Before ending this section we comment on the localization of Majorana end modes in a finite chain. We have seen in Fig. 6 that even with a much larger gap of $\sim 0.1$ eV than the experimentally observed gap in a supported Fe chain, the Majorana states still extends over 30 atoms towards the center of the chain in a 200 atom chain. For shorter chains or smaller gaps, the Majorana modes at the two ends will interfere with each other more strongly and moves further away from zero energy. However, it has been discussed theoretically and been observed experimentally that for chains coupled to a higher-dimensional environment such as the underlying superconductor, the decay of the Majorana modes acquires another power-law factor which makes them more localized, which we will discuss in detail in the following sections.

### IV. HYBRID SYSTEM WITH AN Fe CHAIN COUPLED TO A Pb (110) SUBSTRATE

The experimental setup is not purely one-dimensional. The Fe chain is embedded into a bulk Pb superconductor, and as such the physics of the hybrid system is more complicated than that of a purely one-dimensional chain. This mixture of a one-dimensional magnetic wire in a bulk superconductor has important consequences on many physical properties of the system, including the possible presence of multiple flavors of Majorana end modes, the spatial profile of the Majorana end modes and the presence of other in-gap bands along the wire ("Shiba" bands). This new physics, not present in purely one-dimensional wires, distinguishes the new
platform\textsuperscript{19,27} from all other previously proposed systems hosting Majorana fermions.

In this section we build a more realistic but still simplified model of our system by coupling the Fe tight-binding Hamiltonian to the Pb substrate through a tunneling term. This tunneling term induces in the Fe chain both the Rashba-type spin-orbit coupling and the superconductivity, which are all-important ingredients for Majorana physics but not native to Fe. The geometry of our model hybrid system, shown in Fig. 8 is a commensurate version of the one obtained by comparing DFT calculations and experiments.\textsuperscript{27} Although it is most likely that the Fe atoms form triple chains in the samples investigated in Ref. 27, here we will first focus on results for linear chains, as we have done in the previous sections, to present the conceptually important points, and then discuss results for triple chains in the last part.

\subsection{A. Tight-binding Hamiltonian}

The tight-binding Hamiltonian for the hybrid system reads

\begin{equation}
H_{\text{hybrid}} = H_{\text{Fe}} + H_{\text{Pb}} + H_{\text{Fe-Pb}},
\end{equation}

\begin{equation}
H_{\text{Fe}} = \sum_r d_i^\dagger(\xi_{\text{Fe}}(r)) d_r + \sum_{r_1 \neq r_2} d^\dagger_{r_1} \tau_{\text{Fe}}(r_1 - r_2) d_{r_2},
\end{equation}

\begin{equation}
H_{\text{Pb}} = \sum_r c_i^\dagger(\xi_{\text{Pb}}(r)) c_r + \sum_{r_1 \neq r_2} c^\dagger_{r_1} \tau_{\text{Pb}}(r_1 - r_2) c_{r_2} + \sum_r c^\dagger_r \Delta(r)(c^\dagger_r)^T + \text{h.c.},
\end{equation}

\begin{equation}
H_{\text{Fe-Pb}} = \sum_{r_1, r_2} c^\dagger_{r_1} \tau_{\text{Fe-Pb}}(r_1 - r_2) d_{r_2} + \text{h.c.}.
\end{equation}

Here $d_i^\dagger$ ($c_i^\dagger$) is the vector of electron creation operators for the Fe 3d-orbitals (Pb 6p-orbitals) and spins at site $r$; $\xi$’s, $\tau$’s and $\Delta$ are matrices corresponding to normal on-site, hopping and conventional superconducting pairing terms, respectively. These matrices are explicitly given as follows

\begin{equation}
\xi_{\text{Fe}}(r) = \{[\epsilon_{\text{Fe}}(r) - \mu_{\text{Fe}}]s_0 - J_{\text{Fe}} \cdot s\} \otimes L_0^{(d)},
\end{equation}

\begin{equation}
\xi_{\text{Pb}}(r) = \epsilon_{\text{Pb}}(r)s_0 \otimes L_0^{(p)} + \lambda_{\text{Pb}} \sum_{i=1}^3 s_i \otimes L_i^{(p)},
\end{equation}

\begin{equation}
\tau_{\text{Fe}}(\delta r) = \sum_{\beta=\{\sigma, \pi, \delta\}} E_{dd\beta}(\delta r) A_{dd\beta}(\delta r/|\delta r|) \otimes s_0,
\end{equation}

\begin{equation}
\tau_{\text{Pb}}(\delta r) = \sum_{\beta=\{\sigma, \pi\}} E_{pp\beta}(\delta r) A_{pp\beta}(\delta r/|\delta r|) \otimes s_0,
\end{equation}

\begin{equation}
\tau_{\text{Fe-Pb}}(\delta r) = \sum_{\beta=\{\sigma, \pi\}} E_{pd\beta}(\delta r) A_{pd\beta}(\delta r/|\delta r|) \otimes s_0,
\end{equation}

\begin{equation}
\Delta(r) = \Delta(i\sigma_2) \otimes L_0^{(p)}.
\end{equation}

where $\epsilon_{\text{Fe}}$ and $\epsilon_{\text{Pb}}$ are on-site energies, $\mu_{\text{Fe}}$ is the chemical potential, $J_{\text{Fe}}$ is the magnetization vector in Fe, $\lambda_{\text{Fe}}$ and $\lambda_{\text{Pb}}$ are atomic spin-orbit coupling energies, $E_{dd\beta}$, $E_{pp\beta}$ and $E_{pd\beta}$ are the Slater-Koster bond integrals that depend on the types of bond ($\beta$) and the distance between atoms ($|\delta r|$), $A_{dd\beta}$, $A_{pp\beta}$ and $A_{pd\beta}$ are the real coefficient matrices of Slater-Koster integrals in the cubic harmonic basis and are dependent only on the relative angle between atoms. $\Delta$ is the (real) $s$-wave pairing potential, $s$ and $L$ (the superscripts indicating the type of the orbitals) are spin and orbital angular momentum operators with $s_0$ and $L_0$ the corresponding identity matrices. We use the convention $s = \frac{1}{2} \sigma$ where $\sigma$ is the vector of Pauli matrices, and

\begin{equation}
L_1^{(p)} = \begin{pmatrix}
0 & 0 & 0 \\
0 & 0 & i \\
0 & -i & 0
\end{pmatrix},
\end{equation}

\begin{equation}
L_2^{(p)} = \begin{pmatrix}
0 & 0 & 0 \\
0 & 0 & i \sqrt{3} \\
0 & -i \sqrt{3} & 0
\end{pmatrix},
\end{equation}

\begin{equation}
L_3^{(p)} = \begin{pmatrix}
0 & i & 0 \\
-2i & 0 & 0 \\
0 & 0 & 0
\end{pmatrix}.
\end{equation}

The above Hamiltonian has a very general form. When the Fe atoms lie in a mirror plane of the Pb lattice, as in Fig. 8 for example, and when $\epsilon_{\text{Fe}}(r)$, $\epsilon_{\text{Pb}}(r)$ and $J_{\text{Fe}}$ are all symmetric with respect to the same mirror plane, the Hamiltonian satisfies an anti-unitary symmetry that combines mirror and time-reversal symmetries. Assuming the $xz$ plane to be the mirror plane, the mirror and time reversal symmetry operators, in the cubic harmonic basis for orbitals, are given by

\begin{equation}
M_{xz} = (-1)^l \exp(-i\pi L_2) \otimes \exp(-i\pi s_2) \mathcal{M}(y \rightarrow -y),
\end{equation}

\begin{equation}
T = L_0 \otimes \exp(-i\pi s_2) \mathcal{K},
\end{equation}

where $l$ is the orbital angular momentum quantum number ($l = 1$ for $p$-orbitals; $l = 2$ for $d$-orbitals), $\mathcal{M}(y \rightarrow -y)$ stands for the real-space mirror reflection with respect to the $xz$ plane, and $\mathcal{K}$ is the complex conjugate operator. The invariance of the Hamiltonian under the combined symmetry $M_T = M_{xz} T$ can be broken down
to the following invariance relations:

\[ M_T \xi_{Fe} (x, y, z) M_T^{-1} = \xi_{Fe} (x, y, z), \quad (31) \]
\[ M_{zz} \xi_{Pb} (x, y, z) M_{zz}^{-1} = \xi_{Pb} (x, y, z), \quad (32) \]
\[ T \xi_{Pb} (x, y, z) T^{-1} = \xi_{Pb} (x, y, z), \quad (33) \]
\[ M_{zz} \tau (\delta x, \delta y, \delta z) M_{zz}^{-1} = \tau (\delta x, -\delta y, \delta z), \quad (34) \]
\[ T \tau (\delta x, \delta y, \delta z) T^{-1} = \tau (\delta x, \delta y, \delta z), \quad (35) \]

where \( \tau \) stands for each of \( \tau_{Fe} \), \( \tau_{Pb} \) and \( \tau_{Fe-Pb} \). In addition, the invariance of the superconducting pairing term under \( M_T \) is trivially satisfied. In the Nambu basis, the BdG Hamiltonian satisfies the particle-hole (charge conjugation) symmetry given by

\[ C = L_0 \otimes \exp(-i \pi s_2) \otimes (i \rho_2) K, \quad (36) \]

where \( \rho \) is the vector of Pauli matrices for the particle-hole degree of freedom. The combination of \( M_T \) and \( C \) results in a chiral symmetry

\[ U_\chi = M_T P = M_{zz} \otimes (-i \rho_2), \quad (37) \]

which is unitary and transforms the Hamiltonian as \( U_\chi H_{hybrid} U_\chi^{-1} = -H_{hybrid} \). The implications of these symmetries will be analyzed in detail in Sec. \[ IV \] \[ B \] .

Most of our following results are obtained by performing exact diagonalizations of the above Hamiltonian. In order to maintain a limited yet realistic parameter set, we further assume

\[ \epsilon_{Fe} (r) = \epsilon_{Fe}, \quad \epsilon_{Pb} (r) = \epsilon_{Pb}, \quad (38) \]
\[ J_{Fe} = (0, 0, J_{Fe}), \quad (39) \]
\[ E_{dd\beta} (|\delta r|) = V_{dd\beta} (r_0 / |\delta r|)^{n_{dd\beta}} \quad (|\delta r| \leq a / \sqrt{2}), \quad (40) \]
\[ E_{pp\beta} (|\delta r|) = V_{pp\beta}^1 \quad \text{if} \quad |\delta r| = a / \sqrt{2}, \quad (41) \]
\[ E_{pp\beta} (|\delta r|) = V_{pp\beta}^2 \quad \text{if} \quad |\delta r| = a, \quad (42) \]
\[ E_{pd\beta} (|\delta r|) = V_{pd\beta} \left( \frac{a}{\sqrt{8}} ||\delta r||^{n_{pd\beta}} \quad (|\delta r| \leq \sqrt[3]{8} a), \quad (43) \right. \]

where \( r_0 = 2.383 \AA \) is the nearest neighbor distance in bulk Fe(bcc), and \( a = 4.95 \AA \) is the lattice constant of bulk Pb(fcc). Eqs. \[ 40 \] \[ -43 \] imply that in all types of hopping terms we include up to the second nearest neighbors (cf. Fig. \[ 8 \]). We list all the parameters, except for \( \epsilon_{Fe} \) and \( \Delta \), and their references (if applicable) in Table \[ II \] . Since \( \epsilon_{Fe} \) and \( \mu_{Fe} \) are not actually independent parameters in the model, \( \epsilon_{Fe} \) will be chosen in the linear Fe chain case such that \( \mu_{Fe} = 0 \) corresponds to the center of the minority band, and in the triple Fe chain case according to experiments \[ 22 \].

### B. Multi-Majorana Chains Protected by a Magnetic Symmetry

In this section we investigate new symmetry that could be present in our systems, and which permits the presence of multiple Majorana fermions at the end of the chain. It was first shown in the theoretical part of the supplementary material of \[ 27 \] that in certain cases, multiple Majorana zero modes can appear at the end of the Fe chain. We here explain those results. The conditions needed are: the chain be perfectly straight, with no buckling; the magnetic moment of the iron to have no component perpendicular to the chain and parallel to the Pb surface; the Pb substrate to be disorder free. In this case we show that a magnetic symmetry first proposed in Ref. \[ 28 \] can stabilize an integer number of Majorana fermions at the end of the Fe chain.

For a single Fe chain along the \( x \) direction, on an "infinitely" \( xy \) Pb surface, with the \( z \) direction perpendicular to the surface, and in the absence of any magnetism in the chain, the \( xz \) plane is a mirror plane. We call the mirror operator along that plane \( M_{zz} \) with the properties:

\[ [M_{zz}, H] = 0, \quad M_{zz}^2 = -1 \quad (44) \]

where \( H \) is the superconducting Pb and non-magnetic Fe hybrid structure Hamiltonian operator. Without magnetism, the system is also time-reversal invariant with a spinful time-reversal operator \( T, T^2 = -1 \).

We now add magnetism in the system, on the Fe chain. A magnetic moment breaks time-reversal symmetry. Generically it also breaks the mirror symmetry \( M_{zz} \) – only a magnetic moment polarized along the \( y \) direction does not break \( M_{zz} \), but still breaks \( T \). However, if localized in the \( xz \) plane, the magnetic moment is still invariant under the combination of mirror and time-reversal, a magnetic symmetry \( M_T = M_{zz} T \). This is indeed true as each of the operations flips the magnetic moment so their combination leaves it untouched. This magnetic symmetry was considered first in Ref. \[ 28 \] in a different context, but it was shown that it stabilizes an integer number \( Z \) of Majorana fermions at the vortex core of a crystalline topological insulator. We here repeat the argument to show that this symmetry stabilizes an integer number \( Z \) of Majorana end modes.

The magnetic symmetry \( M_T \) has the properties (since

| Parameters | Ref. | Value | Parameters | Ref. | Value |
|------------|------|-------|------------|------|-------|
| \( \mu_{Fe} \) | ? | | \( \epsilon_{Pb} \) | 35 | 0.97 eV |
| \( \lambda_{Fe} \) | 51 | 0.06 eV | \( \lambda_{Pb} \) | 38 | 0.665 eV |
| \( V_{dd\sigma} \) | 34 | -0.6702 eV | \( V_{p \sigma} \) | 38 | 1.134 eV |
| \( V_{dd\pi} \) | 34 | 0.5760 eV | \( V_{p \pi} \) | 38 | 0.800 eV |
| \( V_{dd\delta} \) | 34 | -0.1445 eV | \( V_{p \delta} \) | 38 | 0.146 eV |
| \( \eta_{dd\sigma} \) | 34 | 3 | \( V_{pd\sigma} \) | 39 | 0 |
| \( \eta_{dd\pi} \) | 34 | 4 | \( V_{pd\pi} / V_{pd\sigma} \) | 39 | -2.17 |
| \( \eta_{dd\delta} \) | 34 | 4 | \( \eta_{pd\delta} \) | 40 | 4 |
| \( J_{Fe} \) | DFT | 2.5 eV | | | |
C. Spatial Extent of the Majorana Fermions From the Shiba Bands

The hybrid 1D-2D nature of our setup is most evident in its influence on the spatial extent of the Majorana end modes. In a purely one-dimensional system, the Majorana modes are exponentially localized at the end of the wire $\exp(-r/L)$. The localization length is $L = t/\Delta_p$ (in units of the chain lattice constant), or the coherence

where $C$ is the charge conjugation operator. Hence $M_T$ acts like spinless time-reversal (squares to 1 and it is antunitary), and it can stabilize multiple majoranas at the edge because any mass terms $i\gamma_5\gamma_k$ between any Majoranas are not allowed due to the $i$ which breaks $M_T$ because of the complex conjugation.

In terms of topological classification, our system falls into the BDI symmetry class because of the presence of both $M_T$ and $P$ symmetries, and hence a chiral symmetry $U_\chi = M_T C$. The bulk of the hybrid system, which is effectively 1D inside the superconducting gap of the Pb substrate, can be classified by a winding number

$$w = i \int_0^{2\pi} \frac{dk}{2\pi} \text{Tr}[h(k)^{-1}\partial_k h(k)],$$

where $h(k)$ is defined such that the Bloch Hamiltonian $H_{\text{hybrid}}(k)$ is brought to the following form by the eigenstates of charge conjugation operator

$$V_\chi^\dagger H_{\text{hybrid}}(k)V_\chi = \begin{pmatrix} 0 & h(k) \\ h(k)^\dagger & 0 \end{pmatrix},$$

$$V_\chi^\dagger U_\chi V_\chi = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}.$$  

Furthermore, the Majorana number $\nu$, defined and investigated in the previous sections (where $\mathcal{M} = (-1)^\nu$ has been used), is related to the winding number as $\nu = w \mod 2$.

We now exemplify the above reasoning in the specific model for Fe chains on the surface of Pb investigated above. As presented previously, the hybrid Hamiltonian [17] is invariant under the magnetic symmetry $M_T$. We therefore expect multiple pairs of Majoranas appearing at the end of the chain. This is indeed confirmed by diagonalizing the Hamiltonian for a finite-size hybrid system. Several such examples are shown in Fig. 9. In addition, we show phase diagrams of such a hybrid structure in Fig. 10 where in particular a phase diagram of the winding numbers (the topological invariant for a Hamiltonian exhibiting $M_T$) as a function of $\mu_{Fe}$ and $V_{pdx}$ is shown in Fig. 10(c).

This new idea could also potentially allow us to experimentally investigate interaction effects in Majorana fermions. While the multiple integer Majorana classification is noninteracting, we expect that interactions will lift the degeneracy of 8 Majoranas providing a $Z \rightarrow Z_8$ classification. With significant experimental effort, this could be potentially tested in the future.
FIG. 10: Phase diagrams of a hybrid structure with a linear Fe chain and a 2D superconducting Pb substrate. Panel (a) shows the band structure (only for the minority band) of the Fe chain when it’s suspended. Panels (b), (c) and (d) are all plotted as a function of $\mu_{Fe}$ and $V_{pd\pi}$, showing the gaps of the hybrid structure, the Majorana number $\nu$, and the topological invariant (winding number) $w$, respectively. The parameter $V_{pd\pi}$ signifies the strength of the hybridization. In order to reduce the errors, we set $\Delta = 0.1$ eV in these calculations. The size of the Pb substrate used here is, in units of unit cell, 21 in $y$-direction and 1 in $z$-direction (infinite in $x$-direction).

length of the $p$-wave. In our system, the $p$-wave wire coherence length is very large, as the induced gap is an order of magnitude smaller than that of the Pb superconductor $\Delta$, of the order $\Delta_p \sim \Delta E_{SO}/J$. If the system was purely one-dimensional, the localization length of the Majorana end states would be larger than the length of the wire. However, when the one-dimensional wire is embedded in the two-dimensional superconductor, the spatial profile of the Majorana end mode is predicted (in a simplified model calculation\textsuperscript{41}) to acquire a powerlaw decay $1/\sqrt{r} \exp(-r/L)$ which significantly decreases the spatial extent of the Majorana end state. We now numerically analyze the decay length of the Majorana end modes in our hybrid one-dimensional Fe chain embedded in the two-dimensional Pb superconductor. In Fig. 11 we show typical evolution of the Majorana wavefunction profile when the coupling between Fe and Pb is varied. It is clearly seen that the deviation of the wavefunction profile from an exponential function becomes more pronounced when the coupling between the 1D and the 2D systems is increased.

D. Phase Diagram of a triple Fe chain hybridized with a 2D Pb Substrate

We now discuss the hybrid structure with a triple Fe chain, which is more relevant to existing experiments presented in Ref. 27. In this case the band structure of a suspended Fe chain is significantly more complicated than that of the linear chain shown in Fig. 2 and Fig. 10(a). STM measurements suggest that the Fermi energy in the triple chain is likely to lie in-between two sets of narrow bands observable in a band structure calculation\textsuperscript{27}. We will refer to this energy as the $\mu_{Fe} = 0$ point in our following presentations. In Fig. 12 we show two phase diagrams in the $\{\mu_{Fe}, V_{pd\pi}\}$ space, in terms of the Majorana numbers and the winding numbers, respectively.
Remarkably, but not surprisingly, although the phase diagram in terms of the Majorana numbers contains almost equal areas for $\nu = 1$ and $\nu = 0$ phases, because of more lifted degeneracies in a triple chain compared with a linear chain, the phase diagram in terms of the winding numbers is still dominated by topologically non-trivial ($w \neq 0$) phases. This implies that Majorana end modes are almost certainly present in the current hybrid structure. To further identify the actual number of these Majorana modes in experiments will be interesting but challenging.

V. DISCUSSION AND CONCLUSIONS

Motivated by recent STM experiments\cite{27} which identified zero-bias peaks in the tunneling density-of-states of iron atomic chains placed on the surface of lead and interpreted them as Majorana states, we have carried out a theoretical study aimed at shedding light on the possibility of developing magnetic transition metal atom chains on the surface of superconductors as a platform for one-dimensional topological superconductivity. Our conclusions are generally speaking optimistic. Even though the exchange spin-splitting on the chain typically exceeds the superconductor’s Clogston limit by orders of magnitude, nano structures of this type typically form gapped superconducting states through a mechanism illustrated schematically in Fig. 1, and these states are often topological.

Our theoretical study aims to identify some general trends and is not exhaustive. We have restricted our attention to transition metal atomic chains. The case of rare earth chains will differ in some important respects and deserves attention. We have also assumed that spin-singlet pairing is dominant on the transition metal chains and treated its strength as a phenomeno-
logical model parameter. Constructing a realistic theory of pairing on the transition metal chain should be feasible, since the pairing mechanism is almost certainly dominated by phonon-mediated attractive electron-electron interactions, but still challenging in several respects and beyond the scope of the present work. In addition we have based our conclusions on models which do not include s orbitals centered on the transition metal atoms. This omission seems to be justified by two different considerations, namely that s-orbitals are both more weakly spin-polarized than d orbitals and more strongly dispersive. Adding s-orbitals to the models we have studied will almost always increase the number of bands which cross the normal state Fermi level by two, and will therefore not alter the topological character of the state.

There is a strong interplay between the possibility of achieving topological superconductivity in transition metal atom chains and the nature of the magnetic order in these chains. In this paper we have addressed the case of ferromagnetic chains with an easy magnetic axis perpendicular to the chain. We have therefore been assuming that the magnetic stiffness along the chain is sufficiently large to justify a macrospin limit and that the magnetic anisotropy is sufficiently strong that the overall spin-orientation does not suffer thermal fluctuations. For Fe on Pb these conclusions are supported by ab initio electronic structure calculations. There is in fact a large experimental and theoretical literature on magnetic order in one-dimensional chains.14–17 Magnetism is influenced by bond lengths, bond angles, band fillings, and substrate among other factors. Chains made from elements that are magnetic in the bulk, do not necessarily have ferromagnetic order and conversely chains made from elements that are not magnetic in the bulk can be ferromagnetic as a chain. It is generally a nontrivial task to experimentally determine the magnetic order of a specific chain. On the theory side, ab initio density functional theory calculations can be helpful in identifying the magnetic order of a chain once its structure and composition is known. Generally speaking transition metal atom chains tend to be ferromagnetic when the atoms are close together and antiferromagnetic when the atoms are far apart. The magnetic interactions in these limits can be interpreted as being dominated by double exchange and super exchange respectively. Helical and other more complex textures tend to occur close to the crossover between these limits. For the particular case of transition metal atoms on lead, however, strong p–d bonding leads to closely spaced transition metal atoms. We expect simple ferromagnetism in nearly every case and this has motivated our restriction to uniform exchange fields.

Our model studies have allowed us to reach two main conclusions which will, we hope, inform efforts to develop ferromagnetic chains on superconducting substrates as a practical Majorana state factory.

- i) Pb is an excellent superconducting substrate. It is a relatively large gap superconductor. Its p-orbitals readily hybridize with d-orbitals in the transition metal chain allowing Cooper pairs to hop from the substrate to the magnetic chain. Its strong spin-orbit coupling not only provides the Rashba spin-orbit coupling required for gapped superconducting states, but also has a favorable influence on chain magnetic properties by enhancing the chain magnetocrystalline anisotropy and by inducing Dzyaloshinskii-Moriya (DM) interactions between the chain magnetic atoms. A large magnetocrystalline anisotropy stabilizes the magnetic order of the chain and is generally desirable. The DM interactions can lead to canted/spiral magnetic order, which, in combination with the on-site spin splitting, can contribute to the effective Rashba spin-orbit coupling.

- ii) The iron atoms chains studied in Ref27 probably do not optimize ferromagnetic chain topological superconductivity. This conclusion motivates a program of experimental and theoretical research aimed at forming topological superconductors with the largest possible gaps and the most robustly reproducible topological character. Our model calculations indicate, for example, that the superconducting state is most likely to be topological when the ferromagnetic atom chain is straight. The structure formed by ferromagnetic atoms on lead is influenced both by the mixture of atoms that are present and by the chain growth conditions. If protocols can be established for growing straight chains, they should enable perfectly reproducible topological behavior. Our model calculations indicate that the one-dimensional superconducting gap is \(\sim \Delta E_{so}/J\). \(\Delta E_{so}\) should be enhanced by strong hybridization with a strongly spin-orbit superconductor like Pb. This formula indicates however that larger superconducting gaps might be achievable in chains with itinerant electron ferromagnetism that is weaker than in iron, perhaps in a chain formed by atoms that are not magnetic in the bulk and barely magnetic in the less coordinated chain geometry.

In summary, we carried of topological superconductivity and Majorana end states in 3d ferromagnetic chain tight-binding models with spin-orbit coupling, inversion symmetry breaking, and s-wave superconductivity pairing. We found that the atomic spin-orbit coupling is in general not sufficient for a p-wave superconducting gap to be open in the ferromagnetic chain, and that one needs to break inversion symmetry or introduce Rashba spin-orbit coupling. This property can be explained with an argument similar to that used for the 3D Weyl semimetals. Motivated by recent experiments, we discussed in detail how a sizable Rashba spin-orbit coupling is induced in the ferromagnetic chain when it is deposited on a strongly spin-orbit coupled substrate. We have constructed topological phase diagram in model parameter
spaces, varying band filling, exchange splitting strength, and chain structural parameters. In straight magnetic chains we find that the half metallicity which appears at strong exchange splitting makes topological superconductivity particularly robust, especially compared to the case of the semiconductor quantum wire Majorana platform. Finally we discussed the decay of the Majorana end modes, the possible appearance of a new symmetry protection an integer number of Majorana modes (where interaction effects could potentially be seen) and of coupling between end states in a finite length chains, on the gap size, the Rashba spin-orbit coupling strength, the pairing amplitude, and hybridization with substrate orbitals.

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Appendix A: Calculation of Majorana number

To calculate the Majorana number (defined below), we need first to write the BdG Hamiltonian into Majorana fermion basis. For any fermion operator \( \psi \) one can define two Majorana operators

\[
\gamma_a = \psi + \psi^\dagger, \quad \gamma_b = -i(\psi - \psi^\dagger).
\]

The Majorana operators fulfill the following relations

\[
\begin{align*}
\gamma_i^\dagger &= \gamma_i, \quad a = a, b \\
\{\gamma_i, \gamma_j\} &= 2\delta_{ij}\delta_{a\beta}.
\end{align*}
\]

By explicitly writing all possible terms in a quadratic fermionic Hamiltonian in the Majorana basis, and considering the hermicity of the coefficients, we can prove that any quadratic fermionic Hamiltonian up to a constant can be written as

\[
H = \frac{i}{2} \sum_{ij} \gamma_i^T A_{ij} \gamma_j, \tag{A3}
\]

where \( \gamma_i \equiv (\gamma_{i,a}, \gamma_{i,b})^T \), and the matrix \( A \) is real and antisymmetric.

The Fourier transform of Majorana fermions is

\[
\gamma_{i,\alpha} = \frac{1}{\sqrt{N}} \sum_k e^{-ikr_i} \gamma_{k,\alpha}, \tag{A4}
\]

which implies that \( \gamma_{k,\alpha}^\dagger = \gamma_{-k,\alpha} \). The Hamiltonian after Fourier transform becomes

\[
H = \frac{i}{2} \sum_k \gamma_k^T \tilde{A} \gamma_k, \tag{A5}
\]

and \( \tilde{A} \) is still antisymmetric but not necessarily real. Eq. (A5) is closely related to the BdG Hamiltonian written in Nambu spinors. Below we follow the prescription given in Ref. [22].

In real space the Majorana spinor \( \gamma_i = (\gamma_{i,a}, \gamma_{i,b}) \) is related to the Nambu spinor \( \Psi_i = (\psi_i, \psi_i^\dagger)^T \) by

\[
\gamma_i = \sqrt{2}U\Psi_i, \quad U = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 1 \\ -i & i \end{pmatrix} \tag{A6}
\]

Therefore after Fourier transform we have

\[
\tilde{A}_k = -iUH_{\text{BdG}}(k)U^\dagger, \tag{A7}
\]

which makes it convenient to obtain \( \tilde{A}_k \) from the BdG Hamiltonian.

The Majorana number \( M \) of an infinite 1D chain is defined as

\[
M = \text{sgn} \left[ \text{Pf}(\tilde{A}_{k=0})\text{Pf}(\tilde{A}_{k=\pi}) \right], \tag{A8}
\]

where \( a \) is the lattice constant, and Pf means Pfaffian of an antisymmetric matrix. When \( M = -1 \), i.e., Pf(\( \tilde{A}_k \)) takes opposite signs at zone center and zone boundary, the chain is topologically nontrivial and there should be isolated zero energy Majorana edge modes in a finite chain.

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