Majoranas in mixed-valence insulators

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Abstract

A physical model for a mixed-valence impurity in a metal must satisfy the Friedel screening theorem for both valences. Such a model is shown, following earlier work which showed low energy singularities in it, to be supersymmetric, leading to a free Majorana and a phase-shifted Majorana excitation. The theory extended approximately to a lattice of mixed-valence ions at appropriate filling gives, without fine-tuning the parameters, a protected gapless Majorana fermion band across the chemical potential, besides the mixed-valence particle and hole bands separated by gaps. In this situation the system is electrically neutral in linear response but has de Haas-van Alphen oscillations. This is used to explain the recently observed magneto-oscillations in mixed-valence insulators as well as their accompanying low energy thermodynamic and relaxation rate anomalies. Some predictions to test the validity of the theoretical results are provided, the most striking of which is that there should be extensive ground state entropy in such compounds.
I. INTRODUCTION

The theory of heavy-fermion and mixed-valence metals and insulators began through understanding the Kondo problem using a variational wave-function for the Anderson model [1] as a resonance obtained by constrained hybridization of the strongly correlated magnetic orbitals obeying local quantum-numbers with the nearly free conduction bands [2, 3]. The problem of the lattice, simply treated as that of conduction electrons hybridizing with a periodic array of such resonances, done in a variety of different ways, for example in [2], [4], [5], [6], [7], [8], is also highly successful in understanding experiments in heavy-fermion metals away from any singularities due the interactions between the correlated orbitals. The reasons are well understood because the excitations are that of a Fermi-liquid obeying Bloch’s counting rules, albeit with quite different relation [10] of Landau parameters to experimental properties from those in He$^3$, the canonical Fermi-liquid. In the case of mixed-valence insulators, predicted by the Bloch’s rules in the same theory based on the same model, this happy state of affairs is called into question by some recent experiments [11–14] with results which are spectacular and call for a new paradigm. Oscillatory magnetization in a magnetic field $H$ with period proportional as in Onsager on metals to $1/H$, and finite value of the Sommerfeld coefficient $\gamma = C_v/T$ with a possibly singular correction at low temperature, are observed at low temperatures in materials which are electrical insulators, of the mixed-valence kind. In this paper, I take these results in context of the fact that the essentially exact solution [15, 16] of a proper physical model for a mixed-valence impurity has singular low energy excitations, unlike the local Fermi-liquid [17] properties of a Kondo impurity. I show here that this solution [15, 16] is equivalent to having Majorana excitations. The theory approximately extended to a lattice of mixed-valent ions gives an insulator obeying the Bloch rules, but one of the branches of Majoranas survives and is in fact protected by the insulating gap. The underlying physics of this Majorana is different from the one-dimensional superconductor model of Kitaev [18]. Although the existence of a Majorana is tantamount to breaking U(1) gauge invariance, there is no implication in the present work for superconductivity of any kind. Arguments for magneto-oscillations in superconductors with odd frequency even parity pairing [19], [20] have already been presented by Baskaran [21] and by Erten et al. [22]. But the materials under discussion are not superconductors of any kind.
The physics of the singularities in the two-channel Kondo problem \[23 –25\] and the two impurity Kondo problem \[26–28\] at specially tuned points may also be expressed in terms of Majoranas. However, in both these problems, the singularities occur at specially tuned points, so that the problems though of theoretical interest are not naturally realizable. The mixed-valence impurity also displays the singularity at a specially tuned point but in a mixed-valence lattice the phenomena occurs over a range of parameters and fine tuning is not required.

What is the difference between a mixed-valence impurity and a Kondo impurity? For a mixed-valence impurity, two different charge states of the impurity are nearly degenerate at the chemical potential while the third is far away in energy \[3\] \[29\] \[30\]. For a Kondo impurity, the Hartree-Fock resonance for one charge state is below the chemical potential while its adjacent charge states on both sides have resonances far above the chemical potential \[1\].

While weak breaking of particle-hole symmetry in the Anderson model \[1\] is known to be irrelevant \[15, 31\], mixed valence requires strong particle-hole asymmetry. In that case, both charge states must be locally screened, which means by the Friedel theorem on local charge neutrality that there should be a phase shift of $\pi$ in the conduction band for two different charge states. This cannot be accomplished by just the one interaction parameters of the Anderson model \[1\] which is sufficient near particle-hole symmetry as in the Kondo impurity. At least another independent parameter is required for screening. The Hartree-Fock mean-field phase diagram of the magnetic impurity with tunable screening interactions \[29\] gives a first order phase transition at the mixed-valence point. This while revealing is insufficient to the problem. The problem was solved by the Wilson numerical renormalization group (RG) \[15\], which for parameters satisfying the Friedel theorem was discovered to have logarithmic low energy singularities similar to the singularities in the two channel Kondo problem and the two Kondo impurity problem. It was further investigated analytically to derive the same singularities using Abelian bosonization in \[16\]. I show in this paper that these results may be expressed in terms of Majorana excitations.

The physical reason for the singularity and the associated Majorana at a mixed-valence may be explained with reference to Fig. (1) in Ref. \[30\] where it is argued that an insulator in rare-earth compounds must with high probability in parameter space have the magnetic ions be in the mixed-valence state rather than of the simple Kondo state. In such compounds the system changes from a fermi-liquid with one phase shift of the fermions when the correlated
orbital is above the chemical potential, i.e. the impurity has one particular valence, to a Fermi-liquid with a different phase shift when the parameters are such that the correlated orbital is below the chemical potential where the impurity has the adjacent valence. The two Fermi-liquids have different symmetries [15] so that one cannot pass continuously from one to the other as the parameters are varied through the mixed-valence condition. Achieving the condition in short-range interaction models requires tuning at least one parameter. In a lattice of correlated orbitals, the singularity pins the chemical potential to the mixed valence condition over a wide region of parameters and temperature [32].

This paper is organized as follows. First the experimental results are very briefly summarized. In Sec. III, the starting Hamiltonian used in [15] and [16] is introduced. In [16], a specific bosonization procedure and rotations or canonical transformations are used to simplify the problem. An alternative canonical transformation is shown to give mathematically similar results. Unlike the two channel Kondo problem but like the two Kondo impurity problem, Abelian bosonization does not reduce the problem to quadrature. A strong coupling procedure introduced for the two Kondo impurity problem [28] is used to show that the mixed valence problem also has super-symmetry, i.e. bosonic and fermionic ground states have identical energy, as do the excitations. This appears necessary to show that the single particle excitations are Majoranas. The approximate extension to the lattice in terms of these variables is presented in Sec. IV. It is shown that when Bloch rules for insulators are satisfied, a band of Majorana hybridizes with local resonances to present a gap in the spectra while another band of Majoranas remains free across the chemical potential. The approximation is to independently perform the transformations done in the single-impurity problem to every site in the periodic lattice. Some justification of this procedure is given. The application to the magneto-oscillations due to the gapless Majorana band, without linear coupling to low energy electromagnetic fields, is explained. This is followed by a brief discussion of some important issues which need further work for a better understanding of the excitations. Important experimental tests of the theory are suggested. Two principal predictions are extensive ground state entropy and the absence of Zeeman splitting of the magneto-oscillations.
II. EXPERIMENTS

The most complete experimental evidence for anomalous properties we are concerned with are available in SmB$_6$ although similar properties are observed in YbB$_{12}$. The symmetry of the band-structure in SmB$_6$ is such that it is also a topological insulator [33] with convincing evidence for surface states [34]. SmB$_6$ was investigated and characterized to be a mixed-valence insulator long ago, in 1968 [35]. Two groups have observed nearly similar magneto-oscillations in this compound. Arguments have been given by one experimental group [36] that the magneto-oscillations in SmB$_6$, claimed to be due to bulk excitations by the other [11] may be due to surface states, while for YbB$_{12}$, there seems to be agreement among both groups [12, 13] for magneto-oscillations due to bulk excitations. I regard the conclusion that the magneto-oscillations periodic in $1/H$, under discussion, in insulating SmB$_6$ are due to bulk excitations as trustworthy for a few reasons. They are accompanied by "electronic" heat capacity in the insulator with magnitude of about 5 mJ/mole K$^2$ at low temperatures. For comparison the specific heat of metallic Cu is 1/2 mJ/mole K$^2$. The amplitude of the oscillations is similar to their diamagnetic susceptibility which is a bulk property. The oscillations are also accompanied by low energy magnetic fluctuations which were already in evidence in $\mu$SR measurements [37]. The $\mu$SR relaxation rate becomes constant below about 4 K down to the lowest measured temperature of 19 mK. $\mu$SR relaxation is a probe for bulk excitations in the limit of zero energy. A constant in temperature relaxation rate is itself a major anomaly.

It is also worth noting that the low temperature electronic specific heat of samples made by different groups [38], [13] are remarkably different. This is further discussed in the last section of the paper.

III. THE MIXED VALENCE IMPURITY

I first recall here some features of Perakis et al. [15] and Sire et al. [16], which are essential for this work. I start with essentially the same Hamiltonian, written in the Wannier orbitals of the form used by Wilson [39] in two different symmetries, the fermions $h_{i\sigma}$ which hybridize with the local orbitals $f_{\sigma}$ which have a large local repulsion parameters, and the screening fermions $s_{i\sigma}$ in a symmetry which is orthogonal to that of the hybridizing channels with a
repulsive interaction between them.

\[ H = H_0 + H_{\text{kin}} \]  \hspace{1cm} (1)

\[ H_0 = \epsilon_f(n_f - 1/2) + U n_f \uparrow n_f \downarrow + t \sum_\sigma f_\sigma^+ h_{0\sigma} + H.C. + V(n_f - 1/2)(n_{s0} - 1/2), \]  \hspace{1cm} (2)

\[ H_{\text{kin}} = \sum_{i,\sigma} t_h h_{i\sigma}^+ h_{i+1\sigma} + t_s s_{i\sigma}^+ s_{i+1\sigma} + H.C. \]  \hspace{1cm} (3)

\( i \) labels the sites of the one-dimensional Wilson chain. The parameter \( V \) is absent in the usual Anderson model \[1\]. It is assumed that both \( U, V >> t \), the hybridization parameter \( t \) for the local orbital. Actually \( U \rightarrow \infty \). The two lowest energy states in \( H_0 \) are multi-particle (excitonic) states,

\[ \zeta^+_\sigma |0 > = |\sigma, 0 >, \quad \text{with energy} \quad E_\zeta = -((\epsilon_f/2 - V/4)^2 + t^2)^{1/2}, \]  \hspace{1cm} (4)

\[ \eta^+ |0 > = |0, 1 >, \quad \text{with energy} \quad E_\eta = -(\epsilon_f/2 + V/4). \]  \hspace{1cm} (5)

Here, the first entry in the bracket is the spin of the charge and spin of the impurity plus the hybridized charge of the neighboring sites in the symmetry of the orbitals of the impurity. The second is the charge of the screening channel. The charge in the screening channel is either 0 or 1 of either spin. This can be properly counted by defining the operator

\[ s_0 = s_{0,\sigma}(1 - n_{s,0,-\sigma}) + s_{0,-\sigma}(1 - n_{0,s,\sigma}), \quad n_{0,s,\sigma} \equiv s_{0,\sigma}^+ s_{0,\sigma}. \]  \hspace{1cm} (6)

The constraint on the states is

\[ \sum_\sigma \zeta^+_\sigma \zeta_\sigma + \eta^+ \eta = 1. \]  \hspace{1cm} (7)

The two states \( \zeta^+_\sigma |0 > \) and \( \eta^+ |0 > \) satisfy the essential requirement of the Friedel theorem.

The effective Hamiltonian in the space of these two states obtained for \( t/V << 1 \) is \[16\],

\[ H_{\text{eff}} = H_{\text{kin}} + \frac{\epsilon}{2}(\sum_\sigma n_{\zeta,\sigma} - n_{\eta}) + \hat{t}(\sum_\sigma \zeta^+_\sigma \eta s_{0\sigma}^+ h_{0\sigma} + H.C.) \]  \hspace{1cm} (8)

\[ + J\zeta^+_\sigma \zeta_\sigma \cdot h_{0\sigma}^+ \sigma h_0 + V_s(n_{\zeta} - 1)(n_{\eta} - 1). \]

In \[8\] \( \epsilon = (E_\zeta - E_\eta) \), and the parameters \( J, V_s \), and \( \hat{t} \) are of similar magnitudes,

\[ J \approx \frac{2t_h^2}{(\epsilon + V)}, \quad V_s \approx \frac{2t_s^2}{(\epsilon + V)}, \quad \hat{t} \approx \frac{2t_h t_s V}{(\epsilon^2 + V^2)}. \]  \hspace{1cm} (9)

The direct hybridization in the initial Hamiltonian disappears in \[8\] in the \( \zeta - \eta \) space and replaced by multi-particle resonances coupling to kinetic energy (K.E.) which carry the effect farther. Secondly, the parameters \( \hat{t}, J, V_s \) are all marginal. The terms in kinetic energy coupling the local resonances to farther and farther Wilson orbitals are successively irrelevant to \( O(\Lambda^{n/2}) \), where \( \Lambda \ll 1 \) is the RG expansion parameter.
A. Bosonization and re-Fermionization

One can represent the one-dimensional hybridizing fermions coupling to the impurity by boson operators $\Phi_{h\sigma}(x)$

$$h_{\sigma}(x) = \frac{e^{-i\Phi_{h\sigma}(x)}}{\sqrt{2\pi a}}. \quad (10)$$

$\Phi_{h\sigma}(x)$ is governed by the appropriate Lagrangian given for example in standard works on bosonization [40]. One may now rotate the obtained Hamiltonian by the operator

$$T_{\sigma} = e^{i(\zeta_{\sigma} - 1/2)\Phi_{h,\sigma}(0)}, \quad (11)$$

and note that $T_{\sigma}$ and $T_{-\sigma}$ commute. The result [16] is the Hamiltonian

$$H = H_{\text{kin}} + \epsilon\left( \sum_{\sigma}(\zeta_{\sigma}^{+} \zeta_{\sigma} - 1/2) - \eta^{+}\eta \right) + \hat{t}\left( s^{+}_{0} \eta \sum_{\sigma} \zeta_{\sigma}^{+} + \text{H.C.} \right) + J \sum_{\sigma} \zeta_{\sigma}^{+} \zeta_{-\sigma}. \quad (12)$$

There are also some additional longitudinal terms introduced (noted in [16]) which do not affect the results obtained here and serve mostly to renormalize $\epsilon$ and so only alter the condition for criticality. In [16], Eq. (12) is used to calculate the free-energy and the response functions and to show the low energy singularities.

The Hamiltonian (12) is equivalent in essential mathematical aspects to that for the two-impurity Kondo problem as treated in [28]. To show this the term proportional to $J$ is written, using the constraint (7) and taking $U \to \infty$, as

$$J \sum_{\sigma} \zeta_{\sigma}^{+} \zeta_{-\sigma} \to J \sum_{\sigma} \zeta_{\sigma}^{+} \eta \gamma^{+} \zeta_{-\sigma}. \quad (13)$$

With this change, $H$ is equivalent to Eq. (4) of Ref. [28] on the two impurity problem (after the rotation to $\Phi_{s} = 0$ in the latter), and the identification of $\eta^{+}\zeta_{\uparrow}$ with $S_{1}^{+}$, $\eta^{+}\zeta_{\downarrow}$ with $S_{2}^{+}$; $\hat{t}$ with $J$ and $J$ with $K$. The other coefficients $J_{z}, J_{m}, J_{mz}$ present in [28] are absent here. They did not play any essential role in [28]. One must also also identify the two channels 1 and 2 in [28] with the channels $s$ and $h$ here. One could define

$$\tau_{\uparrow}^{+} = \eta^{+}\zeta_{\uparrow}, \quad \tau_{\downarrow}^{+} = \eta^{+}\zeta_{\downarrow}, \quad \tau_{\uparrow}^{-} = \eta^{+}\eta - \zeta_{\uparrow}^{+}\zeta_{\uparrow}, \quad (14)$$

e tc. $\tau_{\uparrow}, \tau_{\downarrow}$ are two non-commuting spinors, just as $S_{1}, S_{2}$ in [28].

Just as the two impurity problem, the present problem is not reducible to quadrature by Abelian bosonization. Instead, a strong coupling scheme was developed which I follow below.
1. A different Bosonization and re-fermionization

Before we proceed, it is important to note that $H$ in Eq. (12) is also obtained in terms of somewhat different variables by a different rotation operator. We may bosonize the screening channel fermions also by

$$s(x) = \frac{e^{-i\Phi_s(x)}}{\sqrt{2\pi a}}$$

and introduce charge and spin bosons in the $h$-channel by

$$\Phi_{hc}(x) = \frac{1}{2}(\Phi_{h,\uparrow}(x) + \Phi_{h,\downarrow}(x)); \quad \Phi_{hs}(x) = \frac{1}{2}(\Phi_{h,\uparrow}(x) - \Phi_{h,\downarrow}(x)).$$

The term in (8) proportional to $\hat{t}$ becomes

$$\hat{t} \frac{e^{-i\Phi_s(x)}}{2\pi a} \eta((\zeta_\uparrow^+ + \zeta_\downarrow^+)e^{i\Phi_{hc}(0)}\cos(\Phi_{hs}(0)) + i(\zeta_\uparrow^+ - \zeta_\downarrow^+)e^{i\Phi_{hc}(0)}\sin(\Phi_{hs}(0))) + H.C. \quad (17)$$

A rotation $U' = e^{i(\zeta_\uparrow^+ \zeta_\downarrow^+ - \zeta_\downarrow^+ \zeta_\uparrow)}\Phi_{hs}(0)$, and $U = e^{i\eta^+ \eta\Phi_s(0)}$ puts $\Phi_{hs}(0) \rightarrow 0$ eliminating the term with the difference of the spin-directions as well. One may now transform the Hamiltonian (8) to (12), with $s$ replaced by the fermion obtained by the inverse transformation back to fermion of the operator ($\Phi_{hc}$). In both procedures only one linear coupling of the spin-directions is coupled to the fermions, the other is left free.

If instead, we rotate and eliminate ($\Phi_s - \Phi_{hc}$) out of the Hamiltonian, keeping the spin-fluctuations $\Phi_{hs}$ and fermionizing it, it is not possible to make further progress, primarily because of the exchange term proportional to $J$ which now appears as a product of two spinors and a fermion operator. The basic physics for mixed-valent criticality is in the charge sector. In the two cases, where the procedure works, the effective fermion is the representation of as a screening density dressed with the charge and spin-fluctuations of the hybridizing channel, or the density of the hybridizing channel dressed with the charge density of the screening channel and the spin-density of the hybridizing channel. The mysterious rotations, which are essential for the final simple results, may be thought of as imposing boundary conditions and thereby non-local renormalizations of the channel that is kept. These boundary conditions are the essential ingredients of the conformal field theory solutions of such impurity problems [24].
B. Strong-coupling scheme, supersymmetry and Majoranas

The strong coupling scheme starts with $\hat{t}, J \gg t_h, t_s$, as appropriate in the renormalization group because the successive couplings $t_h, t_s$ in Wilson shells are $O(\Lambda^{n/2})$ irrelevant, while $\hat{t}$ and $J$ are of $O(\Lambda)^0$. So, we first diagonalize only the terms involving the latter. In doing so, one notices that since they are linearly coupled to fermions, $\tau_\sigma$ must also be expressed in terms of fermions. One runs then into the same problem as in [28] that $\tau_\uparrow, \tau_\downarrow$ commute while their fermion representation $d_\uparrow, d_\downarrow$ anti-commute. This is remedied by an effective Jordan-Wigner procedure by which

$$\tau^-_\sigma \rightarrow d_\sigma \left(1 - (1 - i)n_{-\sigma}\right), \quad \tau^+_\sigma \rightarrow \left(1 - (1 + i)n_{-\sigma}\right)d^+_\sigma,$$

$$\tau^z_\sigma = d^+_\sigma d_\sigma - 1/2 = n_\sigma - 1/2. \quad (18)$$

The $d_\sigma$’s then obey the anti-commutation relations while the $\tau_\sigma$’s obey commutation relations. The term proportional to $J$ is not affected by this transformation. The local Hamiltonian in terms of the $d_\sigma$’s is now

$$H_{loc} = \frac{J}{2} \left(d^+_\uparrow d_\downarrow + d^+_\downarrow d_\uparrow\right) + \frac{\hat{t}}{2} \left(cd^+_\uparrow \left(1 - (1 - i)n_\downarrow\right) - cd_\downarrow \left(1 - (1 - i)n_\uparrow\right) + H.C.\right). \quad (19)$$

Here $c$ is the annihilation operator for the local fermion which could be either of the choices made above. $H_{kin} + H_{loc}$ is the exact representation of the mixed valence impurity problem.

One can diagonalize (19) in the space of $n_0 = c^+_0 c_0 = 0, 1; n_\uparrow = 0, 1; n_\downarrow = 0, 1$. The eight states organize into two un-coupled spaces, four with even total number and four with odd total number of ”particles”. The basis vectors for the even sub-space are

$$|0, 0, 0 >, |0, 1, 1 >, |1, 1, 0 >, |1, 0, 1 >,$$

and the odd sub-space are

$$|1, 0, 0 >, |1, 1, 1 >, |0, 0, 1 >, |0, 1, 0 >.$$

The three numbers in the bracket are $n_0, n_\uparrow$ and $n_\downarrow$, respectively. The eigenvalues and the eigenvectors of the Hamiltonians in these sub-spaces are given in an Appendix A, where the following results are derived:

A. The eigenvalues in each subspace split into the ground state $E_G$, a pair of degenerate excited states $E_1 = E_2$ and a higher excited state $E_3$. The energies $E_G, E_1, E_2$ and $E_3$ are identical for the even and the odd sectors.

B. Let us call these states, respectively,

$$|G, e >, |G, o >, |1, e >, |1, o >, |2, e >, |2, o >, |3, e >, |3, o >.$$
The even and the odd sectors may be regarded as bosonic and fermionic respectively, the degeneracy of the two sectors represents a super-symmetry in the problem.

C. Let \( r \equiv J/\hat{t} \). Then for

\[
r\sqrt{r^2 + 2} = 1, \text{ i.e. } J \approx 0.643 \, \hat{t},
\]

which will be considered the condition for mixed-valence criticality,

\[
< G, e|c_0|G, o >= < G, o|c_0|G, e >= < G, e|c_0^\dagger|G, o >= < G, o|c_0^\dagger|G, e > .
\]

This means that \( c_0 \) is a real (Majorana) fermion which may be written as

\[
c_0 = c_0^\dagger = \frac{a_0 + a_0^\dagger}{\sqrt{2}},
\]

The conjugate Majorana

\[
\bar{c}_0 = i\frac{a_0 - a_0^\dagger}{\sqrt{2}}
\]

is un-coupled to the local resonances. \( a_0, a_0^\dagger \) are canonical complex spin-less fermions. \( c_0, \bar{c}_0 \) also obey fermion anti-commutation relations.

D. The matrix elements between the ground state of the even sector and the excited states of the odd sector, and the ground state of the odd sector and the excited states of the even sector of \( c_0 \) have the same property (21) as between the ground state. Similarly all such matrix elements of \( \bar{c}_0 \) are zero. This means that coupling to higher states retains the reality of \( c_0, \bar{c}_0 \). The coupling between the resonances at different sites through the propagating fermions \( c_i \) is therefore absent.

It also follows that \( \bar{c}_0 \), which as shown have no coupling to the degenerate ground states, have no coupling to the excited states as well.

To complete the strong-coupling development, the next Wilson orbitals \( c_1 \) in the kinetic energy is coupled to \( c_0 \) leading to new degenerate ground states, so that \( c_1 \) can be shown to be a Majorana also, and successively for all orbitals \( c_n \) which are increasingly irrelevant to \( O(\Lambda^{n/2}) \). This is also done for the two-channel problem [25] and the two-impurity problem [28] and has its antecedent in the procedure due to Noziéres and Blandin [23]. In their conformal field theory solution of the two-Kondo impurity problem, Affleck and Ludwig [24] showed that the symmetry of the Majoranas in the problem have an Ising symmetry. This is true for the present problem and is different from the symmetry of the Majoranas in the
two-channel problem \[41\]. This is to be contrasted with the Majoranas introduced by Kitaev \[18\] in a one-dimensional superconducting wire, which by construction have \(U(1)\) symmetry.

Since only one linear combination of the local operators \((\tau^\uparrow + \tau^\downarrow)\) is coupled to fermions, and the other \((\tau^\uparrow - \tau^\downarrow)\) is left free, there is ground state entropy \(\frac{1}{2}k_B \ln 2\) for the spin-1/2 mixed-valence impurity problem as there is in the two-channel Kondo impurity problem and the two-impurity Kondo problem at criticality.

Just as in Ref. \[28\], one could perform a mean-field approximation on Eq. \(19\) and obtain an effective Hamiltonian,

\[
H_K + k(d_\uparrow^+ d_\downarrow + H.C.) + ip(d_\uparrow^+ d_\downarrow^+ + d_\sigma d_\sigma^+),
\]

where \(k\) and \(p\) are parameters which depend self-consistently on expectation values such as \(<c_0 d_\sigma>, <c_0 d_\sigma^+>\). At the critical condition \(k = p\), the correlation functions and eigenvalues are same as from the strong coupling solution and the solution with the Wilson numerical RG. The fact that mean-field theory works is as equally surprising in this problem as for the two impurity problem and makes one think that there is some more clever transformation with which the problem is exactly quadratic. We shall not pursue this mean-field theory further here because it does not add to the discussion of the lattice problem.

IV. THEORY FOR THE MIXED-VALENCE LATTICE

In the problem of the heavy-fermion lattice, many particle physics is considered usually only at the level of the single site Kondo problem. The spatial periodicity of the resulting phase shifts of the light bands in the local symmetry of the local moment is then used to generate a band-structure with an energy scale of the Kondo temperature \(T_K\), which is the characteristic universal scale of change of phase shift with energy. This approach is remarkably successful in comparing low energy and low temperature physics with experiments, except when the interactions between the resonances due to their direct interactions with each other are comparable to \(T_K\). A \(1/N\) expansion in the number of channels of fermions and/or number of orbital degree of freedom formally allows a justification. The physical reason for the success of the approximation is that due to the scale of parameters in the problem, with the Kondo temperature much less than the electronic band-width, the self-energy has negligible momentum independence compared to the energy dependence. This
in turn makes vertex renormalizations unimportant. A proof that this procedure works is that experimental Fermi-surfaces\cite{42} of the heavy-fermions have almost the same size and angular dependence as in one-particle calculations but with strongly renormalized mass and velocities. This follows from the theory for the fermi-liquid renormalization when the self-energy satisfies the condition mentioned\cite{10}.

I follow the same approach in using the many-body resonances obtained above for the mixed-valence impurity problem to the periodic array of magnetic ions with local correlated orbitals as well as itinerant fermions. Especially in an insulator and the fact that the Majoranas are free would appear to make the procedure work as well for the metallic states. But ultimately, here as there, this may be proven satisfactory only if the experiments satisfy the predictions of the resulting theory.

Let us first consider the lattice problem in which the mixed-valence problem has been solved at each site independently. The lattice Hamiltonian is

$$H = H_K + G \sum_i \left( |e,i><o,i| + |o,i><e,i| \right) c_i.$$  \hspace{1cm} (25)

$|e,i>$ and $|o,i>$ are the degenerate ground states for the bosonic and the fermionic local Hamiltonians noted above at sites $i$. The second term comes from Eq. \cite{21} at each site $i$. $H_K$ is the kinetic energy of the fermions in terms of the spin-less operators $c_i$ and $\bar{c}_i$. $c_i$ is the local Majorana at site $i$ which couples to them and $\bar{c}_i$ is the local Majorana which does not. $G$ is the gap calculated at the strong coupling limit to be $\hat{t}/(2 + r^2) \approx \hat{t}/\sqrt{2.43}$ but which will have perturbative numerical renormalizations due to coupling to the excited local states.

The meaning of the operators $c_i, \bar{c}_i$ in terms of the fermions in the starting Hamiltonian represented by the operators $s_{i,\sigma}, s_{i,\sigma}^+; h_{i,\sigma}, h_{i,\sigma}^+$ is different in the two procedures described above. Strictly speaking, $c_i$ is the fermion representation of the density operator in the one-dimensional chain terminating at the site $i$ in the screening and the hybridizing channel in the two procedures respectively. We can think of them in the first procedure $c_i$ as the sum over the two spins of the $s_{i,\sigma}$-operator (so that it is a spin-less operator quantized in the $x$-direction), but the bosonization procedure dresses it with a multi-particle density fluctuations as well as the spin-fluctuations of the $h$-fermions. In the second procedure, as discussed above, $c_i$ is the sum over the two spins of the $h_{i,\sigma}$ operators as dressed by the density fluctuations of the $s$-channel and the spin-fluctuations of the $h$-channel. One
is inclined to suspect that the two procedures describe the same effective multi-particle resonances with fermion rules. In either case, this may be justified only by the fact that the correct symmetries are retained. For some rationalization of the procedure, recall the Toulouse\textsuperscript{43} bosonization and refermionization procedure of the Kondo problem. If the final fermion is regarded as the dressed fermion of the hybridizing channel, the correct answers are obtained for the heavy-Fermion lattice. In any event, any further results are only based on objects with symmetry of fermions coupling to the local resonances as derived to get (25).

1. Lattice Majoranas

It is always possible to represent fermions on a lattice by Majorana fermions. Looking at the form of the Hamiltonian (28) and subsequent developments, it is obvious that the Majoranas must be written so that they are spin-less or equivalently as in (27) point in the x-direction only. So we consider an effective free Hamiltonian of spin-less canonical fermions with kinetic energy

\[ H_K = i\tau \sum_{i,n(i)} (\sigma_i^+ a_{i+n} - a_{i+n}^+ \sigma_i). \]  

(26)

\( n(i) \) are neighbors of \( i \). It is convenient as above to take the kinetic energy parameter to be imaginary. On a bi-partite lattice, this is simply a phase shift of \( \pi/2 \) at alternate lattice points. Consider the Majorana operators

\[ c_i = \frac{1}{\sqrt{2}} (\sigma_i + \sigma_i^+), \]  

(27)

\[ \bar{c}_i = i \frac{1}{\sqrt{2}} (\sigma_i - \sigma_i^+). \]  

(28)

Then

\[ H_K = i\tau \sum_{i,n(i)} (c_i c_{i+n} + \bar{c}_i \bar{c}_{i+n}), \]  

(29)

\( n(i) \) denotes neighbors of a site \( i \). (This is different from the Kitaev odd-parity superconducting model in which biquadratic terms off-diagonal in the conjugate Majoranas appear.)

Note that the pairing operators in terms of the fermions cancel out in \( H_K \) although they are present in the two terms separately. Since the local operators couple only to \( c_i \),
we expect to find different spectra for the two terms. Then the two terms in $H_K$ each do have pairing terms. This effectively breaks $U(1)$ invariance but without any implication of superconductivity.

Let us diagonalize $H_K$ by transforming to momentum space. It is best to go back to the original variables to accomplish this. Let us call the two terms in $H_K$ as $H_{K1}$ and $H_{K2}$.

$$H_{K1} = -2t \sum_{k,n} (\sin(k.R_n) - \mu) a_k^+ a_k + 2t \sum_{k,n} \sin(k.R_n) (a_k^+ a_{-k}^+ - a_k a_{-k})$$  \hspace{1cm} (30)

$$H_{K2} = -2t \sum_{k,n} (\sin(k.R_n) - \mu) a_k^+ a_k - 2t \sum_{kn} \sin(k.R_n) (a_k^+ a_{-k}^+ - a_k a_{-k})$$  \hspace{1cm} (31)

Undoing the phase shift introduced earlier, $-\sin(k.R_n)$ changes to $\cos(k.R_n)$. The sum of $H_{K1}$ and $H_{K2}$ has of-corse no pairing term and gives simply the ordinary kinetic energy.

Since $\tilde{c}_i$ does not couple to the local resonances in the Hamiltonian (25), $H_{K2}$ gives the dispersion of one-particle excitations,

$$E_2(k) - \mu = 2t \sum_n \cos(k.R_n),$$  \hspace{1cm} (32)

just that of free-fermions but the eigenvectors are the Majorana fermions $\tilde{c}(k)$.

Taking into account the coupling of the $c_i$ Majoranas to the local resonances in (25) with the parameters $\hat{t}, J$, the dispersion of the bonding and anti-bonding orbitals is

$$E_{1a}(k), E_{1b}(k) = \pm \sqrt{G^2 + (E_1(k) - \mu)^2}$$  \hspace{1cm} (33)

with $E_1(k) = E_2(k)$.

$E_2(k)$ is continuous across the chemical potential while $E_{1a}(k), E_{1b}(k)$ shows a maximum gap of $2G$. Since a dissolution of the Majorana to canonical fermion can occur only if both $c$ and $\tilde{c}$ are found at the same point with the same energy, the Majoranas $\tilde{c}(k)$ are protected. On the other hand, one expects for energies larger than the gap $|G|$ that the eigenvectors are of ordinary fermions. $E_{1a,k}, E_{1b,k}$ is the generic nature of spectrum usually attributed to Kondo insulators. We might however expect that the eigenvectors revert to that of canonical fermions at energies of order $G$ above the gaps (due to the "coherence factors").

The compounds $SmB_6$ and $YbB_{12}$ are topological insulators due to their "inverted" band-structure [33]. This does not invalidate anything in relation to the exceptional bulk excitations derived here. It would of-curse be worthwhile to do the above calculations for the real band-structure and also to see how the bulk Majoranas affect the surface states.
A. Pinning of chemical potential at Mixed-valence

Although achieving a mixed-valence impurity and associated criticality requires fine tuning of parameters, there is a pinning of the chemical potential at mixed-valence for a finite range of parameters. The argument has already been given \cite{15}, taking the lattice problem as a periodic array of non-interacting impurities, and is merely repeated here for completeness. Let the fraction of the ion with valence 1 be \( \langle Q_1 \rangle \). Similarly, let \( \langle Q_0 \rangle \) be the fraction of the ions in valence 0. Both \( \langle Q_0 \rangle \) and \( \langle Q_1 \rangle \) are functions of \( (\epsilon_f - \mu) \) and their sum must satisfy the condition for fixed charge \( \bar{Q} \) for the lattice.

\[
\langle Q_0 \rangle + \langle Q_1 \rangle = \bar{Q} \tag{34}
\]

Near the mixed-valence condition on the chemical potential, the free-energy has a singularity so that

\[
\langle Q_1 \rangle \propto (\epsilon_f - \mu)^{1/\delta} \tag{35}
\]

\( \delta \approx 2.7 \) has been calculated by Wilson RG \cite{15}. Then due to the singularity a self-consistent solution exists for a range of \( \bar{Q} \) at the critical value. This procedure is similar to finding the Pressure-Volume relation in a gas near its critical point. At finite temperature, there will be a cross-over to Fermi-liquid behavior, which has also been discussed \cite{15}.

V. MAGNETO-OSCILLATIONS DUE TO MAJORANAS

The interesting idea that bulk Majorana fermions would produce magneto-oscillations was suggested by Baskaran \cite{21} who used one of the two superfluous free Majoranas in a representation of spin-ful conduction electrons in terms of four Majoranas in a theory for pairing in time-reversal odd singlet superconductors in heavy fermion metals by Coleman et al. \cite{20}. Quite evidently, SmB\textsubscript{6} which is a topological insulator due to its band-structure \cite{33}, with evidence for surface states in agreement with such a band-structure \cite{34}, does not have a pairing gap of any variety. However, the idea that Majoranas do have de Haas van-Alphen oscillations appears to be sound. To seek bulk Majoranas, one must study the nature of mixed-valence which is the common feature in all the insulators which have shown the oscillations. This is what has been done above.
A well defined theory for oscillations in small gap insulators [44] with an inverted band-structure at magnetic fields such that the Zeeman energy is comparable to the gap is not applicable to SmB\textsubscript{6} where oscillations exist for magnetic field substantially smaller. There are also other more speculative ideas [45] also without cognizance of the mixed-valence nature of compounds showing oscillations in the insulating state.

It is essential in the experiments in SmB\textsubscript{6} to have magneto-oscillations without a linear response to an electric field that the system break gauge invariance. Given this, it is worth recapitulating why Majoranas produce de Haas - van Alphen oscillations; this has been explained by Erten et al. [22] particularly clearly. As shown above the Majoranas $\bar{c}(k)$ crossing the chemical potential are a linear equal combination of a canonical particle and anti-particle operators. The linear coupling to a vector potential $A$ changes their energy to

$$\frac{1}{2} \left( E_2(k - \frac{e}{c}A) + E_2(k + \frac{e}{c}A) \right).$$

(36)

The linear response to $A$ (for example electrical conductivity) is then zero but effects quadratic in $A$ are present. The magneto-oscillations are effects due to change in free-energy which are functions of even powers of the magnetic field $B = \nabla \times A$. So, (36) gives the same oscillations as the customary theory. The observed magneto-oscillations in SmB\textsubscript{6} match the fermi-surface of LaB\textsubscript{6} [11], i.e a band-structure similar to that in SmB\textsubscript{6} without the hybridization with local 4f-resonances. This is the result derived above. The specific heat from Majorana excitations is also similar to that of fermions of similar density and mass.

Finite Temperature:

The results for for the mixed-valent impurity used here give the fixed point at $T \to 0$ and prove its validity by calculating the leading correction terms. It is not designed to give the quantitative values of the parameters and especially not the crossovers at higher temperatures. This is important to know because experiments, especially in SmB\textsubscript{6} show such cross-overs. More detailed calculations with study of spectra at various temperatures of the Wilson RG kind [15] may give such information. Application of the methods devised by Affleck and Ludwig [24, 41] might also be attempted. In Ref. [16] such cross-overs are given as well as a dependence of the chemical potential with temperature. The high temperature crossover occurs at the Kondo temperature of the mixed-valence problem which is of $O(J^2 \rho)$ where $\rho$ is the conduction electron density of states as calculated in theories.
without considering screening. This is the temperature below which one would begin to see Majoranas. The crossover to low temperatures is a more delicate matter; it might be related to an exponentially lower scale related to \( \hat{t} \). This and extension of such calculations to the lattice is left for future work. In the experiments there appear to be cross-overs near about 5 K marked by an increase in \( C/T \) and muon relaxation rate and another cross-over below about 1 K where the amplitude of the oscillations and of \( C/T \) increase very rapidly. The detailed temperature dependence of the latter needs to be studied in further experiments.

VI. PREDICTIONS AND FURTHER WORK INDICATED

The most interesting prediction of the theory, following from the approximation that many body effects due to scattering of resonances at different sites are not important, concerns the entropy. As mentioned, half of the degrees of freedom of a mixed-valence impurity does not couple to the fermions if the effective spin is 1/2. In the present theory, this persists for each ion in the lattice. So a ground state entropy of \( O(1/2 \ R \ ln2) \)/mole is to be expected. A confusing situation prevails in the available experimental results. There are samples in which the measured magnetic entropy \([38]\) integrated to 300 K is what is normally expected, and there is no room for ground state entropy. However, in samples which have shown the magneto-oscillations, the entropy at 10 K obtained by integrating \( C/T \) up to that temperature is \([11]\) is about a factor of 5 smaller than in \([38]\), and has not been measured at higher temperatures. The integrated difference of magnetic entropy at 10 K for the two measurements is not inconsiderable, about 0.3 Joules/mole/degree, but about 10 times less than \( 1/2 \ R \ ln \ 2 \)/mole. If the difference in \( C/T \) persists in further measurements to room temperature, there is a case for ground state entropy of the magnitude suggested in the samples showing magneto-oscillations. (This also raises the question of the reason for such remarkable difference and the reason for the large \( C/T \) of about 30 mJ/mole/\( K^2 \) at low temperatures, well below its gap, \([38]\) in an insulator.)

The approximation of non-interacting ions in the theory presented here is bound to break down at low enough temperatures. Mixed valence \( Sm^{2+}/Sm^{3+} \) ions have neither RKKY interactions nor double exchange interactions and neither do \( Yb^{2+}/Yb^{3+} \) ions \([46]\). But small higher order interactions are bound to be present. From the present experiments one can put an upper limit of about 1 K for their effects. Measurements of specific heat at lower
temperatures are suggested.

The magneto-oscillation in SmB$_6$ are also accompanied by low energy magnetic fluctuations in evidence in $\mu$SR measurements [37]. The $\mu$SR relaxation rate becomes constant below about 2 K down to the lowest measured temperature of 19 mK. Magnetic fluctuations which would give a temperature independent relaxation rate are derived for the single mixed valent impurity due to the $1/\tau$ magnetic correlations in imaginary time, (or equivalently $\omega/T$ scaling), derived in in Ref. [16] for the mixed-valence problem. These fluctuations need further investigation and direct measurements by neutron scattering.

A test of the theory is also that the Zeeman splitting of the magneto-oscillations due to a magnetic field should be absent as the Majoranas derived here are spin-less. This is also true of the gapped excitations - so their magnetic character close to the gap should show absence of linear effects in a field.

An obvious prediction is that the magneto-oscillations must be present both in the specific heat and thermal conductivity.

The pair-bilinears in the fermions representation of the diagonal representation in terms of Majorana bands may be detectable in tunneling experiments.

Another result that follows from the present work concerns other materials in which Majoranas may be the proper description of low energy physics. These may be varieties of spin-liquids and the so-called Kitaev compounds or those resembling them. Magneto-oscillations in them should be looked for.

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**VII. APPENDIX**

*Solution of the local Hamiltonian for the single Mixed-valence impurity*
The Hamiltonian $H_{\text{loc}}$ of (19) in the even particle basis

\[ |0, 0, 0 >, |0, 1, 1 >, |1, 1, 0 >, |1, 0, 1 > \] is

\[
H_{\text{even}} = \begin{pmatrix}
0 & 0 & -\hat{t}/2 & 0 \\
0 & 0 & -i\hat{t}/2 & 0 \\
-\hat{t}/2 & i\hat{t}/2 & 0 & J/2 \\
0 & 0 & J/2 & 0 \\
\end{pmatrix}
\] \hfill (37)

The ground has energy $E_0$ and eigenvector

\[ E_0 = -\hat{t}/2\sqrt{2 + r^2}; \quad r = J/i \] \hfill (38)

\[ |0e > = u(|0, 0, 0 > -i|0, 1, 1 >) - v|1, 1, 0 > + w|1, 0, 1 > . \] \hfill (39)

\[ u = \frac{1}{\sqrt{2(2 + r^2)}}, \quad v = \frac{r}{\sqrt{2(2 + r^2)}}, \quad w = \frac{1}{\sqrt{2}}. \]

The next two states are degenerate with zero energy. Their eigenvectors after mutual orthogonalization are

\[ E_{1e} = E_{2e} = 0; \] \hfill (40)

\[ |1e > = \frac{1}{\sqrt{2}}(-i|0, 0, 0 > + |0, 1, 1 >); \] \hfill (41)

\[ |2e > = \left( -\frac{r}{\sqrt{(1 + r^2)}} - i\frac{1}{2}\lambda|0, 0, 0 > + \lambda\frac{1}{\sqrt{2}}|0, 1, 1 > + \frac{1}{\sqrt{1 + r^2}}|101 > \right). \] \hfill (42)

\[ \lambda = -i\frac{r}{\sqrt{1 + r^2}}. \]

The highest state has energy and eigenvectors

\[ E_{3e} = (J/2)\sqrt{2 + r^2}; \] \hfill (44)

\[ |3e > = u(|0, 0, 0 > -i|0, 1, 1 >) + v|1, 1, 0 > + w|1, 0, 1 > . \] \hfill (45)

**Odd charge sector**

The Hamiltonian $H_{\text{loc}}$ of (19) in the odd number particle sector, i.e. in the basis

\[ |1, 0, 0 >, |1, 1, 1 >, |0, 0, 1 >, |0, 1, 0 > \] (46)
The energy levels are identical to the even sector. The even sector is bosonic, the odd is fermionic. So there is supersymmetry.

The ground has energy $E_0$ and eigenvector

$$E_{0o} = -(\hat{t}/2)\sqrt{2 + r^2}; \ |0o> = -u(|1, 0, 0 > - i|1, 1, 1 >) - v|0, 0, 1 > + w|0, 1, 0 > . (48)$$

The next two are degenerate with zero energy. Their eigenvectors after mutual orthogonalization are

$$E_{1o} = E_{2o} = 0; \ |1o> = \frac{r}{\sqrt{1 + r^2}}|1, 0, 0 > + 1/\sqrt{1 + r^2}|0, 0, 1 >$$

$$|2o> = (-\lambda \frac{r}{\sqrt{1 + r^2}} - i/\sqrt{2})|1, 0, 0 > + 1/\sqrt{2}|1, 1, 1 > + \lambda \frac{1}{\sqrt{1 + r^2}}|0, 0, 1 > . (50)$$

$\lambda$ is determined from the orthogonalization of the two degenerate states to be the same as earlier,

$$\lambda = -i \frac{r}{\sqrt{(1 + r^2)}}.$$  

The highest energy state is

$$E_{3o} = (\hat{t}/2)\sqrt{2 + r^2}; \ |3o> = u(|0, 0, 0 > - i|0, 1, 1 >) + v|1, 1, 0 > + w|1, 0, 1 > . (51)$$

The important result is that (just as in the two impurity problem) if

$$u^2 = 2vw,$$

i.e.

$$J \approx 0.634\hat{t}$$

$$< 0e|c_0|0o> = < 0o|c_0|0e > . (52)$$

As discussed in the main text, this means that the fermion operator $c_0$ is purely real and therefore a Majorana.
The matrix element between the ground state and the excited state have exactly the same property, i.e

\[ < 0 | c_{0 \mu} | \alpha, o > = < \alpha, o | c_{0 \mu} | 0 >, \text{ for all } \alpha = 1, 2, 3. \]  
\[ (53) \]

\[ < 0 | c_{0 \mu} | \alpha, e > = < \alpha, e | c_{0 \mu} | 0 >, \text{ for all } \alpha = 1, 2, 3 \text{ also.} \]  
\[ (54) \]

and that \( c_{\alpha\delta} \) has zero matrix elements.

In the above, the diagonal terms which produce difference in the energy of the states were put to zero. The same results are obtained when they are included but with a more complicated condition and coefficients. The mixed-valence condition

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