Dynamic Hubbard Model

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The Hubbard on-site repulsion U between opposite spin electrons on the same atomic orbital is widely regarded to be the most important source of electronic correlation in solids. Here we extend the Hubbard model to account for the fact that the experimentally measured atomic U is different from the one obtained by calculation of the atomic Coulomb integral. The resulting model describes quasiparticles that become increasingly dressed as the number of electrons in the band increases. Superconductivity can result in this model through quasiparticle undressing. Various signatures of this physics in spectroscopies in the normal and superconducting states are discussed. A novel effect in the normal state is predicted to be electroluminescence at the sample-positive counterelectrode boundary.

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The Coulomb repulsion integral for two electrons in a hydrogenic $1s$ orbital for a nucleus of charge Z is

$$U(Z) = \int d^3r\, d^3r' \,|\varphi_{1s}(r)|^2 \frac{e^2}{|r - r'|} |\varphi_{1s}(r')|^2 = \frac{5}{4} Z \times 13.606 \text{ eV}, \quad (1a)$$

$$\varphi_{1s}(r) = \left(\frac{Z^3}{\pi a_0^3}\right)^{1/2} e^{-Zr/a_0} \quad (1b)$$

(a_0 = Bohr radius). However, the effective atomic on-site repulsion $U_{\text{eff}}(Z)$ is obtained by considering the difference in energy between ions with a different number of electrons. For hydrogen ($Z = 1$) and helium ($Z = 2$) the experimental values are [1]

$$U_{\text{eff}}(1) = I - A = 12.86 \text{ eV} = U(1) - 4.15 \text{ eV}, \quad (2a)$$

$$U_{\text{eff}}(2) = I_{II} - I_I = 29.92 \text{ eV} = U(2) - 4.10 \text{ eV}. \quad (2b)$$

Here $I = 13.6$ eV, $A = 0.747$ eV, $I_I = 24.48$ eV, $I_{II} = 54.40$ eV are the ionization energy and electron affinity of H, and the first and second ionization energies of He. Remarkably, the difference between U_{eff} and U is nearly the same for $Z = 1$ and $Z = 2$. Indeed, the same is true for higher Z; for Z between 3 and 8 the difference between U and U_{eff} for the $1s$ atomic orbital, obtained from the appropriate ionization energies [1], is, respectively, in eV, 4.22, 4.22, 4.21, 4.19, 4.15, 4.05. We conclude that for $1s$ orbitals one has approximately

$$U_{\text{eff}}(Z) = U(Z) - 4.1 \text{ eV}, \quad (3)$$

for a large range of Z. A similar reduction from bare U to effective U will be found for other atomic orbitals. This reduction occurs because when the second electron is added to the singly occupied orbital the state of the two-electron system is not the doubly occupied single electron orbital. Rather, the orbital will "expand" to reduce the Coulomb repulsion between electrons, and furthermore the two electrons will develop angular correlations. This effect is, of course, well known in atomic physics, and in its simplest form is approximately described by Slater's rules for the shielding constants [2]: when another electron is added to an atom, the effective Z for the electrons in the same shell is reduced. This effect is, however, ignored in the ordinary Hubbard model [3].

A simple way to describe this physics is by introducing coupling to a fictitious local boson displacement coordinate q_i for atom i that modulates the Hubbard U:

$$U(q_i) = U + \alpha q_i \quad (4)$$

that will relax when double occupancy occurs. As the simplest model we describe the boson dynamics by a harmonic oscillator of frequency $\omega_0 = (K/M)^{1/2}$:

$$H_i = \frac{p_i^2}{2M} + \frac{1}{2} K q_i^2 + (U + \alpha q_i) n_{i\uparrow} n_{i\downarrow}, \quad (5)$$

and the effective on-site repulsion is found by completing the squares as $U_{\text{eff}} = U - \alpha^2/2K$. The equilibrium position of the boson is $q_i = 0$ for the orbital empty or singly occupied, and $q_i = -\alpha/K$ for the doubly occupied orbital.

The reader may argue that the ordinary Holstein model [4]

$$H_i = \frac{p_i^2}{2M} + \frac{1}{2} K q_i^2 + \alpha q_i (n_{i\uparrow} + n_{i\downarrow}) + U n_{i\uparrow} n_{i\downarrow} \quad (6)$$

will also describe a reduction of the bare U to a $U_{\text{eff}} = U - \alpha^2/K$. However, in contrast to Eq. (5), Eq. (6) also describes dressing of electrons in *singly* occupied orbitals by the boson degree of freedom. That is not the physics we are trying to describe here: without electron-phonon interactions or coupling to atomic electrons in other orbitals, the electron in the singly occupied orbital should be undressed.

In terms of boson creation and annihilation operators, the Hamiltonian Eq. (5) is

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$$H_i = \omega_0 a_i^\dagger a_i + [U + g\omega_0(a_i^\dagger + a_i)]n_{i\uparrow}n_{i\downarrow}, \quad (7a)$$

$$U_{\text{eff}} = U - w_0 g^2, \quad (7b)$$

with $g = \alpha/(2K\omega_0)^{1/2}$. The boson degree of freedom describes the electronic excitation of an electron when a second electron is added to the orbital. Hence the frequency ω_0 is related to the excitation energies of the atom, and we expect

$$\omega_0 = cZ^2 \quad (8a)$$

with c a constant of order eV, since the excitation energies in an atom scale with the square of the nuclear charge. From Eqs. (3) and (7b) we conclude

$$g^2 = \frac{c'}{Z^2} \quad (8b)$$

with $c' = 4.1$ eV$/c$. For a lattice system where an electron hops from site i to site j with hopping amplitude t_{ij} the Hamiltonian is then

$$H = -\sum_{ij,\sigma} t_{ij}(c_{i\sigma}^\dagger c_{j\sigma} + \text{H.c.}) + \sum_i [U + g\omega_0(a_i^\dagger + a_i)]n_{i\uparrow}n_{i\downarrow} + \sum_i \omega_0 a_i^\dagger a_i . \quad (9)$$

The physics described by Eq. (3), which led to the Hamiltonian Eq. (9), is a ubiquitous phenomenon, originating in the fact that the spacing between atomic energy levels is always smaller than the strength of the Coulomb repulsion between electrons in a given orbital. Its quantitative importance is determined by the magnitude of the ionic charge Z, as discussed below. Other models, with auxiliary spin degrees of freedom [5] or with only electronic degrees of freedom [6], can be constructed containing the same physics. The model Eq. (9) is a particular case of the generalized Holstein models discussed in Ref. [7].

By construction, the model Eq. (9) is not electron-hole symmetric, even if the band structure defined by t_{ij} is. In particular, a single electron in the empty band does not interact with the boson field at all. For a few electrons in an empty band the effect of the bosons is negligible if the bare Coulomb repulsion U is appreciable, as the probability of double occupancy will be small. In contrast, a single hole in the full band interacts most strongly with the boson field. Treating the four-fermion term in mean field, the electron-boson part of the Hamiltonian Eq. (9) is

$$H_{\text{el-b}} = g(n)\omega_0(a_i^\dagger + a_i)(n_{i\uparrow} + n_{i\downarrow}), \quad (10a)$$

$$g(n) = \frac{n}{2} g, \quad (10b)$$

that is, an ordinary electron-boson coupling with a coupling constant that increases monotonically with band filling. Hence, as the usual electron-phonon interaction, it will give rise to an effective mass enhancement and a quasiparticle weight reduction, which increase as the band filling and hence the effective coupling $g(n)$ increase. There are, however, other dynamical effects of Eq. (9) that are lost in the mean field treatment, Eq. (10).

To study Eq. (9) we perform a generalized Lang-Firsov transformation on the fermion and boson operators [7,8]

$$c_{i\sigma} = e^{g(a_i^\dagger - a_i)\tilde{n}_{i,-\sigma}}\tilde{c}_{i\sigma} \equiv X_{i\sigma}\tilde{c}_{i\sigma}, \quad (11a)$$

$$a_i = \tilde{a}_i - g\tilde{n}_{i\uparrow}\tilde{n}_{i\downarrow}, \quad (11b)$$

and the Hamiltonian Eq. (9) becomes

$$H = -\sum_{ij,\sigma} t_{ij}(X_{i\sigma}^\dagger X_{j\sigma}\tilde{c}_{i\sigma}^\dagger\tilde{c}_{j\sigma} + \text{H.c.}) + \sum_i U_{\text{eff}}\tilde{n}_{i\uparrow}\tilde{n}_{i\downarrow} + \sum_i \omega_0\tilde{a}_i^\dagger\tilde{a}_i, \quad (12)$$

with U_{eff} given by Eq. (7b). The ground state expectation value of the $X_{i\sigma}$ operator is

$$\langle X_{i\sigma}\rangle_0 = e^{-(g^2/2)\tilde{n}_{i,-\sigma}} = 1 + (S-1)\tilde{n}_{i,-\sigma}, \quad (13a)$$

$$S = e^{-g^2/2}. \quad (13b)$$

The part of the fermion operator Eq. (11a) associated with ground state to ground state transitions of the boson field is the coherent part of the operator, the quasiparticle. We have then

$$c_{i\sigma} = |0\rangle\langle 0|[1 + (S-1)\tilde{n}_{i,-\sigma}]\tilde{c}_{i\sigma} + c_{i\sigma}^{\text{incoh}}. \quad (14)$$

The incoherent part of the operator

$$c_{i\sigma}^{\text{incoh}} = \left[\tilde{n}_{i,-\sigma}\sum_{(l,l')\neq(0,0)}|l\rangle\langle l|e^{g(a_i^\dagger - a_i)}|l'\rangle\langle l'| + \sum_{l\neq 0}|l\rangle\langle l|\right]\tilde{c}_{i\sigma} \quad (15)$$

describes processes where the boson field makes transitions to and from excited states $|l\rangle, l \neq 0$, which take place only if $\tilde{n}_{i,-\sigma} = 1$, that is, if the orbital is occupied by another electron of opposite spin.

The quasiparticle weight in this model is, from Eq. (14),

$$z(n) = \left[1 + \frac{n}{2}(S-1)\right]^2 \quad (16)$$

and decreases monotonically with electronic band filling n, $0 \leq n \leq 2$, so that quasiparticles become increasingly dressed as the band filling increases. The factor S is the overlap matrix element of the oscillator ground states with and without site double occupancy [7], and S^2 gives the quasiparticle weight for a hole in the filled band [$n = 2$ in Eq. (16)]. According to Eq. (8b), as the ionic charge Z decreases, S decreases rapidly, implying that hole quasiparticles become increasingly incoherent.

We can estimate S from first principles for a hydrogenlike ion. In the Hartree approximation, S will be given by the overlap matrix element of the electron wave function in the presence and in the absence of another electron in the orbital:

$$S = |\langle \varphi_{1s} \,|\, \bar{\varphi}_{1s} \rangle| = \frac{(1 - \frac{5}{16Z})^{3/2}}{(1 - \frac{5}{32Z})^3} \tag{17}$$

with $\bar{\varphi}_{1s}$ the $1s$ orbital Eq. (1b) with Z replaced by $\bar{Z} = Z - 5/16$, as appropriate for the Hartree wave function. If we use the more accurate Eckart wave function [9,10] $\psi_{\rm Eck}$ for the two-electron ion, which incorporates radial correlations, we can estimate S from the square root of the overlap matrix element of the Eckhart wave function and the wave function of the two electrons in the $1s$ orbital, as

$$S = \sqrt{|\langle \varphi_{1s}\varphi_{1s} \,|\, \psi_{\rm Eck} \rangle|^2} = \sqrt{\frac{2f(Z,Z_1)f(Z,Z_2)}{2[1 + f(Z_1,Z_2)]^{1/2}}}\,, \tag{18a}$$

$$f(Z,Z') = \frac{(ZZ')^{3/2}}{(\frac{Z+Z'}{2})^3}\,. \tag{18b}$$

Here Z_1 and Z_2 are the two orbital exponents for the Eckart wave function obtained by minimization of the energy, which are found to be approximately $Z_1 = 1.14Z - 0.105$, $Z_2 = 0.905Z - 0.622$. The Eckart wave function becomes unstable for $Z < 0.93$.

Figure 1 shows the dependence of S on the ionic charge Z. We expect the Eckart wave function to underestimate and the Hartree wave function to overestimate the value of S for a given Z. Figure 1 also shows S for the dynamic Hubbard model, Eqs. (13b) and (8b), for a value of c' that matches the Eckart wave function results for large Z. While the three curves are different, the qualitative behavior is the same, showing a decrease of S as the ionic charge Z decreases, which describes the increased incoherence of single hole carriers in the system as the ionic charge decreases.

Upon replacement of the operator form Eq. (14) in the Hamiltonian Eq. (12), and ignoring the incoherent part of the operators, we obtain the effective Hamiltonian describing propagation of quasiparticles:

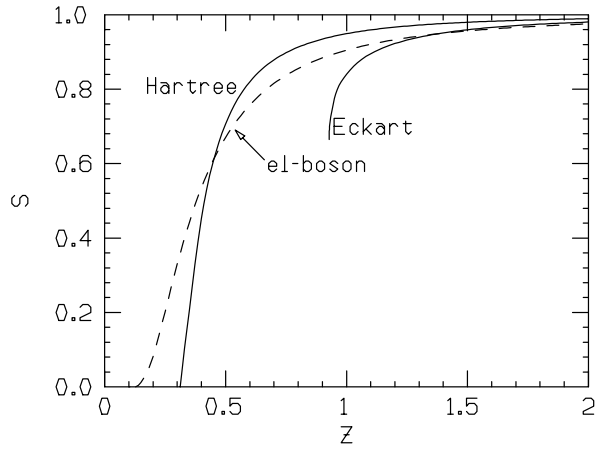

FIG. 1. Parameter S versus ionic charge Z in the Hartree and Eckart approximations, and in the electron-boson model with $c' = 0.2$ [Eqs. (8b) and (13b)]. The deviation of S from 1 indicates the degree of quasiparticle dressing for an almost full band.

$$H_{qp} = -\sum_{ij\sigma} \tilde{t}_{ij}^{\sigma} (\tilde{c}_{i\sigma}^{\dagger} \tilde{c}_{j\sigma} + \text{H.c.}) + \sum_i U_{\rm eff} \tilde{n}_{i\uparrow} \tilde{n}_{i\downarrow}\,, \tag{19a}$$

where the hopping amplitude now will depend on the occupation of the two sites involved in the hopping process:

$$\tilde{t}_{ij}^{\sigma} = t_{ij}[1 + (S-1)(\tilde{n}_{i,-\sigma} + \tilde{n}_{j,-\sigma}) + (S-1)^2 \tilde{n}_{i,-\sigma}\tilde{n}_{j,-\sigma}]. \tag{19b}$$

The effective quasiparticle Hamiltonian Eq. (19) will accurately describe the low energy physics of the full Hamiltonian Eq. (12) in the strong coupling regime, where the Lang-Firsov approximation to the Holstein model becomes accurate. Even in that regime, however, the high energy degrees of freedom described by the full Hamiltonian Eq. (12) still play an important role in ensuring that various sum rules that are violated by the low energy Hamiltonian Eq. (19a) are satisfied.

The hopping amplitude for an electron of spin σ when there are electrons of opposite spin at both sites i and j, i.e., $\tilde{n}_{i,-\sigma} = \tilde{n}_{j,-\sigma} = 1$ is, from Eq. (19b), $t_2 = S^2 t_{ij}$, and when there is one other electron at the two sites, i.e., $\tilde{n}_{i,-\sigma} + \tilde{n}_{j,-\sigma} = 1$, $t_1 = S t_{ij}$. If $S \ll 1$, then $t_2 \ll t_1$. In the limit where t_2 can be neglected with respect to t_1 it becomes obvious that the Hamiltonian Eq. (19) leads to pairing of two holes in a full band: a state where the two holes are separate describes essentially localized holes with zero energy, since $t_2 \sim 0$; a lower energy state results from a linear combination of states where the two holes are on the same or nearest neighbor sites, with energy of order $\epsilon_{\rm pair} \sim -2p \times t_1^2/U_{\rm eff}$ with p the number of nearest neighbors to a site. More generally, an exact criterion can be found for the parameters that will yield a bound state for two holes in a filled band described by the Hamiltonian Eq. (19) [11]:

$$\frac{U_{\rm eff}}{D} \leq 1 - S^2\,, \tag{20}$$

where D is the bare bandwidth of the band defined by t_{ij}. The same criterion is found for existence of superconductivity in the dilute carrier concentration regime in BCS theory [12], a regime where BCS theory is expected to be accurate, and quantitatively close results are obtained from exact diagonalization of small systems [13]. As the atomic charge Z decreases, the coupling g increases [Eq. (8b)], hence S decreases [Eq. (13b)], and furthermore $U_{\rm eff}$ decreases [Eqs. (3) and (1a)]. Both of these effects are in the right direction to satisfy the condition Eq. (20). Furthermore, if the interatomic distance is decreased, t_{ij} and the bare bandwidth D will increase, again in the direction of satisfying the inequality Eq. (20). We conclude that superconductivity induced by this physics will occur in systems where the ionic charge Z is small, the interatomic distances are small, and the Fermi level is close to the top of a band. The parameter regime where the Hamiltonian Eq. (9) yields superconductivity has not yet been established; however, numerical studies of the similar spin-1/2

Hamiltonian [5] have shown that pairing survives well beyond the parameter regime where the mapping to the effective Hamiltonian Eq. (19) is accurate.

The dressing of hole quasiparticles decreases in this model as the hole concentration increases, and correspondingly the hole quasiparticle weight increases, as seen from Eq. (16) or its equivalent in hole representation

$$z_h(n_h) = S^2\left[1 + \frac{n_h}{2}\Upsilon\right] \tag{21}$$

with $n_h = 2 - n$, $\Upsilon = 1/S - 1$. In the normal state, this should be seen in the one-particle Green's function as a transfer of spectral weight from the incoherent part, describing high energy excitations of the boson field on the scale of ω_0, to the quasiparticle peak as the hole doping increases. Correspondingly, a transfer of spectral weight in optical absorption should be seen, from high frequency absorption on the scale of ω_0 to intraband Drude absorption with plasma frequency determined by $t_2(n_h) = t_2 + n_h(t_1 - t_2)$. From the operator relationship for hole quasiparticles derived from Eq. (14),

$$c^{h\dagger}_{i\sigma} = S[1 + \Upsilon\tilde{n}^h_{i,-\sigma}]\tilde{c}^{h\dagger}_{i\sigma}\,, \tag{22}$$

it is seen that the expectation value $\langle c^h_{i\sigma} c^{h\dagger}_{j\sigma}\rangle$ acquires contributions from anomalous expectation values $\langle \tilde{c}^h_{i\sigma}\tilde{c}^h_{j\sigma}\rangle$. This will cause transfer of spectral weight from high to low frequencies in the one- and two-particle Green's functions for fixed hole doping when the system goes superconducting, which should also be observable in photoemission and optical absorption experiments [7].

Nonperturbative theoretical techniques such as dynamical mean field theory [14] and density matrix renormalization group [15] should be able to establish the parameter regime in the Hamiltonian Eq. (9) where the physics of superconductivity through undressing described above takes place. First-principles quantum chemical and density-functional calculations should be able to relate the parameters in Eq. (9) to real materials. The physics discussed here predicts that superconductivity is favored in systems where conduction is through holes in nearly filled bands and through conducting structures that are negatively charged (small ionic charge Z), and that such systems will show undressing of hole carriers both when the system is doped with holes and when it goes superconducting. These effects will be most apparent when Z is small and Υ is large, which also leads to high T_c. The facts that most superconductors show hole carrier transport in the normal state [16], that both MgB_2 and the high T_c cuprates have holes conducting in highly negatively charged substructures [B^- and $(CuO_2)^=$ planes], and that the high T_c cuprates show evidence of "undressing" upon hole doping and upon going superconducting [7,17–19], suggest that the physics of the dynamical Hubbard model may have something to do with the physics of superconductivity in real materials.

In the regime most favorable for superconductivity, i.e., hole conduction in a system with large Υ, the model Eq. (9) predicts that incoherent excitations on electronic energy scales (ω_0) will be induced when holes hop. Hence one would expect nonthermal high frequency radiation to be generated when a dc current circulates in the normal state. This electroluminescence [20] should be most pronounced and easily observable at the positive counterelectrode-sample boundary, where holes are injected into the sample. The intensity of the radiation should correlate with the magnitude of the dressing and hence of T_c, and the frequency distribution will give information on the scale of electronic excitation energies involved in the undressing process that leads to superconductivity.

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