

Electron correlations in one dimension: The Hubbard model

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Applicability of the Hubbard model (HM) to one-dimensional solids is investigated by careful analysis of the introduced approximations and by analytical calculation of the integrals. Consistency with the other approximations implies the neglect of interbond-charge-repulsion integrals. If the interelectronic potential is long range, the extended HM is adequate. On the contrary, for highly screened potentials intersite charge repulsion terms lose their importance in favor of the bond-site terms. The extended HM is then replaced by a new model, which in the mean-field treatment reduces to the simple HM.

Since its proposal,¹ the so-called Hubbard model has enjoyed wide popularity in investigating the properties of a large variety of systems. In fact, originally developed to discuss the *d* and *f* electronic bands in transition metals and oxides,¹ it has then been applied in investigating the properties of, e.g., quasi-one-dimensional (1D) charge-transfer crystals,² conducting polymers,³ and, more recently, high- T_c superconductors.⁴ Even if the approximations of the Hubbard model were discussed in the original papers, their reliability in dealing with systems different from transition metals and oxides has not been carefully analyzed. A very lively debate has recently arisen about the validity of Hubbard model approximations in discussing large bandwidth quasi-1D systems such as *trans*-polyacetylene.⁵⁻¹⁰ In our opinion the question is still open, since the consistency of the approximations has not been carefully checked, and different choices of potentials and wave functions, often not very realistic, have yielded contrasting results. In this paper we reanalyze the problem from the beginning, and with rigorous control of the introduced approximations and of the adopted parameters and wave functions, we try to give a definite answer to the question of the applicability of Hubbard model to quasi-1D solids.

The Hubbard model, the solid-state counterpart of the Pariser-Parr-Pople (PPP) model of molecular physics,¹¹ can be thought of as an improvement of the well-known tight-binding method,¹² the refinement consisting in the relaxation of the one-electron approximation. In both the tight-binding and Hubbard model the electronic structure of the solid is described in terms of few, strongly localized atomic- or molecular-site orbitals, with small overlap between wave functions centered on different sites. More precisely, whereas the atomic or molecular picture is not adequate to describe the properties of the solid due to the finite overlap between wave functions on different sites, this overlap is not so large as to make the localized picture completely inadequate.¹² The small overlap requirement is even more stringent for the one-band version of the Hubbard model usually adopted in dealing with quasi-1D solids. This version explicitly accounts for just one site or-

bit (Ψ_i , centered on site i). The overlap (hence the interaction) between orbitals on different sites has to be small enough to guarantee that the resulting states form a narrow band and do not interact appreciably with states lying on neighboring bands. Therefore, the basic assumption of the Hubbard model is that the overlap between orbitals on nearest-neighbor sites, $S_i = \langle \Psi_i | \Psi_{i+1} \rangle$, is a non-negligible quantity, but it is so small as to make S_i^2 negligible in respect to 1. The neglect of the S_i^2 terms is consistent with a second approximation of the Hubbard model, namely, the neglect of the charge-transfer interaction between orbitals on nonadjacent sites, which stems from the neglect of the corresponding overlap. In fact, in the small S limit the overlap between i and j sites exhibits a nearly exponential decay with the site distance, so that $S'_i = \langle \Psi_i | \Psi_{i+2} \rangle$ is of the same order of magnitude as S_i^2 .

The above considerations can be summarized in the one-electron, tight-binding-like part of the Hubbard Hamiltonian for a linear chain

$$H_e = \sum_{i,s} \epsilon_i a_{i,s}^\dagger a_{i,s} + \sum_{i,s} t_i (a_{i,s}^\dagger a_{i+1,s} + \text{H.c.}), \quad (1)$$

where i runs on the lattice sites and s ($=\alpha, \beta$) is a spin index. ϵ_i is the site energy, and t_i the charge-transfer integral. The $a_{i,s}^\dagger$ ($a_{i,s}$) can be identified as the usual Fermi creation (annihilation) operators for an electron with spin s on site i , only if they refer to an orthonormal set of basis functions. The approximation of considering the site orbitals as virtually orthogonal was introduced by Hubbard himself¹ and is quite commonly adopted,^{8,10} but actually it is not consistent with the basic assumption of the model, i.e., the nonnegligible overlap between orbitals on adjacent sites [$t_i \neq 0$ in Eq. (1)]. Therefore one has to orthogonalize the Ψ_i set, obtaining the following basis set:

$$\phi_i = \Psi_i - \frac{S_i \Psi_{i+1} + S_{i-1} \Psi_{i-1}}{2}, \quad (2)$$

where the Ψ_i have been assumed real and normalized whereas terms of the order or less than S_i^2 and/or S'_i have been neglected. Thus, the ϵ_i and t_i parameters, which in Eq. (1) refer to the ϕ_i set, can also be expressed in terms of the Ψ_i .

In its most general form the electron-electron interaction is introduced as

$$H_{ee} = \sum_{\substack{i,j,m,n \\ s,z}} V(i,j,m,n) a_{i,s}^\dagger a_{j,z}^\dagger a_{m,z} a_{n,s}, \quad (3)$$

where

$$\begin{aligned} V(i,j,m,n) &= \int dr \int dr' \phi_i(r) \phi_j(r') V(r-r') \phi_m(r') \phi_n(r) \\ &= \mathcal{V}(i,j,m,n) - \frac{1}{2} [S_i \mathcal{V}(i+1,j,m,n) + S_{i-1} \mathcal{V}(i-1,j,m,n) \\ &\quad + S_j \mathcal{V}(i,j+1,m,n) + S_{j-1} \mathcal{V}(i,j-1,m,n) + S_m \mathcal{V}(i,j,m+1,n) \\ &\quad + S_{m-1} \mathcal{V}(i,j,m-1,n) + S_n \mathcal{V}(i,j,m,n+1) + S_{n-1} \mathcal{V}(i,j,m,n-1)], \end{aligned} \quad (4)$$

and

$$\mathcal{V}(i,j,m,n) = \int dr \int dr' \Psi_i(r) \Psi_j(r') \times V(r-r') \Psi_m(r') \Psi_n(r),$$

$V(r-r')$ being the interelectronic repulsion potential.

In isolated chains, if the effects of core electrons are disregarded, $V(r-r')$ is the Coulomb potential. On the other hand, in real materials the screening due to electrons on neighboring chains may reduce the range of the electrostatic interaction. In insulators, the screening is in general not very effective and the range of the interelectronic potential is large. In these conditions one can quite safely assume that the overlap integral between the well-localized site functions decays with the site distance more rapidly than the Coulomb repulsion does with the electron distance. The $\Psi_i(r) \Psi_n(r)$ and $\Psi_j(r') \Psi_m(r')$ charge distributions in the $\mathcal{V}(i,j,m,n)$ definition can therefore be mediated to give

$$\begin{aligned} 4\mathcal{V}(i,j,m,n) &= [\mathcal{V}(i,j,j,i) + \mathcal{V}(i,m,m,i) \\ &\quad + \mathcal{V}(n,j,j,n) + \mathcal{V}(n,m,m,n)] \\ &\quad \times \int dr \Psi_i(r) \Psi_n(r) \int dr' \Psi_j(r') \Psi_m(r'). \end{aligned} \quad (5)$$

Equation (5) is the well-known and tested Mulliken approximation,¹³ which allows one to express the off-diagonal elements of the interelectronic potential ($i \neq n$ and/or $j \neq m$) in terms of the diagonal ones. By inserting Eq. (5) in Eq. (4), the $V(i,j,m,n)$ terms with $i \neq n$ and $j \neq m$ (interbond-charge-repulsion terms) turn out to be negligible in respect to the diagonal terms, their ratios being of the order or less than S_i^2 . Terms with $i = n$ and $j \neq m$ or $i \neq n$ and $j = m$ (bond-site repulsion) vanish exactly, so that only the diagonal terms of the interelectronic potential have to be accounted for. The Hamiltonian reduces to the so-called extended Hubbard model (EHM).² Therefore, EHM offers a reliable description of the properties of insulators (more precisely, of materials with non-heavily-screened Coulomb interactions) with the only proviso that the approximations introduced in the definition of the one-electron part of the Hamiltonian are fulfilled. Truncated versions of EHM (Ref. 14) [$V(i,j,j,i)$ terms with $|i-j|$ greater than a threshold value not introduced) or even the simple Hubbard model¹ (SHM) all the $V(i,j,j,i)$ with $i \neq j$ not introduced] constitute further approximations of EHM. These simplified

models are in fact obtained from EHM by neglecting some of the $V(i,j,j,i)$ or through mean-field treatment of the corresponding terms in the Hamiltonian. In any case, the reliability of these models should be carefully checked for each problem at hand and is not of our concern here.

Whereas consensus is emerging about the validity of the EHM for unscreened or slowly varying $V(r-r')$,⁶⁻¹⁰ a clear answer has still to be given in the hypothesis of a very effectively screened potential. Indeed, if the range of $V(r-r')$ is of the same order of magnitude or smaller than the range of the overlap integral, the Mulliken approximation [Eq. (5)] does not apply, and the analysis of H_{ee} [Eq. (3)] is much more difficult. To simplify the problem, we consider the limiting case of infinite screening, i.e., of a δ -function potential. In these conditions only on-site or nearest-neighbor interactions are relevant,⁴ and only terms like $\mathcal{V}(i,i,i,i)$, $\mathcal{V}(i+1,i,i,i)$, $\mathcal{V}(i,i+1,i+1,i)$, and $\mathcal{V}(i,i+1,i,i+1)$ (for short \mathcal{U} , \mathcal{X} , \mathcal{V} , and \mathcal{W} terms, respectively) have to be taken into account. It turns out immediately that $\mathcal{V} = \mathcal{W}$, but the relative magnitude of the other terms, which depends on the actual choice of the site wave functions,^{5,9} is not so obvious. However, acquaintance with molecular-orbital theories¹¹ suggests that, at least for reasonable tight-binding orbitals, $\mathcal{X} \lesssim S^2 \mathcal{U}$ and $\mathcal{W} \lesssim S^2 \mathcal{U}$. To test this hypothesis we have explicitly calculated S , \mathcal{U} , \mathcal{X} and $\mathcal{V} = \mathcal{W}$ on the basis of Slater atomic orbitals. The calculations are performed exactly in the spheroidal-coordinate space¹⁵ and

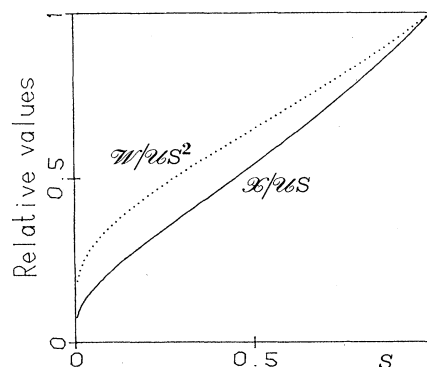


FIG. 1. Values of interbond and bond-site charge-repulsion integrals (\mathcal{W} and \mathcal{X} , respectively) compared with the on-site repulsion \mathcal{U} , as functions of the overlap integral S . A δ -function interelectronic potential is assumed.

choosing as a representative example the $2p\pi$ orbitals (those relevant, e.g., to polyacetylene). In analogy with previously reported results,⁴⁻⁸ we find $\mathcal{U} > \mathcal{X} > \mathcal{V} = \mathcal{W}$. However, our calculations also demonstrate that, whatever the S value (whatever the site separation), the $\mathcal{V} = \mathcal{W}$ terms are negligible in a tight-binding scheme, always be-

ing smaller than $S^2\mathcal{U}$.¹⁶ This important finding is illustrated in Fig. 1, which also shows that \mathcal{X} is of the same order of magnitude as $S\mathcal{U}$, and, therefore, cannot be neglected *a priori*. Thus, by inserting Eq. (4) in Eq. (3) and neglecting terms of the same order or less than S^2 , H_{ee} for $V(r-r') = \delta(r-r')$ reduces to

$$H_{ee} = 8 \sum_i U_i a_{i,\alpha}^\dagger a_{i,\beta}^\dagger a_{i,\beta} a_{i,\alpha} + 8 \sum_{i,s} (a_{i,s}^\dagger a_{i+1,s} + \text{H.c.}) \sum_z (X_i a_{i,z}^\dagger a_{i,z} + X_{i+1} a_{i+1,z}^\dagger a_{i+1,z}) \quad (6)$$

where $U_i = \mathcal{V}(i, i, i, i)$ and

$$X_i = \mathcal{V}(i+1, i, i, i) - \frac{1}{2} S_i \mathcal{V}(i, i, i, i).$$

In this limit the electronic Hamiltonian differs from SHM by the second term of the above equation. The SHM with renormalized t_i is recovered by substituting the summation over z with its mean-field value, but, of course, a mean-field approach can be adopted only after due consideration.

Having discussed the relative magnitude of the $\mathcal{V}(i, j, m, n)$ [and therefore of the $V(i, j, m, n)$] terms in the two limiting cases of a long- and a vanishingly short-range interelectronic potential, we can interpolate the results in intermediate regimes. It turns out that the interbond repulsion terms are always negligible, being of the order of S_i^2 or less in respect to the on-site repulsion energy \mathcal{U} . The intersite repulsion terms $\mathcal{V}(i, j, j, i)$ or $V(i, j, j, i)$ instead can be disregarded only for very short-range, screened potentials. Finally, the bond-site repulsion terms in the nonorthogonal basis [$\mathcal{V}(i, j, j, i+1)$ -like terms] are always non-negligible;¹⁰ however, the corresponding terms in the orthogonal basis [$V(i, j, j, i+1)$] remain of the order of S in the δ -function limit, but vanish exactly for a long-range potential. To summarize, if one starts from orthogonalized site orbitals, EHM offers a reliable description of the properties of quasi-1D systems with unscreened or weakly screened Coulomb potential. On the other hand, when the potential is strongly screened, as in conducting materials, the intersite repulsion terms lose their importance in favor of the bond-site repulsion terms; EHM modifies to a new picture, which in favorable cases reduces to SHM.

As mentioned above, the reliability of EHM in describing systems with long-range interelectronic potential is a result common to various kinds of treatments.⁶⁻¹⁰ However, these treatments start from particular choices of the parameters or wave functions⁶⁻⁹ or disregard the actual nonorthogonality of the basis set.^{8,10} The present discus-

sion puts the above finding on a more sound basis, showing that, whatever the basis set, in the long-range limit EHM does not require additional approximations in respect to those pertinent to a tight-binding scheme.¹² In the short-range limit, on the contrary, the results are strongly dependent on the actual choice of the site wave functions. In this respect, our conclusions for the short-range potential are strictly valid only for $2p\pi$ orbitals, although we believe that they are also applicable to the vast majority of quasi-1D solids. In any case, it has to be kept in mind that only realistic approximations to atomic or molecular site orbitals are actually consistent with the tight-binding approach, particularly in its one-band version; results based on "simplified" site wave functions have to be regarded with some reservation. Of course, if the tight-binding picture is not applicable, the entire problem has to be reconsidered, and such an analysis is beyond the aim of present work.

As final topic we briefly comment on the effects of electron-electron interactions on the dimerization of polyacetylene. The one-electron part of the problem is usually treated in tight-binding approximation due to the smallness of the $2p\pi$ overlap ($S_i = 0.2-0.3$) (Ref. 15) and assuming a σ - π separability. At the light of present results for a long-range potential, EHM holds and, as already found by other authors,¹⁷ weak electron interactions enhance dimerization. In the opposite limit of a very short-ranged potential, interbond- and intersite-repulsion terms are negligible, whereas bond-site terms are expected not to affect dimerization in half-filled systems.^{5,18} Therefore the dimerization instability can be described in terms of SHM which once more predicts^{17,18} enhanced dimerization for weak interelectronic interactions.

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¹P. W. Anderson, Phys. Rev. **115**, 2 (1959); J. Hubbard, Proc. R. Soc. London, Ser. A **276**, 238 (1963).

²J. Hubbard, Phys. Rev. B **17**, 494 (1978), and references therein.

³Z. G. Soos and G. W. Hayden, in *Electroresponsive Molecular and Polymeric Systems*, edited by T. Skotheim (Marcel Dekker, New York, in press).

⁴For a brief account of the work on this subject, see J. Maddox, Nature (London) **329**, 481 (1987).

⁵S. Kivelson, W.-P. Su, J. R. Schrieffer, and A. J. Heeger, Phys. Rev. Lett. **58**, 1899 (1987).

⁶C. Wu, X. Sun, and K. Nasu, Phys. Rev. Lett. **59**, 72 (1988).

⁷D. Baeriswyl, P. Horsch, and K. Maki, Phys. Rev. Lett. **60**, 70 (1988).

⁸J. T. Gammel and D. K. Campbell, Phys. Rev. Lett. **60**, 72 (1988).

⁹S. Kivelson, W.-P. Su, J. R. Schrieffer, and A. J. Heeger, Phys. Rev. Lett. **60**, 73 (1988).

- ¹⁰A. Painelli and A. Girlando, *Solid State Commun.* **66**, 273 (1988).
- ¹¹L. Salem, *The Molecular Orbital Theory of Conjugated Systems* (Benjamin, New York, 1966), and references therein.
- ¹²N. W. Ashcroft and N. D. Mermin, *Solid State Physics* (Holt-Saunders, London, 1976), Chap. 10.
- ¹³R. S. Mulliken, *J. Chim. Phys. (Paris)* **46**, 675 (1949).
- ¹⁴See, for instance, S. Mazumdar, S. N. Dixit, and A. N. Bloch, *Phys. Rev. B* **30**, 4842 (1984), and references therein.
- ¹⁵R. S. Mulliken *et al.*, *J. Chem. Phys.* **17**, 1248 (1949).
- ¹⁶An analogous result has also been found by the authors of Ref. 9. Working with a basis of orthonormalized Gaussian functions and a Gaussian screened potential, they find the interbond-repulsion energy of the order of S^2 in respect to the intrasite repulsion. However, due to the abnormally high value of S (~ 0.6), the interbond-repulsion term has a non-negligible value.
- ¹⁷See, for instance, S. Mazumdar and D. K. Campbell, *Synth. Met.* **13**, 163 (1986), and references therein.
- ¹⁸After submission of this paper, we learned of unpublished work by J. Voit and D. K. Campbell, J. Tinka Gammel, and E. Y. Loh which demonstrates that contrary to the assertion of Ref. 5, the X term couples to Fermi-surface states in the half-filled band. According to these authors, the X term increases dimerization.