

Superconducting T_c enhancement due to negative- U impurities: Monte Carlo study of a local exciton model

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The enhancement of superconductivity by a small concentration of excitonic negative- U centers is studied by a new method which combines diagrammatic perturbation theory and Monte Carlo simulation. Results are given which show how the impurity parameters should be selected in order to obtain the maximum increase in the superconducting transition temperature T_c . We also discuss the underlying physics of these results.

I. INTRODUCTION

It has been suggested some time ago^{1,2} that superconducting transition temperatures of metallic films or alloys can be enhanced by the presence of negative- U centers.³ Such a center consists of a localized electronic orbital which exhibits an attractive on-site interaction, mediated by a coupling to a phonon or excitonic degree of freedom. Due to hybridization with the conduction band of the metallic host material, conduction-electron pairs can tunnel into these centers and participate in the on-site attraction, which, under favorable conditions, may increase the superconducting T_c of the host. It has been suggested that superconductivity in TI-doped PbTe may be due to an impurity-induced pairing mechanism.⁴ More recently,⁵⁻⁷ it has been proposed that negative- U impurities could even be responsible for the high- T_c values found in the perovskite superconductors.⁸

Previous theoretical studies^{1,2} of this effect have employed various perturbative weak-coupling methods to treat the internal dynamics of the negative- U impurity. However, there is by now considerable evidence⁹⁻¹¹ that these systems are quite strongly correlated and exhibit properties very much akin to a Kondo impurity (in parameter regimes of physical interest).

Therefore, nonperturbative methods are needed for their theoretical investigation. We have recently proposed a novel approach to this problem which combines Monte Carlo simulation techniques with a more standard diagrammatic analysis.¹²⁻¹⁵ It allows us to treat such dynamical impurity systems, in principle, exactly, and extract experimentally observable quantities from the model Hamiltonian. Here, we present a more detailed account of this method and results that we have obtained with it for a simple model of a double-valence fluctuating impurity¹⁶ with an exciton-mediated on-site interaction. Specifically, we will discuss the following: (i) the possibility of induced superconductivity due to a small but finite concentration of these impurities in an intrinsically non-superconducting host; (ii) the change of the transition temperature $(dT_c/dc)_{c=0}$ of a superconducting host material in the limit of very small impurity concentrations c ;

and (iii) the impurity spin susceptibility.

The plan of the paper is as follows. In Sec. II we introduce the model Hamiltonian and discuss in simple physical terms the basic mechanism of the exciton-mediated on-site attraction. In Sec. III we outline the diagrammatic formalism that is used to compute superconducting transition temperatures from the Monte Carlo data for certain single-impurity electronic Green's functions. In Sec. IV we describe briefly the Monte Carlo algorithm^{17,18} and its adaption to the present problem. In Sec. V we present our results for the induced transition temperature (Sec. V A) the T_c -enhancement coefficient $(dT_c/dc)_{c=0}$ (Sec. V B), and the impurity spin susceptibility χ_s (Sec. V C). We discuss in detail the dependence of these quantities on the various model parameters and the underlying physics of these results. A summary and concluding remarks are given in Sec. VI.

II. THE EXCITONIC NEGATIVE- U CENTER

A. Model Hamiltonian

The negative- U system that we are considering here is a double-valence fluctuating impurity¹⁶ in a metallic host material. Its Hamiltonian is given by

$$H = H_0 + H_i, \quad (2.1)$$

where

$$H_0 = \sum_{p,s} \epsilon_p c_{ps}^\dagger c_{ps} + \sum_{p,s} N^{-1/2} (V_p d_s^\dagger c_{ps} + \text{H.c.}) \quad (2.2)$$

and

$$H_i = \epsilon_d n_d + \lambda \sigma_x (n_d - 1) + \eta \sigma_x + \frac{1}{2} \Omega \sigma_z. \quad (2.3)$$

The first part of H_0 describes the host lattice conduction band, consisting of Bloch states with momentum p , spin $s = \uparrow, \downarrow$, and energy ϵ_p , measured relative to the Fermi energy μ . The Bloch states are hybridized with a localized impurity orbital, denoted by d in the following. The hybridization matrix elements are given by V_p and N is the number of host lattice sites. The Fermion operators

c_{ps}^\dagger and d_s^\dagger create electrons in a Bloch state (p,s) and in the impurity orbital (d,s) , respectively. In the following, these will be referred to as “ c electrons” and “ d electrons.” The internal structure of the impurity is described by H_i . ϵ_d is the on-site energy of the d orbital, again measured from the Fermi level μ , and n_d denotes the on-site occupation number

$$n_d = n_{d\uparrow} + n_{d\downarrow}, \quad n_{ds} = d_s^\dagger d_s. \quad (2.4)$$

The d electrons are coupled with a strength λ to a two-level excitonic degree of freedom which is here described by a set of Pauli operators

$$\sigma = (\sigma_x, \sigma_y, \sigma_z), \quad (2.5)$$

each with eigenvalues $+1$ and -1 and the usual commutation relations

$$[\sigma_x, \sigma_y] = 2i\sigma_z, \quad (2.6)$$

etc. The σ -operators commute with all c and d fermion operators. The two parameters Ω and η in (2.3) determine both the energy splitting and the polarizability of the two-level system. We shall refer to Ω and η as the exciton frequency and the exciton asymmetry energy, respectively.

As discussed in Ref. 16, such a two-level system could be realized, for example, by a set of two localized electronic orbitals, a and b , say, that are located in a polarizable side group surrounding the central d orbital. For simplicity, one restricts the Hilbert space to those states where this two-orbital side group contains exactly one electron (or one hole). Physically, such a constraint could arise, for example, if there are strong on-site and intersite Coulomb correlations on and between the two orbitals a and b . We introduce it here primarily to simplify our model somewhat without changing its essential physics. Under this constraint, the a - b systems is then described by a two-state Hilbert space: The two eigenstates of the σ_x operator in (2.3), $|\sigma_x = +1\rangle$ and $|\sigma_x = -1\rangle$, are identified with $|n_a = 1, n_b = 0\rangle$ and $|n_a = 0, n_b = 1\rangle$, respectively, where n_a and n_b denote the occupation numbers of the corresponding orbitals a and b . The term $\eta\sigma_x$ in (2.3) describes the difference between the a and b on-site energies $\frac{1}{2}(\epsilon_a - \epsilon_b) \equiv \eta$ at $\lambda = 0$. The term $\frac{1}{2}\Omega\sigma_z$ gives rise to a hybridization between the a and b orbital. The coupling term $\lambda\sigma_x(n_d - 1)$ describes the effect of Coulomb repulsions between the d and the a - b electron with $\lambda = U_{da} - U_{db}$. Here, U_{da} is the (interorbital) repulsion between d and a , and U_{db} is the repulsion between d and b . Assume, for example, that the a orbital is in closer proximity to the d site than the b orbital so that $U_{da} > U_{db}$. If we then introduce a single electron into the d site, it will polarize the a - b two-level system by partially displacing charge from the a to the b orbital. This polarization lowers the effective on-site energy that is needed for a second electron with opposite spin to enter the d orbital. In this way, an effective attraction between the two d electrons is mediated.

Another possible realization of the model (2.3) could arise in certain defect structures in strongly disordered

metals. In such systems, it is possible that some atoms or groups of atoms (i.e., a collective lattice coordinate) exhibit two nearly degenerate minima in their potential energy which can lead to a set of two low-lying energy levels. Let us assume further that the same defect structure also gives rise to a localized electronic orbital in its vicinity. The coupling between this localized “ d orbital” and the strongly anharmonic two-level lattice mode could then be appropriately described by the model Hamiltonian (2.3).

B. Attractive on-site interaction and pair tunneling processes

To get a more detailed physical picture of the excitonic mechanism, it is instructive to discuss a particularly simple, exactly solvable case: the isolated, nonhybridized impurity. For $V_p \equiv 0$, H_i is decoupled from the conduction band and can be straightforwardly diagonalized. The occupation numbers $n_{d\uparrow}$ and $n_{d\downarrow}$ are conserved. For each electronic eigenfunction $|n_{d\uparrow}, n_{d\downarrow}\rangle_e$ there are two excitonic (σ) eigenstates $|l, n_d\rangle_\sigma$ labeled by $l = 0, 1$, which depend only on the total d -site occupation $n_d = n_{d\uparrow} + n_{d\downarrow}$. The total eigenfunction or H_i is then given by the product state

$$|n_{d\uparrow}, n_{d\downarrow}, l\rangle = |n_{d\uparrow}, n_{d\downarrow}\rangle_e \otimes |l, n_d\rangle_\sigma. \quad (2.6a)$$

The state of the two-level system $|l, n_d\rangle_\sigma$ can be expanded in terms of the eigenstates of σ_x , say. In the context of the polarizable two-orbital (a - b) interpretation of H_i , the squares of the corresponding two amplitudes represent the relative charge densities at the a and the b sites in the presence of n_d electrons at the d site. They are hence a direct measure of the a - b polarization due to the d electrons. Without giving a detailed derivation, we note that, as expected, in the case $\lambda = U_{da} - U_{db} > 0$, the a site density in the two-orbital ground state ($l = 0$) decreases whereas the b -site density increases with increasing d -site occupation n_d .

To estimate the effective d - d interaction that results from this polarization, let us turn to the eigenenergies $E_l(n_{d\uparrow}, n_{d\downarrow})$ of the states (2.6), which again depend only on the total d -site occupation n_d and are given by

$$\begin{aligned} E_l(n_{d\uparrow}, n_{d\downarrow}) &= E_l(n_d) \\ &= \epsilon_d n_d - (-1)^l \{ [\lambda(n_d - 1) + \eta]^2 \\ &\quad + \Omega^2/4 \}^{1/2}. \end{aligned} \quad (2.7)$$

Since n_d takes on only the values 0, 1, or 2, we can write the ground-state energy ($l = 0$) as a function of n_d in the form

$$E_0(n_d) = E_0(0) + \epsilon_{d,0} n_d + U n_{d\uparrow} n_{d\downarrow}. \quad (2.8)$$

The renormalized on-site energy $\epsilon_{d,0}$ is the energy needed to introduce one electron into the empty d site,

$$\begin{aligned} \epsilon_{d,0} &= E_0(1) - E_0(0) \\ &= \epsilon_d + [(\lambda - \eta)^2 + \Omega^2/4]^{1/2} \\ &\quad - (\eta^2 + \Omega^2/4)^{1/2}. \end{aligned} \quad (2.9)$$

The effective on-site interaction U is the difference of the energy needed to introduce a second electron into an already singly occupied d site minus the energy for introducing the first electron,

$$\begin{aligned} U &= [E_0(2) - E_0(1)] - [E_0(1) - E_0(0)] \\ &= 2(\eta^2 + \Omega^2/4)^{1/2} - [(\lambda + \eta)^2 + \Omega^2/4]^{1/2} \\ &\quad - [(\lambda - \eta)^2 + \Omega^2/4]^{1/2} \\ &\leq 0. \end{aligned} \quad (2.10)$$

As expected, we find that U is always negative, i.e., it costs less energy to introduce the second d electron than to introduce the first. With increasing λ , $|U|$ increases monotonically, like $2\lambda^2/\Omega$ for $|\lambda|, |\eta| \ll |\Omega|$ and like $2|\lambda|$ for $|\lambda| \gg |\Omega|, |\eta|$.

If we now turn on the hybridization term V_p , electrons will tunnel between the conduction band and the d orbital, thereby taking advantage of the attractive on-site correlations. The enhanced superconducting pairing arises then from the following pair-exchange process: Two conduction electrons with antiparallel spin tunnel into the center, interact via the polarization (i.e., virtual excitation and deexcitation) of the two-level system, and finally tunnel back into the conduction band. This tunneling process is favored very strongly, if the model parameters are such that the initial and final states are almost degenerate, i.e., if $E_0(0) \cong E_0(2)$ (assuming conduction-electron states with ε_p near the Fermi level). The intermediate state ($n_d=1$) of this second-order (in V_p) process has a higher energy than $E_0(0)$, namely, $E_0(1) = E_0(0) + \frac{1}{2}|U|$, if $E_0(0) \cong E_0(2)$. We will discuss the significance of the degeneracy condition further in Sec. II C.

It is interesting to note that, formally, according to (2.10), one can still have a finite on-site interaction $U < 0$ even if the exciton frequency Ω vanishes (as long as $|\eta| < |\lambda|$). This is surprising, since, according to (2.3), the total Hamiltonian (2.1) (including hybridization $V_p \neq 0$) reduces essentially to a noninteracting single-particle problem if $\Omega=0$. σ_x is a conserved quantity in this case and after setting either $\sigma_x = -1$ or $\sigma_x = +1$, the λ term in (2.3) reduces simply to a shift of the d electron on-site energy. In the language of our two-orbital model, there is no hybridization between a and b if $\Omega=0$. Hence, the a - b system cannot be polarized since no charge can be displaced from a to b .

To resolve this paradox, let us assume again $V_p = 0$ and consider the eigenstates of H_i , (2.6), (2.7) for $\Omega=0$. Taking $\lambda > \eta \geq 0$, say, we have $U < 0$ in (2.10). The ground state ($l=0$) for $n_d=0$ corresponds to a two-level state $|l=0, n_d=0\rangle_\sigma$ with $\sigma_x = +1$. It has an energy $E'(0) = -(\lambda - \eta) \cong E_0(0)$. If we now insert one or two electrons into the d orbital, keeping $\sigma_x = +1$ fixed, we end up in states with energies $E'(1) = \varepsilon_d + \eta \cong E_1(1)$ and $E'(2) = 2\varepsilon_d + \lambda + \eta \cong E_1(2)$, respectively. Thus, for $n_d \geq 1$ the $\sigma_x = +1$ state is not the ground state anymore (as for $n_d=0$), but rather, according to (2.7), the excited state. From the difference of the respective energies, we find

$$U' \equiv [E'(2) - E'(1)] - [E'(1) - E'(0)] = 0, \quad (2.11)$$

i.e., indeed no attraction is mediated in this process with fixed $\sigma_x = +1$. The attraction (2.10) will manifest itself only, if the transition $n_d=0 \rightarrow n_d=1 \rightarrow n_d=2$ occurs between the ground-state ($l=0$) configurations of the impurity system. In the present case ($\Omega=0$), this would require a transition of the two-level system from a $\sigma_x = +1$ state to a $\sigma_x = -1$ state which cannot happen since these two states are orthogonal.

This example points out an important dynamical aspect of the excitonic mechanism: The actual strength of the pairing correlations mediated by the two-level system depends not only on the strength of the static on-site attraction (2.10), but also on the ability of the two-level system to respond dynamically to the pair fluctuations of the d -site occupancy, once the hybridization V_p is turned on. This response requires transitions between the $n_d=0$ and $n_d=2$ impurity ground states ($l=0$). The matrix elements for such transitions are therefore governed by the products of the overlaps of the corresponding two-level states involved. To second order in V_p , they have the form (assuming ε_p and $\varepsilon_{p'}$ near the Fermi level)

$$M_l(n_d) \sim \frac{V_p V_{p'}}{E_0(n_d) - E_l(1)} f_l, \quad l=0,1, \quad n_d=0,2, \quad (2.12)$$

where, for states $|l, n_d\rangle_\sigma$,

$$\begin{aligned} f_0 &= {}_\sigma \langle 0,0|0,1\rangle_\sigma {}_\sigma \langle 0,1|0,2\rangle_\sigma, \\ f_1 &= {}_\sigma \langle 0,0|1,1\rangle_\sigma {}_\sigma \langle 1,1|0,2\rangle_\sigma. \end{aligned} \quad (2.13)$$

M_0 and M_1 correspond to transitions between $n_d=0$, $l=0$ and $n_d=2$, $l=0$ via the intermediate states $n_d=1$, $l=0$ or $n_d=1$, $l=1$, respectively. In the case $\Omega=0$, the overlap factors f_0 and f_1 (and hence, M_0 and M_1) vanish. In the strong-coupling limit, $\lambda^2 \gg \Omega^2$, f_0 and f_1 become very small, $O(\Omega^2/\lambda^2)$, whereas for $\lambda^2 \ll \Omega^2$ there is almost perfect ground-state overlap with f_0 approaching unity. Thus, the enhancement of the superconducting pairing strength (as quantified in Sec. III) should reflect two competing effects as a function of increasing coupling strength λ : For small λ ($\lambda \ll \Omega$), the T_c enhancement should increase with λ , since there is almost perfect overlap ($f_0 \cong 1$) and U , (2.10), increases with λ . For $\lambda \gg \Omega$, on the other hand, the enhancement should decrease again, because the overlaps disappear as $f_0, f_1 \sim \Omega^2/\lambda^2$ and, in addition, the energy denominators in (2.12) become large [of order U , assuming $E_0(0) \cong E_0(2)$].

The overlap factors f_0, f_1 entering into (2.12) are a very general feature of an attraction that is mediated by a strong coupling λ to a bosonic degree of freedom with a finite response frequency Ω . In the case of a phonon-mediated attraction,^{12,14} these factors are usually referred to as Franck-Condon factors. In that case,¹¹ they become exponentially small, $f_0, f_1 \sim \exp(-\lambda^2/M\Omega^2)$, in the strong-coupling limit $\lambda \gg \Omega$ (where λ is the electron-phonon coupling strength, Ω is the phonon frequency, and M the mass). This is in contrast to the excitonic system,^{15,16} where f_0 and f_1 vanish only algebraically ($\sim \Omega^2/\lambda^2$). These important effects are, of course,

neglected if one replaces the retarded, boson-mediated interaction by an instantaneous negative U , as was done in earlier treatments² of this problem.

C. Particle-hole symmetry and degeneracy

In the following, we will focus primarily on the case of a particle-hole symmetric system for which H is invariant under a transformation of the form

$$c_{ps} \rightarrow c_{p',s}^\dagger, \quad \varepsilon_{p'} = -\varepsilon_p, \quad (2.14)$$

$$d_s \rightarrow -d_s^\dagger, \quad (2.15)$$

$$\sigma_z \rightarrow \sigma_z, \quad (2.16)$$

$$\sigma_x \rightarrow -\sigma_x, \quad (2.17)$$

$$\sigma_y \rightarrow -\sigma_y \quad (2.18)$$

and hence

$$n_d \rightarrow 2 - n_d. \quad (2.19)$$

For H_i this symmetry holds if and only if

$$\eta = 0, \quad (2.20)$$

$$\varepsilon_d = 0. \quad (2.21)$$

The ground-state energies (2.8) of the unoccupied and the doubly occupied impurity are degenerate,

$$E_0(0) = E_0(2) \quad (2.22)$$

if $\varepsilon_d = \eta = 0$.

Actually, (2.22) can be satisfied under conditions that are less restrictive than (2.20) and (2.21). Namely, from (2.7), it follows that (2.22) is valid if and only if the bare on-site energy ε_d satisfies

$$\varepsilon_d = \frac{1}{2}[(\lambda + \eta)^2 + \Omega^2/4]^{1/2} - \frac{1}{2}[(\lambda - \eta)^2 + \Omega^2/4]^{1/2}. \quad (2.23)$$

We shall make use of this relation later on (Sec. V).

III. PAIRING INTERACTIONS AND SUPERCONDUCTIVITY

A. Low-concentration expansion of the conduction-electron interaction and self-energy

Let us now consider a host lattice doped with a small but finite impurity concentration. By tunneling into the negative- U centers, c electrons participate in the attractive on-site interactions. Formally, this leads to a self-energy Σ_c and an (irreducible) retarded interaction insertion U_c in the c electron one- and two-particle Green's functions, respectively. Our basic approach is now to take disorder averages of these c -electron Green's functions and then expand Σ_c and U_c in powers of the impurity concentration

$$c = N_i/N, \quad (3.1)$$

where N_i is the total number of randomly distributed negative- U impurities. The crucial observation here is

that, to lowest order in c , Σ_c and U_c can be simply expressed in terms of the corresponding d -electron Green's functions of a single impurity embedded in a pure host lattice as described by the Hamiltonian (2.1). Namely, as shown in Fig. 1, we have

$$\Sigma_c(p, i\nu) \cong c |V_p|^2 G_d(i\nu) + O(c^2), \quad (3.2)$$

$$\begin{aligned} U_c(p' i\nu' | p i\nu) &\cong -c T |V_{p'}|^2 |V_p|^2 \Gamma_d(i\nu' | i\nu) + O(c^2) \\ &= c |V_{p'}|^2 |V_p|^2 |G_d(i\nu')|^2 |G_d(i\nu)|^2 \\ &\quad \times [U_d(i\nu' | i\nu) - \delta_{\nu\nu'} |G_d(i\nu)|^{-2} / T], \end{aligned} \quad (3.3)$$

where G_d and Γ_d are the single-impurity d -electron Green's functions

$$G_d(i\nu) = - \int_0^\beta d\tau e^{i\nu\tau} \langle T_\tau d_\uparrow(\tau) d_\uparrow(0) \rangle \quad (3.4)$$

and

$$\begin{aligned} \Gamma_d(i\nu' | i\nu) &= \int_0^\beta d\tau_1 \cdots d\tau_4 e^{i\nu'(\tau_1 - \tau_2) - i\nu(\tau_3 - \tau_4)} \\ &\quad \times \langle T_\tau d_\uparrow(\tau_1) d_\downarrow(\tau_2) d_\downarrow^\dagger(\tau_3) d_\uparrow^\dagger(\tau_4) \rangle. \end{aligned} \quad (3.5)$$

Here, ν and ν' denote odd Matsubara frequencies, and $\beta \equiv 1/T$ is the inverse temperature. In the second line of (3.3), we have decomposed Γ_d into a "connected" and a "disconnected" part by introducing the (reducible) d -electron four-vertex function

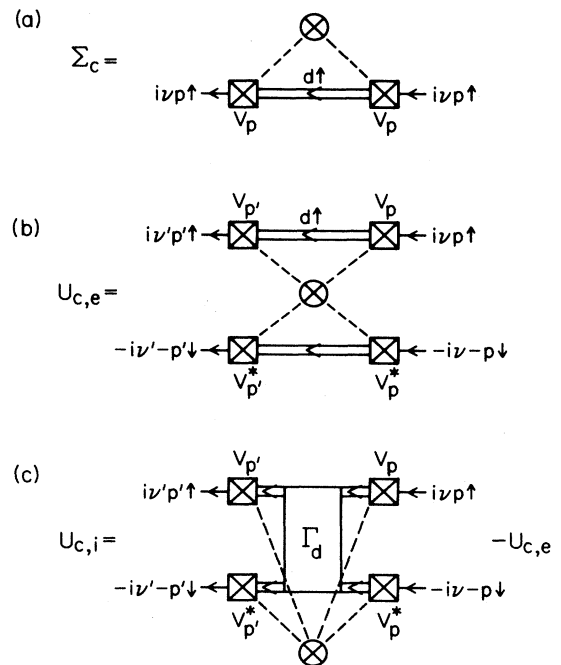


FIG. 1. Conduction electron (a) self-energy (Σ_c), (b) elastic ($U_{c,e}$), and (c) inelastic ($U_{c,i}$) interaction, expanded to first order in c , in terms of the single-impurity Green's functions G_d and λ_d .

$$U_d(i\nu'|i\nu) = -T|G_d(i\nu')|^{-2}|G_d(i\nu)|^{-2} \\ \times [\Gamma_d(i\nu'|i\nu) - \delta_{\nu\nu'}|G_d(i\nu)|^2/T^2]. \quad (3.6)$$

Physically speaking, the $\delta_{\nu\nu'}$ term in (3.3), arising from the disconnected part of Γ_d corresponds to elastic scattering processes from the impurity sit in which no energy is exchanged between the two electrons. The connected part U_d describes truly inelastic processes. Only these inelastic processes enhance T_c , as we will discuss below. Notice that due to Wick's theorem U_d vanishes for the noninteracting ($\lambda=0$) system. For $\lambda \neq 0$, $U_d(i\nu'|i\nu)$ is real, symmetric, and negative (i.e., attractive),

$$U_d(i\nu'|i\nu) = U_d(i\nu|i\nu') < 0, \quad (3.7)$$

as we will show in Sec. IV.

Σ_c and U_c are the basic input for our calculation of superconducting transition temperatures. Notice that, whereas Σ_c and U_c are obtained from fully reducible, single-impurity objects (G_d, U_d), they represent irreducible insertions in the disorder-averaged c -electron Green's functions of the many-impurity system. The single-impurity Green's functions G_d and Γ_d can be obtained in principle with arbitrary accuracy from quantum Monte Carlo simulations. This will be described in Sec. IV.

In the following, we will consider only the simplest case of a momentum-independent hybridization, i.e.,

$$V_p = V = \text{const}. \quad (3.8)$$

Furthermore, we assume that V is small compared to the characteristic energy scales of the conduction band (e.g., the bandwidth D). Then the only detail of the band structure entering into our calculations is the density of states at the Fermi energy $\rho(0)$, where

$$\rho(\epsilon) = N^{-1} \sum_p \delta(\epsilon - \epsilon_p) \quad (3.9)$$

and we assume

$$\rho(0)^{-1} \sim D \gg V. \quad (3.10)$$

Then, G_d becomes

$$\bar{G}_d(i\nu) = 1/[i\nu + i\Delta \text{sgn}(\nu) - \epsilon_d - \Sigma_d(i\nu)] \quad (3.11)$$

with a resonance width

$$\Delta = \pi\rho(0)V^2 \ll D. \quad (3.12)$$

The d -electron self-energy $\Sigma_d(i\nu)$ vanishes in the noninteracting system ($\lambda=0$).

B. Induced superconductivity

To calculate the induced superconducting transition temperature T_c , we carry out a "ladder" simulation with the effective interaction U_c to obtain the c -electron, two-particle t matrix, as shown in Fig. 2,

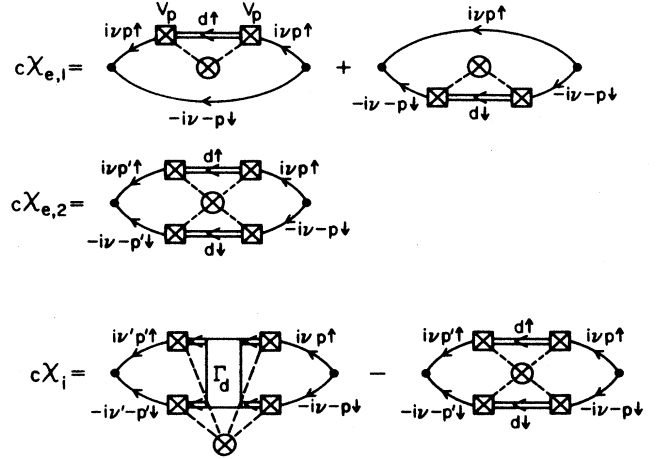


FIG. 2. (a) Elastic and (b) inelastic contributions to the superconducting susceptibilities, Eqs. (3.39)–(3.44), expanded to first order in c .

$$t_c(p', i\nu'|p, i\nu) = U_c(p', i\nu'|p, i\nu) \\ - T \sum_{p'', i\nu''} N^{-1} U_c(p', i\nu'|p'', i\nu'') \\ \times |G_c(p'', i\nu'')|^2 \\ \times t_c(p'', i\nu''|p, i\nu), \quad (3.13)$$

where

$$G_c(p, i\nu) = [i\nu - \epsilon_p - \Sigma_c(p, i\nu)]^{-1} \quad (3.14)$$

is the dressed c -electron Green's function. The superconducting instability occurs at that temperature where t_c diverges, i.e., where the homogeneous equation corresponding to (3.13) has a nonzero solution $\phi(p, i\nu)$:

$$\phi(p', i\nu') = -T \sum_{p'', i\nu''} N^{-1} U_c(p', i\nu'|p, i\nu) \\ \times |G_c(p, i\nu)|^2 \phi(p, i\nu). \quad (3.15)$$

With (3.8), U_c , Σ_c and ϕ become p -independent and, upon carrying out the p summation, Eq. (3.15) attains the form

$$\phi(i\nu') = -T \sum_{i\nu} U_c(i\nu'|i\nu) F(i\nu) \phi(i\nu), \quad (3.16)$$

where, using (3.8)–(3.12),

$$F(i\nu) = N^{-1} \sum_p |G_c(p, i\nu)|^2 \\ \cong \pi\rho(0)/[|\nu| + |\text{Im}\Sigma_c(i\nu)|] \\ = \pi\rho(0)/\left[|\nu| + \frac{c}{\pi\rho(0)}\Delta|\text{Im}G_d(i\nu)|\right]. \quad (3.17)$$

Equation (3.16) is superficially similar to the linearized Eliashberg equation that arises in conventional electron-phonon models of superconductivity where the c electrons are *directly* coupled to host-lattice phonon modes (in the simplest case, with a dispersionless $\omega_q = \omega_0$, constant frequency spectrum, say).¹⁹ In that case, one ap-

proximates the self-energy $\Sigma_{c,ph}$ at low frequencies ($|\nu| \sim T_c \ll \omega_0$) by^{19,20}

$$\text{Im}\Sigma_{c,ph}(i\nu) \cong -\tau_{c,ph}^{-1} \text{sgn}\nu + (1 - Z_{c,ph})\nu + O(\nu^2), \quad (3.18)$$

where the damping term $1/\tau_{c,ph}$ is typically small,

$$\tau_{c,ph}^{-1} \ll T \sim T_c. \quad (3.19)$$

It vanishes, roughly, like $\tau_{c,ph}^{-1} \propto T^2$ for $T \ll \omega_0$ and is therefore neglected. As a consequence, $F(i\nu)$ diverges like $1/|\nu|$ for $T \lesssim |\nu| \rightarrow 0$ and, upon replacing $\phi(i\nu)$ at low frequencies by a constant,²¹ the right-hand side of (3.16) attains its well-known $\ln T$ divergence for arbitrarily small coupling strengths in the limit $T \rightarrow 0$. In the present problem, however, we find

$$\begin{aligned} \tau_{c,i}^{-1} &\equiv |\text{Im}\Sigma_c(i^+)| \\ &= \frac{c\Delta}{\pi\rho(0)} |G_d(i0^+)|^2 [\Delta + |\text{Im}\Sigma_d(i0^+)|] \end{aligned} \quad (3.20)$$

and hence, for example, in a weak-coupling system with particle-hole symmetry

$$\tau_{c,i}^{-1} \sim c/\pi\rho(0) \sim cD. \quad (3.21)$$

This is T independent and typically larger than the induced transition temperature T_c discussed below. It would strongly suppress any low-temperature divergence of (3.16) and superconductivity if $U_c(i\nu|i\nu)$ were a smooth function of its arguments for $T \rightarrow 0$, as in the case of an ordinary electron-phonon system where U_c is given, roughly, by the phonon propagator

$$D(i\nu' - i\nu) \sim -[(\nu - \nu')^2 + \omega_0^2]^{-1}.$$

For our impurity model, however, $U_c(i\nu'|i\nu)$, Eq. (3.3), contains the highly singular elastic term

$$U_{c,e}(i\nu'|i\nu) = -c|V|^4 |G_d(i\nu)|^2 \delta_{\nu\nu'} / T. \quad (3.22)$$

Notice that $U_{c,e}$ is negative (i.e., formally attractive). Hence, it tends to work in favor of the superconducting instability. As it turns out, it cancels the detrimental effect of the large $1/\tau_{c,i}$ term in $\Sigma_c(i\nu)$.

To understand this cancellation in simple physical terms, let us note that, in the electron-phonon system, $1/\tau_{c,ph}$ has a quite different physical origin than $1/\tau_{c,i}$, Eq. (3.20), in our model. $1/\tau_{c,ph}$ describes the damping of the exact noninteracting (Bloch wave) single-particle states due to phonon- and particle-hole-pair creation. In the present model, however, we have formulated our theory in terms of single-particle states (c and d states) which (in the presence of hybridization) are *not* exact eigenstates of the noninteracting Hamiltonian, but rather a superposition of such eigenstates with different energies. This “smearing out” of the single-particle states leads formally to a contribution in $1/\tau_{c,i}$ which is given by the first (Δ) term on the rhs of (3.20). This term is nonzero for $T \rightarrow 0$ and does not vanish as $\lambda \rightarrow 0$. Only the second term in (3.20), involving $|\text{Im}\Sigma_d(i\nu)|$, describes true single-particle damping processes (such as particle-hole pair creation) and can be expected to vanish as $i\nu$ and $T \rightarrow 0$ or $\lambda \rightarrow 0$. Similarly, the effective interaction

U_c exhibits a “hybridization” contribution given by the elastic ($\delta_{\nu\nu'}$) term in the second line of (3.3) which, again arises from our choice of nondiagonal single-particle states. It does not vanish as $\lambda \rightarrow 0$. The true interaction (i.e., two-particle energy transfer) processes are contained in the U_d term in (3.3). Formally, the cancellation of these two terms becomes apparent, if we subtract the elastic term on both sides of (3.16) and carry out the $i\nu$ summation for this term so that

$$\begin{aligned} [1 - c|V|^4 |G_d(i\nu')|^2 F(i\nu')] \phi(i\nu') \\ = -T \sum_{i\nu} U_d(i\nu'|i\nu) \phi(i\nu). \end{aligned} \quad (3.23)$$

We now define

$$\bar{\phi}(i\nu) \equiv \phi(i\nu) [1 - c|V|^4 |G_d(i\nu)|^2 F(i\nu)], \quad (3.24)$$

$$\bar{F}(i\nu) \equiv [\pi\rho(0)]^2 c F(i\nu) / [1 - cV^4 |G_d(i\nu)|^2 F(i\nu)]$$

$$= \frac{c}{\pi\rho(0)} \left/ \left[|\nu| + \frac{c}{\pi\rho(0)} [\Delta |\text{Im}G_d(i\nu)| - \Delta^2 |G_d(i\nu)|^2] \right] \right. \quad (3.25)$$

Then (3.16) becomes

$$\begin{aligned} \bar{\phi}(i\nu') = (-T) \sum_{i\nu} \Delta^2 |G_d(i\nu')|^2 |G_d(i\nu)|^2 \\ \times U_d(i\nu'|i\nu) \bar{F}(i\nu) \bar{\phi}(i\nu). \end{aligned} \quad (3.26)$$

Here, only the inelastic interaction term $U_d(i\nu'|i\nu)$ appears on the rhs. The elastic contribution has been absorbed in $\bar{F}(i\nu)$ which differs from $F(i\nu)$ by the extra term

$$-[c/\pi\rho(0)] \Delta^2 |G_d(i\nu)|^2$$

in the denominator (aside from constant prefactors). Notice that for $i\nu \rightarrow 0$ this term is equal but opposite in sign to the hybridization part of $\tau_{c,i}^{-1}$ [the first term in (3.20)]. Thus, using (3.11), \bar{F} can be written as

$$\begin{aligned} \bar{F}(i\nu) = \frac{c}{\pi\rho(0)} \left/ \left[\left(1 + \frac{c\Delta}{\pi\rho(0)} |G_d(i\nu)|^2 \right) |\nu| \right. \right. \\ \left. \left. + \frac{c\Delta}{\pi\rho(0)} |G_d(i\nu)|^2 |\text{Im}\Sigma_d(i\nu)| \right] \right. \end{aligned} \quad (3.27)$$

If we expand Σ_d at low frequencies as

$$\text{Im}\Sigma_d(i\nu) \cong -\tau_d^{-1} + (1 - Z_d)|\nu| + O(\nu^2) \quad (3.28)$$

and assume that the true d -electron damping is small,

$$\tau_d^{-1} \ll T, \quad |\nu|, T \rightarrow 0, \quad (3.29)$$

then, \bar{F} (3.25) diverges as $1/|\nu|$ for $|\nu|, T \rightarrow 0$ and the lhs of (3.24) diverges as $\ln T$, provided that $U_d(i\nu'|i\nu)$ and $G_d(i\nu)$ approach finite, nonzero values as $T \rightarrow 0$.

For a given value of Δ , c and $\rho(0)$ enter into (3.24) only in the combination $c/\pi\rho(0)$. In the following, we choose the exciton frequency Ω as our unit of energy. We will

therefore express our results in terms of the dimensionless quantity

$$\bar{c} \equiv [\pi\rho(0)\Omega]^{-1}c \quad (3.30)$$

rather than c . Together with the dimensionless parameters T/Ω , Δ/Ω , ε_d/Ω , η/Ω , and λ/Ω , this determines our model completely.

For our numerical treatment, it is convenient to rewrite (3.24) in a symmetrical form

$$\bar{\phi}(i\nu') = \sum_{i\nu} R(i\nu'|i\nu)\bar{\phi}(i\nu) \quad (3.31)$$

by defining

$$R(i\nu'|i\nu) = (-T)\Delta^2 |G_d(i\nu')|^2 |G_d(i\nu)|^2 \times [\bar{F}(i\nu)]^{1/2} U_d(i\nu'|i\nu) \quad (3.32)$$

as a real symmetric matrix of the indices (ν', ν) and

$$\bar{\phi}(i\nu) = [\bar{F}(i\nu)]^{1/2} \phi(i\nu). \quad (3.33)$$

As we lower the temperature or increase the coupling strength, Eq. (3.31) acquires its first nonzero solution when the largest eigenvalue of the matrix R becomes unity. Thus, for fixed impurity parameters $(\Delta, \varepsilon_d, \eta, \Omega, \lambda)$, the induced superconducting transition temperature T_c is determined as a function of the impurity concentration by solving

$$r(\bar{c}, T_c) = 1, \quad (3.34)$$

where r denotes the largest eigenvalue of $R(i\nu'|i\nu)$. Since our single-impurity Monte Carlo algorithm requires the temperature T , but not the impurity concentration \bar{c} , as one of the basic input parameters, we simulate G_d and Γ_d at a specified $T = T_c$, compute $r(\bar{c}, T_c)$ and a function of \bar{c} , and solve for the critical value of \bar{c} at which $r(\bar{c}, T_c) = 1$. This procedure is mathematically equivalent to but less time consuming than specifying \bar{c} and varying T until $T = T_c$. In all cases studied, we have found that $r(\bar{c}, T)$ increases monotonically with \bar{c} and saturates at a finite value

$$\chi_0(T) = TN^{-1} \sum_{i\nu} \sum_p |G_c^{(0)}(p, i\nu)|^2, \quad (3.40)$$

$$\chi_e(T) = \chi_{e,1}(T) + \chi_{e,2}(T), \quad (3.41)$$

$$\chi_{e,1}(T) = TN^{-1} \sum_{i\nu} \sum_p 2|V_p|^2 \text{Re}[G_c^{(0)}(p, i\nu)G_d(i\nu)] |G_c^{(0)}(p, i\nu)|^2, \quad (3.42)$$

$$\chi_{e,2}(T) = TN^{-2} \sum_{i\nu} \sum_{p'} |V_p|^4 |G_c^{(0)}(p', i\nu)|^2, \quad (3.43)$$

$$\chi_i(T) = T^2 N^{-2} \sum_{i\nu, i\nu'} \sum_{pp'} |V_p|^4 |G_c^{(0)}(p', \nu')|^2 |G_d(i\nu')|^2 U_d(i\nu'|i\nu) |G_d(i\nu)|^2 |G_c^{(0)}(p, i\nu)|^2, \quad (3.44)$$

and $G_c^{(0)}(p, i\nu) \equiv (i\nu - \varepsilon_p)^{-1}$ is the bare c -electron Green's function. Here, we have cut off all summations (\sum') over the frequencies $i\nu, i\nu'$ (not the summation over the momenta p, p')²⁵ by the prescription

$$\pi T_{c,0} \sum_{i\nu} |V|^{-1} = \ln(2\gamma\omega_D/\pi T_{c,0}) \quad (3.45)$$

$$r_\infty = r(\bar{c} \rightarrow \infty, T) \quad (3.35)$$

at large \bar{c} . Thus, the solution of (3.34) is unique and exists if and only if $r_\infty > 1$. In the following, the quantity $1/\bar{c}$, determined in this way serves as a convenient measure of the strength of the induced superconductivity and will be discussed as a function of the various model parameters and T_c .

C. T_c enhancement

To calculate the effect of a small concentration of negative- U impurities on the transition temperature of an intrinsically superconducting host lattice, we follow the basic approach of Abrikosov and Gor'kov²² (cf. also Refs. 23 and 24). The Hamiltonian is augmented by a BCS-type interaction

$$H_{\text{BCS}} = N^{-1} \sum_{pkk'} U_0 c_{p+k'}^\dagger c_{p-k}^\dagger c_{p-k} c_{p+k}, \quad U_0 < 0 \quad (3.36)$$

which models in a simple way the intrinsic electron-phonon-mediated c -electron attraction. In the usual mean-field treatment, it leads to a transition temperature of the pure host lattice given by the BCS formula

$$T_{c,0} = \frac{2\gamma}{\pi} \omega_D e^{-1/U_0|\rho(0)}, \quad (3.37)$$

where ω_D denotes the intrinsic (Debye) cutoff of the effective interaction (3.35), and γ is Euler's constant. By extending this mean-field theory in U_0 to include a small concentration of impurities, one obtains the condition²²⁻²⁴

$$1 = U_0 \chi_{\text{sc}}(T = T_c, c). \quad (3.38)$$

To first order in the concentration c , the superconducting susceptibility χ_{sc} is given by the diagrams shown in Fig. 2

$$\chi_{\text{sc}}(T) = \chi_0(T) + c[\chi_e(T) + \chi_i(T)] + O(c^2), \quad (3.39)$$

where

so that (3.38) reproduces the BCS result (3.37) in the limit of the pure host metal ($c \rightarrow 0$). This cutoff in frequency (rather than in momentum p) arises physically from the retarded nature of the phonon-mediated c -electron interaction. It can be justified rigorously by treating the host lattice within the framework of an electron-phonon

model rather than using the BCS Hamiltonian (3.36). Such a treatment will be presented in a forthcoming paper.¹⁵ It gives results that are very similar to those obtained here with the BCS model, and we shall therefore not pursue it any further in the present paper.

From (3.37)–(3.39), we get the T_c -enhancement coefficient in the limit of vanishing impurity concentration as

$$\left[\frac{dT_c}{dc} \right]_{c=0} = \frac{T_{c,0}}{\rho(0)} [\chi_e(T_{c,0}) + \chi_i(T_{c,0})]. \quad (3.46)$$

Upon carrying out the momentum summation, one obtains, using (3.8)–(3.12),

$$\chi_0(T) = \phi \rho(0) T \sum_{iv} '|\nu|^{-1}, \quad (3.47)$$

$$\chi_{e1}(T) = -T \sum_{iv} ' \nu^{-2} \Delta |\text{Im} G_d(i\nu)|, \quad (3.48)$$

$$\chi_{e2}(T) = T \sum_{iv} ' \nu^{-2} \Delta^2 |G_d(i\nu)|^2, \quad (3.49)$$

$$\chi_i(T) = -T^2 \sum_{iv} ' |\nu\nu'|^{-1} \Delta^2 |G_d(i\nu')|^2 U_d(i\nu'|i\nu) \times |G_d(i\nu)|^2. \quad (3.50)$$

Notice that for $T \rightarrow 0$, both $\chi_{e1}(T)$ and $\chi_{e2}(T)$ diverge as $1/T$ but have opposite signs [assuming, as before, that $G_d(i\nu)$ approaches a finite nonzero limit]. Using (3.11), $\chi_e(T)$ becomes

$$\chi_e(T) = (-T) \sum_{iv} \nu^{-2} \Delta [|\nu| + |\text{Im} \Sigma_d(i\nu)|] \times |G_d(i\nu)|^2. \quad (3.51)$$

Thus, the same cancellation as in (3.26) and (3.27) also occurs here, leading to a logarithmic rather than a $1/T$ divergence in $\chi_e(T)$ if $|\text{Im} \Sigma_d(i0^+)|$ vanishes as $T \rightarrow 0$. Note that χ_e is always negative and nonzero even for $\lambda=0$. χ_i , on the other hand, is positive but vanishes for $\lambda \rightarrow 0$. At low T , χ_i diverges as $\ln^2 T$, again assuming that $U_d(i\nu'|i\nu)$ becomes a continuous function of both its arguments as $T \rightarrow 0$. Thus, for $\lambda=0$, the impurities will actually suppress T_c . Physically, the negative contribution χ_e reflects the fact that c electrons which tunnel into an impurity d orbital leave the attractive electron-phonon pairing interaction of the host whole occupying the impurity orbital. Consequently, the impurity must have a certain minimum pairing attraction $|U|$ just to maintain the $T_{c,0}$ of the host. Only if $|U|$ exceeds this minimal value, will impurities enhance T_c .

IV. MONTE CARLO SIMULATIONS

To simulate the single-impurity d -electron Green's functions $G_d(i\nu)$ and $\Gamma_d(i\nu'|i\nu)$, Eqs. (3.4) and (3.5), we have adapted a version of the determinant algorithm¹⁸ that was recently proposed by Hirsch and Fye.¹⁷ The partition function is approximated as

$$Z \simeq Z_L = \text{Tr}[(e^{-\Delta\tau H_0} e^{-\Delta\tau H_1} e^{-\Delta\tau H_2})^L], \quad (4.1)$$

where

$$\Delta\tau = \beta/L.$$

L is a sufficiently large integer, and the Hamiltonian has been broken up into three diagonalizable parts

$$H = H_0 + H_1 + H_2, \quad (4.2)$$

where H_0 is given by (2.2) and

$$H_1 = \varepsilon_d n_d + \lambda \sigma_x (n_d - 1) + \eta \sigma_x, \quad (4.3)$$

$$H_2 = \frac{1}{2} \Omega \sigma_z. \quad (4.4)$$

Notice that this breakup preserves particle-hole symmetry, i.e., H_1 , H_2 , and H_3 are each invariant under the transformations (2.14)–(2.19) if H is invariant. We now insert complete sets of states in (4.1) which are chosen to be eigenstates of σ_x . Upon tracing out the fermions, one obtains the usual determinant representation^{17,26} of Z_L ,

$$\begin{aligned} Z_L &= \sum_{\{\sigma\}} [\det(M\{\sigma\}) e^{-S\{\sigma\}}] \\ &\equiv \sum_{\{\sigma\}} Z_L\{\sigma\}, \end{aligned} \quad (4.5)$$

where

$$M\{\sigma\} = M_\uparrow\{\sigma\} M_\downarrow\{\sigma\}, \quad (4.6)$$

$$\begin{aligned} M_\downarrow\{\sigma\} &= M_\uparrow\{\sigma\} \\ &= \text{Tr} \prod_{l=1}^L e^{-\Delta\tau H_0} e^{-\Delta\tau n_d (\lambda \sigma_l + \varepsilon_d)}, \quad (4.7) \\ e^{-S_B} &= \prod_{l=1}^L e^{-\Delta\tau \Omega / 2 \sigma_l [|\sigma_l + \sigma_{l+1}| \cosh(\Delta\tau \Omega / 2) \\ &\quad - |\sigma_l - \sigma_{l+1}| \sinh(\Delta\tau \Omega / 2)]} \end{aligned} \quad (4.8)$$

and

$$\{\sigma\} \equiv \{\sigma(\tau_2) \cdots \sigma(\tau_L)\}, \quad \tau_j \equiv j\Delta\tau, \quad j=1 \cdots L \quad (4.9)$$

are the time-dependent pseudospin (σ_{x-}) configurations [with $\sigma(\tau_j) = +1$ or -1] to be summed over. In our Monte Carlo procedure, we generate such configurations randomly¹⁷ with a probability

$$P\{\sigma\} = Z_L\{\sigma\} / Z_L. \quad (4.10)$$

Notice that, since $M_\uparrow\{\sigma\} = M_\downarrow\{\sigma\}$,

$$\det M\{\sigma\} = |\det M_\uparrow\{\sigma\}|^2 \geq 0 \quad (4.11)$$

and hence there are no “minus-sign” problems, i.e., for all $\{\sigma\}$

$$0 \leq P_L\{\sigma\} \leq 1. \quad (4.12)$$

Clearly, $M_\uparrow\{\sigma\} = M_\downarrow\{\sigma\}$ holds because in our model system up-spin and down-spin electrons are coupled to the same time-dependent (σ_{x-}) field with identical coupling strength and sign.

The d -electron Green's functions are then given by the following Monte Carlo averages:

$$\begin{aligned} G_d(i\nu)_{L \rightarrow \infty} &= T \sum_{\{\sigma\}} g_{\{\sigma\}}^{(s)}(i\nu|i\nu) P\{\sigma\} \\ &\equiv T \langle g_{\{\sigma\}}^{(s)}(i\nu|i\nu) \rangle_{\text{MC}}, \quad s = \uparrow \text{ or } \downarrow \end{aligned} \quad (4.13)$$

and

$$\begin{aligned} \Gamma_d(i\nu'|i\nu)_{L \rightarrow \infty} &= \sum_{\{\sigma\}} g_{\{\sigma\}}^{(\uparrow)}(i\nu'|i\nu) g_{\{\sigma\}}^{(\downarrow)}(i\nu'|i\nu) P\{\sigma\} \\ &\equiv \langle g_{\{\sigma\}}^{(\uparrow)}(i\nu'|i\nu) g_{\{\sigma\}}^{(\downarrow)}(i\nu'|i\nu) \rangle_{\text{MC}}, \end{aligned} \quad (4.14)$$

where

$$g_{\{\sigma\}}^{(s)}(i\nu'|i\nu) = (\Delta\tau)^2 \sum_{j,k=1}^L e^{i\nu'\tau_j - i\nu\tau_k} g_{\{\sigma\}}^{(s)}(\tau_j|\tau_k) \quad (4.15)$$

and $g_{\{\sigma\}}^{(s)}(\tau_j|\tau_k)$ is the single-particle Green's function for a d electron moving in the time-dependent field configuration $\{\sigma\}$, as defined in Ref. 25,

$$g_{\{\sigma\}}^{(s)}(\tau_i, \tau_j) = M_{(s)}^{-1}\{\sigma\}(\tau_i, \tau_j). \quad (4.16)$$

Again, because up-spin and down-spin electrons couple to the same time-dependent (σ_x) field with identical coupling strength and sign, we have

$$g_{\{\sigma\}}^{(\uparrow)}(i\nu'|i\nu) = g_{\{\sigma\}}^{(\downarrow)}(i\nu'|i\nu). \quad (4.17)$$

Hence,

$$\Gamma_d(i\nu'|i\nu)_{L \rightarrow \infty} = \langle |g_{\{\sigma\}}^{(s)}(i\nu'|i\nu)|^2 \rangle_{\text{MC}} > 0 \quad (4.18)$$

and thus, using (3.6)

$$\begin{aligned} U_d(i\nu'|i\nu)_{L \rightarrow \infty} &= (-T) |G_d(i\nu)|^{-2} |G_d(i\nu')|^{-2} \\ &\quad \times \langle |\Delta g_{\{\sigma\}}^{(s)}(i\nu'|i\nu)|^2 \rangle_{\text{MC}} \\ &< 0, \end{aligned} \quad (4.19)$$

where

$$\Delta g_{\{\sigma\}}^{(s)} \equiv g_{\{\sigma\}}^{(s)} - \langle g_{\{\sigma\}}^{(s)} \rangle_{\text{MC}} \quad (4.20)$$

Thus, we have shown that $U_d(i\nu'|i\nu)$ is indeed real and negative as stated in Eq. (3.7).

Finally, we have simulated the impurity spin susceptibility which is given by

$$\chi_s = -2 \int_0^\beta d\tau \langle g_\downarrow(0, \tau) g_\uparrow(\tau, 0) \rangle_{\text{MC}}. \quad (4.21)$$

For most of our runs we chose $\Delta\tau = \beta/L = 0.25$ (in energy units where $\Omega = 1$). A typical run consisted of 2000 (warm-up) updating sweeps followed by 2000 measurement sweeps. Each measurement was preceded by at least ten further updates of the basic pseudospin configuration $\{\sigma\}$. For a typical chain length of $L = 80$, such a run took several hours on the University of California, Santa Barbara, ST-100 array processor. By sampling all measured quantities after every 200 measurements, we have estimated the statistical error of our results for G_d and Γ_d to be typically a few percent. To test for systematic breakup errors, due to the finite $\Delta\tau$, runs were repeated with $\Delta\tau = 0.125$. The systematic $\Delta\tau$ errors for $G_d(i\nu)$ were less than a few percent, but these errors in $\Gamma_d(i\nu', i\nu)$ were typically of order 5% and could be as

large as 10–15% for the largest coupling strengths λ which were studied. We consider this to be the major source of error in our final results for dT_c/dc and $\bar{\tau}$ presented below. In Fig. 3 we show some results comparing data obtained using $\Delta\tau = 0.25$ and $\Delta\tau = 0.125$.

V. RESULTS AND DISCUSSION

In Figs. 3–6 we display various results as functions of the on-site attraction $|U|$, (2.10), the resonance width Δ , (3.12), the on-site energy ϵ_d , and the asymmetry energy η . The unit of energy for these data was chosen such that the exciton frequency $\Omega = 1$. The frequency cutoff, used in the calculations of $(dT_c/dc)_{c=0}$ [Eqs. (3.43)–(3.49)], corresponds to a host lattice Debye frequency $\omega_D = 0.25$, and the density of states was $\rho(0) = 0.1$.

In Fig. 3(a) we show results for the maximal eigenvalue $r_\infty \equiv r(\bar{c} \rightarrow \infty, T)$ of the Eliashberg matrix (3.30) as a function of the on-site attraction $|U|$ at temperatures $T_c = 0.025, 0.050$, and 0.100 , respectively, using a resonance width $\Delta = 1$ and $\epsilon_d = \eta = 0$. The coupling constant λ was varied according to Eq. (2.10) so as to give the required attraction strength U . For $|U|$ values ranging from $|U| = 0.5$ to $|U| = 5.0$, the corresponding λ values are between $\lambda = 0.56$ and $\lambda = 2.96$, respectively (for $\eta = 0$).²⁷ r_∞ increases with increasing $|U|$. As a function of T , r_∞ increases by approximately constant increments as we lower T by factors of 2 (from 0.100 to 0.050 to 0.025) at fixed $|U| \leq 3$. This corresponds roughly to a $\ln(1/T)$ dependence which is what we would expect according to the discussion in Sec. III B. If $r_\infty(T_c)$ exceeds unity, it is possible to find a solution for the concentration parameter \bar{c} such that the system becomes superconducting at the specified temperature T_c . When r_∞ (as a function of T_c or $|U|$, say) approaches unity from above, the required \bar{c} diverges (i.e., $1/\bar{c} \rightarrow 0$). If r_∞ falls below unity, no solution for \bar{c} exists, i.e., within the framework of our formalism, the system cannot be made superconducting at the specified temperature T , even with the largest impurity concentration.²⁸ This can be seen in Fig. 3(b), where $1/\bar{c}$ is plotted as a function of $|U|$ for the same model parameters and three values of the induced superconducting $T_c = 0.025, 0.050$, and 0.100 . Notice that, as expected, \bar{c} increases monotonically with increasing T_c , i.e., the larger the required T_c , the more impurities are needed to achieve it. Furthermore, a certain minimum strength of attraction is needed in order to be able to reach the specified T_c at all. For $|U|$ is less than this minimum strength there is no solution \bar{c} (i.e., $r_\infty < 1$). If $|U|$ exceeds the minimum strength, then $1/\bar{c}$ first increases with increasing $|U|$, but then reaches a maximum and decrease again for $|U| \gtrsim 3$ (both for $T_c = 0.050$ and 0.100). This is qualitatively in agreement with the discussion in Sec. II B. For $|U| \gtrsim 3$ (corresponding to $|\lambda| \gtrsim 1.9$ with $\Omega = 1$), we should expect to see the strong-coupling effects of the reduced overlap factors f_0, f_1 suppressing the pairing strength (here measured by $1/\bar{c}$). This is indeed what appears to be happening here. In Fig. 3(c) we show the T_c -enhancement coefficient $(dT_c/dc)_{c=0}$, Eq. (3.46), for the same set of model parameters and

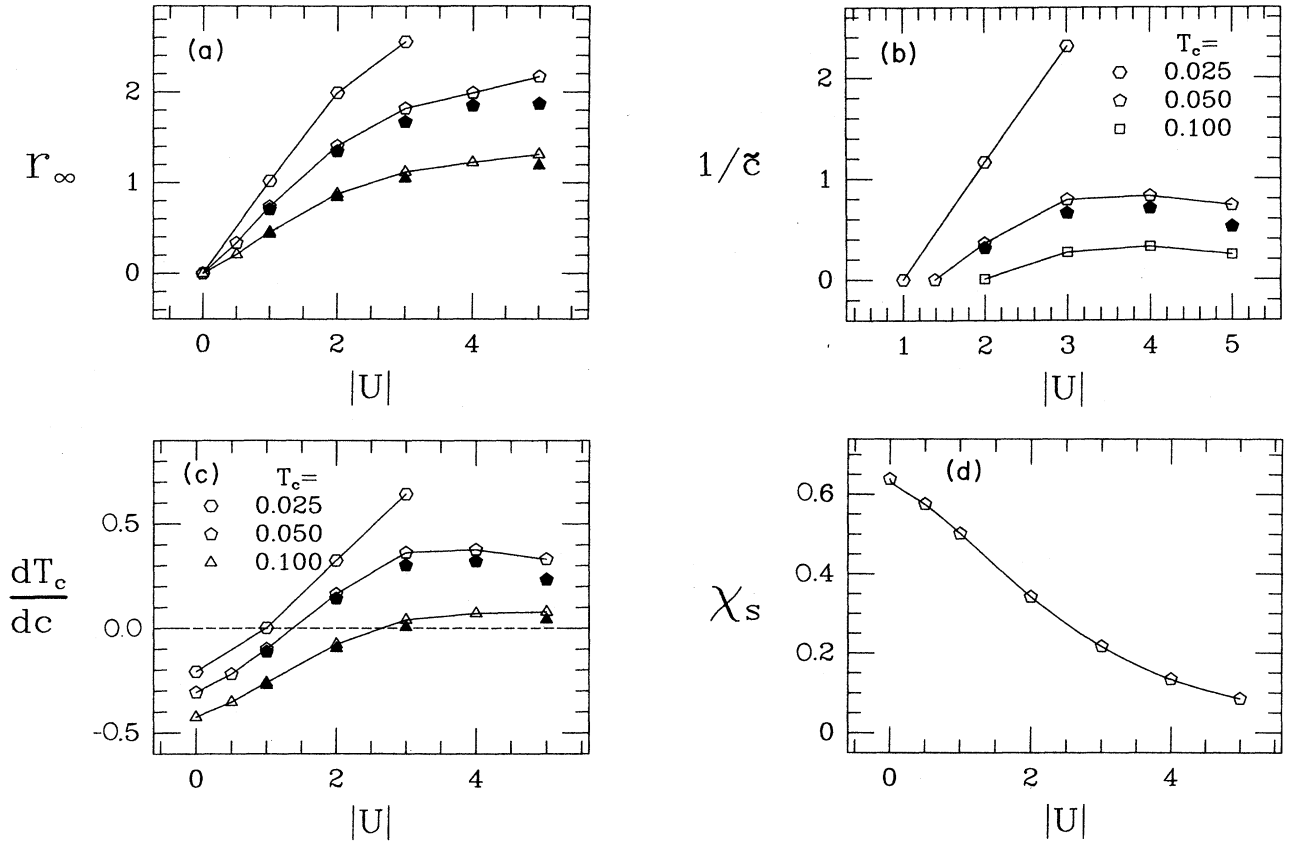


FIG. 3. (a) r_∞ and (b) $1/\bar{c}$ vs $|U|$ for different values of the induced T_c , (c) dT_c/dc vs $|U|$ for different values of the host $T_{c,0}$, $\omega+D=0.25$ and $\rho(0)=0.1$, (d) χ_s vs $|U|$ at $T=0.050$. Here, $\varepsilon_d=\eta=0.0$ and $\Delta=1.0$. The open symbols indicate data obtained with $\Delta\tau=0.25$ and the closed symbols are for $\Delta\tau=0.125$. Here and in all figures to follow, energy is measured in units of Ω .

host-lattice transition temperatures $T_{c,0}=0.025$, 0.050 , and 0.100 . Qualitatively its behavior is very similar to that of $1/\bar{c}$. As discussed in Sec. III C, $(dT_c/dc)_{c=0}$ is actually negative at small $|U|$ and a certain minimum $|U|$ is needed just to maintain the $T_{c,0}$ of the host. Like $1/\bar{c}$, $(dT_c/dc)_{c=0}$ reaches a maximum at larger coupling strengths which we again attribute to the onset of strong-coupling overlap effects.

The d -electron spin susceptibility χ_s is shown as a function of $|U|$ in Fig. 3(d) for a temperature $T=0.050$. With increasing $|U|$, χ_s is rapidly suppressed. Physically, this reflects the fact that for large enough $|U|$ (and $\varepsilon_d=\eta=0$), the low-lying states of the system are composed primarily of impurity configurations with occupation numbers $n_d=0$ or $n_d=2$, neither of which carries a magnetic moment. Thermal and quantum fluctuations into the moment carrying $n_d=1$ configurations are suppressed with increasing $|U|$ since their energy $E_0(1)=E_0(0)+\frac{1}{2}|U|$ is shifted well above $E_0(0)=E_0(2)$. These results are in agreement with Anderson's original conjecture about negative- U centers.³ In Fig. 4, we show $1/\bar{c}$ and $(dT_c/dc)_{c=0}$ as functions of the hybridization strength, measured in terms of the resonance width $\Delta=\pi\rho(0)V^2$. The two data sets for dT_c/dc [Fig. 4(b)] corresponds to $|U|=1$ ($\lambda=0.866$) and $|U|=3$ ($\lambda=1.94$) and the host material has $T_{c,0}=0.05$. Notice that, for

$|U|=1$, dT_c/dc is negative at all values of Δ , indicating that the on-site attraction in the d orbitals is not strong enough to maintain the $T_{c,0}$ of the host. Results for $1/\bar{c}$ [Fig. 4(a)] were obtained only with $|U|=3$ assuming an induced $T_c=0.050$. For $|U|=1$, this T_c could not be reached ($r_\infty < 1$) at any concentration \bar{c} . The on-site energy and asymmetry energy were again $\varepsilon_d=\eta=0$. Clearly, for $|U|=3$, both $1/\bar{c}$ and dT_c/dc exhibit a maximum roughly where the resonance width Δ matches the exciton frequency $\Omega=1$. We believe that this can be understood in terms of the relevant time scales involved: For $\Delta \gg \Omega$, the average time, spent by an electron on the d site, $\tau_\Delta \sim 1/\Delta$, is much shorter than the time $\tau_\Omega \sim 1/\Omega$ which the polarization of the two-level system needs to respond to the presence of the d electron. This polarization response is maximal (of order of the $\Delta=0$ static polarization discussed in Sec. II B) if $\tau_\Delta \gtrsim \tau_\Omega$. On the other hand, if we let $\tau_\Delta \rightarrow \infty$ (i.e., $\tau_\Delta \gg \tau_\Omega$, $1/\omega_D$), the tunneling matrix elements (2.12), and hence, the rate of pair fluctuations will be more and more suppressed, until at $\Delta=0$ (zero hybridization) the impurities are completely decoupled from the host.

All the foregoing results were obtained under conditions of perfect particle-hole symmetry of the impurity (i.e., $\varepsilon_d=\eta=0$) and hence degeneracy $E_0(0)=E_0(2)$, as discussed in Sec. II C. In Fig. 5 we have explored what

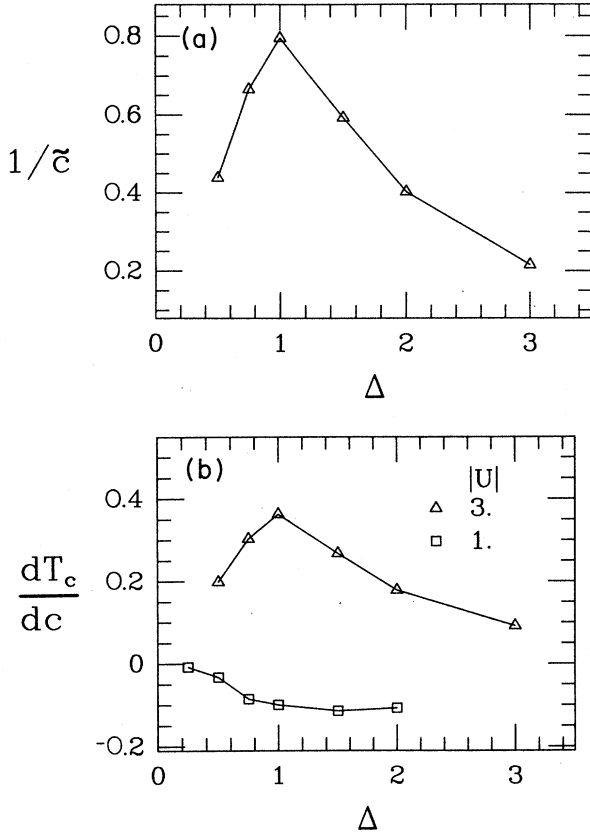


FIG. 4. (a) $1/\bar{c}$ vs Δ for $T_c=0.05$ and $|U|=3.0$, (b) dT_c/dc vs Δ for $T_{c,0}=0.05$, $\omega_D=0.25$, $\rho(0)=0.1$ and two different $|U|$; for all data, $\epsilon_d=\eta=0.0$, $\Delta\tau=0.25$.

happens if this degeneracy is destroyed by shifting the bare on-site energy ϵ_d , keeping $\eta=0$, $|U|=3$ ($\lambda=1.94$), and $\Delta=1$ fixed. Remember that, for $\epsilon_d>0$, we have $E_0(2)>E_0(0)$ so that it becomes energetically unfavorable for a pair electrons near the Fermi energy to tunnel into the empty center. On the other hand, for $\epsilon_d<0$, and hence $E_0(2)<E_0(0)$, the center is mostly doubly occupied, and it is unfavorable for the pair to tunnel back into the conduction band. Indeed we find that both $1/\bar{c}$ [Fig. 5(a)] and dT_c/dc [Fig. 5(b)] are strongly suppressed for $\epsilon_d\neq 0$. Analytical results for related model systems^{1,2,10,14} indicate that the width $\delta\epsilon_d$ of these maxima is of the order of the resonance width ($\Delta\sim\delta\epsilon_d$). From Eq. (2.3), it follows that under a particle-hole transformation (2.15)–(2.18), any Hamiltonian H_i is transformed into an H'_i of the same form (2.3) with ϵ_d and η replaced by

$$\epsilon'_d = -\epsilon_d, \quad (5.1)$$

$$\eta' = -\eta. \quad (5.2)$$

$1/\bar{c}$ and dT_c/dc are invariant under such a transformation. From (5.1) it follows therefore that the data in Figs. 5(a) and 5(b) should be symmetric around $\epsilon_d=0$. We note that, within statistical error, this symmetry is obeyed by our Monte Carlo results.

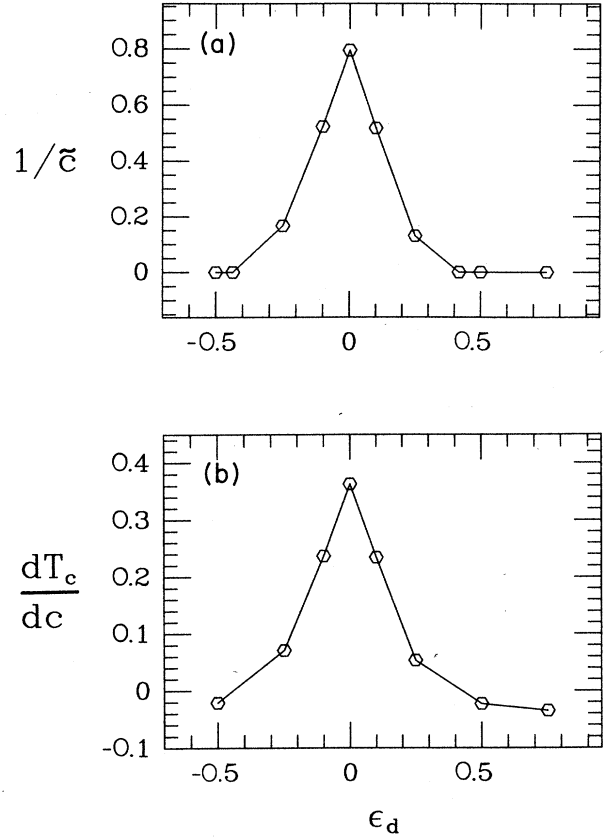


FIG. 5. (a) $1/\bar{c}$ vs ϵ_d for $T_c=0.050$, (b) dT_c/dc vs ϵ_d for $T_{c,0}=0.050$, $\omega_D=0.25$, $\rho(0)=0.1$; for all data $\eta=0$, $|U|=3.0$, $\Delta=1.0$, $\Delta\tau=0.25$.

As discussed in Sec. II C, it is possible in the present model to violate particle-hole symmetry (2.20) and (2.21) without destroying the degeneracy $E_0(0)=E_0(2)$, (2.22), if ϵ_d and η satisfy the condition (2.23). We have explored this possibility in Fig. 6, where $1/\bar{c}$ and dT_c/dc are plotted as functions of η . Together with η , we have varied ϵ_d according to (2.23), in order to keep $E_0(0)=E_0(2)$. Simultaneously, we have adjusted λ according to (2.10) so as to keep on-site attraction at a fixed value $|U|=3$. The suppression of $1/\bar{c}$ and dT_c/dc that we observe in Fig. 6 for $\eta\neq 0$ is therefore *not* the result of a weakened attraction $|U|$. Rather, we believe, that it is again a manifestation of the overlap factors f_0, f_1 discussed in Sec. II B, which, under the present conditions, can be shown to be maximal at the point of particle-hole symmetry $\eta=\epsilon_d=0$. Applying again the particle-hole transformation (2.15)–(2.18), it follows from (5.1), (5.2), and (2.23) that the data in Fig. 6 should be symmetric around $\eta=0$. Within statistical error, this is satisfied.

To estimate typical orders of magnitude for the T_c 's that can be obtained with this mechanism, let us assume a host lattice with a bandwidth $\rho(0)^{-1}=3$ eV, a resonance width $\Delta=0.1$ eV $=\Omega$ (corresponding to a hybridization strength $|V|\sim 0.3$ eV), and an attractive $|U|=0.3$ eV $=3\times\Omega$. Then according to Fig. 3 with a $\bar{c}\simeq(2.3)^{-1}\simeq 0.43$ corresponding to an impurity concentration

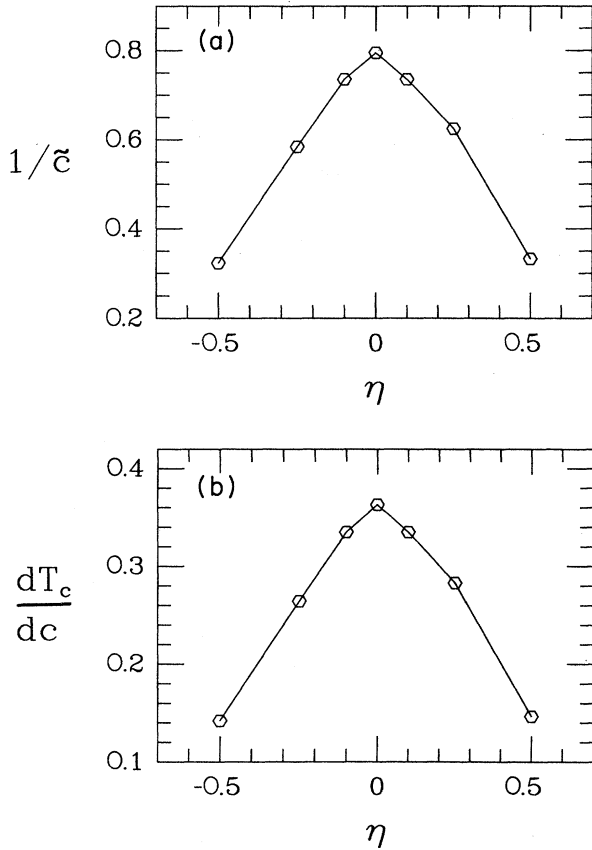


FIG. 6. (a) $1/\bar{\xi}$ vs η for $T_c=0.050$, (b) dT_c/dc vs η for $T_{c,0}=0.050$, $\omega_D=0.25$, $\rho(0)=0.1$; for all data ϵ_d and λ where varied according to Eqs. (2.23) and (2.10), so that $|U|=3$ and $E_0(0)=E_0(2)$, independent of η ; $\Delta\tau=0.25$.

$c = \pi\rho(0)\Omega\bar{c} \simeq 4.5\%$, we would get $T_c \sim 2 \text{ meV} = 20 \text{ K}$.

It is interesting to compare these parameters with those of a conventional BCS superconductor such as aluminum. Al has²⁹ a $T_c=1.2 \text{ K}$, a phonon energy $\Omega=0.034 \text{ eV}$, an inverse density of states $\rho(0)^{-1} \simeq 2.6 \text{ eV}$ and thus, according to the BCS formula, $T_c=1.13\Omega \exp[-1/|U|\rho(0)]$, an attractive $|U|=0.46 \text{ eV}$, about 50% larger than the 0.3 eV assumed above. If we rescale these values for $\rho(0)$, Ω and U to those assumed in our hypothetical “negative- U material,” $\rho(0)^{-1}=3 \text{ eV}$, $\Omega=0.1 \text{ eV}$, and $|U|=0.3 \text{ eV}$, the BCS formula gives an even smaller transition temperature, $T_c=0.05 \text{ K}$. Thus, in the BCS superconductor, T_c is over two orders of magnitude smaller than in the 4.5% doped negative- U material with identical boson frequency Ω , density of states $\rho(0)$, and attraction strength U . The results for the negative- U material are therefore quite surprising, particularly in view of the fact that in the BCS superconductor, *all* lattice sites contribute to the attractive interaction whereas, in the negative- U system, only a small fraction (c) of the sites contributes.

One might suspect that these results are a consequence of the particular excitonic mechanism that mediates the attraction. However, we have also studied a model H_i where the d electron is coupled to a local phonon

mode.^{13,15} We find that, for comparable values of the boson frequency Ω , the effective on-site attraction U , and the resonance width Δ , the results in both models are quite similar. Apparently, the crucial difference between the BCS superconductor and the negative- U system is that in the former, the virtual boson is exchanged directly between the conduction electrons, whereas in the latter, the exchange can take place only after the electrons have tunneled into the impurity orbital. If one estimates perturbatively to lowest order in the coupling the effective attraction^{13,15} one finds that indeed this attraction is enhanced relative to the on-site U by a factor $[\pi\rho(0)\Delta]^{-2} \gg 1$.¹⁵ This is roughly the square of the occupancy time ratio τ_Δ/τ_ρ where again $\tau_\Delta \sim \Delta^{-1}$ is the average time span for which an electron remains at an impurity site after tunneling into the d orbital and $\tau_\rho \sim \rho(0)$ is the (much shorter) time it spends at any lattice site while propagating in the conduction band. The foregoing results show that the negative- U center mechanism may well be capable of producing quite large superconducting T_c 's even with a quite small on-site coupling strength. We should caution, however, that this is achieved only if the model parameters are carefully tuned such that $\Delta \sim \Omega$ and, most importantly, $|\epsilon_d| \sim 0$ ($|\epsilon_d| \ll \Delta$).

VI. SUMMARY AND CONCLUDING REMARKS

In conclusion, we have applied quantum Monte Carlo techniques to study the effects of a small concentration of excitonic impurities on the superconducting T_c of a metallic host material. Combining a standard many-body analysis with results from Monte Carlo simulations we have avoided the lack of adequate analytical approximations for treating such a strongly interacting dynamic local mode embedded in a Fermi sea. Our qualitative analysis in Sec. II and the results in Sec. V show that strong-coupling and retardation effects, such as the overlap factors f_0, f_1 and the finite response time $\tau_\Omega \sim 1/\Omega$ of the bosonic degree of freedom are dominant factors in determining the superconducting pairing strengths in these systems which cannot be adequately described by perturbative weak-coupling techniques² in parameter regions of physical interest.

Specifically, we have demonstrated that excitonic impurities can substantially enhance T_c if their parameters are tuned such that (1) there is near degeneracy between the unoccupied and the doubly occupied configurations of the impurity; (2) the overlap factors for fluctuations between these configurations are maximized by a small asymmetry energy η ; (3) the hybridization is such that the resonance width Δ is of order of the exciton frequency Ω ; and (4) the coupling strength λ has an optimal value which is determined by the competition between the enhancement of the on-site attraction $|U|$ and the suppression of the overlaps f_0, f_1 with increasing λ . On the other hand, the T_c -enhancement effect may rapidly disappear as the model parameters deviate from their optimal values.

On the technical side, our diagrammatic analysis has relied on seemingly quite different approaches in calculating, on the one hand, the T_c -enhancement dT_c/dc at

small concentrations $c \rightarrow 0$ and, on the other, the induced T_c at finite concentration \bar{c} . A more unified treatment (which includes a full Eliashberg-type treatment of the host-lattice electron-phonon coupling, using where necessary realistic phonon spectra) is clearly desirable and will be presented in a forthcoming paper.¹⁵ Therein we will also address the questions of possible interference effects between the electron-phonon coupling of the host and the on-site interaction which are not included in our Monte Carlo simulation.

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²⁷The results for (dT_c/dc) shown in Fig. 4(b) were reported earlier in Ref. 12 and were plotted versus λ rather than versus $|U|$ in Fig. 2 of that paper. Unfortunately, the values of λ that are shown in that plot as well as the λ values quoted in the text (but not the λ values used in the actual simulations) were obtained from the original $|U|$ values by an incorrect conversion formula [based on the incorrect Eq. (3) of Ref. 12]. Thus, any discrepancy between the (correct) λ values presented here and the incorrect values given in Ref. 12 should be ignored. The corresponding values for $|U|$ quoted here and in Ref. 12 are both correct and in agreement. An erratum to Ref. 12 will be submitted.

²⁸We should caution, of course, that, physically, the value of the concentration $c \equiv N_i/N$ may not exceed a certain limit of order (or less than) unity, say. More importantly, however, our basic low-density expansion, Eqs. (3.2) and (3.3), breaks down when c becomes of order unity. We nevertheless feel that in this regime (where $c \lesssim 1$), our results are still qualitatively correct.

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