

Why holes are not like electrons: A microscopic analysis of the differences between holes and electrons in condensed matter

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We give a detailed microscopic analysis of why holes are different from electrons in condensed matter. Starting from a single atom with zero, one, and two electrons, we show that the spectral functions for electrons and for holes are qualitatively different because of electron-electron interactions. The quantitative importance of this difference increases as the charge of the nucleus decreases. Extrapolating our atomic analysis to the solid, we discuss the expected differences in the single-particle spectral function and in frequency-dependent transport properties for solids with nearly empty and nearly full electronic energy bands. We discuss the expected dependence of these quantities on doping, and the physics of superconductivity that results. We also discuss how these features of the atomic physics can be modeled by a variety of Hamiltonians.

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I. INTRODUCTION

The understanding of electronic correlation in solids and its consequences for charge transport and for collective phenomena are fundamental problems in condensed matter physics. At the simplest level, electronic correlation manifests itself in the two-electron atom.¹ In this paper we return to the old problem of the two-electron atom² and show that a fundamental physical principle emerges from it, *electron-hole asymmetry*. We then show that the understanding of electron-hole asymmetry at the atomic level provides insight that implies that this asymmetry has fundamental consequences for the physics of charge transport and collective phenomena of the solid state.

Remarkably, none of the many-body Hamiltonians that are most widely used to study the effect of electronic correlation in solids^{3,4} such as the Hubbard model, extended Hubbard model, degenerate Hubbard model, the Anderson impurity and lattice models, the Kondo model, Falicov-Kimball model, Holstein model, Su-Schrieffer-Heeger model, and *t-J* model, contain this very basic and fundamental aspect of electronic correlation that follows from the atomic analysis. Hence we argue that these models are fundamentally flawed. We propose a variety of other model Hamiltonians that contain this physics, which may be generically called “dynamic Hubbard models.”⁵⁻⁸ These models lead to a new understanding of the physics of charge transport in solids, and to a universal mechanism of superconductivity.⁹⁻¹¹

The observation that electrons and holes in atomic shells are in some sense equivalent was first made by Heisenberg.¹² It is easy to see that in the absence of electron-electron interactions, an atom with *i* electrons in an outer partially filled shell defined by quantum numbers *n*, *l*, has the same multiplet structure as an atom with *p-i* electrons in this shell, with $p=4l+2$ the total number of electrons that can fill this shell. In particular, this is trivially true for an *s* shell ($l=0$), where the state with one electron in the ns^0 shell is *identical* to the state with one hole in the ns^2 shell. Furthermore, all the matrix elements of the Coulomb interaction operator, both diagonal and off-diagonal, between these noninteracting

electron atomic states, are the same for a shell with *i* electrons and one with *i* holes (i.e., *p-i* electrons).¹³ This of course extends also to cases where more than one shell is incomplete. As a consequence, the atomic multiplet structure of a shell with *i* electrons is identical to the one with *i* holes within first-order perturbation theory in the Coulomb interaction between electrons. Thus, to the extent that first-order perturbation theory holds for atoms, electron-hole symmetry exists for the atomic states, and similar arguments can be used to argue for electron-hole symmetry in energy bands in the solid state.¹⁴ This implies that the states of atomic shells that are almost full, and of electronic energy bands that are almost full, can be described in terms of the states of few positively charged holes, instead of the states of many negatively charged electrons. The physical reality of the hole concept for transport in solids was first demonstrated by Hall’s measurement¹⁵ and Peierls’ explanation¹⁶ of positive Hall coefficient in solids with nearly filled electronic energy bands.

However, in this paper we show that electron-hole symmetry in fact does not exist in atoms, and consequently it will not exist in electronic energy bands in solids. Instead, we argue that electrons and holes are *fundamentally different objects*. In some sense, in the light of the above discussion, this can be understood as a failure of first-order perturbation theory. It is of course not surprising that perturbation theory in the electron-electron Coulomb interaction should fail. The electronic structure of noninteracting electrons in atoms is determined by the Coulomb interaction between electrons and ions, which of course has the same coupling constant as the electron-electron Coulomb interaction. Thus, it is *never* true that the spacing between noninteracting electron atomic energy levels is larger than matrix elements of the electron-electron Coulomb interaction, the regime where perturbation theory may be expected to be valid. Despite this, it is fortunate that the qualitative structure of atomic multiplets and their quantum numbers are the same for electrons and holes.¹²

The physics of electron-hole asymmetry that results from electron-electron interactions occurs even for *s* shells, and even for the atomic *1s* shell that is most isolated in energy. This is the case we will analyze in this paper. It is natural to

expect that the physics that we find here should have an even larger effect for atomic states with higher quantum numbers, where shell occupation becomes larger and energy level separation becomes smaller.

Since for an s shell the one-electron state and the one-hole state are the very same state, one may ask how it is possible to understand electron-hole asymmetry based on it. The point is, in considering the process of transport of charge in solids with electrons or holes, we need to consider not only the atom in a given charge state, but also processes where electrons and holes are *created* and *destroyed* as conduction occurs. It is these creation and destruction processes that contain the physics of electron-hole asymmetry even at the level of a single atom and even for s shells.

This paper is organized as follows. In the next section we discuss the electronic state of two electrons in the $1s$ shell of ions of nuclear charge Z . We show that the state of the two-electron atom is strongly influenced by electronic correlation effects, the more so the smaller Z is. In Sec. III we discuss the calculation of the atomic spectral function for electrons and holes, and the qualitative reasons for why they are fundamentally different. Section IV discusses results for the atomic spectral function within the various approximations for the state of the two-electron atom reviewed in Sec. II. In Sec. V we discuss the consequences of these results for the properties of electrons and holes in the solid state, in particular for the single-electron spectral function and for frequency-dependent transport. In Sec. VI we discuss the consequences of this physics for the understanding of superconductivity in solids. Sec. VII discusses several model Hamiltonians that contain the physics of electron-hole asymmetry found at the atomic level. We conclude in Sec. VIII with a summary and discussion of our results, a review of the empirical and experimental evidence in support of this physics as the underlying universal mechanism of superconductivity in solids, and a survey of some of the many open questions and opportunities for further research in this area.

II. THE TWO-ELECTRON ATOM

The wave function for an electron in the lowest-energy state ($1s$) of a hydrogenlike ion of nuclear charge Z is

$$\varphi_Z(r) = \left(\frac{Z^3}{\pi}\right)^{1/2} e^{-Zr} \quad (1)$$

with r measured in units of the Bohr radius a_0 . The ground-state wave function of the two-electron ion is *not*, of course,

$$\Psi(r_1, r_2) = \varphi_Z(r_1)\varphi_Z(r_2) \quad (2)$$

because of electron-electron interactions. Consider the following approximations to the ground state of the two-electron ion.

A. The Hartree wave function

The simplest approximate wave function that takes into account the effect of electron-electron interaction, is of the Hartree form

$$\Psi_H(r_1, r_2) = \varphi_{\bar{Z}}(r_1)\varphi_{\bar{Z}}(r_2), \quad (3a)$$

where

$$\bar{Z} = Z - \frac{5}{16} \quad (3b)$$

results from minimization of the total energy for a variational wave function of the form Eq. (3a). Equation (3) describes an expanded orbital for each electron, due to the partial shielding of the positive nuclear charge by the other electron. In Eq. (3), both electrons reside in the same expanded orbital. A slightly better approximation of the Hartree form is obtained by allowing for the most general single-particle wave function rather than the exponential form Eq. (1). For example, the error in the ground-state energy of the He atom is 1.95% with Eq. (3) and 1.45% with the optimal single-particle wave function in the Hartree wave function.¹

B. The Eckart wave function

A better approximation is obtained by allowing for radial correlations, through the wave function¹⁷

$$\Psi_E(r_1, r_2) = \frac{\varphi_{Z_1}(r_1)\varphi_{Z_2}(r_2) + \varphi_{Z_2}(r_1)\varphi_{Z_1}(r_2)}{2(1+S_{12}^2)^{1/2}}, \quad (4a)$$

$$S_{12} = (\varphi_{Z_1}, \varphi_{Z_2}), \quad (4b)$$

where the exponents Z_1 and Z_2 are again obtained by minimization of the total energy, for a wave function of the form Eq. (4). The numerical results for Z_1 and Z_2 obey the approximate relations

$$Z_1 = 1.14Z - 0.105, \quad (5a)$$

$$Z_2 = 0.905Z - 0.622. \quad (5b)$$

Hence, one of the electrons resides in an orbit of approximately the same radius as that of the single-electron ion, and the second one resides in a substantially enlarged orbit. The minimization procedure resulting in the values of Z_1 and Z_2 becomes unstable for $Z \leq 0.93$. For He, the error in the ground-state energy is now reduced to 0.98%.

C. The Hylleraas wave function

Much more accurate wave functions for the two-electron system are obtained by introducing dependence of the wave function on $r_{12} = |\vec{r}_1 - \vec{r}_2|$ in addition to r_1 and r_2 , which allows for angular in addition to radial correlations. We consider here the simplest wave function of this form, Hylleraas' "dritte Naherung" (third approximation):²

$$\Psi_{Hy}(\vec{r}_1, \vec{r}_2) = N\varphi(2Zks, 2Zkt, 2Zku), \quad (6a)$$

$$\varphi(s, t, u) = e^{-s/2}[1 + c_1u + c_2t^2], \quad (6b)$$

$$s = r_1 + r_2, \quad (6c)$$

$$t = r_2 - r_1, \quad (6d)$$

TABLE I. Orbital exponents and energy (in Ry) of two-electron atom for $Z=1$ (H^+) and $Z=2$ (He) for the Hartree wave function Eq. (3) (\bar{Z} , E_H), the Eckart wave function Eq. (4) (Z_1 , Z_2 , E_E) and the Hylleraas wave function Eq. (6) (Zk , E_{Hy}). The experimental value of the energy (E_{expt}) is also given.

Z	\bar{Z}	E_H	Z_1	Z_2	E_E	Zk	E_{Hy}	E_{expt}
1	0.6875	-0.9453	1.0392	0.2832	-1.0266	0.769	-1.051	-1.0554
2	1.6875	-5.6953	2.1832	1.1885	-5.7513	1.816	-5.805	-5.808

$$u = r_{12}. \quad (6e)$$

The parameters c_1 , c_2 , and k are determined by minimization of the energy, as described in the Appendix A, and N is a normalization constant. Both this as well as the previous wave functions yield upper bounds to the ground-state energy. c_1 and c_2 are found to be positive, indicating that for given $s = r_1 + r_2$ the wave function is larger for large angle between \vec{r}_1 and \vec{r}_2 (angular correlations) and for large $|r_1 - r_2|$ (radial correlations). The error in the He energy with the wave function, Eq. (6), is reduced to 0.05%. Table I summarizes the values of the energy and orbital exponents for the three wave functions discussed for the He ($Z=2$) and the H^+ ($Z=1$) ions compared to the experimental values.

Figure 1 shows the orbital exponents versus ionic charge in the different approximations. The Hylleraas wave function has an orbital exponent similar to the Hartree wave function, while the exponents of the Eckart wave functions are very different. This suggests that even though the Eckart wave function gives better results than the Hartree one for the energy, the Hartree method may give a better representation of the wave function itself. Figure 2 shows the parameters c_1 and c_2 of the Hylleraas wave function, which describe angular and radial correlations, respectively, versus ionic charge. Note that both parameters increase rapidly as the ionic charge decreases, and that angular correlations are much more important than radial correlations for large Z .

The different wave functions discussed above describe attempts of the electronic wave function to reduce the Coulomb repulsion between electrons, without paying unduly in electron-ion energy. The effective Coulomb repulsion between electrons is

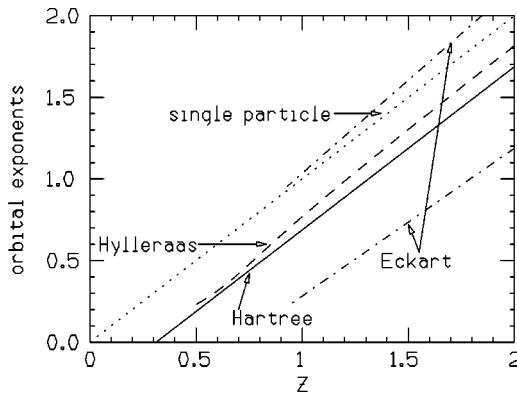


FIG. 1. Orbital exponents for the two-electron atom vs ionic charge Z for the Hartree (full line), Eckart (dot-dashed lines), and Hylleraas (dashed line) wave functions. The dotted line shows the orbital exponent for the one-electron atom ($=Z$).

$$U_{eff}(Z) = E(2) + E(0) - 2E(1) \quad (7)$$

with $E(n)$ the ground-state energy for the ion with n electrons [$E(0)=0$, $E(1)=-Z^2$, with E in Ry=13.6 eV]. For the wave function Eq. (2) with the electrons occupying the same orbitals as in the singly occupied atom

$$U_{eff}(Z) \equiv U = \frac{5}{4}Z, \quad (8a)$$

$$U = \int d^3r d^3r' |\varphi_Z(r)|^2 \frac{e^2}{|r-r'|} |\varphi_Z(r')|^2 \quad (8b)$$

and for the Hartree wave function Eq. (3)

$$U_{eff}^H = \frac{5}{4}Z - \frac{25}{128}, \quad (9)$$

smaller than Eq. (8a) because the wave functions are more expanded (note, however, that this is different from the actual Coulomb integral Eq. (8b) computed with the Hartree wave functions, due to the cost in electron-ion energy paid by the expanded wave functions). For the Eckart and Hylleraas wave functions the effective U becomes progressively smaller, corresponding to the decrease of the two-electron energy $E(2)$ with increasingly better wave functions. Figure 3 shows U_{eff} versus ionic charge in the different approximations.

Figure 4 depicts qualitatively the electrons in the atom in the different approximations. We emphasize that the two-electron wave function in any of the approximations discussed is very different from the one corresponding to non-

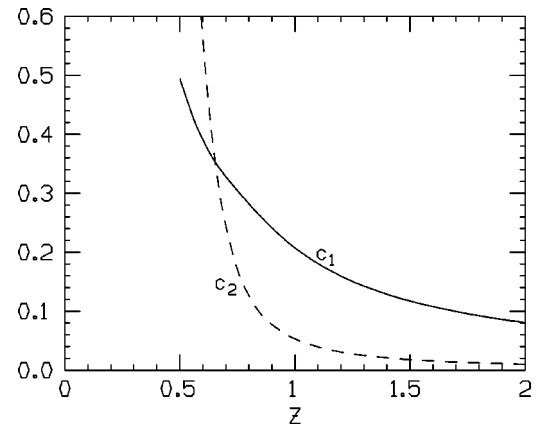


FIG. 2. Parameters in the Hylleraas wave function Eq. (6) describing angular correlations (c_1 , full line) and radial correlations (c_2 , dashed line) vs ionic charge.

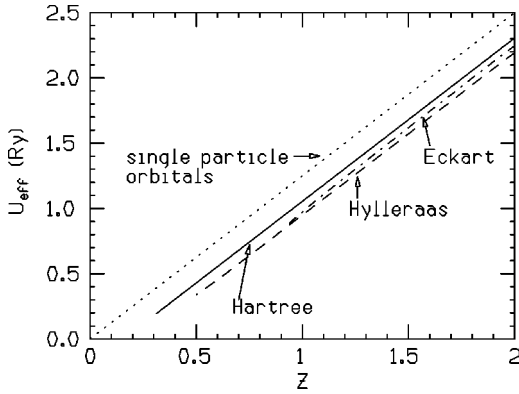


FIG. 3. Effective U [Eq. (7)] vs ionic charge Z for the Hartree (full line), Eckart (dot-dashed line), and Hylleraas (dashed line) wave functions. The dotted line gives the bare U [Eq. (8)] for the two electrons in the single-particle orbital.

interacting electrons, Eq. (2). For the purposes of this paper, any of these wave functions, including the simple Hartree one, describes “electronic correlation,” in the sense that the two-electron wave function is different from the one given in Eq. (2), and is appropriate to illustrate the physics of electron-hole asymmetry. Note also that the difference between these wave functions and the uncorrelated wave function, Eq. (2), increases as the ionic charge Z decreases and the relative importance of electron-electron versus electron-ion interaction strength increases.

It is also worth pointing out that the electron-electron repulsion U_{eff} decreases as the ionic charge Z decreases for all these wave functions, including the uncorrelated one. Hence, everything else being equal, pairing of electrons (or holes)

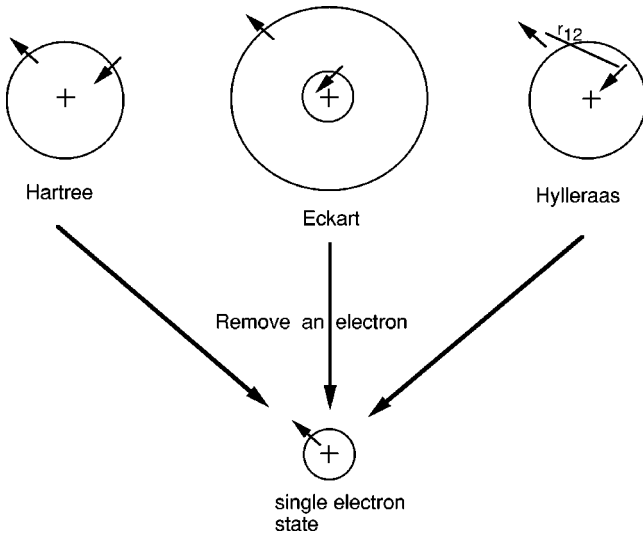


FIG. 4. Qualitative depiction of the two-electron state: in the Hartree wave function, both electrons occupy the same expanded orbital; in the Eckart wave function, the electrons occupy different orbitals; in the Hylleraas wave function, the amplitude of the wave function depends on the relative angular and radial coordinates. When removing an electron from any of these two-electron wave functions, the state of the remaining electron has to change to become the eigenstate of the single-electron atom.

should be favored when the effective ionic charge is small, i.e., with negatively charged ions. This simple fact, which provides some rationale for high-temperature superconductivity being favored in systems with negative ions (O^{-2} in cuprates, B^{-} in MgB_2) has surprisingly not been pointed out before to our knowledge.

III. ATOMIC SPECTRAL FUNCTIONS

Properties of many-electron systems can be studied by consideration of spectral functions. The zero-temperature one-electron spectral function for a many-body system is conventionally defined as

$$A(\omega) = \sum_{n=1}^{\infty} [|\langle n|c_{\alpha\sigma}^{\dagger}|1\rangle|^2 \delta(\omega - (E_n^{N+1} - E_1^{N+1} + \mu_N)) + |\langle n|c_{\alpha\sigma}|1\rangle|^2 \delta(\omega + (E_n^{N-1} - E_1^{N-1} - \mu_{N-1}))], \quad (10a)$$

where $|1\rangle$ is the ground state of the N -electron system, E_1^N its ground-state energy, and $\mu_N = E_1^{N+1} - E_1^N$, $\mu_{N-1} = E_1^N - E_1^{N-1}$. For a metal, $\mu_N = \mu_{N-1} = \mu$, and one can redefine the frequency $\omega \rightarrow \omega + \mu$ so that Eq. (10a) becomes

$$A(\omega) = \sum_{n=1}^{\infty} [|\langle n|c_{\alpha\sigma}^{\dagger}|1\rangle|^2 \delta(\omega - (E_n^{N+1} - E_1^{N+1})) + |\langle n|c_{\alpha\sigma}|1\rangle|^2 \delta(\omega + (E_n^{N-1} - E_1^{N-1}))] \quad (10b)$$

and the zeros of the δ -function arguments occur at the excitation energies of the system. To have a smooth transition between the metal and atomic spectral functions we will here define the atomic spectral functions as Eq. (10b) rather than Eq. (10a). The first term describes the response of the system when an electron of spin σ is created in the single-particle state α , into the ground state with N electrons. E_n^{N+1} is the n th excited-state energy of the many-electron system with $N+1$ electrons. Similarly, the second term describes the response of the system when an electron of spin σ at the single-particle state α is destroyed from the ground state of the N -electron system, and E_n^{N-1} are the excited state energies of the resulting $(N-1)$ -electron system. Generically, in many-body systems the one-electron spectral function is of the form¹⁸

$$A(\omega) = z \delta(\omega - (\epsilon - \mu)) + A_{inc}(\omega), \quad (11)$$

where the first term describes the quasiparticle, with quasiparticle weight z , $0 \leq z \leq 1$, and the second term describes a continuum of incoherent excitations at higher energies. For a small system such as an atom, however, the spectral function will consist of only discrete δ functions. Nevertheless, we can identify the lowest-energy δ function as corresponding to the quasiparticle, and its coefficient as the quasiparticle weight.

The fundamental asymmetry between electrons and holes follows immediately from consideration of these spectral

functions. Consider the spectral function for creating an electron in the empty atom, $N=0$. From Eq. (10b), it is simply

$$A_{el}(\omega) = \delta(\omega) \quad (12)$$

so that it is totally coherent, with quasiparticle weight $z=1$.

Consider next the spectral function for creating a hole in the full $1s$ shell

$$A_h(\omega) = \sum_n |\langle n|c_{\alpha,\uparrow}|1\rangle|^2 \delta(\omega + E_n^1 - E_1^1). \quad (13a)$$

The excitation energies in Eq. (13a) are the ones of the singly occupied atom,

$$E_n^1 = -\frac{Z^2}{n^2} \quad (13b)$$

and the matrix elements are

$$\langle n|c_{\alpha,\uparrow}|1\rangle \equiv S_n = \int d^3r_1 d^3r_2 \Psi(\vec{r}_1, \vec{r}_2) \varphi_\alpha(r_1) \varphi_n(r_2) \quad (13c)$$

with Ψ the two-electron ground-state wave function, φ_n the wave function for the n th excited state of the singly occupied atom, and φ_α the single-particle wave function of state α . The important qualitative point is, because Ψ is not given by the product form of single-electron wave functions Eq. (2), the spectral function Eq. (13a) *necessarily* consists of a *sum* of δ functions rather than a single one as Eq. (12):

$$A_h(\omega) = z\delta(\omega) + \sum_{n \neq 1} S_n^2 \delta(\omega + E_n^1 - E_1^1), \quad (14a)$$

$$z = S_1^2. \quad (14b)$$

Hence, the spectral function for hole creation Eq. (14a) is *qualitatively different* from the one for electron creation Eq. (12).

The foregoing remarks are true for *any* single-particle wave function φ_α . Which is the appropriate φ_α to use to define the hole spectral function? We argue that it is reasonable to use the single particle wave function that maximizes the quasiparticle weight of the hole spectral function, S_1^2 (such a hole wave function will have minimal kinetic energy in the solid). For the Hartree wave function, Eq. (3a), it is simply given by

$$\varphi_\alpha(r) = \varphi_{\bar{Z}}(r) \quad (15a)$$

and

$$S_1 = \int d^3r \varphi_1(r) \varphi_{\bar{Z}}(r) = \frac{(Z\bar{Z})^{3/2}}{\left(\frac{Z+\bar{Z}}{2}\right)^3} \quad (15b)$$

with $\bar{Z} = Z - 5/16$. For the Eckart and Hylleraas wave functions, we use a single-particle wave function of the form Eq. (15a), with \bar{Z} determined by maximization of the function

$$S_1(\bar{Z}) = \int d^3r_1 d^3r_2 \Psi(\vec{r}_1, \vec{r}_2) \varphi_{\bar{Z}}(r_1) \varphi_1(r_2). \quad (16)$$

Note that the hole spectral function as defined by Eq. (13) satisfies

$$\int_0^\infty d\omega A_h(\omega) = \sum_n S_n^2 = \int d^3r_1 \left[\int d^3r_2 \Psi(r_1, r_2) \varphi_\alpha(r_2) \right]^2. \quad (17)$$

In the Hartree approximation

$$\int_0^\infty d\omega A_h(\omega) = 1, \quad (18)$$

while with the more accurate wave functions, the frequency integral of the hole spectral function is less than unity. This is because there is also a nonzero probability of creating an *electron* in the single-particle state φ_α into the two-electron atom. However, that probability is found to be small.

Finally, the atomic spectral function for the singly occupied atom is of interest. We consider separately the positive and negative frequency parts. The spectral function for destruction of an electron in the singly occupied atom is

$$A'_{el}(\omega) = \sum_n |\langle n|c_{\alpha,\uparrow}|1\rangle|^2 \delta(\omega + E_n^0 - E_1^0), \quad (19)$$

which is of course also given by

$$A'_{el}(\omega) = \delta(\omega) \quad (20)$$

and the spectral function for destruction of a hole in the singly occupied atom, or equivalently creation of an electron in the singly occupied atom, is

$$A'_h(\omega) = \sum_n (S'_n)^2 \delta(\omega - (E_n^2 - E_1^2)), \quad (21)$$

where E_n^2 are the excitation energies of the doubly occupied atom, and

$$S'_n = \int d^3r_1 d^3r_2 \varphi_\alpha(r_1) \varphi_{\bar{Z}}(r_2) \Psi_n(r_1, r_2) \quad (22)$$

with Ψ_n the wave functions for the excited states of the two-electron atom. Once again, the spectral function A'_h is qualitatively different from A'_{el} , as it contains an incoherent part. The spectral function for the singly occupied atom as defined by Eq. (10b) will be either Eq. (20) or Eq. (21) depending on the value of σ in Eq. (10b) and of the spin of the electron in the singly occupied atom.

To estimate S'_n we need the excited-state wave functions for the doubly occupied ion. The excited states are approximately described by one electron in the ground state and the other electron in an excited state of the ion with orbital exponent \bar{Z} , $\varphi_{n\bar{Z}}$, with \bar{Z} given by Slater's rules:¹

$$\bar{Z} = Z - 0.85, \quad n=2, \quad (23a)$$

$$\bar{Z} = Z - 1, \quad n=3,4,\dots \quad (23b)$$

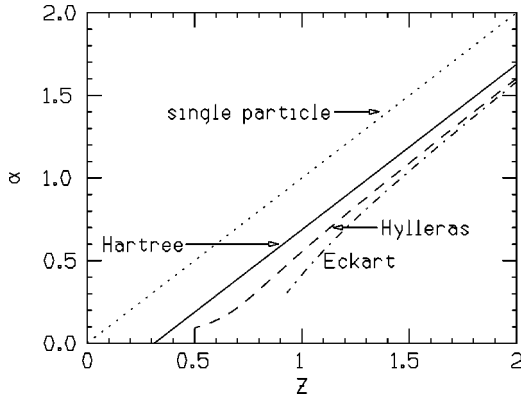


FIG. 5. Orbital exponent of the “hole wave function” φ_α , defined as the single-particle wave function that yields maximal quasiparticle weight for the hole spectral function, Eq. (14), for the various approximations to the two-electron wave function. The orbital exponent of the single-electron wave function is also shown (dotted line).

The matrix elements are then given by (for $n > 1$)

$$S'_n = \int d^3r \varphi_\alpha(r) \varphi_{n\bar{z}}(r) \quad (24)$$

and the excitation energies by

$$E_n^2 = -Z^2 - \frac{\bar{Z}^2}{n^2}. \quad (25)$$

IV. RESULTS FOR THE ATOMIC SPECTRAL FUNCTIONS

As discussed in the previous section, we calculate the hole spectral function for that single-particle wave function φ_α that maximizes the quasiparticle weight, which we will call the “hole wave function.” Figure 5 shows the orbital exponent of that state, α , versus Z . For the Hartree approximation $\alpha = \bar{Z}$, for the Eckart and Hylleraas approximations α is somewhat smaller, i.e., the hole wave function is somewhat more extended. In all approximations the hole wave function becomes more diffuse as the ionic charge Z decreases, as expected. Figure 6 shows the quasiparticle weight for the hole, from Eqs. (14b) and (16). The Hartree wave function somewhat overestimates and the Eckart wave function somewhat underestimates the quasiparticle weight given by the Hylleraas wave function, which presumably is the most accurate one. As the ionic charge decreases the quasiparticle weight for the hole decreases in all the approximations.

To obtain the full spectral function for hole creation we compute the matrix elements S_n , Eq. (13c). Because φ_α is spherically symmetric, only the excited atomic s states give nonzero results for the integral. They are given by

$$\varphi_n(r) = \left(\frac{(Z/n)^3}{\pi} \right)^{1/2} \sum_{l=0}^{n-1} (-1)^l a_l \left(\frac{Zr}{n} \right)^l e^{-Zr/n}, \quad (26a)$$

$$a_l = \frac{(n-1)! 2^l}{(n-l-1)! (l+1)! l!}. \quad (26b)$$

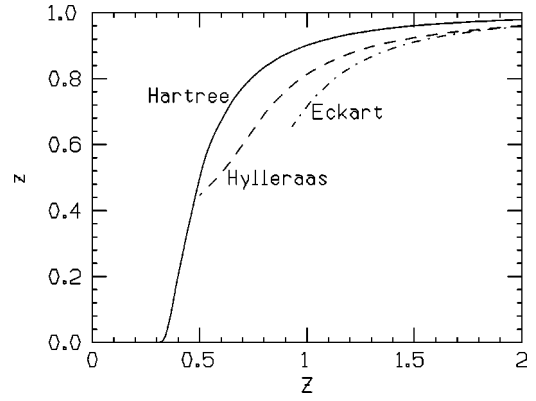


FIG. 6. Quasiparticle weight for the hole, z , vs ionic charge Z , for the various approximate two-electron wave functions. The difference between these curves and 1, the quasiparticle weight for the electron, measures the importance of electron-hole asymmetry for given ionic charge.

The integrals for all the approximate wave functions considered can be done analytically, as described in Appendix B.

Figure 7 shows the spectral function for hole creation in the full $1s$ shell, Eq. (13a), for various values of Z . We show results for both the Hartree and Hylleraas wave functions; the results for the Eckart wave function are similar. For $Z = 2$, $A_h(\omega)$ is close to a δ function at $\omega = 0$, of weight unity; the incoherent part occurs at very high energies and has very small weight. As Z decreases, the weight of the $\omega = 0$ peak (quasiparticle) gradually decreases, and the weight of the higher-energy peaks (incoherent part) gradually increases; in addition, the incoherent peaks shift to lower frequency. In Fig. 8 we show results with the Hartree wave function for an even smaller Z , $Z = 0.4$ (the procedure to obtain the Hylleraas wave function does not converge for such a small Z), showing that here the incoherent contribution is bigger than the quasiparticle part.

Similarly, we can calculate the spectral function for hole destruction (electron creation) in the ion with one hole (i.e., with one electron), from Eqs. (23)–(25). The excited states wave functions are given by Eq. (26) with Z replaced by \bar{Z} given in Eq. (23). The matrix elements turn out to be similar to the case of hole creation, but the excitation energies here are much lower. Hence the incoherent part of the spectral function is shifted to much lower energies for these processes. Figure 9 shows the calculated spectral function for hole destruction for $Z = 2$ and $Z = 1$.

Note that it is meaningless to calculate the spectral function for hole destruction for the isolated atom for $Z < 1$. In that case, all the excited states of the two-electron ion are unbound. However, the situation is different in the solid state. There, the negative ion (e.g., O^{-2} or B^{-}) will be surrounded by positive cations, and excited states can be formed where the excited electron is still confined in the neighborhood of the anion and the surrounding cations.

V. CONSEQUENCES FOR THE SOLID STATE

We have seen in the last section that the spectral functions for electrons and holes in the atom will be either single δ

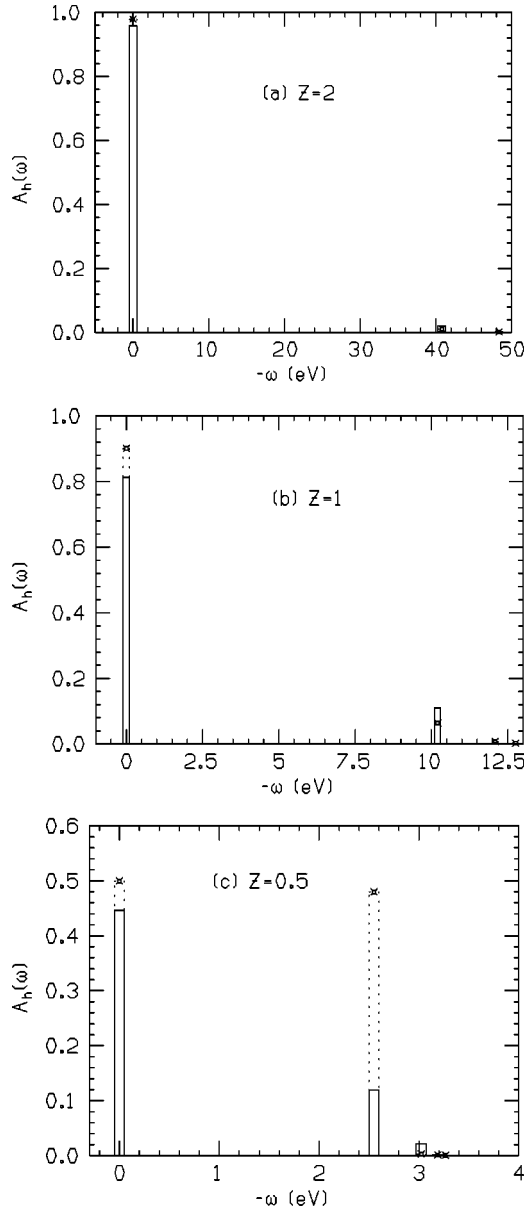


FIG. 7. Spectral function for hole creation for various values of the ionic charge Z . The full lines indicate the magnitude of the coefficients of the δ functions within the Hylleraas wave function, the dotted lines and symbols give the results for the Hartree wave function. The “width” of the δ functions is arbitrary. As the ionic charge decreases the quasiparticle peak (δ function at $\omega=0$) decreases and the “incoherent parts” (δ functions at negative frequencies) increase. At the same time the energy of the incoherent excitations decreases in absolute value.

functions or sums of δ functions depending on the charge state of the atom. In this section we discuss the fundamental consequences of this for the solid state.

When we bring together the atoms to form a solid, orbitals overlap and bands are formed. Consider for simplicity the lowest band, formed by overlapping $1s$ orbitals, well separated from other bands if the interatomic distance is large. The kinetic energy operator for an electron in such a band, in second quantized formalism, is

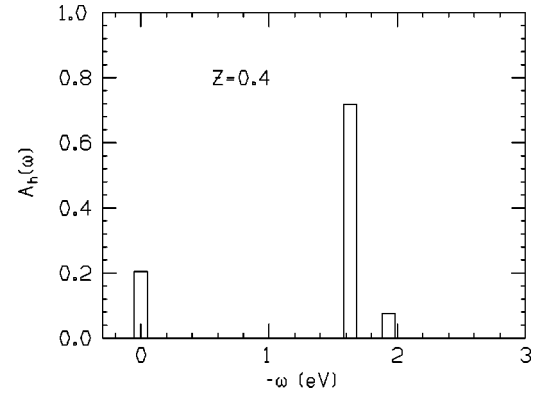


FIG. 8. Spectral function for hole creation within the Hartree approximation for ionic charge $Z=0.4$. Here the quasiparticle has smaller weight than the incoherent excitations.

$$H = - \sum_{i,j} t_{ij} c_{i\sigma}^\dagger c_{j\sigma}, \quad (27a)$$

where t_{ij} is the Fourier transform of the Bloch band energy

$$t_{ij} = \frac{1}{N} \sum_{k} e^{ik(R_j - R_i)} \epsilon_k \quad (27b)$$

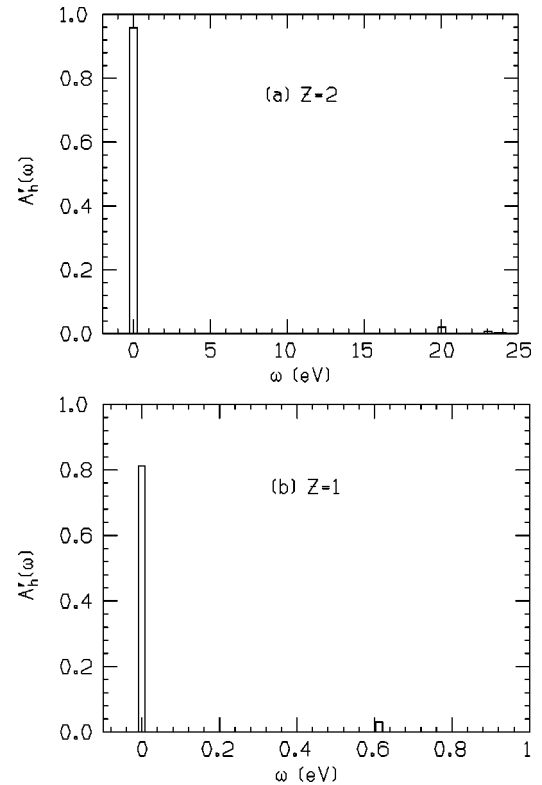


FIG. 9. Spectral function for hole destruction (electron creation) in the singly occupied atom within the Hylleraas approximation. Note that the energies where the incoherent contributions appear are much lower for hole destruction than for hole creation for the same Z . The quasiparticle peak has the same height for hole destruction and hole creation.

and $c_{i\sigma}^\dagger$ creates an electron in Wannier orbital i , a linear combination of nearby atomic orbitals with largest amplitude at site i . In the simplest tight-binding approximation the hopping matrix element for a single electron can be obtained from

$$t_{ij} = \frac{-(\varphi_i, h\varphi_j) + S_{ij}(\varphi_i, h\varphi_i)}{1 - S_{ij}^2}, \quad (28a)$$

$$S_{ij} = (\varphi_i, \varphi_j) \quad (28b)$$

with

$$h = -\nabla^2 - \frac{2Z}{|r-R_i|} - \frac{2Z}{|r-R_j|} \quad (29)$$

the single electron Hamiltonian (in atomic units). Equation (28) reproduces quite accurately the spacing between bonding and antibonding states of the single-electron diatomic molecular ion in a wide range of interatomic distances and ionic charges.¹⁹ However, we emphasize that Eq. (27) is generally valid for any Bloch band: away from the tight-binding limit the hopping t_{ij} will involve many neighboring atoms and differ from Eq. (28), and the Wannier orbital will be a linear combination of many atomic orbitals. We will focus on the tight-binding limit here for simplicity, but expect the qualitative physics to survive beyond that limit.

A. Spectral function

1. General considerations

Consider the spectral function for electrons in this band, $A(k, \omega)$. For the empty band, we use Eq. (10) with $c_{\alpha\sigma}$ replaced by

$$c_{k\sigma} = \frac{1}{\sqrt{N}} \sum_i e^{ikR_i} c_{i\sigma}. \quad (30)$$

When $c_{k\sigma}^\dagger$ acts on the ground state (the empty band), it yields a single-electron Bloch function, an eigenstate of the Hamiltonian Eq. (27a). Hence the spectral function is simply given by

$$A(k, \omega) = \delta(\omega - (\epsilon_k - \mu)), \quad (31a)$$

$$\epsilon_k = \frac{1}{N} \sum_{i,j} e^{ik(R_i - R_j)} t_{ij} \quad (31b)$$

where μ is the chemical potential (equal to the bottom of the band for the empty band).

For the full band instead, the situation is *much* more complicated. We wish to compute Eq. (10) with the operator

$$c_{k\sigma}^\alpha = \frac{1}{\sqrt{N}} \sum_i e^{ikR_i} c_{i\sigma}^\alpha, \quad (32)$$

where the atomic destruction operator $c_{i\sigma}^\alpha$ destroys an electron in the single-electron atomic state α with wave function φ_α as discussed in the preceding section. The ground state $|0\rangle$ is given by

$$|0\rangle = |\uparrow\downarrow\rangle_1 |\uparrow\downarrow\rangle_2 \dots |\uparrow\downarrow\rangle_i \dots |\uparrow\downarrow\rangle_N, \quad (33)$$

where $|\uparrow\downarrow\rangle_i$ is the correlated two-electron ground state of the i th atom, described, e.g., by the Hylleraas wave function. When $c_{i\sigma}^\alpha$ operates on this state we obtain

$$c_{i\uparrow}^\alpha |\uparrow\downarrow\rangle_i = S_1 |\downarrow\rangle_i + \sum_{n>1} S_n |\downarrow^n\rangle_i, \quad (34)$$

where the matrix elements S_n are given by Eqs. (13c) and (B7), and $|\downarrow^n\rangle_i$ denotes the n th excited state of the single-electron ion with energy given by Eq. (13b), and $|\downarrow\rangle \equiv |\downarrow^1\rangle$. Hence,

$$c_{k\uparrow}^\alpha |0\rangle = \frac{S_1}{\sqrt{N}} \sum_i e^{ikR_i} |\downarrow\rangle_i + \frac{1}{\sqrt{N}} \sum_i e^{ikR_i} \sum_{n>1} S_n |\downarrow^n\rangle_i, \quad (35)$$

which is, not surprisingly, *not* an eigenstate of the Hamiltonian Eq. (27a). [In Eq. (35), the state vectors for all sites $j \neq i$, $|\uparrow\downarrow\rangle_j$, are omitted for clarity.] Thus the spectral function for a single hole in the full band is *not* a single δ function and hence is qualitatively different from the spectral function of a single electron in the empty band, similarly to the case for the single atom.

The first term in Eq. (35) denotes a Bloch wave for a single hole in the full band. This is also not an exact eigenstate of the Hamiltonian, Eq. (27a), because every time the hole hops to a neighboring site there is a finite probability amplitude that the final state has the atoms in excited states, as discussed in the preceding section. Nevertheless, within the approximation where those processes are excluded, the energy of the itinerant hole will be given by

$$\epsilon_k^h = S_1^2 \epsilon_k = z \epsilon_k \equiv \tilde{\epsilon}_k. \quad (36)$$

Separating this contribution from the rest we have for the single-hole spectral function

$$A_h(k, \omega) = z \delta(\omega - (\tilde{\epsilon}_k - \mu)) + A'(k, \omega), \quad (37)$$

where $A'(k, \omega)$ contains all contributions to the spectral function with atomic excited states resulting from the second term in Eq. (35). Hence it will involve the high-energy part of the atomic spectral function discussed in the previous sections. In a solid, we expect that this contribution will not have a strong k dependence and that the atomic δ functions will broaden to give rise to the ‘‘incoherent’’ part of the spectral function, $A'(k, \omega)$.

The derivation of Eq. (37) is not rigorous, and hence the expressions for z and $\tilde{\epsilon}_k$ are not exact. Nevertheless, the general form, Eq. (37), possibly with some k dependence to the quasiparticle weight z , is expected to be correct for a many-body system.¹⁸ In fact, Sham has shown rigorously²⁰ that the spectral function for a single hole in a full band has a δ -function quasiparticle contribution that is separated from the continuum of incoherent excitations. We believe that the k -independent z and the form of $\tilde{\epsilon}_k$ obtained are reasonable approximations at least in the tight-binding limit. In particu-

lar, this implies that the quasiparticle weight z and the effective mass renormalization for a hole

$$\frac{m^*}{m} = \frac{1}{z} \quad (38)$$

will have the qualitative dependence on the ionic charge Z discussed in the previous section.

2. Quasiparticle operators

In the foregoing discussion we considered the spectral function for a single electron in the empty band and for a single hole in the full band. To generalize this analysis to other band fillings we define quasiparticle operators. The atomic electron operator can be written in terms of atomic states as

$$c_{i\uparrow} = |0\rangle\langle\uparrow| + S_1|\downarrow\rangle\langle\uparrow\downarrow| + \sum_{(n,n') \neq (0,0)} S_{nn'}|\downarrow^n\rangle\langle\uparrow\downarrow^{n'}|, \quad (39)$$

where $|\downarrow^n\rangle$ and $|\uparrow\downarrow^{n'}\rangle$ are excited states of the singly and doubly occupied ion, respectively, and

$$S_{nn'} = \int d^3r d^3r' \Psi_{n'}(r_1, r_2) \varphi_\alpha(r_1) \varphi_n(r_2) \quad (40)$$

with $S_{n1} = S_n$, $S_{1n'} = S'_n$, as discussed in the previous section. We write Eq. (39) as

$$c_{i\sigma} = [1 + (S_1 - 1)\tilde{n}_{i,-\sigma}]\tilde{c}_{i\sigma} + c'_{i\sigma}, \quad (41)$$

where the ‘‘quasiparticle operator’’ $\tilde{c}_{i\sigma}$ acts as if electronic correlations did not exist,

$$\tilde{c}_{i\sigma}^\dagger|0\rangle = |\sigma\rangle \quad (42a)$$

$$\tilde{c}_{i\sigma}^\dagger|-\sigma\rangle = |\uparrow\downarrow\rangle \quad (42b)$$

and obeys usual anticommutation relations. $\tilde{n}_{i\sigma} = \tilde{c}_{i\sigma}^\dagger \tilde{c}_{i\sigma}$. The operator $c'_{i\sigma}$ is the ‘‘incoherent part’’ of the bare fermion operator $c_{i\sigma}$, given by the last term in Eq. (39). From Eq. (41), we obtain that the quasiparticle weight for a band with band filling of n electrons per atom is approximately given by

$$z(n) = \left[1 + (S_1 - 1) \frac{n}{2} \right]^2 \quad (43)$$

decreasing monotonically from 1 to S_1^2 as n increases from 0 to 2.

3. Quasiparticle Hamiltonian

The effective low-energy Hamiltonian for quasiparticles (kinetic energy part only) is obtained by replacing the bare fermion operators in Eq. (27a) in terms of their form Eq. (41) and neglecting the ‘‘incoherent part’’ of the operators that would leave the atoms in excited states. Hence, it describes only ground state to ground-state transitions (diagonal transitions in the language of small polaron theory)

$$H_{qp} = - \sum_{ij} t_{ij}^\sigma \tilde{c}_{i\sigma}^\dagger \tilde{c}_{j\sigma}, \quad (44a)$$

$$t_{ij}^\sigma = t_{ij} [1 - (1 - S_1)(\tilde{n}_{i,-\sigma} + \tilde{n}_{j,-\sigma}) + (1 - S_1)^2 \tilde{n}_{i,-\sigma} \tilde{n}_{j,-\sigma}]. \quad (44b)$$

In a mean-field approximation, the quasiparticle energy is simply given by taking the expectation value of Eq. (44b), yielding

$$\tilde{\epsilon}_k = z(n) \epsilon_k. \quad (45)$$

To simplify the notation, we omit to denote explicitly the n dependence of $\tilde{\epsilon}_k$ on the left side of Eq. (45). Equation (45) implies that the relation Eq. (38) between effective mass and quasiparticle weight is valid for any band filling, and that the quasiparticle mass increases and the effective bandwidth decreases with increasing band filling.

4. Phenomenological model for the spectral function

From the considerations in the previous sections we conclude that a reasonable model for the spectral function in the solid that contains the physics discussed is of the form

$$A(k, \omega) = z(n) \delta(\omega - (\tilde{\epsilon}_k - \mu)) + A'(\omega), \quad (46)$$

where $A'(\omega)$ is the incoherent part describing the atomic excitations, and we have ignored its k dependence. The quasiparticle weight $z(n)$ and energy $\tilde{\epsilon}_k$ are given by Eqs. (43) and (45), respectively. The atomic spectral functions discussed in Sec. III will be broadened in the solid state, and we assume the Gaussian forms

$$A_h(\omega) = \frac{1}{\sqrt{2\pi}\Gamma_1} \exp\left(-\frac{(\omega + \epsilon_1)^2}{2\Gamma_1^2}\right), \quad (47a)$$

$$A'_h(\omega) = \frac{1}{\sqrt{2\pi}\Gamma_2} \exp\left(-\frac{(\omega - \epsilon_2)^2}{2\Gamma_2^2}\right). \quad (47b)$$

corresponding to hole creation (negative ω) and hole destruction (positive ω), respectively. ϵ_1 and ϵ_2 are mean excitation energies of the singly occupied ion and the doubly occupied ion, hence $\epsilon_1 > \epsilon_2$, and we assume the broadening Γ_i is proportional to ϵ_i . The relative weights of A_h and A'_h in A' will be determined by the probabilities of doubly and singly occupied sites, respectively, in the solid for band filling n . The probabilities for empty, singly occupied, and doubly occupied sites p_e , p_s , p_d can be written as

$$p_e(n) = \left(1 - \frac{n}{2}\right)^2 - \left(\frac{n}{2}\right)^2 \alpha, \quad (48a)$$

$$p_s(n) = n \left(1 - \frac{n}{2}\right) + 2\alpha \left(\frac{n}{2}\right)^2, \quad (48b)$$

$$p_d(n) = \left(\frac{n}{2}\right)^2 (1 - \alpha) \quad (48c)$$

for $n \leq 1$, and

$$p_e(n) = p_d(2 - n), \quad (49a)$$

$$p_s(n) = p_s(2 - n), \quad (49b)$$

$$p_d(n) = p_e(2 - n) \quad (49c)$$

for $n > 1$. Here, α is a parameter that describes the suppression of double occupancy due to the onsite repulsion U , which we assume to be approximately n independent and to interpolate smoothly between the limits $\alpha(U=0)=0$ and $\alpha(U=\infty)=1$. As discussed earlier, the magnitude of U depends on the ionic charge Z . The relative probabilities of singly and doubly occupied sites are then

$$P_s(n) = \frac{p_s(n)}{p_s(n) + p_d(n)}, \quad (50a)$$

$$P_d(n) = 1 - P_s(n) \quad (50b)$$

and the incoherent part of the spectral function in Eq. (46) is given by

$$A'(\omega) = [1 - z(n)][P_s(n)A'_h(\omega) + P_d(n)A_h(\omega)]. \quad (51)$$

In Fig. 10 we show the qualitative behavior of the spectral function Eq. (46) versus band filling for one set of parameters. As the band filling starts increasing from zero, the quasiparticle peak starts decreasing and a peak at positive frequencies forms, corresponding to the excited states of the doubly occupied ion upon creation of electrons in singly occupied ions. Only at higher fillings, and particularly beyond half filling, where the number of doubly occupied atoms becomes appreciable, does the peak at negative frequencies start to form, corresponding to the excited states of the singly occupied ion resulting from destruction of an electron in the correlated ground state of the two-electron atom. The peak at positive energies decreases as the full band is approached, because we are not considering the possibility of creation of electrons in higher-energy states of the doubly occupied atom. The quasiparticle peak height decreases monotonically as the band filling increases, approaching S_1^2 as the band becomes completely full. In the limit $\alpha \rightarrow 1$, corresponding to very strong intra-atomic Coulomb repulsion (i.e., very large ionic charge Z) the peak at negative energies only starts to form for $n > 1$. Note also, as discussed in the previous section, that the relative magnitude of the quasiparticle and the incoherent parts will depend on the ionic charge Z , with the incoherent contributions becoming more important for small Z . Furthermore, the energy scale of the incoherent excitations decreases with decreasing Z .

B. Frequency-dependent conductivity

On general grounds we expect that the frequency-dependent conductivity will be given by a δ function at zero frequency broadened to a Drude form by disorder and electron-phonon interactions if the spectral function is of the δ -function form, Eq. (31a), i.e., for the case of electrons in an almost empty band. On the other hand, as the band becomes full and the single-electron spectral function develops incoherent contributions we expect the frequency-dependent

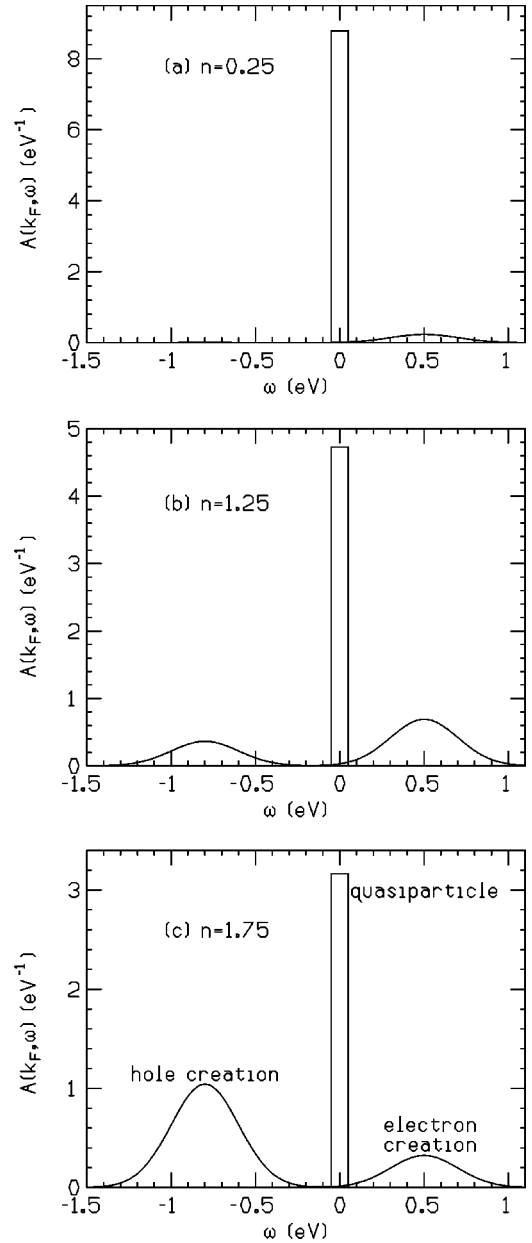


FIG. 10. Dependence of the phenomenological one-electron spectral function on band filling, for \vec{k} the Fermi wave vector. Parameters used in Eqs. (43) and (46)–(51) are: $S_1=0.5$, $\epsilon_1=0.8$, $\Gamma_1=0.2$, $\epsilon_2=0.5$, $\Gamma_2=0.2$, $\alpha=0.5$. The zero-frequency δ function is drawn with width $\Delta\omega=0.1$, so that $A(k_F, \omega=0)=10 \text{ eV}^{-1}$ is the maximum height (for $z=1$). As the band is filled with electrons (increasing n), the quasiparticle weight $z(n)$ decreases and incoherent contributions appear, first at positive energies (electron creation in the singly occupied atom) and at higher n at negative energies (electron destruction in the doubly occupied atom). Electron creation in the empty atom and electron destruction in the singly occupied atom give no incoherent contributions.

conductivity to develop high-frequency contributions reflecting incoherent absorption processes where the atoms i and/or j end up in excited states when an electron absorbs a photon and jumps from atom i to atom j . A convenient form for the frequency-dependent conductivity that reflects this physics is

given by the form derived within dynamical mean field theory²¹

$$\sigma_1(\omega) = \pi e^2 \int_{-\infty}^{\infty} d\epsilon \int_{-\infty}^{\infty} d\omega' \rho(\epsilon) A(\epsilon, \omega') A(\epsilon, \omega + \omega') \times \frac{f(\omega) - f(\omega + \omega')}{\omega}. \quad (52)$$

Here, $f(\omega)$ is the Fermi function and $A(\epsilon_k, \omega)$ is the single-electron spectral function. $\rho(\epsilon)$ is the electronic density of states for the quasiparticle band. Equation (52) is exact in the limit of infinite dimensions, and is believed to be a reasonable approximation for finite dimensions.

We evaluate Eq. (52) for the phenomenological spectral function given by Eqs. (46) and (51). For the quasiparticle band density of states we choose for simplicity a triangular form

$$\begin{aligned} \rho(\epsilon) &= \frac{2}{D} \left(1 + \frac{\epsilon}{D/2} \right); & -\frac{D}{2} < \epsilon < 0 \\ &= \frac{2}{D} \left(1 - \frac{\epsilon}{D/2} \right); & 0 < \epsilon < \frac{D}{2} \end{aligned} \quad (53)$$

with bandwidth $D = z(n)D_0$, and D_0 the 'bare' bandwidth for electrons in the almost empty band. The "effective bandwidth" D becomes progressively smaller as the band filling increases, corresponding to the progressive reduction in the quasiparticle hopping amplitude

$$t(n) = t_0 z(n) \quad (54)$$

with t_0 the hopping for the almost empty band. The Fermi energy is related to the band occupation by

$$\begin{aligned} \epsilon_F &= \frac{D}{2} (-1 + \sqrt{n}), & n \leq 1 \\ &= \frac{D}{2} (1 - \sqrt{2-n}), & n > 1 \end{aligned} \quad (55)$$

in this model. The frequency-dependent conductivity has three contributions

$$\sigma_1(\omega) = \sigma_1^1(\omega) + \sigma_1^2(\omega) + \sigma_1^3(\omega). \quad (56)$$

At zero temperature, they are given by

$$\sigma_1^1(\omega) = \pi e^2 z^2(n) \rho(\epsilon_F) \frac{1}{\pi} \frac{\Gamma}{\omega^2 + \Gamma^2}, \quad (57a)$$

$$\begin{aligned} \sigma_1^2(\omega) &= \frac{\pi e^2 z(n)}{\omega} \int_{-\omega}^0 [A'(\omega + \omega') \rho(\epsilon_F + \omega') \\ &+ A'(\omega') \rho(\epsilon_F + \omega + \omega')], \end{aligned} \quad (57b)$$

$$\sigma_1^3(\omega) = \frac{\pi e^2}{\omega} \int_{-\omega}^0 d\omega' A'(\omega') A'(\omega + \omega'). \quad (57c)$$

In Eq. (57a), we have replaced the $\omega=0$ δ function by a Drude-like lorentzian with relaxation time $\tau = 1/\Gamma$ as would be expected in the presence of impurities or electron-phonon scattering.

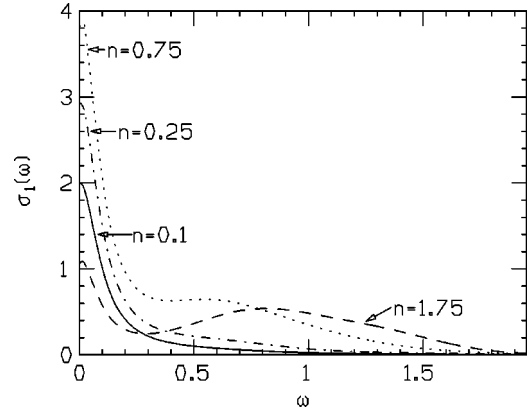


FIG. 11. Frequency-dependent conductivity $\sigma_1(\omega)$, Eq. (52), for the parameters of the single-electron spectral function used in Fig. 10. As the band filling n increases, spectral weight shifts from the low-frequency Drude part to the high-frequency incoherent part. The zero-frequency conductivity is high for electrons (small n) and low for holes (large n).

The physical content of the different contributions to $\sigma_1(\omega)$ is as follows. σ_1^1 describes the intraband optical absorption of the quasiparticles, where the atoms remain in their ground state when the electron hops, and in particular gives the zero-frequency conductivity. Note that it is proportional to $z(n) = 1/m^*$ as expected in the Drude model (one of the powers of $z(n)$ is canceled by the density of states factor). σ_1^2 has two contributions; the first term has a nonzero contribution from the incoherent part of the spectral function at positive frequencies: it corresponds to processes where an electron hops to a singly occupied site, and the resulting doubly occupied atom ends up in an excited state, while the atom where the electron hopped from (initially doubly or singly occupied) remains in the ground state; similarly, the second term in σ_1^2 has a nonzero contribution from the incoherent part of the spectral function at negative frequencies, corresponding to processes where an electron hops from a doubly occupied site and the resulting singly occupied atom ends up in an excited state, while the atom the electron hops to (either singly or unoccupied initially) ends up in the ground state. Finally, σ_1^3 describes processes where an electron hops from a doubly occupied site to a singly occupied site and the atoms at both sites end up in excited final states.

Figure 11 shows the obtained frequency-dependent conductivity for one set of parameters using the phenomenological spectral function discussed in the previous subsection. For low band filling, with the spectral function dominated by the quasiparticle part, the optical conductivity is largely given by the intraband Drude part, and the zero-frequency conductivity is high. In other words, the system is a "good metal," with small resistivity. As the band filling increases, the intraband conductivity first increases as the number of electrons increases, however, at the same time some of the increased absorption occurs at higher frequency due to the incoherent part of the spectral function. At even higher band filling where the intraband conductivity becomes holelike, the Drude part becomes much smaller as does the zero-frequency conductivity; at the same time, a large incoherent

contribution to the conductivity develops; the spectral weight of the incoherent part arises from the reduced intraband contribution due to the reduced quasiparticle weight. The system is now a “bad metal,” with high resistivity and largely incoherent optical absorption.

It should be pointed out that our calculated conductivity certainly does not satisfy the “global” conductivity sum rule¹⁸

$$\int_0^\infty d\omega \sigma_1(\omega) = \frac{\pi e^2 n}{2m}, \quad (58)$$

which states that the total conductivity spectral weight should increase with the number of electrons in the system (m is the bare electron mass). This is because our model does not take into account most interband transitions, and because it does not allow for absorption processes where the atomic final state contains three electrons. Nevertheless, the model correctly describes the transfer of optical spectral weight from intraband to higher-frequency incoherent absorption as the bandfilling progressively increases.

C. dc conduction

As a consequence of this physics, it is clear that the process of electrical conduction in a hole metal is intrinsically more complicated than that in an electron metal. When a hole hops from a site to a neighboring site, there is a finite probability amplitude for the atoms to end up in excited states rather than the ground state. That is what gives rise to the reduced dc conductivity as expressed by the enhanced effective mass in the Drude formula. Thus the conduction cannot be described as an entirely coherent process, as in the case of electrons, where the phase of the wave function is well defined over a mean free path. In the case of the hole, only the part of the conduction associated with the quasiparticle part of the spectral function can be described as coherent. When the quasiparticle weight is small, the transport of current is largely incoherent.

It is of course true that in a perfect translationally invariant crystal the many-body eigenstates are also eigenstates of the crystal momentum operator,²⁰ and one might argue that such a state with finite \vec{k} could carry current without dissipation. However, any imperfections in the crystal would make such arguments invalid, unless the system goes into the superconducting state and acquires rigidity.

One may expect new physical phenomena associated with this incoherent transport. If an atom ends up in an excited state after the hole hops, it amounts to creating an electronic excitation in the system, just as the electron-phonon interaction can give rise to creation of a phonon. In the electron-phonon case this phonon emission gives rise to Joule heating that dissipates part of the energy supplied to the system by the external potential. Similarly, here the electronic excitation should decay through *photon* emission, with the photon frequency determined by the electronic excitation energies involved. Because of conservation of energy it is clear that such photon emission cannot occur in every single hopping process for the moderate voltages applied. However, one

would expect emission of nonthermal high-frequency radiation at locations in the solid where translational symmetry is broken, i.e., impurities and boundaries. In particular, electroluminescence²² (at visible and infrared frequencies) would be expected to occur in this picture at the sample-*positive* electrode boundary, where holes are injected into the hole-metal sample. The effect should be the strongest in samples where the holes are highly dressed in the normal state, i.e., where the band is close to full and the ionic charge Z is small. Such systems should also give rise to high- T_c superconductivity, as discussed in the following section. When the system goes superconducting transport becomes coherent and the photon emission should disappear.

Furthermore, the physics of hole conduction discussed here suggests that the contact resistance between an electron-metal electrode and a highly dressed hole-metal sample should be nonsymmetric. When an electron is injected into the hole metal it needs to excite the other electron in the orbital, while when an electron is removed from the hole metal the remaining electron relaxes to a lower energy state. Hence electron injection into the hole metal should offer more resistance than electron removal, giving rise to a rectifying contact where the resistivity is lower at the positive electrode-hole metal contact.

VI. HOLE SUPERCONDUCTIVITY

The physics discussed earlier leads to a mechanism for superconductivity.⁹⁻¹¹ Consider the low-energy effective Hamiltonian for quasiparticles, Eq. (44): the hopping amplitude for a quasiparticle depends on the occupation of the sites involved in the hopping process. For zero, one, and two other electrons in these sites, the hopping amplitude for an electron is respectively

$$t_{ij}^0 = t_{ij}, \quad (59a)$$

$$t_{ij}^1 = S_1 t_{ij}, \quad (59b)$$

$$t_{ij}^2 = S_1^2 t_{ij} \equiv \tilde{t}_{ij} \quad (59c)$$

becoming progressively smaller as the occupation increases, due to the progressive reduction in quasiparticle weight. It is convenient to rewrite the quasiparticle kinetic energy in terms of hole rather than electron operators through a particle-hole transformation (that does not change the physics). The quasihole Hamiltonian is then

$$H_{qh} = - \sum_{i,j,\sigma} [\tilde{t}_{ij} + \Delta t_{ij}(\tilde{n}_{i,-\sigma} + \tilde{n}_{j,-\sigma})] \tilde{c}_{i\sigma}^\dagger \tilde{c}_{j\sigma} + \sum_{i,j} U_{ij} \tilde{n}_i \tilde{n}_j, \quad (60a)$$

$$\Delta t_{ij} = t_{ij}^1 - t_{ij}^2 = \left(\frac{1}{S_1} - 1 \right) \tilde{t}_{ij} \equiv Y \tilde{t}_{ij}. \quad (60b)$$

Here, the operators are hole rather than electron operators. We have also added a term describing density-density Coulomb repulsion between holes U_{ij} , of which the largest will be the onsite repulsion $U \equiv U_{ii}$. Furthermore, we have omitted the term describing hopping of a hole in the presence of

two other holes, which should be negligible for low hole density due to Coulomb repulsion.

Superconductivity will occur for this model Hamiltonian in the regime of low hole density (band almost full) for a range of parameters, driven by lowering of kinetic energy when hole carriers pair.^{9,10} For simplicity, we now restrict ourselves to the case of nearest-neighbor hopping and interactions only. The hole quasiparticle Hamiltonian is

$$H = - \sum_{\langle ij \rangle, \sigma} [t + \Delta t(n_{i, -\sigma} + n_{j, -\sigma})] (c_{i\sigma}^\dagger c_{j\sigma} + \text{H.c.}) + U \sum_i n_{i\uparrow} n_{i\downarrow} + V \sum_{\langle ij \rangle} n_i n_j. \quad (61)$$

We have omitted the “tilde” on the hole quasiparticle operators. This “correlated hopping” Hamiltonian has been extensively studied in recent years by approximate and exact techniques, and the reader is referred to the references for detailed information.^{9,23–32} The condition for superconductivity in the limit of low hole concentration is³²

$$K > \sqrt{(1+u)(1+w)} - 1, \quad (62)$$

where $K = 2z\Delta t/D$, $u = U/D$, $w = zV/D$, with z the number of nearest neighbors to a site and D the (renormalized) bandwidth. Within BCS theory the same condition is found, with $1/D$ replaced by $g(\epsilon_F)$, the density of states at the Fermi energy, in the definition of the parameters in Eq. (62).⁹ The reader is referred to the literature for discussion of the particular features of the superconducting state (e.g., energy-dependent gap function) and for results for various observables (e.g., density and pressure dependence of T_c , thermodynamics, tunneling, nuclear magnetic resonance, disorder effects, etc.) that can be understood from this low-energy effective Hamiltonian.^{9,10}

Here we wish to focus the discussion on the fundamental aspect of the physics related to the high-energy degrees of freedom that are not contained in the low-energy quasiparticle Hamiltonian.^{33,11} The key to superconductivity lies in the relation between the relative weights of the coherent and incoherent parts of the spectral function discussed in Sec. III and the site occupation, or the band filling. As we have seen, as the electronic site occupation increases the spectral function becomes more incoherent. Consider the Cooper pair wave function for a hole pair in the full band,

$$\Psi = \frac{1}{\sqrt{N}} \sum_{i,j} f_{ij} c_{i\uparrow}^\dagger c_{i\downarrow}^\dagger |0\rangle, \quad (63)$$

where $|0\rangle$ is the full band, and $c_{i\sigma}^\dagger$ is a hole creation operator. In the limit where the size of the Cooper pair (i.e., the superconducting coherence length) goes to infinity the holes become uncorrelated and $f_{ij} \sim 1/\sqrt{N}$ (N denotes number of sites in the system). For short coherence length instead, $f_{ij} \sim O(1)$ for $|i-j|$ small. In particular, the amplitude for the holes to be on the same site or on neighboring sites becomes of order unity rather than being negligible. Thus, the spectral function for a hole in such a state will have a larger coherent part and a smaller incoherent part than the spectral function

of a hole that is not bound in a pair. In other words, holes “undress,” i.e., become more coherent, when they pair.¹¹ Because electrons (quasiparticles when the band is almost empty) are more coherent than holes (quasiparticles when the band is almost full) we may also say that holes become more “like electrons” when they bind in a Cooper pair. Naturally, if pairing and superconductivity are associated with such quasiparticle “undressing,” it will occur when the quasiparticles in the normal state are holelike (band close to full) and will not occur when they are electronlike (band close to empty).³⁴

Intimately related to the increased coherence of the hole bound in a Cooper pair is the fact that the hole has an increased hopping amplitude when it hops to or from a site where there is another hole, due to its increased quasiparticle weight. When a hole forms a Cooper pair the probability for another hole to be nearby increases, and the increased hopping amplitude that occurs on the average gives rise to a lowering of the hole kinetic energy upon pairing, which provides the binding energy of the Cooper pair if it can overcome the increased cost in ordinary Coulomb energy arising from the decreased distance between like charges.³⁵

Finally, consider the process of optical absorption when the band is almost full. An incident photon causes an electron to hop from a site to a neighboring site. If the electron is part of a hole Cooper pair, it is far more likely to hop to or from a site that is *not occupied* by another electron, than if it is uncorrelated. If the electron hops to or from an unoccupied site, it has a larger contribution from the coherent part of the spectral function and hence gives a larger contribution to the “intra-band” part of σ_1 rather than to the high-frequency incoherent part. Hence, optical spectral weight will shift from the high-frequency incoherent part of the spectrum to the low-frequency Drude part when pairing occurs. Because in the superconducting state the lowest-frequency part of the Drude absorption (below twice the energy gap Δ) collapses into the zero-frequency δ function that determines the penetration depth, the δ function acquires an “anomalous” extra contribution transferred from the high-energy incoherent optical absorption spectrum rather than from the frequency region below 2Δ , and an “apparent violation” of the conductivity sum rule results.³⁵

In summary, the superconducting transition driven by the physics of electron-hole asymmetry discussed here has associated with it these anomalous spectral weight transfers in one- and two-particle (optical conductivity) spectral functions, caused by the dependence of the single-particle spectral function on site occupation discussed in Sec. III, *together with the fact that the site occupation changes when pairing occurs*. The spectral weight is transferred from an energy range that is not related to the magnitude of the superconducting energy gap Δ , rather it is related to the much larger energy scale of intra-atomic electronic excitations. To study quantitatively these spectral weight transfer processes, it is useful to consider model Hamiltonians as discussed in the following section.

VII. MODEL HAMILTONIANS

To go beyond the phenomenological model discussed in the previous section it is useful to construct model Hamilto-

nians that contain the physics of interest, that are amenable to theoretical studies by various techniques. We consider here three classes of model Hamiltonians.

A. Hamiltonians with auxiliary oscillator degrees of freedom

A variety of generalizations of the commonly used Holstein model describing coupling of a local boson (usually phonon) degree of freedom to the local electronic charge density can be constructed to contain the essential physics discussed here.⁷ As the simplest example, consider an electronic model with a single orbital per site and a local boson degree of freedom, with site Hamiltonian

$$H_i = \frac{p_i^2}{2M} + \frac{1}{2}Kq_i^2 + (U + \alpha q_i)n_{i\uparrow}n_{i\downarrow} \quad (64)$$

describing the coupling of a local oscillator q_i of frequency $\omega_0 = \sqrt{K/M}$ to the atomic *double occupancy*. Completing the squares yields

$$H_i = \frac{p_i^2}{2M} + \frac{1}{2}K \left(q_i + \frac{\alpha}{K} n_{i\uparrow}n_{i\downarrow} \right)^2 + U_{eff} n_{i\uparrow}n_{i\downarrow}, \quad (65a)$$

$$U_{eff} = U - \frac{\alpha^2}{2K} \equiv U - \omega_0 g^2 \quad (65b)$$

so the equilibrium position of the oscillator is $q=0$ for the empty and singly occupied site, and $q = -\alpha/K$ for the doubly occupied site. The reduction from U to U_{eff} due to the change in the oscillator equilibrium position parallels the reduction from U to U_{eff} in the atomic problem due to the modification of the electronic wave function in the doubly occupied atom by correlations.

The states of the site can be written as direct product of the electronic state in occupation number representation and the boson state. We denote by $|n^l\rangle$ the l th excited state of the oscillator when there are n electrons at the site ($n=0, 1$ or 2), and $|n^0\rangle \equiv |n\rangle$ the ground state. The site ground states are then $|0\rangle|0\rangle, |\uparrow\rangle|1\rangle, |\downarrow\rangle|1\rangle, |\uparrow\downarrow\rangle|2\rangle$. Because the oscillator is not affected by single occupancy, $|0^l\rangle = |1^l\rangle$. The matrix elements S_l defined in Eq. (13c) and excitation energies Eq. (13b) are given by

$$S_{l+1} = \langle 1^l | 2 \rangle = \frac{e^{-g^2/2} g^l}{(l!)^{1/2}}, \quad (66a)$$

$$E_l^1 = \omega_0 l \quad (66b)$$

and the spectral function for hole creation in the doubly occupied site $A_h(\omega)$ has the form given by Eq. (14), with quasiparticle weight

$$z = S_1^2 = e^{-g^2}. \quad (67)$$

The spectral functions for electron creation in the empty site and electron destruction in the singly occupied site A_{el} and A'_{el} are single δ functions, as in the case of the atom, because the oscillator is not affected by single occupancy. Finally, the

spectral function for hole destruction (electron creation) in the singly occupied site $A'_h(\omega)$ is a sum of δ functions like Eq. (21), with

$$S'_l = (-1)^l S_l, \quad (68a)$$

$$E_l^2 = E_l^1. \quad (68b)$$

In an atom, the energy level spacing is proportional to Z^2 , with Z the nuclear charge. If we assume similarly

$$\omega_0 = cZ^2, \quad (69a)$$

and we also assume

$$g^2 = \frac{c'}{Z^2}, \quad (69b)$$

(c, c' constants) then the reduction from U to U_{eff} in Eq. (65b) is independent of Z , which is what is found in real atoms.¹ Furthermore, as Z decreases g increases and the quasiparticle weight Eq. (67) will decrease, similarly as found in the atomic problem in Sec. III. For the solid we take then as model Hamiltonian

$$H = - \sum_{ij} t_{ij} c_{i\sigma}^\dagger c_{j\sigma} + \sum_i H_i \quad (70)$$

and argue that this model Hamiltonian describes the same physics as the real solid discussed earlier. In particular, the low-energy effective Hamiltonian is of the same form as Eq. (44), and the same processes of spectral weight transfer discussed earlier will occur here. Quasiparticle operators are easily defined using a generalized Lang-Firsov transformation.^{11,33}

This Hamiltonian can be studied by standard theoretical techniques. Some initial studies have already been performed.^{11,8} Further studies with nonperturbative techniques such as dynamical mean field theory^{21,36} and numerical methods such as density-matrix renormalization group³⁷ should be able to determine quantitatively the parameter regime where superconductivity occurs in this model, as well as provide substantial insights into the physics of electron-hole asymmetry and spectral weight transfer under discussion here.

It should be pointed out, however, that there is a difference between this Hamiltonian and the atomic case previously discussed. Namely, both the excitation spectrum and matrix elements here are the same for hole destruction in the doubly occupied site and electron creation in the singly occupied site, unlike the case of the real atom. However, we do not believe that this difference will qualitatively change the physics.

It is also possible to extend the Hamiltonian, Eq. (64), so that it will also describe dressing of electrons in singly occupied sites,⁷ by including coupling to the electronic charge density as in the ordinary Holstein model. As long as the coupling to double occupancy is nonzero, or through other terms that break electron-hole symmetry such as anharmonicity,⁷ the essential physics of interest here, that as the band filling increases the coupling strength and hence the

dressings of the quasiparticle increases, will be contained in the Hamiltonian. Such a generalized Holstein model would be useful if one is interested in describing the smaller dressing effects of the first electron in a shell due to coupling to electrons in inner shells.

B. Electronic Hamiltonian

An electronic Hamiltonian without auxiliary degrees of freedom that contains the physics of electron-hole asymmetry and undressing under consideration here needs to have at least two orbitals per site. A simple such Hamiltonian for the site is⁶

$$H_i = U n_{i\uparrow} n_{i\downarrow} + U' n'_{i\uparrow} n'_{i\downarrow} + V n_i n'_i + \epsilon n'_i - t' \sum_{\sigma} (c_{i\sigma}^{\dagger} c'_{i\sigma} + \text{H.c.}), \quad (71)$$

where the primed (unprimed) orbitals refer to electrons in the upper (lower) energy orbital, assumed orthogonal to each other. (An alternative description would assume $t'=0$ and nonorthogonal orbitals). We assume all parameters in Eq. (71) positive, and the ordering

$$U' + 2\epsilon < V + \epsilon < U \quad (72a)$$

$$U, U', V \gg \epsilon \gg t'. \quad (72b)$$

These conditions ensure that a single electron resides primarily in the lower level and two electrons reside primarily in the upper level. Hence this Hamiltonian mimics the physics of the Hartree-Fock solution of the atomic problem discussed previously. The effective onsite repulsion defined by Eq. (7) is $U_{eff} = U' + 2\epsilon$ to lowest order in t' .

It is simple to diagonalize the site Hamiltonian exactly; however, for illustration purposes we restrict ourselves here to the lowest-order perturbation theory in t' . The ground states of the singly and doubly occupied sites, $|\sigma \gg\rangle$ and $|\uparrow\downarrow\rangle\rangle$ and their energies, are respectively

$$|\sigma \gg\rangle = |\sigma\rangle|0\rangle + \delta_1 |0\rangle|\sigma\rangle, \quad E = 0, \quad (73a)$$

$$|\uparrow\downarrow\rangle\rangle = |0\rangle|\uparrow\downarrow\rangle + \delta_2 \frac{|\uparrow\rangle|\downarrow\rangle + |\downarrow\rangle|\uparrow\rangle}{\sqrt{2}}, \quad E = U' + 2\epsilon, \quad (73b)$$

where the first ket refers to the lower and the second ket to the upper orbital, and

$$\delta_1 = \frac{t'}{\epsilon}, \quad (74a)$$

$$\delta_2 = \frac{\sqrt{2}t'}{V - U' - \epsilon}. \quad (74b)$$

The excited state of the singly occupied atom is

$$|\sigma^{(2)}\rangle\rangle = \delta_1 |\sigma\rangle|0\rangle - |0\rangle|\sigma\rangle, \quad E = \epsilon \quad (75)$$

and the excited states of the doubly occupied atom are

$$|\uparrow\downarrow^{(2)}\rangle\rangle = \frac{|\uparrow\rangle|\downarrow\rangle + |\downarrow\rangle|\uparrow\rangle}{\sqrt{2}} + \delta_3 |\uparrow\downarrow\rangle|0\rangle - \delta_2 |0\rangle|\uparrow\downarrow\rangle, \quad E = V + \epsilon, \quad (76a)$$

$$|\uparrow\downarrow^{(3)}\rangle\rangle = |\uparrow\rangle|\downarrow\rangle - |\downarrow\rangle|\uparrow\rangle\sqrt{2}, \quad E = V + \epsilon, \quad (76b)$$

$$|\uparrow\downarrow^{(4)}\rangle\rangle = |\uparrow\downarrow\rangle|0\rangle - \delta_3 |\uparrow\rangle|\downarrow\rangle + |\downarrow\rangle|\uparrow\rangle\sqrt{2}, \quad E = U, \quad (76c)$$

with $\delta_3 = \sqrt{2}t'/(U - V - \epsilon)$. The spectral functions to create an electron in the empty site and to destroy an electron in the singly occupied site are single δ functions, as in the atomic case. The ‘‘hole wave function’’ φ_{α} that maximizes the hole quasiparticle weight is given, to this order in t' , simply by the wave function of the upper state. The spectral function for hole creation in the doubly occupied atom is then of the general form Eq. (14)

$$A_h(\omega) = z \delta(\omega) + S_2^2 \delta(\omega + \epsilon), \quad (77a)$$

$$z = S_1^2 = \left(\delta_1 + \frac{\delta_2}{\sqrt{2}} \right)^2, \quad (77b)$$

$$S_2 = - \left(1 - \frac{\delta_1 \delta_2}{\sqrt{2}} \right) \quad (77c)$$

and the spectral function for destroying a hole in the singly occupied atom, i.e., creating an electron, is

$$A_h'(\omega) = z \delta(\omega) + [(S_2')^2 + (S_3')^2] \delta(\omega - (V - U' - \epsilon)) + (S_4')^2 \delta(\omega - (U - U' - 2\epsilon)), \quad (78a)$$

$$S_2' = \frac{1}{\sqrt{2}} - \delta_1 \delta_2, \quad (78b)$$

$$S_3' = \frac{1}{\sqrt{2}}, \quad (78c)$$

$$S_4' = -\frac{\delta_3}{\sqrt{2}}. \quad (78d)$$

Hence the site spectral functions are of the same form as in the atomic problem discussed previously. The ‘‘quasiparticle operators’’ are then $c_{i\sigma}$ or $c'_{i\sigma}$ depending on whether the site is singly or doubly occupied. We may take as lattice Hamiltonian

$$H = - \sum_{ij} t_{ij} [c_{i\sigma}^{\dagger} c_{j\sigma} + c'_{i\sigma} c'_{j\sigma} + (c'_{i\sigma})^{\dagger} c_{j\sigma} + (c_{i\sigma})^{\dagger} c'_{j\sigma}] + \sum_i H_i, \quad (79)$$

where we have assumed for simplicity the same hopping amplitude for the unprimed and primed orbitals. Projection of the Hamiltonian Eq. (79) to the lowest site energy states yields a low-energy effective Hamiltonian of the form Eq. (44), which will give rise to superconductivity in certain pa-

parameter ranges. Furthermore, the spectral weight transfer processes discussed previously should occur for this Hamiltonian. Because it has a relatively small number of states per site this Hamiltonian should be amenable to study particularly by exact diagonalization methods. Parameters in this Hamiltonian can be related fairly directly to realistic parameters obtained from quantum chemical calculations of real atoms.

C. Hamiltonians with auxiliary spin degrees of freedom

The physics of interest here was first studied in the context of an electronic Hamiltonian with an auxiliary spin 1/2 degree of freedom^{5,38} to represent the other electron(s) in the atom, with site Hamiltonian

$$H_i = [V(n_{i\uparrow} + n_{i\downarrow}) - \omega_0]\sigma_z^i + \Delta\sigma_x^i + Un_{i\uparrow}n_{i\downarrow} \quad (80)$$

with $V > \omega_0$ and $\Delta \ll \omega_0, V$, and all parameters positive. For such parameters, the auxiliary spin in the ground state will point predominantly up if $n_{i\uparrow} = n_{i\downarrow} = 0$ and down otherwise. That situation describes then a *hole* Hamiltonian, where the first hole causes a large disruption in the “background” degree of freedom (the spin) and the second a small one. We can, however, also use this Hamiltonian with the operators representing *electrons* if we choose the parameter range $V < \omega_0 < 2V$ instead, so that the first electron will not change the state of the spin and the second one will. The lattice Hamiltonian

$$H = - \sum_{ij} t_{ij} c_{i\sigma}^\dagger c_{j\sigma} + \sum_i H_i \quad (81)$$

also has as low-energy effective Hamiltonian the generic form Eq. (44) that gives rise to correlated hopping.³⁹ Exact diagonalization studies of this Hamiltonian on small clusters³⁸ show that it gives rise to pairing in a wide range of parameters. Furthermore, the optical conductivity was calculated in a simple case³³ and the results show the spectral weight transfer process discussed earlier, as one would expect.

The site spectral functions are also simple to calculate. There is a difference with the atomic case discussed previously in that the single-electron spectral function for the empty site is not a single δ function here because some modification of the background spin degree of freedom occurs even when the first electron is created at the site. Nevertheless, for the parameter range discussed the change in the state of the background is much larger for the second electron, hence the quasiparticle weight is much smaller for a hole than for an electron and the same qualitative physics of electron-hole asymmetry and undressing occurs. Here again, this Hamiltonian should be amenable to detailed study by exact diagonalization.

Finally, a site Hamiltonian analogous to the oscillator Hamiltonian, Eq. (64), can also be constructed with auxiliary spin degrees of freedom,

$$H_i = [Vn_{i\uparrow}n_{i\downarrow} - \omega_0]\sigma_z^i + \Delta\sigma_x^i + Un_{i\uparrow}n_{i\downarrow}, \quad (82)$$

which will contain the physics of interest here for $V > \omega_0$. This Hamiltonian does not “dress” the single electron as Eq. (80) does. A two-parameter version that resembles closely the oscillator Hamiltonian would be

$$H_i = \omega_0\sigma_z^i + g\omega_0[1 - 2n_{i\uparrow}n_{i\downarrow}]\sigma_x^i + Un_{i\uparrow}n_{i\downarrow}, \quad (83)$$

which is analogous to the oscillator Hamiltonian, Eq. (64), which in terms of boson creation and annihilation operators reads

$$H_i = \omega_0 a_i^\dagger a_i + [U + g\omega_0(a_i^\dagger + a_i)]n_{i\uparrow}n_{i\downarrow}. \quad (84)$$

For large g , the Hamiltonians, Eqs. (83) and (84), give rise to small quasiparticle weight for the hole.

In summary, a large variety of model Hamiltonians can be constructed that contain the essential physics of interest here, and we discussed some particular simple examples. Study of these Hamiltonians should yield interesting insights and clarify the physics further. However, this physics will only exist for certain parameters in the models, and not for others. In particular, the models need to break electron-hole symmetry. Instead, if one takes for example the spin Hamiltonian, Eq. (80), with $V = \omega_0$, or the Holstein Hamiltonian with only coupling to the local charge density, the physics of interest is lost because the models in those cases are electron-hole symmetric.

VIII. DISCUSSION

In this paper we have addressed the microscopic reasons for why holes are not like electrons in condensed matter. We have shown that there are qualitative differences between electrons and holes in atoms that have fundamental consequences for the physics of the solid state. We have proposed that the essential physical difference relates to the relation between the coherent (quasiparticle part) and incoherent parts of the one-electron spectral function, and the electron versus hole character of the quasiparticle. Namely, we have argued that, reflecting the physics at the atomic level, as the filling of a band increases the quasiparticle becomes progressively less coherent while at the same time the character of the quasiparticle changes from electronlike to holelike. Furthermore, the effective mass of the quasiparticle is inversely proportional to the degree of coherence (quasiparticle weight) and hence increases as the band filling increases.

This physics naturally leads to a mechanism of superconductivity, since (1) superconductivity involves pairing of quasiparticles, and (2) when hole quasiparticles pair, the *local density of electrons decreases*. Hence, as holes bind in a Cooper pair they become more coherent, and more mobile, and more like electrons, and the superconducting state is stabilized by the accompanying lowering of kinetic energy. As a result the superconducting state is more coherent than the normal state, and spectral weight at low energies in one- and two-particle spectral functions increases while incoherent spectral weight at high energies decreases. In other words, quasiparticles “undress” when they pair.¹¹

The informed reader may wonder about the relation between the parameters in the low-energy effective Hamil-

tonian, Eq. (44), and the ones calculated in our earlier work on hopping amplitudes in the diatomic molecule.¹⁹ For example, Eq. (44) implies that $t_2/t_1 = t_1/t_0$, with t_i the hopping amplitude for an electron when there are i other electrons at the two sites involved in the hopping process. In fact, the results found in Ref. 19 do not generally obey this relation. The answer is, the calculation in Ref. 19 is certainly expected to be more accurate. However, the derivation here reflects the essential physics in a clearer way and allows one to discuss the fundamental processes of spectral weight transfer. The two calculations are of course intimately related, in particular recall that in the calculations in Ref. 19 the difference in hopping amplitudes went to zero as the atomic charge became large or if one artificially constrained the atomic orbitals to not change with occupation, in agreement with the physics discussed here.

One may argue that the difference between electrons and holes discussed here is strictly speaking only a *qualitative* difference for the lowest $1s$ band. For higher bands, even a single electron in an empty band will be partially dressed from interactions with electrons in lower bands (not to mention electron-phonon interactions). While this is true, the considerations in this paper certainly imply that within a given band

$$z(n) > z(2-n) \quad (85)$$

for $n \leq 1$, that is, the hole at band filling $(2-n)$ is always more dressed than its counterpart electron at band filling n . Hence, the mechanism of superconductivity whereby holes in a band pair to “undress” and become more like the electrons in that band should still be operative.

There is in fact another qualitative difference between electrons and holes in energy bands, i.e., between electrons at the bottom and electrons at the top of the band. Namely, the wave function for the quasiparticle at the bottom of the band has a large amplitude in the region between the atoms, thus providing stability to the lattice (bonding state). Instead, the wave function for the quasiparticle at the top of the band has vanishing amplitude in the region between the atoms, as it has highest energy and is orthogonal to all the band states below it (antibonding state). Correspondingly, the amplitude of the wave function at the atoms is larger for electrons at the top than for electrons at the bottom of the band, and as a consequence the dressing due to intraatomic Coulomb repulsion also from electrons in other atomic orbitals is larger for electrons at the top of the band.

The phase space of model Hamiltonians that can be written down and studied as possible models for condensed matter phenomena is infinite. What makes some models more suitable to describe real materials than others? We propose that a useful criterion to validate one Hamiltonian over another is whether it can be derived from a more fundamental Hamiltonian that describes physics on a larger energy scale. In particular, the low-energy Hamiltonian, Eq. (44) [or Eq. (61)], describes an *increase* in low-energy spectral weight when carriers pair.³⁵ By itself, it does not contain the high-energy degrees of freedom where that spectral weight is coming from. However, it can be derived from a more fundamental Hamiltonian (e.g., the models discussed in Sec.

VII) that does contain the high-energy degrees of freedom where the spectral weight comes from. In contrast, the attractive Hubbard model, for example, can also describe pairing of carriers, and it describes an associated *decrease* in low-energy spectral weight (because the effective mass increases upon pairing); however, it is not clear that it is possible to derive an attractive Hubbard model from a more general Hamiltonian that would describe a corresponding *increase* in high-energy spectral weight.

As we have discussed, there are a variety of models that one can study that contain the physics of interest here. Thus, the issue is not the validity of a given model Hamiltonian, rather it is the validity of a very general paradigm. Namely, that the conventional description of energy bands in solids needs to be augmented, beyond the knowledge of the ϵ vs k relation and the quasiparticle wave function, to the description of the behavior of the coherent and incoherent parts of the one-particle spectral function as function of band filling, and that these quantities have the particular dependence on band filling discussed here.

The concepts discussed here are clearly not restricted to one particular class of solids but rather are generally applicable to all solids, just as the concept of energy bands is. Thus, it is unreasonable to expect that the mechanism of superconductivity that results from these concepts would apply to only one material or any one class of materials, or even that it would apply to most but not all superconducting materials. In a sense it is like superconductivity itself: the collective state is robust because it forms a coherent whole, and cannot be destroyed by local impurities or imperfections in a given solid. Similarly, the theory discussed here is a seamless web, that cannot be destroyed by individual examples that seemingly contradict it: it either applies to all superconductors or to none, and the apparent counterexamples (e.g., superconductors that seem to have only *electron* carriers in the normal state, or superconductors that exhibit seemingly incontrovertible evidence for an electron-phonon mechanism) will eventually be explainable within the same framework, if the framework is valid. So what is the evidence in favor of this framework?

Most importantly, there is significant empirical evidence that the presence of hole carriers favors superconductivity.³⁴ Moreover, the materials with highest T_c (high- T_c cuprates and MgB_2) have holes conducting through negative ion networks (O^{-2} and B^-), i.e., small ionic charge Z , which favors superconductivity within this framework. Moreover, the high T_c cuprates show clear evidence for “undressing,” both in the normal state as holes are added and at fixed hole concentration as the system becomes superconducting,^{40–45} as described (in fact *predicted*^{9,33}) by the present framework. Moreover, the dependence of T_c on doping in transition metal intermetallics⁴⁶ follows the behavior predicted by this framework.^{47,48} Moreover, the general empirical relation observed between superconductivity and lattice instabilities follows naturally from the fact that *antibonding* states need to be occupied in order to have hole carriers. Other experimental evidence in support of hole superconductivity is discussed in the references.^{9,10,35,49}

There are many open questions within the framework discussed in this paper. A convenient starting point for the discussion are the model Hamiltonians discussed in Sec. VII. First, are there other, similar or otherwise, model Hamiltonians that should be studied, possibly more appropriate than those? Next one can move from there in two opposite directions. In one direction, the study of the properties of these Hamiltonians by various theoretical techniques. In particular, dynamical mean field theory³⁶ is likely to be a very fruitful approach. One should calculate the most basic physical properties such as phase diagram, quasiparticle weight, spectral functions, and various correlation functions. How do the basic superconductivity parameters such as coherence length, superfluid weight, etc. depend on the Hamiltonian parameters? How do the various spectral weight transfer processes depend on the parameters? And in particular, which observable properties should be calculated that can differentiate this mechanism from others? In the opposite direction, one would like to connect the model Hamiltonians to real materials. What quantities should one evaluate in a first-principles calculation of a given solid that would be relevant to fix the parameters in the model Hamiltonians? Once that question is clarified a vast area of study will open up where any given existing or proposed material could be tested to see where its parameters lie, in particular concerning its superconducting properties.

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APPENDIX A: HYLLERAAS DRITTE NAHERUNG

For the convenience of the reader we summarize here the equations that determine the parameters in the Hylleraas wave function Eq. (5)². The energy (in Ry) is given by $E = Z^2\lambda$, with

$$\lambda = -\frac{L^2}{4NM}, \quad (\text{A1})$$

$$M = 8 + 50c_1 + 96c_2 + 128c_1^2 + 584c_1c_2 + 1920c_2^2, \quad (\text{A2a})$$

$$N = 4 + 35c_1 + 48c_2 + 96c_1^2 + 308c_1c_2 + 576c_2^2, \quad (\text{A2b})$$

$$L = 16 - \frac{5}{Z} + \left(120 - \frac{32}{Z}\right)c_1 + \left(192 - \frac{36}{Z}\right)c_2 + \left(288 - \frac{70}{Z}\right)c_1^2 + \left(1120 - \frac{192}{Z}\right)c_1c_2 + \left(2304 - \frac{312}{Z}\right)c_2^2. \quad (\text{A2c})$$

Minimization of λ yields the coefficients c_1 and c_2 in the wave function, and the orbital exponent k is given by

$$k = \frac{L}{2M}. \quad (\text{A3})$$

APPENDIX B: CALCULATION OF MATRIX ELEMENTS S_N IN THE VARIOUS APPROXIMATIONS

For the Hartree wave function we have for the overlaps Eq. (13c)

$$S_n^H = \int d^3r \varphi_{\bar{Z}} \varphi_n(r) = (\varphi_{\bar{Z}}, \varphi_n) \equiv S_n(Z, \bar{Z}). \quad (\text{B1})$$

These integrals are simply evaluated for the wave functions Eq. (26) and yield

$$S_n^H = \frac{4 \left(\frac{Z}{n}\right)^{3/2}}{\left(\bar{Z} + \frac{Z}{n}\right)^3} \sum_{l=0}^{n-1} (-1)^l (l+2)! a_l \frac{\left(\frac{Z}{n}\right)^l}{\left(\bar{Z} + \frac{Z}{n}\right)^l} \quad (\text{B2})$$

with a_l given by Eq. (26b).

For the Eckart wave function Eq. (4) we have simply

$$S_n^E = \frac{S_1(Z_1, \bar{Z}) S_n(Z_2, Z) + S_1(Z_2, \bar{Z}) S_n(Z_1, Z)}{[2(1 + S_1(Z_1, Z_2)^2)]^{1/2}}. \quad (\text{B3})$$

For the Hylleraas wave function, Eq. (6), we use the relation

$$\int d^3r_1 d^3r_2 F = 2\pi^2 \int_0^\infty ds \int_0^s du \int_0^u dt (s^2 - t^2) F \quad (\text{B4})$$

valid for any symmetric function $F(\vec{r}_1, \vec{r}_2)$, with s, t, u given by Eq. (6). The integrals needed are of the form

$$I(p, q, r, a, b) = \int_0^\infty ds \int_0^s du \int_0^u dt (s^2 - t^2) e^{-as} e^{-bt} s^p t^q u^r \quad (\text{B5})$$

and yield

$$I(p, q, r, a, b) = \frac{1}{b^{p+q+r+3}} \left\{ \sum_{j=0}^q \frac{q!}{(q-j)!} \times \left[\sum_{i=1}^{q+r+1-j} \frac{1}{\left(\frac{a}{b} + 1\right)^{p+i}} \frac{(p+i-1)!(q+r+1-j)!}{(i-1)!} - \frac{p!}{\left(\frac{a}{b} + 1\right)^{p+1} (q+r-j)!} \right] + \frac{q!(p+r+1)!}{(r+1) \left(\frac{a}{b}\right)^{p+r+2}} \right\} \quad (\text{B6})$$

and the overlaps are given by

$$\begin{aligned}
 S_n = & \frac{\pi}{(2Zk)^6} \frac{\left(\bar{Z}^3 \left(\frac{Z}{n}\right)^3\right)^{1/2}}{b^6} \sum_{l=0}^{n-1} (-1)^l \frac{a^l}{b^l} \frac{1}{(4kn)^l} \sum_{i=0}^l \frac{l!}{i!(l-i)!} \left([I(2+l-i, i, 1, a, b) - I(l-i, 2+i, 1, a, b,)] \right. \\
 & + (-1)^{i+l} \{I(2+l-i, i, 1, a, -b) - I(l-i, 2+i, 1, a, -b)\} + \frac{c_1}{b} [I(2+l-i, i, 2, a, b) - I(l-i, 2+i, 2, a, b,)] \\
 & - (-1)^{i+l} \{I(2+l-i, i, 2, a, -b) - I(l-i, 2+i, 2, a, -b)\} + \frac{c_2}{b^2} [I(2+l-i, 2+i, 1, a, b) - I(l-i, 4+i, 1, a, b,)] \\
 & \left. + (-1)^{i+l} \{I(2+l-i, 2+i, 1, a, -b) - I(l-i, 4+i, 1, a, -b)\} \right) \quad (B7)
 \end{aligned}$$

with

$$a = \frac{1 + \lambda_1 + \lambda_2}{2}, \quad (B8a)$$

$$b = \frac{\lambda_2 - \lambda_1}{2}, \quad (B8b)$$

$$\lambda_1 = \frac{\bar{Z}}{2Zk}, \quad (B8c)$$

$$\lambda_2 = \frac{1}{2kn}. \quad (B8d)$$

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