Fundamental properties, localization threshold, and the Tomonaga–Luttinger behavior of electrons in nanochains

Adam Rycerz and Jozef Spałek
Marian Smoluchowski Institute of Physics, Jagiellonian University, Reymonta 4, 30-059 Kraków, Poland, e-mail: adamr@th.if.uj.edu.pl, ufspalek@if.uj.edu.pl

Abstract. We provide a fairly complete discussion of electronic properties of a nanochain within the recently proposed approach combining Exact Diagonalization in the Fock space with an Ab Initio calculations (EDABI method). In particular, the microscopic parameters of the second–quantized Hamiltonian are determined and the evolution of the system properties is traced in a systematic manner as a function of the interatomic distance (the lattice parameter, $R$). Both the many–particle ground state and the dynamical correlation functions are discussed within a single scheme. The principal physical results are: (i) the evolution of the electron momentum distribution and its analysis in terms of the Tomonaga–Luttinger scaling, (ii) the appearance of mixed metallic and insulating features (partial localization) for the half–filled band case, (iii) the appearance of a universal renormalized dispersion relation of electron energy, and (iv) the transformation from a highly–conducting nanometallic state to the charge–ordered nanoinulator in the quarter–filled case. The analysis is performed using the adjustable Gaussian 1s–like basis set composing the Wannier functions, as well as includes the long–range Coulomb interaction.

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1 Introduction

Recent development in computational, as well as analytical methods has lead to a successful determination of electronic properties of semiconductors and metals starting from LDA [1], LDA+U [2], and related [3] approaches. Even strongly correlated systems, such as V$_2$O$_3$ (undergoing the Mott transition) and high–temperature superconductors, have been treated in that manner [4]. However, the discussion of the metal–insulator transition of the Mott–Hubbard type is not as yet possible in a systematic manner, particularly for low–dimensional systems. These difficulties are caused by the circumstance that the electron–electron interaction is comparable, if not stronger than the single–particle energy. In effect, the procedure starting from the single–particle picture (band structure) and including subsequently the interaction via a local potential might not be appropriate then. In this situation, one resorts to parametrized models of correlated electrons, where the single–particle and the interaction-induced aspects of the electronic states are treated on equal footing. The single–particle wave–functions are contained in the formal expressions for the model parameters. We have proposed [5] to combine the two efforts in an exact manner, at least for some model systems.

In our method of approach (EDABI), we determine first rigorously the ground–state energy $E_G$ of the system of interacting particles in occupation–number representation, that is expressed as a function of microscopic parameters. Second, we optimize this energy with respect to the wave–functions contained in those parameters by deriving the self–adjusted wave equation for them. Physically, the last step amounts to allowing the single–particle wave functions relax in the correlated state. In practice, we propose the particular class of those functions, which are obtained by minimizing the ground–state energy $E_G$.

The EDABI method has been overviewed in number of papers [6,7,8], so we concentrate here on its application to one–dimensional (1D) nanochains of $N \leqslant 16$ atoms, close to the metal–insulator crossover transition. The paper complements our recent study of such systems [9,10] with the systematic analysis of both half– and quarter–filled band cases, as well as with the analysis of its transport properties. Throughout the paper we are using the adjustable Wannier functions composed of Gaussian basis set (STO–3G), that are determined explicitly from the minimization of the system ground–state energy $E_G$ as a function of the interatomic distance $R$.

The question of delocalization of atomic states has also a practical relevance. Namely, in dealing with electronic properties of quantum dots one usually assumes
the existence of the effective–mass states. The question for which systems this assumption is well founded, can be answered only by determining the critical interatomic distance, above which the states are localized. In this context, we address this question here for model systems composed of $s$–like states.

The structure of the paper is as follows. In the next Section we present briefly the basic idea of the EDABI method. Then, in Section 3 we provide the numerical ground–state analysis of nanochains with the long–range Coulomb interaction. Namely, we discuss the electron momentum statistical distribution function for the half–filled case and analyse it in terms of Tomonaga–Luttinger scaling (including the logarithmic correction), illustrate the charge–density wave ordering for the quarter filling, as well as analyze the $N$–particle wave function localization according the method developed by Resta [9]. In Section 4 we calculate the system charge and spin gaps, as well as perform the finite–size scaling with $1/N \to 0$ on these quantities. We also analyze the spectral density and extract from it the renormalized dispersion relation for the interacting electrons in a nanochain. To the best of our knowledge, such an exact renormalized one–electron band structure has not been determined before. Finally, the application of the present scheme to the higher ($ns$–like) valence orbital systems would make possible a direct comparison with the experimental results for nanowires made of noble and alkaline elements. Also, the correspondence between the localization criteria inferred from the ground–state properties on one side, as well as from the dynamical correlation functions, is established there.

2 The combined exact diagonalization ab–initio (EDABI) method

The basic idea of EDABI method [58] is illustrated on the block–diagram exhibited in Fig. 1. We start from choosing the initial Wannier basis set $\{w_i(\mathbf{r})\}$, composed of atomic–like wave functions (here a trial Gaussian basis set) with their radii $a_i$. Next, we write down the system Hamiltonian in the second–quantization form and determine the ground–state energy $E_0$ and the corresponding state in the Fock space $|\Psi_0\rangle$ by e.g. employing the Lanczos procedure. Next, the Wannier basis set $\{w_i(\mathbf{r})\}$ is optimized with respect to the atomic radii $a_i$, contained in the atomic wave functions composing $w_i(\mathbf{r})$, until the minimal ground-state energy $E_G$ is reached [5] for given lattice parameter $R$. On the right, the renormalized quantities (for the optimized basis) are listed.

3 The correlated electrons in a nanochain

We consider the system of $N_e$ electrons on $N$ lattice sites arranged periodically, each site containing a single valence orbital and an infinite–mass ion (i.e. we start from hydrogenic–like atoms). The Hamiltonian including all the Coulomb–interaction terms and neglecting other (e.g. exchange terms), can be written down (up to the constant) in the form

$$H = \epsilon_a^e \sum_i n_i + t \sum_{\sigma} \left( a_i^\dagger a_{i+1\sigma} + H.C. \right) + U \sum_i n_i n_{i+1} + \sum_{i<j} K_{ij} \delta n_i \delta n_j,$$

where $\delta n_i = n_i - 1$, $\epsilon_a^e = \epsilon_a + N^{-1} \sum_{i<j}(2/R_{ij} + K_{ij})$ (in Ry) is the effective atomic level, $R_{ij}$ is the distance between the $i$–th and $j$–th atoms, $t$ is the nearest–neighbor hopping, $U$ and $K_{ij}$ are the intra– and inter–site Coulomb repulsions, respectively. Thus, all the mean–field Coulomb terms are collected in $\epsilon_a^e$, whereas the last term in the above Hamiltonian represent the correlation part of the long–range interactions.

Hamiltonian (1) is diagonalized in the Fock space with the help of Lanczos technique. As the microscopic parameters $\epsilon_a^e$, $t$, $U$, and $K_{ij}$ are calculated numerically in the Gaussian basis, the orbital size of the $1s$–like state expressed in this basis is subsequently adjusted to obtain the minimal ground state energy $E_G$ as a function of the interatomic distance $R$. Earlier, we have shown [5] that such a combined exact diagonalization – ab initio study of the one dimensional system provides the localization threshold, the electron–lattice couplings, and the dimerization magnitude. Moreover, the utilization of the Gaussian–type orbitals leads to variational procedure that converges rapidly with the lattice size $N$ [7,10], so one can extrapolate the optimal orbital parameters for larger $N$ using those obtained for small systems (i.e. for $N = 6 \div 10$) and speed up the computation remarkably.

3.1 Statistical distribution and the Tomonaga–Luttinger scaling: The half–filled case

We discuss now the electron momentum distribution of 1D chain of $N = 6 \div 16$ atoms to address the question whether the system composes either the Luttinger–liquid or forms the insulating (Mott–Hubbard) state. We first summarize,
following Voit [11], the salient properties of 1D conductors, which include the two principal characteristics:

(i) A continuous momentum distribution function, showing the singularity near the Fermi level \( k \to k_F \) in the form (Solyom, Ref. [11])

\[
n_{k,\sigma} = n_F + A|k_F - k|^\theta \, \text{sgn}(k_F - k),
\]

where \( \theta \) is a non-universal (interaction-dependent) exponent; in consequence, it leads to the absence of fermionic quasi-particles (the quasi-particle residue in vanishes as \( z_k \sim |k_F - k|^\theta \) when \( k \to k_F \)). In other words, the Fermi ridge is absent in this case.

(ii) Similar power-law behavior of all the other physical properties, particularly of the single-particle density of states \( N(\omega) \sim |\omega - \mu|^\theta \) (pseudogap), that implies a finite Drude weight \( D > 0 \) for \( \theta < 1 \).

In the case of lattice models, such as the (extended) Hubbard model, the Luttinger liquid behavior is predicted by the renormalization group (RG) mapping onto Tomonaga–Luttinger model [11]. Through such mapping, one can also expect, with the increasing \( N \), the gradual convergence of the discrete momentum distribution \( n_{k,\sigma} \) into the continuous power-law form [2]. This hypothesis was first checked numerically for the Hubbard model by Sorella et al. [12].

Here we present the approach to a finite 1D chain with long-range Coulomb interaction, as described by the following Voit [11], with a simultaneous evaluation of the model parameters by optimizing the single-particle wave functions contained in those parameters [5]. The discrete electron–momentum distribution for the half-filling \((N_e = N)\) is depicted in Fig. 2a, whereas in Fig. 2b we replot it in the log-log scale together with the fitted theoretical curves, as explained below. In order to obtain those results we use the boundary conditions (BC) that minimize the ground-state energy for a given \( N \) (namely, the periodic BC for \( N = 4n + 2 \) and the antiperiodic BC for \( N = 4n \), at the half-filling).

To extract the exponent \( \theta \) accurately from the data for finite \( N \), it was necessary to include also the higher scaling corrections to [2]. They can be obtained from the Tomonaga mapping in the form of an expansion in the powers of \( \ln(\pi/|k_F - k|) \), namely,

\[
\ln |n_F - n_{k,\sigma}| = -\theta \ln z + b \ln \ln z + c + O(1/\ln z),
\]

where \( z = \pi/|k_F - k| \). This singular form of the expansion is required by the especially slow approach to the RG fixed point (Solyom, Ref. [11]). Obviously, by neglecting the logarithmic corrections one reaches the asymptotic form [2] for \( k \approx k_F \). The solid lines in Fig. 2a represent the formula [3] : the fitted values of the parameters \( \theta \), \( b \), and \( c \) are also listed in Table 1. The quality of the fit is decisively worse for the points far away from the Fermi momentum, and depends on \( N \), as the Fermi wave vector is \( N \)-dependent, i.e. \( k_F^N = k_F^\infty (1 - 2/N) \), where \( k_F^\infty = \pi/(2R) \) represents the Fermi wave vector for \( N \to \infty \). The exponent \( \theta \) is also plotted in Fig. 2a as a function of the lattice parameter \( R \) showing that it crosses the critical value \( \theta = 1 \) (corresponding to the metal–insulator boundary in 1D) for \( R_c = 2.60a_0 \) (\( a_0 = 0.529 \) Å is the Bohr radius). We also supply the residual sum of squares (cf. inset in Fig. 2a) to show, that the fit quality becomes worst for \( R \approx R_c \), where the system approaches the localization threshold.

The results for the half-filled system with the on-site Hubbard repulsion only, but with the atomic energy part included explicitly as a function of \( R \) [13], are qualitatively very similar to those displayed in Fig. 2. The critical value of the lattice parameter in that case is \( R_c = 2.16a_0 \), and also does not differ drastically from the previous one (cf. Table 2 for the corresponding values of all the fitted parameters in the Hubbard–model case). This is because such nanoscopic systems always have a finite conductivity in the large-density limit, since the external electron tunnels through a finite potential barrier. Therefore, such

| Table 1. The parameters of the expansion [3] for the half-filled chain with long-range Coulomb interactions. The corresponding standard deviations \( \sigma \) are also specified. |
| --- |
| \( R/a_0 \) | \( \theta \) | \( b \) | \( c \) | \( \sigma(\theta) \) | \( \sigma(b) \) | \( \sigma(c) \) |
| 1.5 | 0.138 | 0.015 | 0.147 | 0.024 | -0.567 | 0.115 |
| 2.0 | 0.387 | 0.055 | 0.425 | 0.089 | -0.346 | 0.053 |
| 2.5 | 0.803 | 0.122 | 0.971 | 0.196 | 0.084 | 0.118 |
| 3.0 | 1.307 | 0.128 | 1.315 | 0.207 | 0.357 | 0.125 |
| 4.0 | 1.455 | 0.186 | 1.113 | 0.290 | -0.032 | 0.180 |
| 5.0 | 1.413 | 0.133 | 0.943 | 0.214 | -0.823 | 0.129 |

![Table 1. The parameters of the expansion [3] for the half-filled chain with long-range Coulomb interactions. The corresponding standard deviations \( \sigma \) are also specified.](image)
half-filled systems, both with and without inclusion of the long-range interactions can be regarded as close to the metal–insulator transition, in no apparent contradiction with the infinite–chain RG result by Fabrizio [14], and with the Hubbard–model solution by Lieb and Wu [15]. This discussion is complete only after calculating the distribution function with the Hubbard–model solution by Lieb and Wu [15], in which we have interpreted the distribution in an almost flat manner for the interatomic distance $\sigma$. The points are arranged in an almost localized Fermi liquid. The points are arranged in an almost flat manner for the interatomic distance $\sigma$. The points are arranged in an almost flat manner for the interatomic distance $\sigma$. The points are arranged in an almost flat manner for the interatomic distance $\sigma$. The points are arranged in an almost flat manner for the interatomic distance $\sigma$. The points are arranged in an almost flat manner for the interatomic distance $\sigma$. The points are arranged in an almost flat manner for the interatomic distance $\sigma$. The points are arranged in an almost flat manner for the interatomic distance $\sigma$. The points are arranged in an almost flat manner for the interatomic distance $\sigma$. The points are arranged in an almost flat manner for the interatomic distance $\sigma$. The points are arranged in an almost flat manner for the interatomic distance $\sigma$. The points are arranged in an almost flat manner for the interatomic distance $\sigma$. The points are arranged in an almost flat manner for the interatomic distance $\sigma$. The points are arranged in an almost flat manner for the interatomic distance $\sigma$. The points are arranged in an almost flat manner for the interatomic distance $\sigma$. The points are arranged in an almost flat manner for the interatomic distance $\sigma. Finally, it should be noted that a well-defined spin–density–wave state develops with the increasing $R$ for the half-filled case, as discussed elsewhere [7,13]. The system ground–state energy as a function of $R$ is also provided there.

3.2 Onset of the charge–density wave state for the quarter filling

The electron quasi–momentum distribution for the quarter–filled (QF) case ($N_e = N/2$) is shown in Fig. 3. The available number of datapoints is too small to fit the singular expansion (3) to a reasonable accuracy. In effect, the lines on the plot are a guide to the eye only. However, the smooth behavior of the Luttinger–liquid type is evident for $R \lesssim 4a_0$, and changes dramatically for the larger values of $R$. This change reflects the onset of the charge–density–wave ordering, as illustrated in Fig. 4a in QF chain of $N = 16$ atoms (cf. Fig. 3). The charge is almost uniformly distributed for $R \lesssim 3a_0$, but the charge density wave (CDW) sets in very rapidly in the range $R/a_0 = 4/5$. The CDW order parameter, defined as $\theta_{\text{CDW}} \equiv \delta n(k_{\sigma})/\langle \delta n(k_{\sigma}) \rangle$, is drawn as a guide to the eye only. ABC and PBC denotes the antiperiodic and periodic boundary conditions.

We allow ourselves for one specific suggestion (if not speculation) at this point. Namely, the results shown in Fig. 2 (and the discussion in the remaining part of the paper) point to the possibility that the system with small $R \lesssim 2a_0$ can be analyzed as a Landau–Fermi liquid (albeit with discrete momentum states [16]), whereas the system with $2a_0 \lesssim R \lesssim 2.5a_0$ is closer to the Tomonaga–Luttinger–Solyom limit. For $R > 2.5a_0$ the electrons can be regarded as effectively localized. Such a division into three physically distinct regimes requires a further discussion, carried out, to some extent, below.

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3.3 Ground–state wavefunction localization

The approach \[9\] to the electron localization in the correlated state is based on the idea that although the insulating or the metallic states of matter are usually characterized by their excitation spectrum, the qualitative difference in dc conductivity must also reflect a qualitative difference in the organization of the electrons in their ground state. Such a concept was first emphasized by Kohn in a milestone paper \[17\], but a complete treatment, related to the Berry–phase theory of polarization, was proposed over 30 years later by Resta and Sorella (cf. Ref. \[18\]). In their approach the complex number \(z\) cannot be expressed as a single–particle operator (like \(X\)) and is rather a genuine many–body operator.

The numerical evaluation of the complex number \(z\), and the resulting \(\langle x^2 \rangle_c\), within the Lanczos algorithm is straightforward, since the operator \(e^{i(2\pi/L)\hat{X}}\) in Eq. \(1\) is diagonal in the position representation. The results for 1D system with long–range Coulomb interaction are shown in Fig. \(4\) for both the half– and the quarter–filled cases (cf. Fig. \(5\a\) and \(5b\), respectively). To avoid confusion by changing the system length \(L\), we plot the localization data in the units of lattice parameter \(R\), namely \(\langle x^2 \rangle_c/R^2\), instead of \(\langle x^2 \rangle_c\). The values of the localization parameter, depicted in Fig. \(3\a\), decay gradually with growing \(R\) for all available numbers of atoms \(N\). However, the dramatic change of the decay character takes place around the value of the lattice parameter \(R \approx 2.5a_0\) (cf. inset in Fig. \(3\a\)), where the curves for different \(N\) join together and forms a single one for \(R \geq 2.5a_0\). In contrast, for lower values of \(R\), the curves are well separated, showing the divergence of the localization parameter with \(N\) for \(R \lesssim 2a_0\). The results for the Hubbard model (not shown) again does not differ qualitatively from those presented in Fig. \(3\a\); the coalescence point is located than near the value \(R \approx 2.2a_0\). The positions of the joining points for both the models (with and without inclusion of the long–range Coulomb interactions) are very close to the corresponding critical
values \( R_c \) obtained form the Tomonaga–Luttinger scaling at the beginning of this Section.

The numerical results for the quarter–filled case, shown in Fig. 5b, are of lesser accuracy than those for the half–filling. This is because the complex expectation value \( z_{N_z} \), defined by Eq. (1), is itself a sum of many complex numbers with different phases, when calculated in the position representation. If the resulting \( z_{N_z} \) is close to zero, which is the case for QF for all examined values of \( R \), it is, in turn, strongly affected by the computer roundoff errors, which are also amplified by taking the logarithm of \( \langle z^2 \rangle \), from Eq. (6). Nevertheless, the evolution of the wavefunction localization parameter versus \( R \) is qualitatively similar to that for the half–filled case: the curves for different system sizes \( N \), depicted in Fig. 5b, get very close to each other for \( R \lesssim 4.5a_0 \), where the charge–density wave state is formed, as discussed in the preceding subsection.

The apparent correspondence between the wavefunction localization properties and the nature of electron momentum distribution, both discussed in this Section, suggests that a significant reorganization of the ground state takes place when the nanochain is close to the localization threshold. These observations are supplemented with an analysis of the system energy gap, the spectral function, and transport properties in the next Section.

4 Spectral and transport properties

4.1 The charge and the spin gaps

For a further verification, whether the system is quasi–metallic or insulating in the Luttinger–liquid like regime, we perform first an extrapolation with \( 1/N \to 0 \) of the charge–gap defined (for the half–filling) as

\[
\Delta E_C(N) = E_G^{N+1} + E_G^{N-1} - 2E_G^N, \tag{6}
\]

where \( E_G^N \) is the ground-state energy of the system containing \( N \) electrons. The corresponding numerical results are shown in Fig. 6 where we use again the proper boundary conditions (periodic or antiperiodic) that minimize the ground–state energy. The extrapolation with \( 1/N \to 0 \) performed using the 2–nd and the 3–rd order polynomials in \( (1/N) \) provides a nonzero value of \( \Delta E_C \) for wide range of the lattice parameter \( R \). Only for the lowest examined value of \( R = 1.5a_0 \), the gap \( \Delta E_C \) becomes zero within the extrapolation error; for \( R > 1.5a_0 \) it is clearly nonvanishing. The gap is also significantly smaller than the corresponding Hartree–Fock value in the regime \( R \lesssim 4.5a_0 \), suggesting that some kind of reorganization is present in the dielectric properties, e.g. a crossover from the Slater– to the Mott–type insulator, as discussed for the parametrized models [13]. This hypothesis is verified by estimating the spin gap below.

The situation changes completely when we consider the quarter–filled band case, \( N_z = N/2 \) (cf. Fig. 7). The parabolic extrapolation with \( 1/N \to 0 \) provides now the value of the charge–gap \( \Delta E_C \approx 0 \) (within the errorbars) for the lattice parameter \( R \lesssim 2a_0 \). In the range of \( R/a_0 = 2.5 \div 4.5 \) the gap develops (it is significantly greater than the corresponding errorbars), but a random dispersion of the datapoints suggests an inaccuracy of the performed extrapolation due to the nonanalytic behavior of \( \Delta E_C \) when the system approaches the localization threshold. For \( R \gtrsim 4.5a_0 \) the gap grows smoothly to a limiting value corresponding to that for the insulating charge–density wave state, identified earlier. The more precise position of the localization point is determined later in this Section, where we calculate the system Drude weight.

For a sake of completeness we now provide, in Fig. 8, the values of the system spin gap, which is defined as

\[
\Delta E_S \equiv E_G(S_z = 1) - E_G(S_z = 0), \tag{7}
\]

where \( E_G(S_z) \) denotes the lowest eigenenergy in the subspace with a given total \( z \)-component of spin \( S_z \). Through the finite–size scaling with \( 1/N \to 0 \), we obtain the spin gap \( \Delta E_S \approx 0 \) for both the half– and the
quarter-filled cases (cf. Figs. 8a and 8b, respectively) and in the whole examined range of the interatomic distance \( R \). These results show clearly that the insulating phase of the system is of the Mott type in the large-\( N \) limit. No indications of the Slater-type phase, for which \( \Delta E_C = \Delta S > 0 \), was found. However, for a nanosystem containing \( N \sim 10 \) atoms, one can note that the so-called correlated insulator (\( \Delta E_C > \Delta S > 0 \)), existing for small values of \( R \) (cf. insets to Figs. 8a and 8b), transforms gradually into the Mott insulator with the increasing \( R \). This evolution should be contrasted with the evolution of bulk three-dimensional systems where the Slater antiferromagnet evolves into the Mott insulator.

4.2 Spectrum of single-particle excitations: renormalized bands vs. Hubbard subbands

The evolution of the single-particle spectral density function \( A_k(\omega) \) with the increasing \( R \) is shown in Fig. 9a for the half-filled (\( N_e = N \)) nanochain described by the Hamiltonian \( \hat{H} \). The spectral function is defined in the standard manner, namely

\[
A_k(\omega) = \sum_n \left| \langle \Psi^{N\pm}_n | c_{k\sigma} \rangle \right|^2 \delta \left[ \omega - \left( E^{N\pm}_n - E^0_0 \right) \right],
\]

where the upper (lower) sign correspond to \( \omega > \mu \) (\( \omega < \mu \)), respectively, \( \langle \Psi^{N}_n \rangle \) is the \( n \)-th eigenstate of the system containing \( N \) particles, \( E^{N}_n \) is the corresponding eigenenergy, and the matrix element \( \langle \Psi^{N\pm}_n | c_{k\sigma} \rangle \), with \( c_{k\sigma} = \alpha_k \) and \( \beta_k \), is calculated within the Lanczos technique set up by Dagotto [21]. For plotting the purposes, we have used analytical representation of Dirac delta function \( \delta(x) \to (1/\pi)\epsilon/(x^2 + \epsilon^2) \) with \( \epsilon = 0.01 \) Ry. In the nanometric range (\( R \lesssim 2.5a_0 \)), the quasiparticle peaks are well defined, but incoherent tails are always present and grow in strength with the increasing \( R \). In effect, in the intermediate regime of \( R \sim 3a_0 \) the lower and the upper Hubbard bands are formed, which, in turn, continuously evolve into discrete atomic levels located at the positions \( \omega = \epsilon_a \) and \( \omega = \epsilon_a + U \), when \( R \to \infty \). Those limiting peak positions correspond to the ground (\( H^0 \)) and excited (\( H^- \)) atomic levels. Probably, the most interesting feature of this spectrum is its incoherent nature for \( R \sim 3a_0 \), where the band and the interaction energies are comparable and where the Luttinger liquid exponent crosses the critical value \( \theta = 1 \) (cf. Section 3.1), corresponding to the localization threshold.

A direct picture of the spectrum evolution is provided by the renormalized dispersion relation, obtained from the spectral function by extracting the major quasiparticle peak position for each momentum \( k \), and plotted in Figs. 9a–d. We again easily identify: (i) the nanometric range (cf. Fig. 9a) for \( R = 1.5a_0 \), for which the charge gap is of the same order as the energy discretization due to the geometrical quantization of the quasiparticle momenta, (ii) the intermediate regime (cf. Fig. 9b, \( R = 3a_0 \)) where the gap become significantly wider, and (iii) the atomic limit (cf. Fig. 9c, \( R = 8a_0 \)), in which two dispersionless manifolds located at the energies \( \omega = \epsilon_a \) and \( \omega = \epsilon_a + U \) appear. One should also note that the corresponding results for the antiferromagnetic Hartree–Fock solution match closely those obtained within the EDABI method, both for the atomic and for the nanometric limits (particularly for the upper Hubbard band in the latter case). The electron–correlation effects, in contrast, appear clearly (near the Fermi momenta) for the intermediate range of \( R \), where the Hartree–Fock charge gap is significantly larger than the exact one (cf. preceding Section).

Another interesting feature of the renormalized dispersion relation is that the datapoints for different \( N = 10 \) and 12 compose a single (universal) dispersion curve \( \bar{c}_k \) provided that the proper boundary conditions, which minimize the ground–state energy for a particular \( N \), are applied. The results for \( \bar{c}_k \) and those for the distribution func-

**Fig. 8.** Spin gap for the half-filled (a) and the quarter-filled (b) nanochains. The results obtained through the finite-size scaling are also shown with the corresponding errorbars.

**Fig. 9.** Spectral functions \( A_k(\omega) \) for the nanochain of \( N = 10 \) atoms (a) and the corresponding renormalized dispersion relations for the lattice parameter \( R = 1.5a_0 \) (b), \( R = 3a_0 \) (c), and \( R = 8a_0 \) (d). The quasiparticle energies for antiferromagnetic Hartree–Fock solution (solid lines) are also shown for the comparison.
tion $n_{ks}$ (cf. Fig. 2a) characterize in a fundamental manner the salient features of electronic states for the quantum nanoliquid. They are supplemented with the results for the transport properties, which are considered next.

### 4.3 Drude weight and optical conductivity

The real part of the optical conductivity at zero temperature is determined by the corresponding real part of the linear response to the applied electric field and can be written as $\sigma(\omega) = D\delta(\omega) + \sigma_{\text{reg}}(\omega)$, where the regular part is

$$\sigma_{\text{reg}}(\omega) = \frac{\pi}{N} \sum_{n \neq 0} \frac{|\langle \Psi_n | j_p | \Psi_0 \rangle|^2}{E_n - E_0} \delta(\omega - (E_n - E_0)), \quad (9)$$

whereas the Drude weight (the charge stiffness) $D$ is defined by

$$D = -\frac{\pi}{N} \langle \Psi_0 | T | \Psi_0 \rangle - \frac{2\pi}{N} \sum_{n \neq 0} \frac{|\langle \Psi_n | j_p | \Psi_0 \rangle|^2}{E_n - E_0}, \quad (10)$$

with the kinetic–energy term $T$ as the second term in Eq. (4) and the diamagnetic current operator defined as usual: $j_p = it \sum_{\sigma} \langle \Psi_{\sigma} | a_{\sigma} a_{\uparrow \downarrow} - \text{HC} \rangle$. Here the states $|\Psi_0\rangle$ in Eqs. (9) and (10) are the eigenstates of Hamiltonian corresponding to the eigenenergies $E_n$, again with the boundary conditions that minimize the ground–state energy for a given system size $N$. Matrix elements $\langle \Psi_n | j_p | \Psi_0 \rangle$ are calculated within the Lanczos method [20]. For plotting purposes, we also use again the analytic representation of Dirac delta function $\delta(x) \to (1/\pi\epsilon)/\sqrt{x^2 + \epsilon^2}$, with $\epsilon = 0.01$ Ry.

For finite system of $N$ atoms $D$ is always nonzero due to a nonzero tunneling probability through a potential barrier of finite width. Because of that, the finite–size scaling with $1/N \to 0$ has to be performed on $D$. Here we use, after Góra et al. [21], the following parabolic extrapolation

$$\ln |D_N^a| = a + b(1/N) + c(1/N)^2, \quad (11)$$

where $D_N^a$ denotes the normalized Drude weight $D^* = -(N/\pi)D / \langle \Psi_0 | T | \Psi_0 \rangle$ for the system of $N$ sites, that provides the value in the range $0 \leq D^* \leq 1$, and thus can be regarded as an alternative order parameter for the transition to the localized (atomic) state.

The results for 1D system of $N = 6 \div 14$ atoms in the half–filled chain case are shown in Fig. 11. The values of $D_N^a$ used for the scaling (11) are listed in Table 3 together with the resulting $D_N^a$ and its relative error (we stop at the lattice parameter $R$ for which $D_N^a = 0$ within the range of errorbars). We also provide, for comparative purposes, the data for the system with the on–site Coulomb interaction only (i.e. for the Hubbard model) in Table 4. In both cases with the long–range (cf. Table 3) and the on–site only (cf. Table 4) interactions, the extrapolated Drude weight $D_N^a$ becomes significantly greater than zero of 2σ value only for small lattice parameter, $R \leq 2.6a_0$ and $R \leq 2.1a_0$, respectively. The limiting values match nicely those for which the Luttinger–liquid exponent crosses the critical value $\theta = 1$, corresponding to the localization–delocalization boundary. The above results suggest again the localization onset in these 1D systems at half–filling. However, the optical conductivity $\sigma_{\text{reg}}(\omega)$, drawn in Fig. 10, shows the isolated Hubbard peak at $\omega \approx U$ and no intraband transitions present in delocalized state. Because of this fact, and also because of the nonzero value of the charge–gap for any $R$ (cf. above), one should regard both the half–filled systems studied here as the Mott insulators in the large $N$ limit. Nevertheless, the finite–$N$ results show, that the conductivity of the nanoscopic chain diminishes by two orders of magnitude when the corresponding increase of the lattice parameter $R$ is in the range of $40 \div 50\%$. So, one can consider such system as undergoing a transformation either from a nanoliquid to the localized spin system at the half–filling or from an intrinsically partially localized state, since the intraband transitions are absent even in the small–$R$ range. It would be very interesting to confirm experimentally these results.

The situation becomes again completely different at the quarter–filling (QF). Namely, the normalized Drude weight of the QF systems of $N = 8 \div 16$ atoms, depicted
in Fig. 11, shows a highly conducting behavior \( (D^* \approx 1) \) for \( R \lesssim 3.5a_0 \) and gradually transforms to zero in the range \( R/a_0 = 4/5 \). Also, the regular part of conductivity \( \sigma_{\text{reg}}(\omega) \) \( (\text{cf. Fig. 11b}) \) comprises intraband transitions in the quasi–metallic range, particularly near the onset of the charge–density wave state \( (N = 16) \). Such a behavior provides the model case for the transformation from a nanometal in the small–R range to the charge–ordered system \( (\text{cf. Fig. 4}) \) for larger \( R \).

5 A brief overview: New features

We have provided a fairly complete description of electronic states in a finite 1D chain within the framework of EDABI method, which combines the exact diagonalization of many–fermion Hamiltonian in the Fock space with a subsequent \( \textit{ab initio} \) readjustment of the single–particle (Wannier) functions. Both the ground–state and dynamical properties have been obtained as a function of the variable lattice parameter \( (\text{interatomic spacing}) \) \( R \). Our approach thus extends the current theoretical treatments of band and strongly correlated systems within the parametrized \( (\text{second–quantized}) \) models by determining those parameters and, in turn, analyzing the correlated state explicitly as a function of \( R \). The single–particle wavefunction is allowed to readjust in the correlated state within the EDABI method thus unifies the second and the first quantization aspects of the many–particle states into a single scheme.

We start from analyzing the situation with one valence electron per atom \( (\text{the half–filled case}) \) and includes the long–range Coulomb interaction. The Luttinger–liquid type of the electron momentum distribution suggests a crossover transition from the quasi–metallic to the insulating \( (\text{spin–ordered}) \) state with the increasing \( R \) (the same is true about the system without the long–range interaction \( 14 \), but the quasi–metallic behavior is manifested to much stronger degree when the long–range part of the Coulomb interactions is included). The finite–size scaling with \( 1/N \rightarrow 0 \), performed on the charge–energy gap shows the insulating nature of the ground state for the large \( N \) limit, in agreement with the renormalization–group results for the infinite system with two Fermi points \( 14 \). Such an apparently dychotomic nature \( (\text{localized vs. itinerant}) \) of the nanoscopic systems is confirmed by their transport properties. On one hand, the Drude weight is nonzero in the small \( R \) limit and the localization threshold agrees with those obtained from the Luttinger–liquid exponent, but the regular part of the optical conductivity exhibits the insulating behavior. This is the reason we coined the term: partly localized quantum nanoliquid. The most fundamental features of the electrons as a quantum nanoliquid is provided in Figs. 2b and 10–d, where Fermi–like distribution, as well as the renormalized band structure appear for small interatomic spacing. These features evolve with \( R \rightarrow R_0 \) into atomic–like through the regime with split Hubbard–like subbands.

An illustrative example of the nanoscopic system with a clear transformation from nanometal to nanoininsulator with the charge–density wave order is provided with the quarter–filled nanochain \( (\text{when including again the long–range Coulomb interaction}) \). For that system, the Drude weight is reduced gradually from its maximal value to zero and other properties evolve analogously with the increasing lattice parameter \( R \). The intermediate range of \( R \), where the crossover takes place, also shrinks rapidly with the increasing \( N \), suggesting the existence of a sharp zero–temperature transition in the large \( N \) limit.

The above analysis, for both the half– and the quarter–filled cases is very sensitive to the choice of the boundary

### Table 3. Normalized Drude weight \( D_N \), the extrapolated value \( D_N^\infty \), and its relative error for 1D half–filled system with long–range Coulomb interaction.

| \( R/a_0 \) | \( D_{14}^1 \) | \( D_{12}^1 \) | \( D_{10}^1 \) | \( D_{8}^1 \) | \( D_{6}^1 \) | \( D_{4}^1 \) | \( D_{2}^1 \) | \( D_{0}^1 \) | \( \sigma(D_N^\infty)/D_N^\infty \) |
|---|---|---|---|---|---|---|---|---|---|
| 1.5 | 0.9225 | 0.9420 | 0.9563 | 0.9727 | 0.9822 | 0.8008 | 0.019 |
| 2.0 | 0.6245 | 0.7105 | 0.7875 | 0.8660 | 0.9222 | 0.2567 | 0.129 |
| 2.5 | 0.1839 | 0.2812 | 0.4109 | 0.5813 | 0.7526 | 0.0087 | 0.420 |
| 2.6 | 0.1269 | 0.2096 | 0.3315 | 0.5065 | 0.7009 | 0.0033 | 0.489 |
| 2.7 | 0.0840 | 0.1508 | 0.2595 | 0.4312 | 0.6441 | 0.0012 | 0.566 |
| 3.0 | 0.0196 | 0.0461 | 0.1047 | 0.2314 | 0.4575 | 0.0000 | – |

### Table 4. Normalized Drude weight \( D_N^\infty \), the extrapolated value \( D_N^\infty \), and its relative error for 1D half–filled system described by the Hubbard model.

| \( R/a_0 \) | \( D_{14}^\infty \) | \( D_{12}^\infty \) | \( D_{10}^\infty \) | \( D_{8}^\infty \) | \( D_{6}^\infty \) | \( \sigma(D_N^\infty)/D_N^\infty \) |
|---|---|---|---|---|---|---|
| 1.5 | 0.6173 | 0.6742 | 0.7342 | 0.7973 | 0.8640 | 0.3294 | 0.070 |
| 2.0 | 0.1529 | 0.2259 | 0.3276 | 0.4631 | 0.6331 | 0.0092 | 0.364 |
| 2.1 | 0.0991 | 0.1598 | 0.2527 | 0.3884 | 0.5731 | 0.0032 | 0.449 |
| 2.2 | 0.0619 | 0.1094 | 0.1896 | 0.3190 | 0.5123 | 0.0010 | 0.540 |
| 2.5 | 0.0124 | 0.0294 | 0.0687 | 0.1561 | 0.3372 | 0.0000 | – |
conditions. This problem is widely studied in the existing literature and its relation to the spontaneous magnetic flux appearing in the mesoscopic rings of $N = 4n$ atoms 22 has been established before 23. The EDABI method implement here can be applied to discuss also the coupling of electrons the lattice and the dimerization (for a discussion see the third paper in Ref. 5). Also, one should incorporate the properties of chain with odd number of electrons (the boundary conditions will involve then the complex number domain). Furthermore, the dynamics with single holes and impurities in the nanochain would make the system more realistic as a quantum wire. Finally, the application of the present scheme to the higher (ns–like) valence orbital systems would make possible a direct comparison with the experimental results quantum nanowires made of noble and alkaline elements. We should be able to see a progress along these lines soon.

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References

1. P.C. Hohenberg, W. Kohn, L.I. Sham, in Adv. Quantum Chemistry, edited by S.B. Trickey, vol. 21 (Academic, San Diego, 1990), p. 7; W. Temmerman et al., in Electronic Density Functional Theory: Recent Progress and New Directions, edited by J.F. Dobson et al. (Plenum, New York, 1998), p. 327.
2. V.I. Anisimov, et al., Phys. Rev. B 44, 943 (1991); P. Wei and Z.Q. Qi, ibid. 49, 10864 (1994).
3. A. Svane and O. Gunnarson, Europhys. Lett. 7, 171 (1988); Phys. Rev. Lett. 65, 1148 (1990).
4. S. Ezhov, et al., Phys. Rev. Lett. 83, 4136 (1999); K. Held et al., ibid. 86, 5345 (2001).
5. J. Spalek, et al., Phys. Rev. B 61, 15676 (2001), and unpublished; A. Rycerz and J. Spalek, ibid. 63, 073101 (2001); ibid. 65, 035110 (2002); J. Spalek and A. Rycerz, ibid. 64, R161105 (2001).
6. J. Spalek, et al., Acta Phys. Polon. B 31, 2879 (2000); ibid. 32, 3189 (2001).
7. A. Rycerz, et al., in Lectures on the Physics of Highly Correlated Electron Systems VI, edited by F. Mancini, AIP Conf. Proc. vol. 629 (New York, 2002) p. 213; ibid. vol. 678 (New York, 2003) p. 313.