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Microscopic model of the Mott-Hubbard localization

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We devise a variational approach to the metal-insulator transition (MIT) that combines the Mott and Hubbard aspects of localization. Starting from the Gutzwiller approach, we optimize the ground-state energy not only with respect to the double occupancy η, but also with respect to the single-particle wave functions, which enter the energy via expressions for the Coulomb interaction U and for the bare bandwidth W. In effect, we obtain a theory of the MIT without resorting to a parametrization in terms of U/W. The effective mass close to the MIT is strongly enhanced even when the transition is discontinuous.

In this paper we propose an approach to the metal-insulator transitions[1] (MIT) for correlated electrons, which obviates the need for parametrizations involving the transfer integral t_{ab} (i.e., bare bandwidth W) and the Hubbard repulsion U between electrons located on the same site. This objective is achieved by adjusting the radial extension of the Wannier functions which enter the expression for the ground-state energy of the correlated state via the parameters t_{ab} and U. In other words, both single-particle (band-structure) and strong-Coulomb-interaction aspects of electron structure are incorporated into a single scheme. Through this methodology we calculate the energy of both metallic (M) and insulating (I) states in terms of the lattice parameter a_0, and then determine the critical interatomic distance at which the Mott-Hubbard transition takes place. As an automatic consequence we find that near the transition to the I state the effective mass of charge carriers is strongly enhanced. We also discuss the relation between the Mott[1] and Hubbard[2] criteria for the MIT driven by electron-electron interactions. As a concrete application we determine the localization boundary along the $3d$ series of monoxides rationalized earlier[3] in an empirical manner.

We start with the expression for the ground-state energy of correlated itinerant electrons[4]

$$E_G=\sum_{i,\sigma} n_\sigma \int d^3r\, H(\mathbf{r})|w(\mathbf{r}-\mathbf{R}_i)|^2 + \sum_\sigma q_\sigma n_\sigma(1-n_\sigma)\sum_{ij}{}' \int d^3r\, w^*(\mathbf{r}-\mathbf{R}_i)V_1(\mathbf{r})w(\mathbf{r}-\mathbf{R}_j) + \eta\sum_i \int d^3r\, d^3r'\, |w(\mathbf{r}-\mathbf{R}_i)|^2(e^2/|\mathbf{r}-\mathbf{r}'|)|w(\mathbf{r}'-\mathbf{R}_i)|^2 . \tag{1}$$

Here $n_\sigma \equiv \langle n_{i\sigma}\rangle$ is the number of particles in the Wannier state $w_i(\mathbf{r})=w(\mathbf{r}-\mathbf{R}_i)$ with spin $\sigma=\pm 1$, $\eta=\langle n_{i\uparrow}n_{i\downarrow}\rangle$ is the probability that the state $w_i(\mathbf{r})$ is doubly occupied, $H(\mathbf{r})$ is the atomic part of the single-particle Hamiltonian, and $V_1(\mathbf{r})$ is the potential acting on a particle in the state $w_i(\mathbf{r})$ from all neighboring atoms. For the half-filled band case of interest the band narrowing factor is given by[4] $q_\sigma=\Phi=8\eta(1-2\eta)$. The first term in (1) represents the atomic part of the energy, the second is the single-particle (band) part in the correlated state, and the last term accounts for the short-range part of the Coulomb interaction. The primed summation excludes terms with $i=j$.

Equation (1) is obtained in the scheme[2] in which the Wannier functions $\{w_i(\mathbf{r})\}$ entering the definition of the field operator are not specified explicitly. Additionally, as the MIT is approached the band and interaction parts of the total energy become of comparable magnitude.[5] Therefore, the single-particle and the interaction parts should be treated on the same footing. The former is characterized by the wave function $w_i(\mathbf{r})$, the latter, by the two-particle correlation function η. Hence, E_G should be optimized with respect to both $\{w_i(\mathbf{r})\}$ and η. To allow the wave function to readjust in the correlated state, we consider E_G as a functional of $\{w_i(\mathbf{r})\}$. One must therefore derive the Lagrange-Euler equation for the functional (1) under the condition that the renormalized wave function be normalized. This procedure leads to the following nonlinear integrodifferential wave equation:

$$H(\mathbf{r})w_i(\mathbf{r})+\Phi\sum_{j(i)} V_1(\mathbf{r})w_j(\mathbf{r}) + \eta w_i(\mathbf{r})\int d^3r'\,(e^2/|\mathbf{r}-\mathbf{r}'|)|w_i(\mathbf{r}')|^2=\lambda w_i(\mathbf{r}) , \tag{2}$$

where λ is an eigenvalue. One sees that in the Mott insulating state (i.e., with double occupancies excluded) Eq. (2) reduces to the Schrödinger equation for atomic states. However, these reference atomic states are realized *in the solid;* hence, the effect of surrounding ions must be included in the $H(\mathbf{r})$ part, as discussed below.

Equation (2) can only be solved numerically and even then requires an additional minimization of E_G with respect to η. To construct a simpler workable scheme that permits a discussion in physical terms we solve Eq. (2) variationally by constructing Wannier functions from atomiclike functions with an adjustable radius R using the tight-binding methodology. Since the validity of the Hubbard model is limited to narrow-band systems with a small overlap, we can write $w_i(\mathbf{r})$ in the asymptotic form

$$w(\mathbf{r}-\mathbf{R}_i)=\Phi_a(\mathbf{r}-\mathbf{R}_i)-\tfrac{1}{2}\sum_{j(i)} S_{ij}\Phi_a(\mathbf{r}-\mathbf{R}_j)+o(S_{ij}^2)\ , \tag{3}$$

where $S_{ij}=\langle i|j\rangle$ is the overlap integral involving the atomiclike wave functions $\Phi_a(\mathbf{r}-\mathbf{R}_i)$ and $\Phi_a(\mathbf{r}-\mathbf{R}_j)$. The wave function (3) can be transformed to the Bloch representation in the standard manner. The Bloch functions so obtained are then used to calculated the bare-particle energies

$$E_{\mathbf{k}}=\tilde{\epsilon}_a+(\langle a|V_1|a\rangle+\epsilon_{\mathbf{k}})/(1+S_{\mathbf{k}})\ ,$$

where

$$\epsilon_{\mathbf{k}}=\sum_{j(i)} t_{ij}\exp[i\mathbf{k}\cdot(\mathbf{R}_i-\mathbf{R}_j)]\ ,$$

$$S_{\mathbf{k}}=\sum_{j(i)} S_{ij}\exp[i\mathbf{k}\cdot(\mathbf{R}_i-\mathbf{R}_j)]\ ,$$

and

$$\langle a|V_1|a\rangle=\int d^3r|\Phi_a(\mathbf{r}-\mathbf{R}_i)|^2\sum_{j(i)}(-Z^*e^2/|\mathbf{r}-\mathbf{R}_j|)\ . \tag{4}$$

In the above expression $\tilde{\epsilon}_a$ is the atomic energy of an electron in the presence of surrounding ions, t_{ij} is the transfer integral involving atomic states located on the sites i and j, and Z^*e is the effective nuclear charge of neighboring atoms attracting the electron located on site i. One should notice that close to localization every ion will be screened strongly by electrons, one of which will eventually localize on it.

In the small overlap limit one can represent the atomiclike wave function by the s-type functions

$$\Phi_a(\mathbf{r}-\mathbf{R}_i)=(\pi R^3)^{-1/2}\exp(-|\mathbf{r}-\mathbf{R}_i|/R)\ ,$$

where R is an adjustable wave-function radius. For the sake of simplicity we introduce two further assumptions: The hopping integral t_{ij} is taken only between the nearest neighbors, and the shape of the bare density of states is taken as featureless when calculating the total energy. The first leads to the expression $\epsilon_{\mathbf{k}}=zt_{ab}\gamma_{\mathbf{k}}$, where z is the number of nearest neighbors, t_{ab} is the corresponding hopping integral, and $\gamma_{\mathbf{k}}$ is a geometric factor dependent on the crystal structure. The second assumption should not drastically affect the results since the global energy calculation involves integration over the density of states. In effect, the ground-state energy takes the form

$$E_G=\tilde{\epsilon}_a+\Phi\bar{\epsilon}+U\eta\ , \tag{5}$$

where $\bar{\epsilon}$ (<0) is the average bare-band energy per particle. Additionally, the parameters t_{ab}, S_{ab}, and $\langle a|V_1|a\rangle$ can be calculated explicitly by adopting the corresponding expressions[6] for the H_2^+ ion. Finally, the Coulomb repulsion U between the two electrons on the same atom can be calculated in the same manner as is done[7] for the ground state of He: $U=(5e^2/8R)$. In this manner, E_G becomes a function of two variables, $\omega\equiv a_0/R$ and η. To make our computations relevant to real systems we now consider a concrete example.

The canonical compounds whose valence ($3d$) electrons are in the Mott localized state are the later transition metal monoxides.[1] Here, the oxygen O^{2-} anions produce a crystal field acting on $3d$ electrons. This is so because in the insulating state the covalency effects lead at most to a readjustment of the spatial extent of the $3d$ orbitals; any significant $2p$-$3d$ charge transfer would invariably lead to a stable M state. We presume that the assumption about the passive role of anion $2p$ states does not invalidate our main conclusions.[8] From a physical point of view the assumption means that the bare $2p$ states are separated energetically from the $3d$ states. Additionally, we set the number of electrons in the $3d$ shell equal to D, so that the Coulomb energy difference between the atomic configurations with $(D+1)$ and D electrons is UD.[9] Only one out of the D electrons delocalizes at the MIT boundary. Furthermore, the anions repel the electrons located on the neighboring $3d$ orbitals. Therefore, we have to add the energy $\langle a|V_1'|a\rangle$ due to anions to $\langle a|V_1|a\rangle$ since the anions reduce the attraction of the electron to neighboring cations. The cations form an fcc lattice, and each of them is in the octahedral environment of O^{2-} anions. In this situation the relevant quantities entering (5) have the following form: (a) the transfer integral

$$t_{ab}=-Z^*(e^2/a_B)(1/a)\omega(1+\omega/\sqrt{2})\exp(-\omega/\sqrt{2})\ ; \tag{6}$$

(b) the overlap integral

$$S_{ab}=(1+\omega\sqrt{2}+\omega^2/6)\exp(-\omega/\sqrt{2})\ ; \tag{7}$$

and (c) the Coulomb integrals

$$\langle a|V_1|a\rangle=Z^*(e^2/a_B)z[(\omega/\sqrt{2}+1)\times\exp(-\omega\sqrt{2})-1](\sqrt{2}/a)\ , \tag{8}$$

and

$$\langle a|V_1'|a\rangle=2(e^2/a_B)z'[1-(1+\omega/2)\exp(-\omega)](2/a)\ . \tag{9}$$

In Eqs. (6)–(9), $a\equiv a_0/a_B$, a_B is the Bohr radius, and z' is the number of nearest-neighboring anions to a cation. Substituting the above expressions to (5) we transform E_G into a function of ω and η, with a and Z^* (Z^* is taken as Z_M and Z_I in the metallic and insulating states, respectively) as the only parameters. Minimization with respect to η yields $\eta=\eta_0=\frac{1}{4}(1-U/U_C)$, where $U_C=8|\bar{\epsilon}|$. One sees that as $U\rightarrow U_C$, the probability $\eta\rightarrow 0$, i.e., the transition to the Mott insulating state is approached.[10,11,4] Substituting the optimal value η_0 into (5) we obtain $E_G/N=\tilde{\epsilon}_a+(1-U/U_C)^2\bar{\epsilon}$.

The optimal E_G values for specified Z_M and Z_I for $D=5$ are displayed as solid lines in Fig. 1 as a function of a. The dashed line represents the energy $E_I=\epsilon_a+\langle a|V_1|a\rangle+\langle a|V_1'|a\rangle$ of the I state, ϵ_a is the atomic part of its energy. A continuous MIT occurs at the crossing (coexistence) point of the solid and dashed lines. It should be underlined that the reference energy $\tilde{\epsilon}_a$ takes into account the presence of neighboring ions,

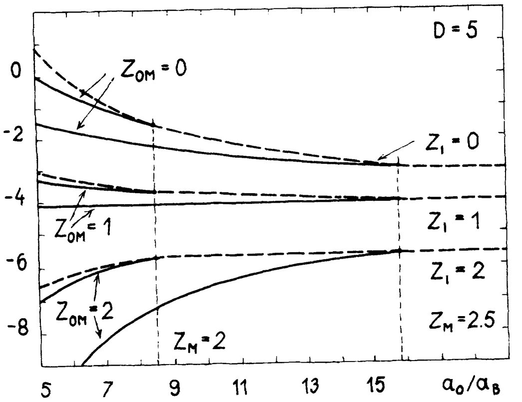

FIG. 1. The energies of insulating (dashed lines) and metallic (solid lines) phases as a function of relative lattice constant $a = a_0/a_B$. The explanation is provided in the text.

and differs from the bare atomic energy ϵ_a. Hence, our approach differs in this respect from the standard tight-binding scheme, for which the reference energy is ϵ_a. In the numerical calculations we have also considered the case where the effective charge Z_I on the neighboring cations is different in the expressions for $\tilde{\epsilon}_a$ and E_I, being equal to Z_{0M} and Z_I, respectively. This distinction reflects the difference between the M and I states, treated here as different phases.[12,5] The anion charge $Z_A = -2$ is fixed in both phases.

The choice of Z_M specifies the Mott-Hubbard boundary, as marked by vertical dashed lines in Fig. 1. The termination points (with $\eta = 0$) in this figure represent *continuous* MIT's, which take place when $Z_I = Z_{0M}$. The continuous nature of the transition in this situation is easy to understand since the reference energy ($\tilde{\epsilon}_a$) is the same in the metallic and insulating phases; hence, the MIT is specified only by the condition $\eta = 0$. However, if the symmetry in the insulating state is lower than in the metallic state then $Z_I = Z_{0M} + \delta$ with $\delta > 0$, and the transition is always *discontinuous*. This can be visualized by noting that with an increase of Z_I the dashed curve is lowered and hence crosses the solid line above its termination point. Furthermore, one can expect that $\delta \ll 1$; then, the effective mass enhancement, defined as[4,10] $m^*/m_B = \Phi^{-1}$ is large in the vicinity of the MIT, as displayed in Fig. 2. Note also that in the case of a discontinuous MIT the metallic state becomes unstable before η vanishes. Hence the question[13] whether the state of $\eta = 0$ can be achieved for finite U/U_C is not of primary importance.

The value $Z_M \sim 2$ reflects the situation in which the electrons are almost localized, i.e., they screen the cationic charge so as to produce a configuration close to the $M^{2+}O^{2-}$ ionic state. Also, the value $Z_I = 0$ is in accordance with the commonly adopted assumption, when considering magnetic insulators, that the electron states in the localized regime are influenced only by the nearest anions. In other words, the electrostatic fields of more distant cations and anions almost compensate each other. However, for the sake of completeness we have plotted in Fig. 1 also the $E_I(a)$ dependence for $Z_I > 0$; the I state with $Z_I > 1$ is unstable. Similar results are obtained for $D = 4$ and 3. The localization boundary for $D = 1$ is shifted towards much higher a_c and corresponds well with the observed absence of localization for the earlier monoxides. On the basis of the above results one can conclude that our approach reproduces the universal features of the later $3d$ monoxides with the critical spacing $a_c \sim 4$–5 Å, as observed in experiment.[3] Hence, even though the approach still requires a detailed analysis of the screening leading to the effective charges $Z_M \cong 2$ and $Z_I \cong 0$, as well as of the inclusion of the $2p$-$3d$ hybridization, it leads to a proper starting point of a quantitative model for the electronic structure calculations near the Mott-Hubbard boundary.

In the inset A (Fig. 2) we display the bare bandwidths $W = 2z|t_{ab}|$ and

$$\overline{W} = W[1 + z(\langle a|V_1|a\rangle + \langle a|V_1'|a\rangle)S_{ab}] ,$$

without and with inclusion of S_{ab}, respectively. These two quantities become very small when the MIT's were continuous.

The minimization of E_G with respect to ω yields the results for η and R displayed in Figs. 3(a) and 3(b). The orbit shrinks with growing a_0. The insets A and B display the evolution with a of the quantity $\omega \equiv a_0/R$, of the overlap (on a logarithmic scale), and of the U/U_C ratio. Both U/U_C and R change linearly with a as the system approaches the insulating boundary. In the case of a symmetry change, R and η jump at the values noted by arrows; the magnitude of these jumps corresponds to the critical spacing a_c marked in Fig. 2 for which the mass enhancement in the metallic phase at the transition is $m^*/m_B \cong 10$. We see that close to MIT, $S_{ab} \ll 1$; this result justifies *a posteriori* the expansion (3) adopted at the outset. Also, the MIT takes place for nonzero t_{ab}. However, in the correlated state the bare-transfer integral is renormalized by the factor Φ which plays the role of many-body band narrowing[4] and vanishes as the MIT is approached.

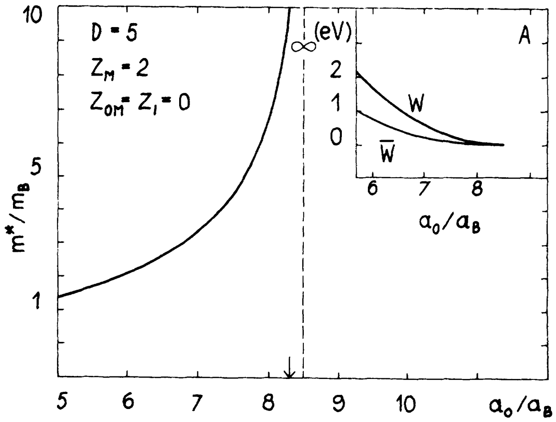

FIG. 2. The mass enhancement due to correlations a. The inset A displays bare bandwidths W and $\overline{W}$.

From Fig. 2 and from the insets $A-C$, one can see clearly that our approach combines different features of previous treatments[1,2,4,10] into a consistent scheme. It confirms the original suggestion[1] that the MIT is of first order, though here it is driven by the details of the balance between the atomic, band, and Coulomb repulsion parts of the total energy. We show that the transition takes place for $U \sim U_C$.[10–12] The effective mass is largely enhanced in M phase close to localization, a feature which is absent in the Mott and Hubbard approaches but is present in the Gutzwiller-Brinkman-Rice scheme. This combination of properties resolves a long-standing problem of unifying the earlier treatments and is possible only because we have combined the Mott concepts that stress the atomic state stability for a single electron, with the theory of electron correlations having its origin in the Gutzwiller approach,[10] which stresses the competitive nature of band and short-range Coulomb interaction parts in the total energy. As an automatic consequence of our approach we obtain for $D=5$ the Mott criterion[2] for MIT in the form $n_c^{1/3}a_H=(1/a_c)R/a_B=\omega^{-1}\sim 0.04$. We emphasize also that we cannot neglect the atomic part of the total energy since it changes with a, due to the wave-function readjustment with changing η. If the atomic energy part were disregarded, the transition at zero temperature would always be continuous as is found within the standard Gutzwiller approach.[10,5]

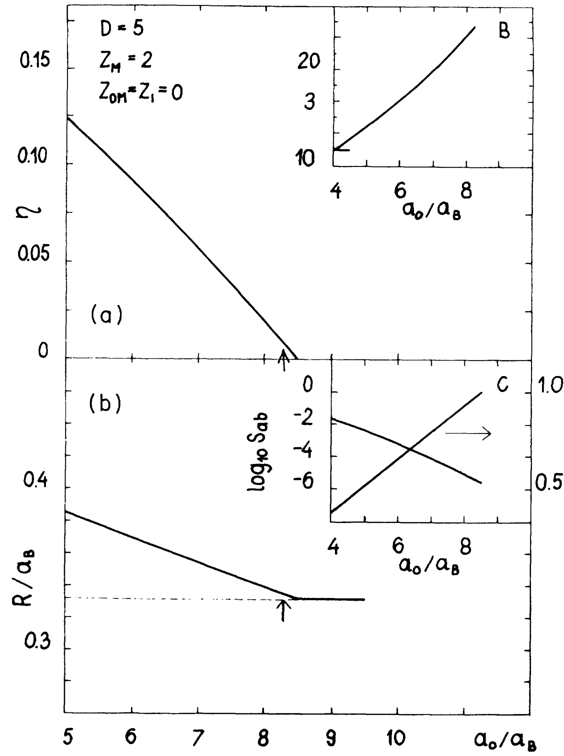

FIG. 3. (a) The optimal value of correlation function η vs a; (b) radial extent of the wave function $\Phi_a(\mathbf{r}-\mathbf{R}_i)$ vs a. The insets B and C display the a dependence of ω, overlap S_{ab}, and U/U_C.

In summary, we have analyzed a model of correlated electrons in which both optimization of the intra-atomic two-particle correlation function and a single-particle wave-function readjustment have been treated on an equal footing. An MIT signaling the localization is accompanied by a diminution of the wave-function radius R and by the disappearance of the metallic state composed of heavy quasiparticles. From the formal point of view we have replaced the parametrization in terms of U/W by the systematic analysis as a function of the lattice parameter a_0. The validity of the present approach is not limited to the Gutzwiller approximation. Further refinement would require a formulation going beyond the Gutzwiller analysis, as well as a more realistic treatment of both the single-particle (periodic) potential and of the filled $(2p)$ bands. Additionally, the inclusion of antiferromagnetic exchange interactions in the regime $S_{ab} \ll 1$ would specify stability criteria for antiferromagnetic M and I phases. Also, inclusion of the lattice part of the total energy would allow for a calculation of the equilibrium spacing a_0.

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