Electron localization in one dimension obtained from combined exact diagonalization - \textit{ab initio} approach

Jozef Spalek and Adam Rycerz
Marian Smoluchowski Institute of Physics, Jagiellonian University, ulica Reymonta 4, 30-059 Kraków, Poland
(June 4, 2001)

Exact ground-state properties are presented by combining the diagonalization in the Fock space (and taking \textit{all} hopping integrals and \textit{all} two-site interactions) with the \textit{ab initio} optimization of the Wannier functions. Electrons are essentially localized for the interatomic distance \( R \sim 2.0 \, \text{Å} \) for \( s \)-like states, when the quasiparticle mass is divergent. The momentum distribution dispersion is proposed to define the localization \textit{order parameter}. Dimerization and zero-point energies are also discussed. The method provides convergent results for \( N \geq 8 \) atoms.

PACS Nos. 71.10.Fd, 71.15.Fv, 31.25.Nj

One dimensional systems range from organic metals \[1\] to quantum rings and wires \[2\], and to nanotubes \[3\]. In their description the role of the long-range Coulomb interaction is crucial because of reduced dimensionality, for which the charge screening becomes less effective \[4\]. The existing exact solutions of the parametrized models with inclusion of intersite interactions \[4,5\] prove the existence of the metal-insulator transition for the half-filled-band case, in contradistinction to the corresponding Hubbard-model solution \[6\], for which the system is insulating even for an arbitrarily small Coulomb repulsion. The existence of such metal-insulator the transition has been also discussed \[7\] within the density-matrix renormalization group (DMRG) method when the second-neighbor hopping is included. A separate question concerns the appearance of the Tomonaga-Luttinger behavior \[8\] in the metallic state, for which some evidence has been gathered \[9\]. In brief, the search for a proper description of those systems as quantum liquids (and their instabilities) is one of the basic problems in the physics of low-dimensional systems.

In the above theoretical analysis \[1-8\] the solutions have been discussed as a function of the microscopic parameters, which are not easy to measure. Therefore, one assumes that they should be determined first from a separate single-particle approach. In following this route one must avoid counting twice the interaction, as discussed carefully in the papers implementing the LDA+U \[6\] and SIC \[10\] methods. We have proposed \[11\] a new method in which the single-particle (Wannier) wave functions are allowed to relax in the correlated state and thus are determined by optimizing the exact ground state energy obtained from the diagonalization in the Fock space. In other words, we treat properly the interactions first due to their strongly nonperturbative nature and then readjust the single-particle functions \( \{w_i(r)\} \) by setting Euler equation for them, which plays the role of the renormalized wave equation for a particle in the correlated ground state. In such approach the problem of double counting the interaction does not arise \textit{at all}. Additionally, we include \textit{all} the hopping integrals and \textit{all} two-site interactions to make the solution more complete. The method is executable on a desktop server for the number of atoms \( N \leq 12 \). What is probably the most remarkable formal feature of these calculations is that the electronic correlations make the wave function more tightly bound to the atoms and thus limiting the interaction range. In effect, the results are converging very fast for \( N \geq 8 \) atoms meaning that the \textit{optimized} Wannier functions and the interaction parameters are relevant at most up to the \textit{third} neighbors. The results are detailed below and to the best of our knowledge they represent the first analysis of the strong correlation effects as a function of the lattice parameter within the exact account of both the interaction and the wave function \textit{without limiting the range of either the hopping processes or the two-site interactions}. The obtained results show that the method is particularly useful for accurate studies of electronic correlations in quantum dots and rings.

FIG. 1. Momentum distribution \( n(k) \) for electrons in linear ring of \( N = 10 \) atoms; the interatomic distance \( R \) is specified in units of Bohr radius \( a_0 \). The continuous line represents the parabolic interpolation, which is of the same type for both \( k > k_F \) and \( k < k_F \).
The nature of the electron momentum distribution \( n_{k\sigma} = \langle a_{k\sigma} \dagger a_{k\sigma} \rangle \) is shown in Fig. 1 for \( N = 10 \) atoms (we use the periodic boundary conditions). For the interatomic distance \( R = 3a_0 \), where \( a_0 \) is the 1s Bohr radius (setting the length scale), this is essentially the Fermi-Dirac function with a tail extending to the Brillouin zone boundary. The smearing out of the distribution with increasing \( R \) suggests that the electronic states transform from itinerant to localized states, as exemplified for \( R = R_c \approx 3.929 \). The continuous line represents the parabolic fit of the same type for both \( k \leq k_F \) and \( k \geq k_F \). A natural question to be dealt with is whether the Fermi ridge disappearance at \( R = R_c \) is reflected in any singularity in other properties.

To distinguish quantitatively between these states we plot in Fig. 2, the following basic quantities (as a function of \( R \)) defined in both itinerant and localized states: (i) the site spin magnitude \( \Theta_M = (4/3) \langle S_i^2 \rangle \), where \( S_i = (S_i^+, S_i^-, S_i^z) = (a_i^\dagger a_{i\uparrow}, a_i^\dagger a_{i\downarrow}, (n_{i\uparrow} - n_{i\downarrow})/2) \) is the electron spin on site \( i \), (ii) the spin correlation function \( \Theta_{AF} = -\langle S_i \cdot S_{i+1} \rangle \), and (iii) \( \Theta_{MI} = 4\sigma^2 \{n_{k\sigma}\} \), where \( \sigma^2 \{n_{k\sigma}\} \) is the dispersion of the statistical distribution defined as:

\[
\sigma^2 \{n_{k\sigma}\} = \frac{1}{2N} \sum_{k\sigma} n_{k\sigma}^2 - \left( \frac{1}{2N} \sum_{k\sigma} n_{k\sigma} \right)^2 . \tag{1}
\]

The averages are for the ground state, which is determined via an exact diagonalization in the Fock space. The quantity \( (\Theta_M = 1 - 2 \langle n_{i\uparrow} n_{i\downarrow} \rangle) \) takes the value \((1/2)\) in the ideal gas limit and approaches unity in the atomic limit, where we have a Pauli spin on each atom. \( \Theta_{AF} \) approaches the value \((3/4)\) for the singlet configuration of atomic spins, whereas \( \sigma^2 \{n_{k\sigma}\} \) acquires the value 1 in the gas limit \((n_{k\sigma} = \Theta (\mu - \epsilon_k)) \) and vanishes for an even momentum distribution \((n_{k\sigma} = 1/2)\), when the particle position is sharply defined on atom, i.e. for the localized electron states characterized by atomic states. Thus, the quantity \( \Theta_{MI} \) plays the role of the order parameter for this crossover behavior; since it clearly distinguishes between the complementary momentum and position representations of the system quantum states. From Fig. 2 it follows that for \( R/a_0 = 5 \) all three parameters acquire (within 5%) their asymptotic values for purely atomic states.

![FIG. 2. Correlations function versus distance R, depicting the crossover from itinerant to localized state (see main text), for \( N = 6 \) to 10 atoms. The shaded areas are drawn to illustrate the convergence of the results in the large \( R \) limit.](image)

The analysis of metal-insulator transition induced by electron-electron interaction started with the works of Mott [4] and Hubbard [3]. The first of them introduced the critical carrier concentration for the transition to take place in a discontinuous manner, whereas the second introduced the critical bandwidth to interaction ratio (of the order of unity). Our method of approach can be used to relate the above criteria, as we discuss next. Namely, to relate our method to the original ideas of Mott and Hubbard, we have plotted in Fig. 3 the ratio of bandwidth \( W = 2\sum_{ij} t_{ij} \) where \( t_{ij} \) is the hopping integral between the neighbors \((ij)\) (calculated through the relation \( t_{ij} = \langle w_i | H_1 | w_j \rangle \) for the basis \( \{w_i\} \) optimized in the correlated state and for full single-particle potential in \( H_1 \)), to the effective short range Coulomb interaction \( U - K \), where \( U = \langle w_i w_j V_{12} w_i w_j \rangle \) and \( K = \langle w_i w_{i+1} V_{12} w_i w_{i+1} \rangle \). The value \( W/(U - K) = 1 \)

![FIG. 3. The bandwidth-to-interaction ratio versus \( R \); the Hubbard point for localization [15] is marked. The inset provides the optimal size \( \alpha^{-1} \) (in units of \( a_0 \) for \( s \) atomic orbitals composing the optimized Wannier function.](image)
marked in this figure represents roughly the dividing line between metallic and Mott insulating states for three-
dimensional systems [1]. This point, achieved for $R \approx 2.7a_0$, does not reflect any characteristic point for our system. Instead, the localization is practically achieved for the distance about twice as large, as is the size of the atomic states composing the Wannier function [2] (characterized by the quantity $a^{-1}$, see the inset), which nears its atomic value for the s-like state. Again, the results for $N = 8$ and $N = 10$ are very close to each other; this is the reason why we have shadowed the areas between the corresponding curves in both Figs. 2 and 3.

On the basis of Figs. 2 and 3 we can estimate the localization threshold for our system. The corresponding Mott criterion [13], generalized to $d$ dimensions takes the form $n^{1/d}a_H \approx 0.2$, where $n_c$ is the carrier concentration, and $a_H$ is the size of the states at the localization threshold. In our situation of neutral chain: $n_c = 1/R$, and $a_H = \alpha^{-1}$ so that for $R \approx 5a_0$ this criterion takes the form $(a_0/R)(\alpha^{-1}/a_0) \approx 0.95/5 \approx 0.2$, a suprisingly close value to that of Mott (which reflects the long-range nature of the Coulomb interaction). Thus, our results provide a support for the Mott criterion rather than for the Hubbard one [14]. In other words, the metallicity extends well beyond the $W = U$ limit and this must be caused by the inclusion of more distant hopping processes. One may also say that the Mott-criterion universality originates from the long-range nature of the interaction, which imitates the higher-lattice dimensionality.

Hence, the conclusion [1] about the universality of the insulating state for the Hubbard chain does not extend to the $1d$ models with a realistic account of the electronic structure. This conclusion is very important also because it removes one of the main objections against using the itinerant (or even effective mass) states for quantum dots [2].

We can determine directly the effective mass at the Fermi level. Namely, the calculated band mass $m_F$ is about 40% enhanced near the localization threshold. The quasiparticle mass $m_F^*$ is found from the relation $m_F^* = (\Delta n_{k_F})^{-1}m_F$, where the first factor is the usual Fermi-liquid $Z^{-1}$ enhancement (the discontinuity at the Fermi level marked in Fig.1). The results are shown in Fig. 4. A clear critical behavior is detected: $m_F^* = A[R - R_c]^{-\gamma}$, with $A = 10.2, R_c = 3.92$, and $\gamma = 4/3$. This quantum critical behavior is obtained, since we emulate the discrete distribution $n_k$ with a continuous parabolic interpolation when determining $\Delta n_{k_F}$. The localization threshold $R_c$ is about 10% higher for $N = 8$. It is tempting to speculate that with the increasing $N \to \infty$ the Mott and the Hubbard criteria for $R_c$ may coalesce.

The one-dimensional systems are unstable with respect to the dimerization [10]. We have determined the ground state energy of such a state on the same level of precision as above and have additionally minimized it with respect to the amplitude of the lattice distortion. In Fig. 5 (bottom) we have compared the energy contribution $\Delta E$ due to the dimerization with that due to the zero-point motion (top). Both the dimerization amplitude and $\Delta E$ are strongly reduced for $R/a_0 > 5$, a feature inevitably connected with the long-range nature of Coulomb interactions, which drives the system towards spatially periodic state (the Mott insulating state on the lattice replaces the Wigner-crystal state [11] for the electron gas). Therefore, our results and conclusions above should remain intact for longer chains. Additionally, the zero-point energy overcomes the dimerization energy for a light (hydrogen) chain and has been estimated in the following manner.

In the harmonic approximation, the phonons have energy $\omega_k = 2(C/M)^{1/2} \sin(\pi k/N)$, where $M$ is ionic mass, and the elastic constant is calculated by a numerical differentiation $C = N^{-1}\partial^2E_G/\partial R^2$. Formally, these formulae are valid only if the energy has an absolute minimum. Here we assume that the system is closed in a box of length $NR$ and thus the global repulsive interaction between the atoms (the situation with $\partial E_G/\partial R < 0$ for given $R$) is balanced out by the environment. Also, as the $k=0$ mode is a Goldstone mode, we include only the modes with $k \neq 0$. The phononic contribution to the ground state energy (in the atomic units) is then

$$\Delta E_{G}^{th} = \left(\frac{2m}{M}\right)^{1/2} \left(\frac{1}{N} \frac{\partial^2E_G}{\partial R^2}\right)^{1/2} \sum_{k=1}^{N-1} \sin \left(\frac{\pi k}{N}\right),$$

where $m$ is the bare electron mass. On the basis of the relation for the $k$-th mode $(1/2)M\omega_k(\Delta R_k)^2 = \hbar \omega_k/2$, where $(\Delta R_k)^2$ is the mode contribution to the zero-point vibrations, we can easily estimate the total amplitude $(\Delta R)^2$, which in the atomic units has the form
\[(\Delta R)^2 = \frac{1}{N} \left( \frac{m}{2M} \right)^{\frac{1}{2}} \left( \frac{1}{N} \frac{\partial^2 E_G}{\partial R^2} \right) \sum_{k=1}^{N-1} \frac{1}{\sin(\pi k/N)}. \]

(3)

In the \( N \to \infty \) result gives \((\Delta R)^2 \sim \log N\), providing the dynamical lattice instability in one dimension. At the localization threshold (i.e., for \( R/a_0 \approx 5 \)) and for \( N = 8 \), we have that \( \Delta R \approx 0.12 \), a substantial. By comparison, the shift due to the dimerization is \( \approx 0.06 \). Also, the Peierls distorted state extends to the localized state (up to \( R \approx 6.5 a_0 \)).

In summary, we have determined the microscopic criteria for the transition from the itinerant to the localized states in a one-dimensional system of a finite size and have illustrated those findings on the example of a correlated quantum ring. The new method of optimizing the single-particle wave functions in the correlated state \([12]\) proves thus valuable in the exact treatment of nanoscopic systems. We have calculated all the properties as a function of the lattice parameter. The work was supported by KBN Grant No. 2PO3B 092 18.

---

[1] D. Jerome and H. J. Schulz, Adv. Phys. 31, 299 (1982); cf. also Correlated Electron Systems, edited by V. Emery (World Scientific, Singapore, 1993).
[2] L. Jacak, P. Hawrylak and A. Wójs, Quantum Dots (Springer Vlg., Berlin 1998); F. Ge, et al., Ann. Phys. (Leipzig) 9, 1 (2000); A. Sekiyama et al., Phys. Rev. B 51, R13899 (1995); A. Goni et al., Phys. Rev. Lett. 70, 1151 (1993).
[3] J. W. Mintmire, B. I. Dunlap, and C. T. White, Phys. Rev. Lett. 68, 631 (1992).
[4] A. A. Ovchinnikov, Zh. Eksp. Teor. Fiz. 64, 342 (1973) [Sov. Phys. - JETP 37, 176 (1973)]; J. Kondo and K. Yamaaji, J. Phys. Soc. Jpn. 43, 424 (1977); J. Hubbard, Phys. Rev. B 17, 494 (1978); S. Caponi, D. Poiblanc and T. Giamarchi, Phys. Rev. B 61, 13410 (2000).
[5] R. Strack and D. Vollhardt, Phys. Rev. Lett. 70, 2637 (1993); L. Arachea and A. A. Aligia, Phys. Rev. Lett. 73, 2240 (1994); A. A. Ovchinnikov, Mod. Phys. Lett. B 7, 1397 (1993); K. Michielssen, H. De Raedt and T. Schneider, Phys. Rev. Lett. 68, 1410 (1992); D. Poiblanc et al., Phys. Rev. B 56, R1645 (1997).
[6] E. H. Lieb and F. Y. Wu, Phys. Rev. Lett. 20, 1445 (1968).
[7] S. Daul and R. M. Noack, Phys. Rev. B 61, 1646 (2000).
[8] H. J. Schulz, Phys. Rev. Lett. 71, 1864 (1993); J. Voit, Rep. Prog. Phys. 57, 977 (1995).
[9] B. Dardel et. al. Europhys. Lett. 24, 687 (1993); A. Sekiyama et al., et al., Ref. [10].
[10] V. I. Anisimov, J. Zaanen and O. K. Andersen, Phys. Rev. B 44, 943 (1991); V. I. Anisimov, E. Aryasetiawan, and A. I. Lichtenstein, J. Phys: Condens. Matter 9, 767 (1997).
[11] W. M. Temmerman et. al., in Electronic Density Functional Theory Recent Progress and New Directions, edited by J. F. Dobson et. al., (Plenum, New York, 1998); A. Svane et. al., Int. J. Quantum Chem. 77, 799 (2000).
[12] J. Spalek et. al., Phys. Rev. B 61, 15676 (2000); A. Rycerz and J. Spalek, Phys. Rev. B 63, 073101 (2001).
[13] The statistical distribution within the Hubbard model (for \( d = 1 \)) was analysed in: J. Carmelo and D. Baeriswyl, Phys. Rev. B 37, 7541 (1988); M. Ogata and H. Shiba, ibid., B 41, 2326 (1990). For \( d = 2 \): J. Bonča et al. Solid State Commun. 78, 109 (1991); W. Stephan and P. Horsh, Phys. Rev. Lett. 66, 2258 (1991).
[14] N. F. Mott, Proc. Phys. Soc. A 62, 416 (1949); N. F. Mott, Metal-Insulator Transitions (Taylor & Francis, London, 1990).
[15] J. Hubbard, Proc. Roy. Soc. (London) A 281, 401 (1964).
[16] W. F. Brinkman and T. M. Rice, Phys. Rev. B 1, 4302 (1970); J. Spalek, A. Datta, and J. M. Honig, Phys. Rev. Lett., 59, 728 (1987).