The combined exact diagonalization- \textit{ab initio} approach and its application to correlated electronic states and Mott-Hubbard localization in nanoscopic systems

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Abstract. We overview the EDABI method developed recently and combining the exact diagonalization and \textit{ab initio} aspects of electron states in correlated systems and apply it to nanoscopic systems. In particular, we discuss the localization-delocalization transition for the electrons that corresponds to the Mott-Hubbard transition in bulk systems. We show, that, the statistical distribution function for electrons in a nanochain evolves from the Fermi-Dirac-like to the Luttinger-liquid-like with the increasing interatomic distance. The concept of Hubbard subbands is introduced to nanoclusters, and corresponds to the HOMO-LUMO splitting in the molecular and organic solid states. Also, the nanochains exhibit magnetic splitting (Slater-like), even without the symmetry breaking, since the spin-spin correlations extend over the whole system. Thus, the correlated nanoscopic systems exhibit unique and universal features, which differ from those of molecular and infinite systems. These features define unique properties reflecting "the Mott physics" on the nanoscale. We also employ the EDABI method to the transport properties in nanoscopic systems. For example, we show that the particle-hole symmetry is broken when the tunneling conduction through $H_2$ molecule is calculated.

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1. Introduction

The studies of nanosystems are becoming increasingly important in view of their application in quantum nanoelectronics and related fields of research. Of particular importance are their quantum electronic properties, since they determine their behavior as concrete devices: quantum nanowire connectors and semiconducting elements, single-electron transistors, spin valves etc. Under these circumstances, solid-state and molecular nanophysics is developing very rapidly to provide proper quantitative (and qualitative) characteristics of their static, transport, and optical properties [1].

Independently of the applications, the research in nanophysics is important for its own fundamental sake. Namely, the nanosystems are finite systems and therefore, most of the limiting situations considered in the condensed matter physics and involving the limit for the number of atoms \( N \to \infty \), is simply inapplicable. Furthermore, the role of boundary conditions is very nontrivial, as they should reflect the system actual configuration. Also, and probably most importantly, the question of electron-electron interactions, particularly for extended states, should be taken into account on equal footing with the single-electron aspects of their quantum states, since the screening processes are very often highly ineffective. Nevertheless, given the circumstances, the role of physics is to single out universal properties of the systems such as nanowires, clusters, quantum dots, etc. Such research involves also determining the conditions, under which the bulk-solid concepts are applicable, since then the description can be simplified remarkably.

In this article we present our recent and earlier results concerning the studies of nanosystems containing as an intrinsic property the electron correlation effects induced by the Coulomb interactions, within the devised EDABI method combining both exact diagonalization and \textit{ab initio} aspects of electronic states, as well as their transport properties [2]. This approach allows for discussing the evolution of the physical properties of e.g. nanowires or clusters, both as a function of their interatomic distance, as well as to determine the values of microscopic single-particle and interaction parameters. The visualization of the properties as a function of interatomic distance is particularly important for nanometer size systems, as they are studied customarily by placing them on a substrate with the lattice parameter, which differs from their equilibrium interatomic distance (sometimes the substrate even stabilizes them).

Our most interesting results can be summarized as follows. First, we show how the system properties evolve from the Fermi-liquid-like to the atomic-like states for nanowires containing up to \( N = 16 \) simple atoms, passing through the Luttinger-liquid-like state, with the increasing interatomic distance \( R \). This evolution is determined by calculating directly the system statistical distribution function \( n_{k\sigma} \) of electrons and their dynamical spectral function. Finite-size scaling properties are introduced to determine the \textit{Mott critical interatomic distance} ( \textit{the Mott criterion} ) for the transition from the delocalized to the localized states. Secondly, we show that the electronic states in nanosystems of \( N \sim 10 \) atoms exhibit a magnetic splitting reminiscent of
the Slater splitting in antiferromagnetic metallic systems. This type of symmetry change is associated with the breakdown of the discrete translational symmetry, as the antiferromagnetism sets in. In the case of nanosystems such symmetry breakdown is not required. It turns out, that the splitting appears if the spin-spin correlation length is of the system size. The splitting should be detected e.g. in nanowires containing strongly correlated electrons in a half-filled valence band configuration. Thirdly, the question arises whether with the increasing interatomic distance one should not observe the Hubbard split-band structure of nanowire and molecular (e.g. $H_N$ or $Li_N$) clusters? We show that nanocluster levels group into multiple Hubbard subbands (in bulk systems such a grouping is termed as HOMO and LUMO structures). Finally, in the case of a quantum dot composed of e.g. $H_2$ molecule attached to the semimacroscopic electrodes we show, that the electron-hole symmetry in the tunneling transport through the molecule is not preserved and is due to the difference in electronic binding energy of $H_2^+$ and $H_2^-$ states. Such result is not obtained if a parameterized model of a quantum dot properties is used.

The structure of this paper is as follows. In the next Section we overview the EDABI method, as well as discuss some of the many-electron general properties adopted to the analysis carried out in the next Sections. We also compare the method with the configuration interaction (CI) approach used in quantum chemistry. In Section 3 we discuss atomic systems and $H_N$ nanoclusters, whereas in Section 4 the results for nanochains containing up to $N = 16$ atoms are elaborated in detail. In Section 5 we employ the EDABI method to calculate the tunneling conductivity through the $H_2$ molecule and the Drude weight for the nanochains. We also discuss the role of boundary conditions there.

The present method and the research grew out of our earlier work on the thermodynamics of the Mott-Hubbard transition in correlated systems. There, the principal question was if the metallic and magnetic insulating states can be regarded as separates phases in the thermodynamic sense? The affirmative answer to the above question provided a partial answer to the Sir Nevill Mott question: What is a metal? In this article the corresponding principal question: how small a piece of metal can be? In other words, can a nanochain composed of e.g. $N = 10$ Cu atoms be regarded already as a metallic system and in what sense? The answer is ‘yes’, but above a critical value of voltage applied to the chain and for not too large interatomic distance.

2. Exact diagonalization combined with an ab initio approach

2.1. General features

The second-quantization language is used when we have an interaction between the quantum physical fields representing the classical particles composing the system. The approach is usually formulated in the occupation-number representation, expressing the possible occupations of a given (complete in quantum mechanical sense) set of single-
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particle states, between which there are transitions induced by their mutual interaction. Explicitly, the single-particle basis \( \{\Phi_i(r)\} \) defines the field operator \( \hat{\Psi}(r) \), in terms of which the many-particle Hamiltonian (or Lagrangian) is defined. In the nonrelativistic case, the Hamiltonian is defined as \[ \hat{H} = \int d^3r \hat{\Psi}^\dagger(r) H_1(r) \hat{\Psi}(r) + \frac{1}{2} \int d^3r d^3r' \hat{\Psi}^\dagger(r) \hat{\Psi}^\dagger(r') V(r - r') \hat{\Psi}(r') \hat{\Psi}(r) \equiv \hat{T} + \hat{V} \] (1)

with

\[ \hat{\Psi}(r) = \sum_i \Phi_i(r) a_i. \] (2)

\( H_1(r) \) represents Hamiltonian for a single particle in the assembly of \( N \) indistinguishable particles, \( V(r - r') \) is the interaction between a single pair of particles, \( a_i \) is the annihilation operator of the particle in the single particle state \( \Phi_i(r) \). One should underline that the basis \( \{\Phi_i(r)\} \) should be complete, but otherwise arbitrary (it does not have to be orthogonal \[10\]).

The complete set of \( \{\Phi_i(r)\} \) in (2) is in practical calculations not infinite, so we have to resort to a finite subset of \( \{\Phi_i(r)\} \) when performing explicit computations, i.e. constructing \textit{many-particle models}. In this manner, we make the basis \textit{incomplete} in the quantum-mechanical sense, even though the model may be well justified on physical grounds as it may contain principal dynamic processes involved. In the first step, we diagonalize \( H \) in the Fock space for given trial basis \( \{\Phi_i(r)\} \). Then, as a next step, one can optimize the finite (incomplete) subset taken by e.g. minimizing the ground state energy \( E_G \equiv \langle \Phi_0 | \hat{H} | \Phi_0 \rangle \) (where \( |\Phi_0\rangle \) is the ground state wave function in the Fock-space representation), with respect to the selected subset \( \{\Phi_i(r)\} \). Such procedure is highly nontrivial, since the determination of \( E_G = E_G\{\Phi_i(r), \nabla \Phi_i(r)\} \) requires first the diagonalization of the parameterized Hamiltonian \[11\] in the Fock space \[11\] (with the microscopic parameters containing both \( \{\Phi_i(r)\} \) and \( \{\nabla \Phi_i(r)\} \)) and, only after that, setting up an effective wave equation for each \( \Phi_i(r) \), with \( E_G \) treated as a functional of the trial basis \( \{\Phi_i(r)\} \). The resultant renormalized or \textit{self-adjusted wave equation} (SWE) should have a universal meaning to the same degree, as has the starting Hamiltonian \[11\] in that incomplete basis. We call this method of approach EDABI (a combined Exact Diagonalization - AB Initio approach). In this manner, only then the approach to the interacting system can be regarded as \textit{completed}, particularly in the situation when the interparticle interaction cannot be regarded as weak, e.g. for \textit{correlated systems}. Obviously, when the correlations are weak, the approach reduces to the Hartree-Fock approximation. This approach has been implemented so far to some exactly soluble models of correlated electrons and to nanochains \[12,13,14\] containing up to \( N = 16 \) atoms using as a trial basis, with adjustable Slater or Gaussian orbitals \[4\]. Here we present a rather extensive analysis of our method, applicable to both fermion and boson systems, as well as construct explicitly the multiparticle wave function is the simplest
atomic situations. The last aspect of the work may be applied to both atomic and molecular systems providing e.g. a systematic approximation scheme in the quantum-chemical calculations. In particular, the explicit many-particle wave-function construction allows for a comparison with the method of multiconfigurational interaction (MCI) approach utilized in quantum chemistry. Simply put, we develop a relatively straightforward (but not simple!) workable scheme, which is applicable to both many-electron atoms, molecules and molecular ions, as well as to clusters and nanoscopic systems.

One can summarize important features of our approach as follows. First, the interaction and the single particle terms in the many-particle Hamiltonian are treated on an equal footing. Second, the single-particle wave function appears in a nonexplicit form in the expression for the microscopic parameters and is determined explicitly from the variational principle for the ground-state energy $E_G = \langle \hat{T} \rangle + \langle \hat{V} \rangle \equiv E_G\{\Phi_i(r)\}$, which leads to the self-adjusted wave equation \[16\]. Third, the explicit construction of the multiparticle wave function $\Psi(r_1, ..., r_N)$ in terms of the field operators \[17\] provides a way of systematizing the approximation schemes. Fourth, one does not count twice the interaction, which should be taken with care in e.g. in LDA+U method. All of these features are particularly important for the systems, for which the interaction cannot be treated as a perturbation. Among such systems are cluster and various correlated Fermi and Bose systems, particularly of low dimensionality. Probably the most important formal feature of the present approach is that by reversing the order of solving the problem (treating first the interaction in the Fock space and only then determining the single particle wave function in the Hilbert space), we complete the treatment of strongly correlated systems. Unfortunately, our approach is executable so far only in limited number of situations. As a side result we obtain also the values of microscopic parameters for the parametrized models \[18\]. In effect, the physical properties can be analyzed as a function of interatomic distance, not only as a function of model parameters, and thus provide us with the global minimum for system at hand and for given interatomic distance.

The self-adjusted wave equation (SWE), as we shall see, is of nonlocal and nonlinear nature. Hence, it is very difficult to solve it directly. Nonetheless, the main purpose of the present paper is to present the solution in the closed variational form and illustrate its character in simple situations, ranging from the atomic physics to nanophysics.

### 2.2. Renormalized (self-adjusted) wave equation (SWE)

We start with Hamiltonian \[11\] and write down in the explicit-spin basis, in which the spin is regarded as an additional coordinate, i.e. in the form

$$
\hat{H} = \sum_{\sigma} \int d^3r \hat{\Psi}_{\sigma}^\dagger (r) H_1(r) \hat{\Psi}_{\sigma} (r)
$$

$$
+ \frac{1}{2} \sum_{\sigma_1 \sigma_2} \int d^3r_1 d^3r_2 \hat{\Psi}_{\sigma_1}^\dagger (r_1) \hat{\Psi}_{\sigma_2}^\dagger (r_2) V(r_1 - r_2) \hat{\Psi}_{\sigma_2} (r_2) \hat{\Psi}_{\sigma_1} (r_1).
$$

(3)
We define the spin-dependent field operator as

$$\hat{\Psi}_\sigma(r) = \sum_{i=1}^{M} w_i(r) \chi_\sigma a_i^\sigma, \quad (4)$$

where \{w_i(r)\} is a complete single-particle basis with the set of quantum numbers denoted by $i$. Note that we regard the Hamiltonians $H_1(r)$ and $V(r_1 - r_2)$ as spin independent (it is straightforward to generalize the formalism to the case with spin-dependent Hamiltonian, i.e. when magnetic field or spin-orbit interaction are included). Substituting (4) into (3) we obtain the usual form of the Hamiltonian

$$H = \sum_{ij\sigma} t_{ij} a_i^\sigma a_j^{\sigma^\dagger} + \frac{1}{2} \sum_{ijkl\sigma_1\sigma_2} V_{ijkl} a_i^{\sigma_1} a_j^{\sigma_2} a_l^{\sigma_2} a_k^{\sigma_1}, \quad (5)$$

with the microscopic parameters defined by

$$t_{ij} \equiv \langle w_i | H_1 | w_j \rangle \equiv \int d^3r w_i^*(r) H_1(r) w_j(r), \quad (6)$$

and

$$V_{ijkl} \equiv \langle w_i w_j | V | w_k w_l \rangle \equiv \int d^3r_1 d^3r_2 d^3r_3 d^3r_4 w_i^*(r_1) w_j^*(r_2) V(r_1 - r_2) w_k(r_3) w_l(r_4) \quad (7)$$

In the standard form (5) of the many-particle Hamiltonian the single- and many-particle aspects of the problem are separated in the sense that the calculation of the hopping parameter $t_{ij}$ and their interaction correspondants $V_{ijkl}$, both containing the single-particle wave-functions \{\psi_i(r)\}, is separated from the diagonalization procedure of the Hamiltonian in the Fock space [19]. The latter procedure is dependent only on the nature of the commutation relation between the annihilation ($a_i^{\sigma^\dagger}$) and creation ($a_i^\sigma$) operators. Thus this two-step procedure can be seen explicitly when we calculate the system ground-state energy

$$E_G \equiv \langle H \rangle = \sum_{ij\sigma} t_{ij} \langle a_i^{\sigma^\dagger} a_j^{\sigma} \rangle + \frac{1}{2} \sum_{ijkl\sigma_1\sigma_2} V_{ijkl} \langle a_i^{\sigma_1} a_j^{\sigma_2} a_l^{\sigma_2} a_k^{\sigma_1} \rangle, \quad (8)$$

where the averaging $\langle \ldots \rangle$ takes place over all accessible occupancies of given single particle states $|i\sigma_1\rangle$, $|j\sigma_2\rangle$, $|k\sigma_1\rangle$, and $|l\sigma_2\rangle$. Obviously, if we want to consider all occupancies (a grand canonical ensemble), we diagonalize $H - \mu N$, where $N$ is the total number of particles and only a posteriori impose the conditions that $N = \sum_{i\sigma} \langle n_{i\sigma} \rangle$, with $n_{i\sigma} \equiv a_i^{\sigma^\dagger} a_i^{\sigma}$.

So far, the approach is standard [9,10]. We have proposed [2,12,13,14] to close the solution (i.e. the complete calculation of e.g. $E_G$) with the determination of the single-particle basis \{\psi_i(r)\} by treating the expression (6) as a functional of the set of functions \{\psi_i(r)\} and their gradients. In such situation the renormalized (self-adjusted) wave equation is determined from the Euler equation for the functional

$$E\{\psi_i(r)\} \equiv E_G\{\psi_i(r)\} - \mu N - \sum_{i \geq j} \lambda_{ij} \left( \int d^3r w_i^*(r) w_j(r) - \delta_{ij} \right), \quad (9)$$
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where

\[ N = \sum_{\sigma} \int d^3 \langle \hat{\Psi}^\dagger_{\sigma}(\mathbf{r}) \hat{\Psi}_{\sigma}(\mathbf{r}) \rangle = \sum_{ij\sigma} \int d^3 \mathbf{r} w^*_i(\mathbf{r}) w_j(\mathbf{r}) \langle a^\dagger_{i\sigma} a_{j\sigma} \rangle, \]

\( N \) is the number of particles in the system, and \( \lambda_{ij} \) are the Lagrange multipliers, when the single-particle basis is nonorthonormal.

The general form of this equation in the stationary case and in the grand canonical-ensemble formalism is

\[ \frac{\delta (E_G - \mu N)}{\delta w^*_i(\mathbf{r})} - \nabla \frac{\delta (E_G - \mu N)}{\delta (\nabla w^*_i(\mathbf{r}))} - \sum_{i \geq j} \lambda_{ij} w_j(\mathbf{r}) = 0. \tag{10} \]

We will make a \textit{fundamental} postulate concerning this equation: \textit{As this equation does not contain explicitly the (anti)commutation relations between the creation and annihilation operators, it is equally valid for both fermions and bosons and determines a rigorous, within the class of states included in the definition of \( \hat{\Psi}(\mathbf{r}) \), wave equation for a single particle wave function in the ground state, in the milieu of remaining \((N-1)\) particles. Additionally, as is implicit in the treatment above, we have defined one global spin-quantization axis for all single particle states used to define \( \hat{\Psi}_{\sigma}(\mathbf{r}) \). In some spin noncolinear systems this is insufficient and will require a more refined treatment. Also, if we use the particle conserving approach to calculate \( E_G \), then we put \( \mu \equiv 0 \) in (10). Likewise, for the orthonormal basis \( \{w_i(\mathbf{r})\} \) used to define \( \hat{\Psi}_{\sigma}(\mathbf{r}) \) in (4), one puts \( \lambda_{ij} \equiv 0 \). In the latter case the system (10) represents a set of Euler equations for renormalized Wannier functions. In what follows we discuss examples of application of this equation to fermion systems (it can be applied to Bose systems in the same manner). But first, we define the renormalized many particle wave function as complementing the above renormalized single particle states \( \{w_i(\mathbf{r})\} \) and then discuss the differences with the MCI approach.}

\[ 2.3. \text{Multiparticle wave function from the second-quantization approach} \]

The general \( N \)-particle state \( |\Phi_N\rangle \) in the Fock space can be defined through the corresponding \( N \)-particle wave function \( \Psi_\alpha(\mathbf{r}_1, \ldots, \mathbf{r}_N) \) in the Hilbert space in the following manner [9, 17]

\[ |\Phi_N\rangle = \frac{1}{\sqrt{N!}} \int d^3 \mathbf{r}_1 \ldots d^3 \mathbf{r}_N \Psi_N(\mathbf{r}_1, \ldots, \mathbf{r}_N) \hat{\Psi}^\dagger(\mathbf{r}_1) \ldots \hat{\Psi}^\dagger(\mathbf{r}_N) |0\rangle, \tag{11} \]

where \( |0\rangle \) is the vacuum state. One can reverse this relation and a simple algebra yields the following expression for the wave function \( \Psi_\alpha(\mathbf{r}_1, \ldots, \mathbf{r}_N) \) in terms of \( |\Phi_N\rangle \)

\[ \Psi_\alpha(\mathbf{r}_1, \ldots, \mathbf{r}_N) = \frac{1}{\sqrt{N!}} \langle 0 | \hat{\Psi}(\mathbf{r}_1) \ldots \hat{\Psi}(\mathbf{r}_N) |\Phi_N\rangle. \tag{12} \]

In other words, to obtain the wave function in the coordinate representation, we not only annihilate \( N \)-particles from the state \( |\Phi_N\rangle \), but also project out thus obtained result onto the Fock vacuum state and normalize it by the factor \((N!)^{-1/2}\). Usually, the formula (12) is not used as we proceed from first to second quantization. Now,
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\[ \sum_j H_{ij} w_j(r) = \epsilon_i w_i(r) \]

\[ \{w_i(r)\} \]

\[ \Psi(r), \Psi^\dagger(r) \]

\[ H = |\Psi_0\rangle E_G \langle \Psi_0| + \ldots \]

\[ \Psi_{\text{ren}}(r), (\Psi_{\text{ren}})^\dagger(r) \]

\[ \Psi_{\text{ren}}^0(r_1, \ldots, r_N) \]

\textit{Renormalized $N$-particle wave function}

\textbf{Figure 1.} Flow-chart describing the scheme of the EDABI method. For details see main text. When selecting the Gaussian starting single-particle set, the topmost block should be disregarded.

\emph{the crucial point} is based on the observation that if we substitute in the field operator $\hat{\Psi}(r)$ the renormalized wave functions obtained from Eq. (10), then we should obtain the renormalized field operator and as a consequence, the renormalized multiparticle wave function $\Psi_\alpha(r_1, \ldots, r_N)$ from relation (12). This last step of inserting renormalized field operator completes the procedure of a formal treatment of many-particle system, which avoids writing down explicitly the N-particle Schrödinger equation. The whole approach is schematically represented in Fig. 1. This scheme provides an exact renormalized single-particle wave function from Eq. (10) and the exact $N$-particle wave function provided we can diagonalize the second-quantized model Hamiltonian (5) for the problem at hand. We shall see next, that we can approach the true solution also step by step.

\subsection*{2.4. Finite-basis approximation for the field operator: Difference with the multiconfiguration interaction (MCI) approach}

The field operator $\hat{\Psi}(r)$ defined in terms of the sum over a complete basis $\{w_i(r)\}$ contains an infinite number of single-particle states. We assume that, in general, we represent the field operator by $M$ wave functions $\{w_i(r)\}$. Explicitly,

\[ \hat{\Psi}(r) \equiv \sum_{i=1}^{\infty} w_i(r) a_i \simeq \sum_{i=1}^{M} w_i(r) a_i, \quad (13) \]

with $i$ representing a complete set of quantum numbers and $M$ being a finite number. This approximation represents one of the most \textit{fundamental} features of constructing theoretical models. The neglected states usually represent highly excited (and thus negligible) states of the system. We can then write the approximate N-particle wave
function \((N \leq M)\) in the following manner

\[
\Psi_{\alpha}(\mathbf{r}_1, \ldots, \mathbf{r}_n) = \frac{1}{\sqrt{N!}} \sum_{i_1, \ldots, i_N=1}^{M} \langle 0 | a_{i_N} \ldots a_{i_1} | \Phi_N \rangle w_{i_1}(\mathbf{r}_1) \ldots w_{i_N}(\mathbf{r}_N). \tag{14}
\]

Recognizing that within the occupation-number space spanned on the states \(\{ |i_k\rangle \}_{k=1 \ldots M}\), we have the \(N\)-particle state in the Fock space of the form

\[
| \Phi_N \rangle = \frac{1}{\sqrt{N!}} \sum_{j_1, \ldots, j_N=1}^{M} C_{j_1 \ldots j_N} a_{j_1}^\dagger \ldots a_{j_N}^\dagger | 0 \rangle, \tag{15}
\]

where \(C_{j_1 \ldots j_N}\) represents the coefficients of the expansion to be determined from a diagonalization procedure. Substituting (15) to (14) we obtain

\[
\Psi_{\alpha}(\mathbf{r}_1, \ldots, \mathbf{r}_N) = \frac{1}{N!} \sum_{i_1, \ldots, i_N=1}^{M} \sum_{j_1, \ldots, j_N=1}^{M} \langle 0 | a_{i_1} \ldots a_{i_N} a_{j_1}^\dagger \ldots a_{j_N}^\dagger | 0 \rangle C_{j_1 \ldots j_N} w_{i_1}(\mathbf{r}_1) \ldots w_{i_N}(\mathbf{r}_N). \tag{16}
\]

The expression provides \(N!\) nonzero terms each equal to \((-1)^P\), where \(P\) represents the sign of the permutation of quantum numbers \((j_1 \ldots j_N)\) with respect to selected collection \((i_1 \ldots i_N)\). In other words, we can write that

\[
\Psi_{\alpha}(\mathbf{r}_1, \ldots, \mathbf{r}_N) = \frac{1}{N!} \sum_{i_1, \ldots, i_N=1}^{M} C_{i_1 \ldots i_N} (A, S)[w_{i_1}(\mathbf{r}_1) \ldots w_{i_N}(\mathbf{r}_N)]. \tag{17}
\]

We have the same expansion coefficients for both wave function in the fock space \(| \Phi_N \rangle\) and that in Hilbert space \(\Psi_{\alpha}(\mathbf{r}_1, \ldots, \mathbf{r}_N)!\) Therefore, the above expression represents the multiconfigurational-interaction wave function of \(N\) particles distributed among \(M\) states with the corresponding weights \(C_{i_1 \ldots i_N}\) for each configuration, and \((A, S)\) represents respectively the antisymmetrization (Slater determinant) or the symmetrization (simple product \(w_{i_1}(\mathbf{r}_1) \ldots w_{i_N}(\mathbf{r}_N)\)) for the fermions and bosons, respectively. Whereas MCI used in quantum chemistry \([20]\) bases on variational optimizations of both the coefficients \(C_{i_1 \ldots i_N}\) and the basis \(\{ w_{i}(\mathbf{r}) \}\), here the coefficients \(C\) are determined from diagonalization in the Fock space, spanned on \(M\) states in the Hilbert space and determined from \((10)\). The presence of SWE \((10)\) thus supplements the usual MCI approach.

Summarizing, the differences between the EDABI and the MCI methods, both of which belong to the class of multi-determinant expansion of \(N\)-particle wave function, are threefold:

i) **Historical.** MCI evolved from variational methods of quantum physics and chemistry to include the electronic correlations and hence, to obtain lower value of \(E_G\) by starting from many-particle Schrödinger equation. EDABI represents a procedure of calculating single-particle wave function starting from parameterized models of strongly correlated electrons.
ii) **Technical.** In MCI, we optimize simultaneously the coefficient expressing the weights of different determinants (representing different micro-configurations), as well as the parameters of the trial single-particle basis. In EDABI, we diagonalize the Hamiltonian expressed in the Fock space (with the help of either analytic or numerical methods), combined with a simultaneous optimization of the orbital size in the resultant ground state.

iii) **Essential.** In the case of analytically soluble models, EDABI leads formally to the explicit form of the renormalized wave equation, which represents a *nonlinear Schrödinger equation of nonlocal type*. This circumstance opens up a new direction of studies in *mathematical quantum physics*. Additionally, it allows for a direct determination of dynamical correlation functions, transport properties, etc. in the convenient, second-quantization, language.

2.5. **An interpretation of the approach: rationale behind the self-adjusted wave function in the many-body system**

Usually, the choice of starting single-particle basis \( \{ w_i(r) \} \) is dictated by the physics of the system at hand. Since the creation and annihilation processes are characterized only by the quantum numbers \( i \) of those starting single-particle states, one can say that they represent a *particle language* characterizing transitions between those states. The ground state energy obtained from the diagonalization in the Fock space defines resultant single-particle states, which can be called the *self-adjusted* states, after the optimization of the single-particle wave function has been carried out via solving the *self-adjusted wave equation* (SWE)\(^{21, 22}\) or its variational version. In other words, we allow the initial particle wave function \( w_i(r) \) to adjust to the correlated state. In such scheme the particle and the wave aspects of the single-particle states are intertwined formally, illustrating among others the particle-wave complementarity, this time in a formal manner. For example, the Born probability density of finding a particle is taken here as \( \sum_{\sigma} \langle \hat{\Psi}_\sigma^\dagger(r) \hat{\Psi}_\sigma(r) \rangle / N \). In what follows we essentially illustrate the method on concrete examples and apply it to nano systems.

One may ask the basic question: Why to revert the usual sequence of solving the single-particle wave equation first, and only then constructing the field operators in the second-quantization Hamiltonian (or Lagrangian), by solving the many-particle Hamiltonian first and only then readjusting the orbitals? The reason for this is as follows. As said above, in many cases (e.g. for correlated and/or low-dimensional fermionic systems) we encounter the situation when the interaction cannot be regarded as a perturbation and therefore should be treated *at least* on equal footing with the single-particle aspect of the problem. This is because, in general, the interaction may change the class of the stationary-state wave function. Such a situation is beautifully illustrated on example of metal-insulator phase transition of the Mott-Hubbard type, at which the metallic state represented by the Bloch-type wave functions switches to the localized (Wannier-type) states even though those representations are regarded as equivalent from a single-particle
point of view. In other words, the interaction determines the particle wave function. Furthermore, the electron as a separate entity (lepton) is preserved even in the highly correlated milieu of other particles and therefore, constructing the self-consistent wave equation (SWE) has a sense as it provides its wave function adjusted to the environment.

2.6. Single-particle basis selection and the particle-density space profiles

As we have already mentioned, the selected single-particle basis \( w_i(x) \equiv \{ \Phi_i(x) \} \) is determined from the variational principle for \( E_G \{ \Phi_i(x), \nabla \Phi_i(x) \} \), and it should satisfy the self-adjusted wave equation. Here we solve this equation variationally and take a trial basis \( \{ \Phi_i(\alpha; x) \} \) dependent on a finite number of parameters \( \alpha \equiv \{ \alpha_p \}_{p=1,\ldots,K} \). Moreover, if the basis is orthonormal, then the equation can be simplified then to the form

\[
\frac{\delta (E_G - \mu N)}{\delta \alpha} = 0. 
\] (18)

In most applications we select adjustable atomic orbitals as the basic functions \( \{ \Phi_i(\alpha; x) \} \), which need to be orthonormalized with a special kind of orthonormalization procedure. Additionally, if the number of particles \( N \) is conserved by the Hamiltonian \( H \) then the term \( \mu N \) in (18) is absent, and the equation reduces to the ordinary energy minimization \( E_G \equiv \langle H \rangle \) with respect to the variation parameters \( \{ \alpha_p \} \).

2.7. A remainder: Wannier basis for an extended periodic system

Let us consider the multi-particle systems for a single-band case for atoms located at positions \( \{ R_i \} \) and the basic wave functions \( \{ \Phi_i(\alpha; x) \} \) of the form \( \{ \Phi(\alpha; x-R_i) \} \). The orthonormalization procedure for periodic structures can be obtained by starting with the expression for the Bloch function

\[
\Phi_q(\alpha; x) = N_q \sum_{j=1}^N e^{i q \cdot R_j} \Phi_j(\alpha; x), \tag{19}
\]

where \( N_q \) is a normalization coefficient. The normalization condition then takes form

\[
\langle \Phi_q(\alpha; x) | \Phi_{q'}(\alpha; x) \rangle = N_q^* N_{q'} \sum_{j} e^{-i q \cdot R_j + i q' \cdot R_j} \langle \Phi_j(\alpha; x) | \Phi_{l}(\alpha; x) \rangle 
= N_q^* N_{q'} \sum_{j} e^{i (q' - q) \cdot R_j} \sum_{l} e^{i q' \cdot (R_l - R_j)} S_{ij} \equiv \delta_{qq'}, \tag{20}
\]

where \( S_{ij} \) is an overlap integral. The last sum does not depend on the relative distance, hence

\[
\langle \Phi_q(\alpha; x) | \Phi_{q'}(\alpha; x) \rangle = N_q^* N_{q'} N \delta_{qq'} \sum_{l} e^{i q' \cdot (R_l - R_j)} S_{ij} \equiv \delta_{qq'}, \tag{21}
\]

and thus

\[
|N_q| = (N \sum_l e^{i q \cdot (R_l - R_j)} S_{ij})^{-1/2}. \tag{22}
\]
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As we can see, the above wave functions \( \{ \Phi_q(\alpha; r) \} \) are the Bloch functions, from which we can construct the Wannier functions \( \{ w_l(\alpha; r) \} \) in the usual manner, i.e.

\[
\begin{align*}
    w_l(\alpha; r) &= \frac{1}{\sqrt{N}} \sum_q e^{-i\mathbf{q} \cdot \mathbf{R}_l} \Phi_q(\alpha; r) \\
    &= \frac{1}{\sqrt{N}} \sum_q e^{-i\mathbf{q} \cdot \mathbf{R}_l(A)} \sum_j e^{i\mathbf{q} \cdot \mathbf{R}_j} \Phi_j(\alpha; r) \\
    &= \sum_j \Phi_j(\alpha; r) \left( \frac{1}{\sqrt{N}} \sum_q N_q e^{-i\mathbf{q} \cdot (\mathbf{R}_l - \mathbf{R}_j)} \right) \\
    &\equiv \sum_j \beta_{lj} \Phi_j(\alpha; r),
\end{align*}
\]

where

\[
\beta_{lj} = \frac{1}{N} \sum_q \frac{e^{-i\mathbf{q} \cdot (\mathbf{R}_l - \mathbf{R}_j)}}{\sqrt{\sum_m e^{-i\mathbf{q} \cdot (\mathbf{R}_n - \mathbf{R}_m)} S_{mn}}}. \quad (24)
\]

The orthonormal Wannier set \( \{ w_l(\alpha; r) \} \) obtained with the help of the above procedure is thus a set of linear combinations of the originally non-orthonormal atomic orbitals. Moreover, the coefficients \( \{ \beta_{lj} \} \) depend only on \( \mathbf{R}_l - \mathbf{R}_j \) and satisfy the relation \( \beta_{lj} = \beta_{lj}^* \).

2.8. Wannier functions for finite systems

The above procedure can be applied with modifications to finite cluster systems. We start from the decomposition

\[
\begin{align*}
    w_l(\alpha; r) &= \sum_{j=1}^{M} \beta_{lj} \Phi_j(\alpha; r), \quad (25)
\end{align*}
\]

with the normalization condition in the form

\[
\langle w_l(\alpha; r) | w_l(\alpha; r) \rangle = \sum_{jk} \beta_{lj}^* \beta_{lk} \langle \Phi_j(\alpha; r) | \Phi_k(\alpha; r) \rangle = \sum_{jk} \beta_{lj}^* \beta_{lk} S_{kj} \equiv \delta_{ll}. \quad (26)
\]

In the matrix language, this condition can be rewritten as

\[
\beta S \beta^+ = 1, \quad (27)
\]

or, equivalently as

\[
\beta^+ \beta = S^{-1}. \quad (28)
\]

We choose the \( \beta \) matrix in the form \( \beta = \beta^+ \); in effect this choice leads to the relation

\[
\beta = S^{-1/2}. \quad (29)
\]

The above method is known as the Löwdin method of determining the orthonormal basis, and for the overlap integral matrix becomes unity if elements of the system are separated from each other at large distances. So, the \( \beta \) matrix then can be written down as

\[
\beta = 1 + \sum_{n=1}^{\infty} \frac{(-1)^n \Delta^n}{2^n n!} \prod_{k=1}^{n} (2k - 1) = 1 + \sum_{n=1}^{\infty} \Delta^n \prod_{k=1}^{n} \left( \frac{1}{2k} - 1 \right), \quad (30)
\]
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where $\Delta = S - 1$. However, the above series does not converge in the tight binding approach and it has to be modified to the form

$$ \beta = \left( \frac{(1 + C)S}{1 + C} \right)^{-1/2}, $$

(31)

and thus

$$ \beta = (1 + C)^{-1/2}[1 + \sum_{n=1}^{\infty} \Delta_{C}^{n} \prod_{k=1}^{n} \left( \frac{1}{2k} - 1 \right)], $$

(32)

where $\Delta_{C} \equiv S/(1 + C) - 1$. The parameter $C$ allows us to manipulate convergence of the series, for it appears in the convergence condition

$$ \| \Delta_{C} \| < 1, $$

(33)

that needs to be satisfied for any kind of the $\| \cdot \|$ metrics. Therefore, we choose the metrics

$$ \| \Delta_{C} \|_{\infty} \equiv \max_{ij} \{ \frac{|S_{ij}|}{1 + C} - \delta_{ij} \} = \max\{ \frac{C}{1 + C} ; \frac{\max_{i \neq j} |S_{ij}|}{1 + C} \}. $$

(34)

As we can see, the metrics satisfies the condition when the parameter $C$ is equal to

$$ C = \max_{i \neq j} |S_{ij}|. $$

(35)

The method, we have just shown, can be applied to both single-band and to multiple-band systems. The method can also be applied to disordered systems. In what follows we will select as a starting atomic basis $\{ \Phi_{i}(r) \}$ either Slater or Gaussian (STO-3G) basis when constructing the Wannier function, and subsequently, optimize their size in the correlated state.

2.9. Particle density profiles in space

In the previous Section we dealt with the N-particle wave function $\Psi(r_1, ..., r_N)$. Here we show how it can be applied to the evaluation of particle density $n(r)$. We start with the usual definition of the probability density for a single particle:

$$ \rho(r_N) = \int d^3 r_1 ... r_{N-1} |\Psi(r_1, ..., r_N)|^2. $$

(36)

We utilize now the expression (4) for the wave function we obtained in Section II. In effect,

$$ |\Psi(r_1, ..., r_N)|^2 = \frac{1}{N!} \langle \Phi_N | \hat{\Psi}^+(r_N) ... \hat{\Psi}^+(r_1) |0\rangle \langle 0 | \hat{\Psi}(r_1) ... \hat{\Psi}(r_N) |\Phi_N \rangle. $$

(37)

We have the particle-number conservation and hence we can rewrite (37) as

$$ |\Psi(r_1, ..., r_N)|^2 = \frac{1}{N!} \langle \Phi_N | \hat{\Psi}^+(r_N) ... \hat{\Psi}^+(r_1) \hat{\Psi}(r_1) ... \hat{\Psi}(r_N) |\Phi_N \rangle. $$

(38)
The expectation value of the particle-number operator \( \sum_n |N\rangle \langle N| \) instead of \( |0\rangle \langle 0| \). The expression for the field operator \( \hat{\Psi} (r) \), defined with the help of the orthonormal basis \( \{w_i (r)\} \) in (4), leads to the following relation

\[
\hat{\Psi}^+ (r) \hat{\Psi} (r) = \sum_{i_1 \sigma_1 i_2 \sigma_2} w^*_{i_1} (r) \chi^*_{\sigma_1} w_{i_2} (r) \chi_{\sigma_2} a^+_{i_1 \sigma_1} a_{i_2 \sigma_2},
\]

and thus

\[
\hat{\Psi}^+ (r) \hat{\Psi} (r) = \sum_{i \sigma} w^*_{i_1} (r) w_{i_2} (r) a^+_{i \sigma} a_{i \sigma}.
\]

Therefore, we can apply the above relation to the expression for \( \rho (r_N) \). Namely, by noting that

\[
\rho (r_N) = \int d^3 r_2 ... r_{N-1} (\int d^3 r_1 |\Psi (r_1, ..., r_N)|^2),
\]

we can obtain the following series of helpful identities:

\[
\frac{1}{N!} \sum_{i_1 i_2 ...} (\int d^3 r_1 w^*_{i_1} (r_1) w_{i_2} (r_1)) \langle \Phi_N | \hat{\Psi}^+ (r_2 ... r_N) \rangle \langle \hat{\Psi} (r_1 ... r_N) | \Phi_N \rangle = \frac{1}{N!} \sum_{i_1 i_2 ...} n_{i_1} n_{i_2} \cdots \langle \hat{\Psi} (r_2 ... r_N) | \Phi_N \rangle.
\]

The expectation value of the particle-number operator \( \sum_{i \sigma} n_{i \sigma} \) is equal to unity for the multi-particle state \( \hat{\Psi} (r_2 ... r_N) |\Phi_N \rangle \sim | \Phi_{N=1} \rangle \). Obviously, the subsequent procedure applied \( N - 2 \) times leads to the net result

\[
\rho (r_N) = \frac{1}{N} \langle \Phi_N | \hat{\Psi}^+ (r_N) \hat{\Psi} (r_N) | \Phi_N \rangle.
\]

This result can be understood if we introduce explicitly the particle-density operator

\[
\hat{n} (r) \equiv \hat{\Psi}^+ (r) \hat{\Psi} (r),
\]

and thus the particle density is

\[
n (r) \equiv N \rho (r) = \langle \Phi_N | \hat{\Psi}^+ (r) \hat{\Psi} (r) | \Phi_N \rangle.
\]

Hence, we obtain the explicit expression for the density of particles using Eq.(4), i.e.

\[
n (r) = \sum_{i_1 i_2} w^*_{i_1} (r) w_{i_2} (r) \langle \Phi_N | a^+_{i_1 \sigma} a_{i_2 \sigma} | \Phi_N \rangle,
\]

or, equivalently

\[
n (r) = \sum_i |w_i (r)|^2 \langle n_i \rangle + \sum_{i_1 \neq i_2} w^*_{i_1} (r) w_{i_2} (r) \sum_\sigma \langle a^+_{i_1 \sigma} a_{i_2 \sigma} \rangle,
\]

where averages \( \langle ... \rangle \) are taken with the N-particle ground state \( | \Phi_N \rangle \).

The first of two terms represents the contribution of the particle-number operator to the total density of particles and appears in the Hartree-Fock approach as the only term. The second term can provide a significant contribution when the averages \( \langle a^+_{i_1 \sigma} a_{i_2 \sigma} \rangle \) is
of the same magnitude as the first contribution. Explicitly, if the N-particle function has the form of a simple determinant

$$\Psi_{i_1 \ldots i_N}(r_1, \ldots, r_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} w_{i_1}(r_1) & \ldots & w_{i_N}(r_1) \\ \vdots & \ddots & \vdots \\ w_{i_1}(r_N) & \ldots & w_{i_N}(r_N) \end{vmatrix},$$

then the occupancies $\langle n_i \rangle \equiv 1$ in (47) and $\langle a_1^\dagger a_2^\sigma \rangle \equiv 0$ for $i_1 \neq i_2$. This is not the case when the multi-configurational form (12) of $\Psi(r_1, \ldots, r_N)$ is taken, as we shall see in the following. In the remaining part of this paper we discuss the results obtained within this method of approach for various nanosystems.

3. Atomic systems and nanoclusters

In this Section we start with the simplest examples of lightest atoms and ions to illustrate the specific features of the EDABI method, as well as to provide an elementary example of the renormalized wave equation. In particular, we systematically enrich up the trial basis to build up the Fock space.

3.1. A didactic example: He atom

We start by selecting as $\{w_i(r)\}$ just two 1s-like states for the He atom $\Phi_\sigma(r) = (\alpha^2/\pi)^{1/2} \exp(-\alpha r) \chi_\sigma$, where $\alpha$ is the effective inverse radius of the states. In other words, the simplest trial field operator is of the form

$$\hat{\Phi}(r) = \Phi_\uparrow(r) a_\uparrow + \Phi_\downarrow(r) a_\downarrow,$$

where $a_\sigma$ is the annihilation operator of particle in the state $\Phi_\sigma(r)$. The Hamiltonian in the second quantization for this two-element basis has then the form

$$H = \epsilon_a (n_\uparrow n_\downarrow) + Un_\uparrow n_\downarrow,$$

where $n_\uparrow = a_\uparrow^\dagger a_\uparrow$, whereas

$$\epsilon_a = \langle \Phi_\sigma | H_1 | \Phi_\sigma \rangle,$$

and

$$U = \langle \Phi_\sigma \Phi_\sigma^\dagger | V | \Phi_\sigma \Phi_\sigma \rangle$$

are the matrix elements of the single-particle part defined as

$$H_1 = -\frac{\hbar^2}{2m} \nabla_1^2 - \frac{\hbar^2}{2m} \nabla_2^2 - \frac{2e^2}{\kappa_0 r_1} - \frac{2e^2}{\kappa_0 r_2} \equiv -\nabla_1^2 - \nabla_2^2 - \frac{4}{r_1} - \frac{4}{r_2}$$

and of the Coulomb interaction

$$V = \frac{e^2}{\kappa_0 |r_1 - r_2|} \equiv \frac{2}{|r_1 - r_2|^{\frac{5}{2}}}$$

with the corresponding definitions in atomic units after the second equality sign. The only eigenvalue of (50) is obtained for the state $a_\uparrow^\dagger a_\downarrow^\dagger |0\rangle$ and is $E = 2\epsilon_a + U$. This
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total energy is then minimized with respect to $\alpha$ to obtain the well-known variational estimate of both $\alpha$ and the ground state energy $E_G$, as discussed before [2]. However, we may look at the problem differently. As the approximate field operator can be defined in an arbitrary basis, we may regard the eigenvalue $E$ as a functional of $\Phi_\sigma(r)$, since the functions are under the integral expressions. Therefore, the true wave function is obtained from the Euler equation for the functional under the proviso that the wave function is normalized. This means that we minimize the functional

\[ E\{\Phi_\sigma(r)\} = \sum_\sigma \int d^3r \Phi_\sigma^*(r) H_1(r) \Phi_\sigma(r) \]

\[ + \frac{1}{2} \sum_\sigma \int d^3r d^3r' |\Phi_\sigma(r)|^2 V_{12}(r - r') |\Phi_\sigma(r')|^2. \]

In effect, the Euler equation take the form of he unrestricted Hartree-Fock equations for $\Phi_\sigma(r)$

\[ \left( \nabla^2 - \frac{2e^2}{\kappa_0 r} \right) \Phi_\sigma(r) + \Phi_\sigma(r) \int d^3r' \frac{e^2}{\kappa_0 |r - r'|} |\Phi_\sigma(r')|^2 = \lambda \Phi_\sigma(r). \]

Thus we can see that taking in the simplest case just two spin orbitals we obtain either well-known variational estimate [24] for $\alpha$ and $E_G$ for He atom: $\alpha = 27/(16a_0)$ and $E_G = -5.695\text{Ry}$, where $a_0 \simeq 0.53\text{Å}$ is the 1s Bohr orbit radius.

Obviously, the proposed expression (49) of the field operator is the simplest one, though it leads to nontrivial results even though the trial atomic basis $\{\Phi_\sigma(r)\}$ is far from being complete in the quantum-mechanical sense. However, we can improve systematically on the basis by selecting a reacher basis than that in (49). The further step in this direction is discussed next.

3.2. The basis enrichment for the lightest atoms and ions: He, Li

We can expand the field operator in the basis involving the higher order irreducible representations of the rotation group with $n = 2$, which in the variational scheme involve including, apart from the $\Psi_{1s}(r)$ orbital, also the higher $\Psi_{2s}(r)$ and $\Psi_{2pm}(r)$, with $m = \pm 1, 0$ (i.e. the next shell); all of them involving the adjustment of the corresponding orbital characteristics $\alpha_i; i = 1s, 2s$ and $2pm$. The field operator is then

\[ \hat{\Psi}(r) = \sum_\sigma \left[ w_{1s}(r) \chi_{1s,a_1} + w_{2s}(r) \chi_{2s,a_2} + \sum_{m=-1}^{+1} w_{2pm}(r) \chi_{m,a_{2pm}} \right] \]

\[ \equiv \sum_{i\sigma} w_i(r) \chi_{i\sigma} a_{i\sigma}, \]

where $w_i(r)$ are orthogonalized orbitals obtained from the nonorthogonal atomic [23] basis $\{\Psi_i(r)\}$ in a standard manner. The Fock space spanned on $2 + 2 + 6 = 10$ trial spin orbitals contains $D = (2M)^N$ dimensions, where $M = 5$ now and $N_e = 2, 3$ is the number of electrons for He and Li, respectively. This means that $D = 45$ and 120 in those two cases and we have to diagonalize the Hamiltonian matrices of that size to determine
the ground and the lowest excited states. One should note that we construct and subsequently diagonalize the $\langle i | H | j \rangle$ matrix in the Fock space for (fixed) parameters $\epsilon_a, t_{ij}$, and $V_{kl}$. After the diagonalization has been carried out, we readjust the wave function and start the whole procedure again until the absolute minimum is reached (cf. Fig. 1).

By diagonalizing the corresponding Hamiltonian matrices and subsequently, minimizing the lowest eigenvalue with respect to the parameters $\alpha_i$ - the inverse radial extensions of the corresponding wave functions, we obtain the results presented in Table 1 (the values $a_{pmn}$ are all equal within the numerical accuracy $\sim 10^{-6}$). For example, the ground state energy of He is $E_G = -5.794$ Ry, which is close to the accepted "exact" value $-5.8074$, given the simplicity of our approach. Further improvement is feasible by either including the $n = 3$ states or by resorting to the Gaussian basis; these are not performed in this Part (see next Sections). Instead, we elaborate on two additional features.

First, we can represent the ground-state two-particle spin-singlet wave function for He atom taking $\hat{\psi}(\mathbf{r})$ in the form (57), which has the following form (6)

$$\Psi_0^He = (-0.799211 a_{1s\downarrow}^+ a_{1s\uparrow}^+ + 0.411751 a_{1s\downarrow}^+ a_{2s\uparrow}^+ - 0.411751 a_{1s\uparrow}^+ a_{2s\downarrow}^+) (58)$$

$$-0.135451 a_{2s\downarrow}^+ a_{2s\uparrow}^+ + 0.0357708 a_{2p\downarrow} a_{2p\uparrow} + 0.0357641 a_{2p\uparrow} a_{2p\downarrow}$$

$$-0.0357641 a_{2p\uparrow} a_{2p\downarrow}) |0\rangle,$$

Similarly, the $S^z = +1/2$ state for Li atom is of the form

$$\Psi_0^Li = (0.997499 a_{1s\downarrow}^+ a_{1s\uparrow}^+ a_{2s\uparrow}^+ - 0.0570249 a_{1s\downarrow}^+ a_{2s\uparrow}^+ a_{2s\downarrow}^+$$

$$+0.0339591 a_{1s\downarrow}^+ a_{2p\downarrow} a_{2p\uparrow} + 0.03395902 a_{1s\downarrow}^+ a_{2p\uparrow} a_{2p\downarrow} - 0.03395894 a_{1s\downarrow}^+ a_{2p\uparrow} a_{2p\downarrow}$$

$$-0.0237806 a_{2s\downarrow} a_{2p\uparrow} a_{2p\downarrow} + 0.0237806 a_{2s\downarrow} a_{2p\uparrow} a_{2p\downarrow}) |0\rangle.$$

We see that the probability of encountering the configuration $1s^2$ in He is less than $2/3$, whereas the corresponding configuration $1s^22s$ for Li almost coincides with that for the hydrogenic-like picture. The reason for the difference is that the overlap integral

| $a_{1s}$ | $a_{2s}$ | $a_{2p}$ | $S$ | $E_G$ (Ry) |
|---------|---------|---------|-----|-------------|
| $H$     | 1       | 2       | 2   | 0           | -1 |
| $H^+$   | 0.9696  | 1.6485  | 1.017 | -0.1 | -1.0487 |
| $He$    | 0.4274  | 0.5731  | 0.4068 | -0.272 | -5.79404 |
| $He^+$  | 1.831   | 1.1416  | 0.4354 | -0.781 | -5.10058 |
| Li      | 0.3725  | 1.066   | 0.2521 | -0.15  | -14.8334 |
| $Be^+$  | 0.2708  | 0.683   | 0.1829 | 0.109  | -28.5286 |
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Table 2. Microscopic parameters (in Ry) of the selected atoms and ions are all quantities are calculated for the orthogonalized atomic states. \( t \) is the \( 1s\rightarrow2s \) hopping magnitude, \( U_i \) is the intraorbital Coulomb interaction \( (i=1s(1),2s(2),m=0(3),\text{ and }m=\pm1(p)) \), whereas \( K_{ij} \) and \( J_{ij} \) are the interorbital Coulomb and exchange interaction parameters.

|     | \( t \)  | \( U_1 \) | \( U_2 \) | \( U_3 \) | \( U_p \) | \( K_{12} \) | \( K_{13} \) | \( K_{23} \) | \( J_{12} \) | \( J_{13} \) | \( J_{23} \) |
|-----|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| \( H^- \) | 0.057  | 1.333  | 0.369  | 0.77   | 0.728  | 0.519  | 0.878  | 0.457  | 0.061  | 0.138  | 0.035  |
| \( He \)  | 1.186  | 3.278  | 1.086  | 1.924  | 1.821  | 1.527  | 2.192  | 1.289  | 0.212  | 0.348  | 0.115  |
| \( He^+ \) | -1.1414| 1.232  | 0.764  | 1.798  | 1.701  | 0.929  | 1.421  | 1.041  | 0.269  | 0.28   | 0.102  |
| \( Li \)  | -0.654 | 3.267  | 0.533  | 3.105  | 2.938  | 0.749  | 3.021  | 0.743  | 0.06   | 0.606  | 0.014  |
| \( Be^+ \) | -0.929 | 4.509  | 0.869  | 4.279  | 4.049  | 1.191  | 4.168  | 1.175  | 0.105  | 0.837  | 0.025  |

between \( 1s \) and \( 2s \) states \( S = \langle 1s|2s \rangle \) in the former case is large and the virtual transitions \( 1s \Leftrightarrow 2s \) do not involve a substantial change in of the Coulomb energy. Those wave functions can be used to evaluate any ground-state characteristic by calculating \( \langle \Psi_G|\hat{O}|\Psi_G \rangle \) for \( \hat{O} \) represented in the 2nd quantized form. For example, the atom dipole moment operator is \( \hat{d} = e \int d^3r \bar{\Psi}^\dagger(r) x \Psi(r) \), etc.

The second feature is connected with determination of the microscopic parameters \( V_{ijkl} \) in our Hamiltonian, since their knowledge is crucial for atomic cluster calculations, as well as the determination of physical properties of extended systems as a function of the lattice parameter. Namely, we can rewrite the Hamiltonian (5) for the case of single atom within the basis (67) in the form

\[
H = \sum_{i\sigma} \epsilon_i n_{i\sigma} + t \sum_{\sigma} \left( a_{2\sigma}^\dagger a_{1\sigma} + a_{1\sigma}^\dagger a_{2\sigma} \right) + \frac{1}{2} \sum_{i\neq j} K_{ij} n_{i\uparrow} n_{j\downarrow} + \frac{1}{2} \sum_{i\neq j} J_{ij} \left( S_i \cdot S_j - \frac{1}{2} n_i n_j \right) + \sum_{i\neq j} J_{ij} a_{i\uparrow}^\dagger a_{i\downarrow} a_{j\downarrow}^\dagger a_{j\uparrow} + \sum_{i\neq j} V_{ij} n_{i\sigma} a_{i\sigma}^\dagger a_{j\sigma} (60)
\]

t is the hopping integral between \( 1s \) and \( 2s \) states, \( U_i \) are the intraorbital Coulomb interactions, \( K_{ij} \) are their interorbital correspondants, \( V_{ij} \) is the so-called correlated hopping integral, and \( J_{ij} \) is the direct exchange integral, for states \( i \) and \( j = 1,\ldots,5 \). The principal parameters for the atoms and selected ions are provided in Table 2.

We can draw the following interpretation from this analysis. The calculated energy difference \( \Delta E \) for \( He \) between the ground state singlet and the first excited triplet is \( \Delta E = 2.3707 - (-5.794) \approx 3.423\text{Ry} \) (the singlet \( 1s \uparrow 2s \downarrow \) is still 1 Ry higher). The corresponding energy of the Coulomb interaction in \( 1s^2 \) configuration is \( U_1 = 3.278 \), the value comparable to \( \Delta E \). Additionally, the Coulomb interaction in \( 1s \uparrow 2s \downarrow \) state is \( \approx 1.5\text{Ry} \), a substantially lower value. The relative energetics tells us why we have a substantial admixture of the excited \( 1s \uparrow 2s \downarrow \) state to the singlet \( 1s^2 \). In other words, a substantial Coulomb interaction ruins hydrogenic-like scheme, although the actual values could be improved further by enriching still the trial basis.

One may ask how the renormalized wave equation would look in the present situation? The answer to this question is not brief already for the basis containing
$M = 5$ starting states \{\(w_i(r)\)\}; we return to this question in a slightly simpler case of molecular states we consider next.

### 3.3. \(H_2\) molecule and the \(H^-_2\) and \(H^+_2\) ions

In this Subsection we consider \(H_2\) and \(Li_2\) molecules, and \(H^-_2\) ion molecule. For the illustration of the method we have plotted in Fig. 2 the level scheme for the \(H_2\) and \(H^-_2\) systems. We consider first the situation with only one 1s-like orbital per atom. For \(H_2\) we have \(\binom{4}{2} = 6\) two particle states \[2\]. For that purpose, we start with the parameterized Hamiltonian \[60\], where subscripts ”i” and ”j” label now the two atomic sites and hence \(U_1 = U_2 = U\), \(K_{12} = K\), \(J_{12} = J\), \(V_{12} = V\), and \(\epsilon_1 = \epsilon_2 = \epsilon_a\). The lowest eigenstate for \(H_2\) is

\[
E_G \equiv \lambda_5 = 2\epsilon_a + \frac{1}{2}(U + K) + J - \frac{1}{2}\left[(U - K)^2 + 16(t + V)^2\right]^{1/2}, \tag{61}
\]

and the corresponding singlet ground state in the Fock space has the form

\[
\left|G\right> = \frac{1}{\sqrt{2D(D - U + K)}} \times
\frac{4(t + V)}{\sqrt{2}} \left\{ \frac{(a_{1\uparrow}^+a_{2\downarrow}^+ - a_{1\downarrow}^+a_{2\uparrow}^+)}{\sqrt{2}} - \frac{(D - U + K)}{\sqrt{2}} (a_{1\uparrow}^+a_{2\downarrow}^+ + a_{1\downarrow}^+a_{2\uparrow}^+) \right\} |0\rangle, \tag{62}
\]

**Figure 2.** The level scheme of the \(H_2\) ground state and the lowest \(H^-_2\) states as a function of the interatomic distance \(R\). The hopping electron illustrates the relevance of \(H^-_2\) ionic configuration when measuring tunneling conductivity of \(H_2\) system.
where
\[
D \equiv \left[ (U - K)^2 + 16(t + V)^2 \right]^{1/2}.
\]
The lowest spin-singlet eigenstate has an admixture of symmetric ionic state $\frac{1}{\sqrt{2}}(a_{1\uparrow}^\dagger a_{2\downarrow}^\dagger + a_{1\downarrow}^\dagger a_{2\uparrow}^\dagger)$. Therefore, to see the difference with either the Hartree-Fock or Heitler-London approach to $H_2$ we construct the two-particle wave function for the ground state according to the prescription

\[
\Phi_0(r_1, r_2) \equiv \frac{1}{\sqrt{2}} < 0 | \Psi(r_1) \Psi(r_2) | G > .
\]

Taking $\Psi(r) = \sum_{i=1}^{2} \sum_{\sigma=\uparrow} \Phi_i(r) \chi_\sigma(r)$, we obtain that

\[
\Phi_0(r_1, r_2) = \frac{2(t + V)}{\sqrt{2D(D - U + K)}} \Phi_\epsilon(r_1, r_2) - \frac{1}{2} \sqrt{\frac{D - U + K}{2D}} \Phi_\gamma(r_1, r_2),
\]

where the covalent part is

\[
\Phi_\epsilon(r_1, r_2) = w_1(r_1) w_2(r_2) + w_1(r_2) w_2(r_1) \left[ \chi_\uparrow(r_1) \chi_\downarrow(r_2) - \chi_\downarrow(r_1) \chi_\uparrow(r_2) \right],
\]

whereas the ionic part takes the form

\[
\Phi_\gamma(r_1, r_2) = w_1(r_1) w_1(r_2) + w_2(r_1) w_2(r_2) \left[ \chi_\uparrow(r_1) \chi_\downarrow(r_2) - \chi_\downarrow(r_1) \chi_\uparrow(r_2) \right].
\]

The ratio of the coefficients before $\Phi_\epsilon(r_1, r_2)$ and $\Phi_\gamma(r_1, r_2)$ can be regarded as the \textit{many-body covalency $\gamma_{mb}$}. This value should be distinguished from the \textit{single-particle covalency $\gamma$} appearing in the definition of the orthogonalized atomic orbital $w_i(r)$:

\[
w_i(r) = \beta \left[ \Phi_i(r) - \gamma \Phi_j(r) \right],
\]

with $j \neq i$. The two quantities are drawn in Fig. 3. The many-body covalency $\gamma_{mb}$ represents a true degree of multiparticle configurational mixing.

In Table 3 we list the energies and the values of the microscopic parameters for $H_2$ system with optimized orbitals, whereas in Table 4 the same is provided for $H^-_2$ molecular ion. One should notice a drastic difference for the so-called \textit{correlated hopping} matrix element $V$ in the two cases. The same holds true for the direct exchange integral $J$ (ferromagnetic). This exchange integral is always decisively smaller than that for the antiferromagnetic kinetic exchange, $J_{kex} = 4(t + V)^2/(U - K)$. The virtual interatomic hopping processes leading to the strong kinetic exchange are the source of the singlet nature of the $H_2$ ground state. The $H^-_2$ ground state is unstable with respect to the dissociation into $H_2$ and $e^-$, contrary to the $H^-_2$ case. However, the energetics of such state is important when calculating e.g. the metallization of molecular hydrogen or determining the tunnelling conductivity through $H_2$ molecule, as shown schematically in Fig. 2. This last Figure illustrates the method of determining the energetics of excited states of $H_2$ by measuring e.g. the tunnelling conductivity (i.e. via $H^-_2$ intermediate...
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Figure 3. The single-particle ($\gamma$) and many-body ($\gamma_{mb}$) covalency factors for the $H_2$ wave functions. For details see main text.

For the sake of completeness, we have provided in Fig. 4 the energy levels vs. $R$ for $H_2, H_2^-$, and $H_2^+$ ions and have labeled both the bonding (B) and antibonding (AB) level positions. We see that the distance between $H_2$ and $H_2^-$ levels is much smaller then the distance between $H_2$ and $H_2^+$ states. This will lead to the asymmetry in the tunneling conductivity when reversing the bias voltage sign, as discussed in detail in Section 5.

3.4. Hydrogen clusters, $H_N$

As next application we consider hydrogen-cluster $H_N$ systems, with $N \leq 6$ atoms. We take the atomic-like 1s orbitals $\{\Phi_i(r)\}$ of an adjustable size $a \equiv \alpha^{-1}$, composing the orthogonalized atomic (Wannier) functions $\{w_i(r)\}_{i=1,\ldots,N}$. The cluster of $N$ atoms with $N$ electrons contains $\binom{2N}{N}$ states and the second-quantized Hamiltonian is of the form (60), with 3- and 4-site terms added. The 3- and 4-site interaction terms are difficult to calculate in the Slater basis (see below). Therefore, we have made an ansatz [7] namely, we impose the condition on the trial Wannier function that the 3- and 4-site matrix elements $V_{ijkl}^\prime$ vanish. This allows for an explicit expression of the 3- and 4-site matrix elements $V_{ijkl}$ in the atomic representation via the corresponding one- and
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Figure 4. Position of $H_2^+$ bonding (B) and antibonding (AB) energy levels with respect to those of $H_2$ and $H_2^-$, drawn as a function of intermolecular distance.

Table 3. Ground-state energy and microscopic parameters (in Ry) for $H_2$ molecule. The last column represents the kinetic exchange integral characterizing intersite antiferromagnetic exchange.

| $R/a$ | $E_G/N$ | $\epsilon_a$ | $t$ | $U$ | $K$ | $V$ [mRy] | $J$ [mRy] | $\frac{4(t+V)^2}{V-K}$ [mRy] |
|-------|---------|-------------|-----|-----|-----|-----------|----------|-----------------|
| 1.0   | -1.0937 | -1.6555     | -1.1719 | 1.8582 | 1.1334 | -13.5502  | 26.2545  | 7755.52         |
| 1.5   | -1.1472 | -1.7528     | -0.6784 | 1.6265 | 0.9331 | -11.6875  | 21.2529  | 2747.41         |
| 2.0   | -1.1177 | -1.722      | -0.4274 | 1.4747 | 0.7925 | -11.5774  | 16.9218  | 1130.19         |
| 2.5   | -1.0787 | -1.6598     | -0.2833 | 1.3769 | 0.6887 | -12.0544  | 13.1498  | 507.209         |
| 3.0   | -1.0469 | -1.5947     | -0.1932 | 1.3171 | 0.6077 | -12.594   | 9.8153   | 238.939         |
| 3.5   | -1.0254 | -1.5347     | -0.1333 | 1.2835 | 0.5414 | -12.8122  | 6.9224   | 115.143         |
| 4.0   | -1.0127 | -1.4816     | -0.0919 | 1.2663 | 0.4854 | -12.441   | 4.5736   | 55.8193         |
| 4.5   | -1.006  | -1.4355     | -0.0629 | 1.2579 | 0.4377 | -11.4414  | 2.8367   | 26.9722         |
| 5.0   | -1.0028 | -1.3957     | -0.0426 | 1.2539 | 0.3970 | -9.9894   | 1.6652   | 12.9352         |
| 5.5   | -1.0012 | -1.3616     | -0.0286 | 1.2519 | 0.3623 | -8.3378   | 0.9334   | 6.1455          |
| 6.0   | -1.0005 | -1.3324     | -0.01905| 1.251 | 0.3327 | -6.7029   | 0.5033   | 2.8902          |
| 6.5   | -1.00024| -1.3073     | -0.0126 | 1.2505 | 0.3075 | -5.2242   | 0.2626   | 1.3452          |
| 7.0   | -1.0001 | -1.2855     | -0.0083 | 1.2503 | 0.2856 | -3.9685   | 0.1333   | 0.6197          |
| 7.5   | -1.00004| -1.2666     | -0.0054 | 1.2501 | 0.2666 | -2.9509   | 0.066    | 0.2826          |
| 8.0   | -1.00002| -1.25       | -0.0035 | 1.2506 | 0.25   | -2.1551   | 0.032    | 0.1277          |
| 8.5   | -1.00001| -1.2353     | -0.0023 | 1.2503 | 0.2353 | -1.5501   | 0.0152   | 0.0572          |
| 9.0   | -1.2222 | -0.0015     | 1.2501 | 0.2222 | -1.1005  | 0.0071   | 0.0254         |
| 9.5   | -1.2105 | -0.0009     | 1.2501 | 0.2105 | -0.7725  | 0.0033   | 0.0112         |
| 10.0  | -1.2   | -0.0006     | 1.25 | 0.2    | -0.5371 | 0.0015   | 0.0049         |
two-site elements. In Figs. 5 and 6 we present the results for the ground- and excited-states energies for the square and face-centered-square (fcs) configurations, \( N = 4 \) and \( 5 \), respectively. The states are grouped into manifolds, which are characterized by the number of double occupancies of a single state \( w_i(r) \), appearing in the system. The horizontal lines mark the ground state, states with one and two double electron occupancies in the atomic limit (i.e. for large interatomic distance). The manifolds thus correspond to the Hubbard subbands introduced for strongly correlated solids \([25]\). As far as we are aware of, our results are the first manifestation of the energy manifold evolution into well separated subbands with the interatomic distance increase. The first two subbands correspond to HOMO and LUMO levels determined in quantum-chemical calculation \([20]\). In Fig. 7 and 8 we represent the renormalized Wannier function profiles for the face centered square configuration of \( N = 5 \) atoms, for the central and the corner positions, respectively. Note the small negative values on the nearest-neighbor sites to assure the orthogonality of the functions centered on different sites. Obviously, the atom in the center of the square is inequivalent to the remaining four corner atoms, as can be see explicitly in Fig. 9 where the density profile \( n(r) \) in the cluster plane, according to formula \([17]\), has been drawn. The electron density near the central atom is decisively smaller, a clear sign of electron-correlation effects induced by the repulsive Coulomb interaction. This assessment is corroborated in Fig. 10.
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Figure 5. Ground- and excited states energies for the $H_4$ square configuration as a function of the interatomic distance.

where the difference to the Hartree-Fock part of the density profile has been presented. These densities should be possible to be determined with the help of scanning tunneling microscopy (STM).

3.5. Energetically stable $H_4$ clusters and fermionic nanoladders

The $H_N$ clusters of regular-polygon shape are not stable energetically, as the ground state energies in Figs. 5 and 6 at the minimum (per atom) is above that for the $H_2$ case. This is because a stable, say, $H_4$ cluster will reflect strong molecular bonding of each pair of $H_2$ molecules to saturate the covalent character of the bonding. To prove that this is indeed the case we have considered an example of a rectangular cluster differentiating between the lateral distance (say, along the bond of the length $a$) and the
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Figure 6. Ground- and excited states energies for the $H_5$ face-centered-square (fcs) configuration as a function of the interatomic distance.

horizontal intermolecular distance $b$. We consider both the planar and the twisted by 90° configurations, as drawn in Fig. 11. The Gaussian STO-3G basis of an adjustable size $\alpha^{-1}$ has been used in this case, so the 3- and 4- site interaction terms in the atomic basis are included explicitly. Additionally, the Hamiltonian in the second quantization, only containing the principal one- and two- site interactions, is taken in the form

$$H = \epsilon^\text{eff}_a \sum_{i\sigma} n_{i\sigma} + \sum_{i\neq j} t_{ij} a_{i\sigma}^\dagger a_{j\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow} + \frac{1}{2} \sum_{i\neq j} K_{ij} \delta n_i \delta n_j,$$

(68)

where $\delta n_i = 1 - n_i$, $n_i = \sum_{\sigma} n_{i\sigma}$ and

$$\epsilon^\text{eff}_a = \epsilon_a + \frac{1}{2N} \sum_{i\neq j} \left( K_{ij} + \frac{2}{R_{ij}} \right),$$

(69)
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with the last term in the parenthesis representing the Coulomb repulsion (in atomic units) between the protons placed at the distance $R_{ij}$, together with the electron-electron intersite repulsion $K_{ij}$ (such a redefinition is necessary to achieve the proper atomic limit, when the nearest-neighbor distance $R \to \infty$. Also, we have to take into account three different hopping integrals: between the nearest neighbors $t_1 = t_{12} = t_{34}$, between the second neighbors $t_2 = t_{13} = t_{24}$, and the third neighbors $t_3 = t_{14} = t_{23}$. Likewise, we have three intersite Coulomb interactions $\{K_n\}_{n=1,2,3}$. The basic ground-state characteristics for the two spatial arrangements is provided in Tables 5 and 6.

The results are listed as a function of intermolecular distance and include: the bond length $a_{\text{min}}$, the inverse Gaussian-function size $\alpha$, the energy of $H_4$ and the energy of two $H_2$ molecules (per atom). The principal feature of these results is that the system is energetically stable against the dissociation into two $H_2$ molecules (cf. the last row in the two situations). The global minima are:

i) for the planar geometry: $b_{\text{min}} = 4.32a_0$, $a_{\text{min}} = 1.4303a_0$, $\alpha_{\text{min}} = 1.1937a_0^{-1}$, and $E_{G_{\text{min}}}^{\text{N}} = -1.149061\text{Ry}$; and

ii) for the twisted $90^\circ$ geometry: $b_{\text{min}} = 4.13a_0$, $a_{\text{min}} = 1.4318a_0$, $\alpha_{\text{min}} = 1.11927a_0^{-1}$, and $E_{G_{\text{min}}}^{\text{N}} = -1.150396\text{Ry}$. 

*Figure 7.* The renormalized Wannier function profile for the central atom in the fcc structure.
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Figure 8. The renormalized Wannier function profile for for the corner atom in the fcs structure.

Table 5. The optimal bond length $a_{\text{min}}$, inverse orbital size $\alpha_{\text{min}}$, and the ground-state energy $E_G$ per atom for the planar H$_4$ cluster ($i$). The corresponding energy of the molecular dimer $E_G(2\text{H}_2)$ is also provided.

| $b/a_0$ | $a_{\text{min}}/a_0$ | $\alpha_{\text{min}}a_0$ | $E_G/N$ | $E_G(2\text{H}_2)/N$ |
|---------|-----------------------|--------------------------|---------|----------------------|
| 1.7     | 1.3627                | 1.2231                   | -0.928424 | -0.922411          |
| 2.0     | 1.3291                | 1.2395                   | -1.019152 | -1.016365          |
| 2.5     | 1.3518                | 1.2304                   | -1.098551 | -1.097314          |
| 3.0     | 1.3829                | 1.2157                   | -1.131770 | -1.131167          |
| 3.5     | 1.4075                | 1.2041                   | -1.144613 | -1.144317          |
| 4.0     | 1.4238                | 1.1969                   | -1.148598 | -1.148454          |
| 5.0     | 1.4373                | 1.1911                   | -1.148093 | -1.148056          |
| 6.0     | 1.4390                | 1.1908                   | -1.145975 | -1.145964          |
| 8.0     | 1.4375                | 1.1924                   | -1.143651 | -1.143649          |
| 10.0    | 1.4366                | 1.1929                   | -1.142756 | -1.142755          |
| 20.0    | 1.4357                | 1.1940                   | -1.141908 | -1.141908          |
| $\infty$| 1.4356                | 1.1943                   | -1.141783 |          |
So, the geometry (ii) is the most stable in vacuum and should constitute a building block for $H_2$ molecular crystal. Note we have not included the zero point motion of the nuclei [2]. The ratio $b/a$ is roughly four, so substantial molecular identity of $H_2$ pairs survives.

As in all cases before, the knowledge of microscopic parameters is crucial for the larger-cluster or solid-state configurations (Hamiltonian [68] provides whole dynamics within the subspace with one orbital per atom). Therefore, in 7 and 8 we list them for the two configurations considered, as a function of intermolecular distance $b$ (the last row represents the corresponding values for $H_2$ in the ground state).

The stability of the $H_4$ cluster raises a very interesting question of stability of $H_{2N}$ ladders, which can be regarded as the simplest fermionic ladders with the frustration of electron spins in the twisted configuration.
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Figure 10. Difference between the calculated density of states and the Hartree-Fock results for the $H_5$ fcs structure.

Figure 11. Schematic representation of the $H_4$ cluster geometries: (i) parallel and (ii) perpendicular orientation of $H_2$ molecules. Geometrical parameters of the cluster are: the bond length $a$ and the intermolecular distance $b$. The numbering order of the lattice sites $j$ is also provided.
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Table 6. The optimal bond length $a_{\text{min}}$, inverse orbital size $\alpha_{\text{min}}$, and the ground-state energy $E_G$ per atom for the cluster geometry (\textit{ii}). The corresponding energy of the molecular dimer $E_G(2H_2)$ is also provided.

| $b/a_0$ | $a_{\text{min}}/a_0$ | $\alpha_{\text{min}}a_0$ | $E_G/N$  | $E_G(2H_2)/N$ |
|---------|----------------------|-------------------------|----------|----------------|
| 1.6     | 1.5796               | 1.1568                  | -0.928235 | -0.923390      |
| 2.0     | 1.3759               | 1.2206                  | -1.038891 | -1.037968      |
| 2.5     | 1.3725               | 1.2193                  | -1.108116 | -1.107803      |
| 3.0     | 1.3947               | 1.2091                  | -1.136931 | -1.136809      |
| 3.5     | 1.4153               | 1.2000                  | -1.147566 | -1.147519      |
| 4.0     | 1.4292               | 1.1937                  | -1.150310 | -1.150293      |
| 5.0     | 1.4397               | 1.1894                  | -1.148674 | -1.148672      |
| 6.0     | 1.4400               | 1.1897                  | -1.146200 | -1.146200      |
| 8.0     | 1.4377               | 1.1926                  | -1.143705 | -1.143705      |
| 10.0    | 1.4367               | 1.1929                  | -1.142774 | -1.142774      |
| 20.0    | 1.4357               | 1.1940                  | -1.141908 | -1.141908      |
| $\infty$ | 1.4356               | 1.1943                  | -1.141783 |                |

Table 7. Microscopic parameters (in Ry) for the H$_4$ cluster configuration (\textit{i}) calculated in the Gaussian STO–3G basis. Corresponding values of the inverse orbital size $\alpha_{\text{min}}$ and the bond length $a_{\text{min}}$ are provided in Table 5.

| $b/a_0$ | $e_{\alpha}^{\text{eff}}$ | $t_1$  | $t_2$  | $t_3$  | $U$     | $K_1$   | $K_2$   | $K_3$   |
|---------|---------------------------|--------|--------|--------|---------|---------|---------|---------|
| 1.7     | -0.2354                   | -0.8610| -0.6622| 0.0822 | 1.811   | 1.027   | 0.947   | 0.728   |
| 2.0     | -0.3088                   | -0.8791| -0.5137| 0.0617 | 1.802   | 1.032   | 0.872   | 0.692   |
| 2.5     | -0.4233                   | -0.8390| -0.3268| 0.0352 | 1.748   | 1.007   | 0.750   | 0.619   |
| 3.0     | -0.4925                   | -0.7983| -0.2067| 0.0220 | 1.702   | 0.984   | 0.649   | 0.553   |
| 3.5     | -0.5319                   | -0.7685| -0.1290| 0.0150 | 1.671   | 0.967   | 0.567   | 0.497   |
| 4.0     | -0.5533                   | -0.7492| -0.0785| 0.0103 | 1.653   | 0.957   | 0.500   | 0.449   |
| 5.0     | -0.5689                   | -0.7316| -0.0267| 0.0037 | 1.639   | 0.949   | 0.401   | 0.373   |
| 6.0     | -0.5707                   | -0.7275| -0.0084| 0.0007 | 1.638   | 0.948   | 0.334   | 0.318   |
| 8.0     | -0.5692                   | -0.7269| -0.0006| -0.0000| 1.640   | 0.949   | 0.250   | 0.243   |
| 10.0    | -0.5684                   | -0.7268| -0.0000| -0.0000| 1.641   | 0.950   | 0.200   | 0.197   |
| 20.0    | -0.5673                   | -0.7272| -0.0000| -0.0000| 1.642   | 0.951   | 0.100   | 0.100   |
| $\infty$| -0.5671                   | -0.7273| 0       | 0       | 1.642   | 0.951   | 0       | 0       |
Figure 12. Ground–state energy per atom for the planar ladder of $N=12$ atoms (a) with a fixed intermolecular distance $b$ (specified in the units of Bohr radius $a_0$), and (b) the corresponding values of the optimal inverse orbital size $\alpha_{\text{min}}$. Periodic boundary conditions are used. The results for the atomic chain (dashed lines) with a lattice parameter $a \lesssim b_{\text{crit}}$ are shown for the comparison.

For that purpose we have considered planar (i) and $90^\circ$ twisted (ii) ladder composed of $8 \div 12$ atoms. In Fig. 12 we display the ground state energy (per atom) for the nanoladder containing $N = 10$ atoms with periodic boundary conditions. The insets provide the values of the optimal bond length $a_{\text{min}}$ (left) and the inverse atomic (Gaussian) orbital size $\alpha_{\text{min}}$ (right). The Gaussian orbitals (STO-3G basis) have been used to define the single-particle basis. The horizontal dashed line marks $H_2$ ground state energy. One should also note that due to the closed-shell molecular-crystal configuration ($b/a \sim 4$) of the ground state, the data almost do not depend on the system size (e.g. analogical results for $N = 8$ fit onto those shown in Fig. 12 up to the pixel size). The characteristics of the global minima are:

i) for the planar geometry: $b_{\text{min}} = 4.00a_0$, $a_{\text{min}} = 1.422a_0$, $\alpha_{\text{min}} = 1.189a_0^{-1}$, and $E_G^{\text{min}}/N = -1.1626\text{Ry}$; and
ii) for the twisted 90° geometry: $b_{min} = 3.67a_0$, $a_{min} = 1.426a_0$, $\alpha_{min} = 1.178a_0^{-1}$, and $E_G^{min}/N = -1.1680\text{Ry}$.

These values lead to the binding energies of the molecules in the nanoladders: $\Delta E_G^{(i)}/N = 20.8m\text{Ry}$ and $\Delta E_G^{(ii)}/N = 26.2m\text{Ry}$, respectively, i.e. about three times larger than for the $H_4$ clusters.

One can also draw some conclusions about the nature of electronic states in those nanoladders. Namely, by calculating the so called charge stiffness (Drude weight) and the charge gap (cf. Ref. [5]) one can draw a phase diagram shown in Fig. 13 for a planar nanoladder on the plane $a-b$. For either $a$ or $b$ large we expect the Mott insulating state of spins $S = 1/2$. However, it is interesting to note that for bond lengths in the range $2 \div 3$ and an appropriate intermolecular distance ($b \sim a$) a quasimetallic state is possible and is followed by a band insulator for small $b < a$. The metal phase sandwiching the two, band and Mott insulating phases appears well beyond the optimal configuration for the nanoladder (see the dashed line representing $a = a_{min}$ as a function of $b$). So it can appear only when nanoladder is artificially made on a supporting substrate. The dotted line marks the model of qurted-filled (QF) band system discussed in Ref. [5].
4. Monoatomic nanowires: from nanometal to Mott insulator

4.1. Ground state properties

The EDABI method was applied first to nanochains starting with Slater basis of atomic states \[^{5, 13, 12}\]. In this Section we present the new results starting from STO-3G "atomic" basis of adjustable size. The selection of this basis makes the inclusion of 3- and 4-site interactions possible. We limit here to the situation with one electron per atom. Strictly speaking, we study a nanochain of hydrogen atoms, which can also model the behavior of single valence electron nanowires.

We start again with Hamiltonian (68) describing the so-called extended Hubbard model for a system with one orbital per atom (here the orbitals are taken as Gaussians of an adjustable size, out of which we compose the Wannier functions). The diagonalization in the Fock space is performed with the help of Lanczos method described in detail elsewhere \[^{5, 6}\]. In Fig. 14 we plot the ground state energy of chains containing \(N = 6 - 10\) hydrogen atoms, as a function of interatomic distance \(R\) (in units of \(a_0\)). The Wannier functions are calculated in the tight-binding approximation, with six attractive atomic Coulomb wells representing the periodic potential. In the inset we display the inverse size \(\alpha\) (in units of inverse \(a_0\)) of the Gaussian functions (note that the actual size of atoms is reduces in the correlates state). The continuous \(E_G\) lines INS and M represent respectively to the Mott insulating state represented by \(E_{G}^{\text{INS}} = \epsilon_a^{\text{eff}},\) and to the ideal metallic state, for which

\[
E_G^M = \epsilon_a^{\text{eff}} - \frac{4|t|}{\pi} + \frac{1}{2N} \sum_{i \neq j} K_{ij} \langle \delta n_i \delta n_j \rangle, \tag{70}
\]

where the correlation is taken for the one-dimesional ideal gas

\[
\langle \delta n_i \delta n_j \rangle = 2 \frac{\sin^2(\pi|i-j|/2)}{(\pi|i-j|)^2}. \tag{71}
\]

For the sake of completeness, we have also included the Hartree-Fock (HF) result for \(E_G\) (the dotted line) calculated for the antiferromagnetic (Slater) state; it provides a better estimate of \(E_G\) than either M or INS curves. For discussing HF solution we take the Hamiltonian (68) in the form

\[
H^{\text{HF}} = \epsilon_a^{\text{eff}} \sum_{i\sigma} n_{i\sigma} + t \sum_{i\sigma} \left( a_{i\sigma}^\dagger a_{i+1\sigma} + \text{h.c.} \right) + \\
+U \sum_i \left( \langle n_{i\uparrow} \rangle n_{i\downarrow} + \langle n_{i\downarrow} \rangle n_{i\uparrow} - \langle n_{i\uparrow} \rangle \langle n_{i\downarrow} \rangle \right) + \\
\sum_{i<j} K_{ij} \left( \langle \delta n_i \rangle \delta n_j + \delta n_i \langle \delta n_j \rangle - \langle \delta n_i \rangle \langle \delta n_j \rangle \right) - \\
\sum_{i<j,\sigma} K_{ij} \left( \langle a_{i\sigma}^\dagger a_{j\sigma} \rangle a_{j\sigma}^\dagger a_{i\sigma} + \langle a_{j\sigma}^\dagger a_{i\sigma} \rangle a_{i\sigma}^\dagger a_{j\sigma} - |\langle a_{i\sigma}^\dagger a_{j\sigma} \rangle|^2 \right). \tag{72}
\]
Table 8. Microscopic parameters (in Ry) for the H$_4$ cluster configuration (ii) calculated in the Gaussian STO-3G basis. Corresponding values of the inverse orbital size $\alpha_{\text{min}}$ and the bond length $a_{\text{min}}$ are provided in Table 6.

| $b/a_0$ | $\epsilon^{eff}_0$ | $t_1$ | $t_2$ | $t_3$ | $U$  | $K_1$ | $K_2$ | $K_3$ |
|--------|-------------------|-------|-------|-------|------|-------|-------|-------|
| 1.6    | -0.5352           | -0.5423 | -0.2986 | -0.2986 | 1.650 | 0.911 | 0.816 | 0.816 |
| 2.0    | -0.4511           | -0.7496 | -0.2230 | -0.2230 | 1.732 | 0.991 | 0.772 | 0.772 |
| 2.5    | -0.4863           | -0.7820 | -0.1451 | -0.1451 | 1.711 | 0.986 | 0.680 | 0.680 |
| 3.0    | -0.5221           | -0.7721 | -0.0923 | -0.0923 | 1.683 | 0.972 | 0.598 | 0.598 |
| 3.5    | -0.5467           | -0.7558 | -0.0571 | -0.0571 | 1.661 | 0.961 | 0.530 | 0.530 |
| 4.0    | -0.5613           | -0.7423 | -0.0342 | -0.0342 | 1.646 | 0.953 | 0.473 | 0.473 |
| 5.0    | -0.5715           | -0.7293 | -0.0115 | -0.0115 | 1.637 | 0.947 | 0.387 | 0.387 |
| 6.0    | -0.5719           | -0.7264 | -0.0038 | -0.0038 | 1.636 | 0.947 | 0.326 | 0.326 |
| 8.0    | -0.5692           | -0.7269 | -0.0003 | -0.0003 | 1.640 | 0.949 | 0.247 | 0.247 |
| 10.0   | -0.5685           | -0.7268 | -0.0000 | -0.0000 | 1.641 | 0.950 | 0.198 | 0.198 |
| 20.0   | -0.5673           | -0.7272 | -0.0000 | -0.0000 | 1.642 | 0.951 | 0.100 | 0.100 |
| $\infty$ | -0.5671        | -0.7273 | 0       | 0       | 1.642 | 0.951 | 0     | 0     |

Figure 14. Ground state energy per atom vs. $R$ for the linear chain with $N = 6 \div 10$ atoms with periodic boundary conditions. The STO-3G Gaussian basis for representation of atomic orbitals forming the Wannier function has been used. The inset provides a universal behavior of the inverse size $\alpha$ of the orbitals. For details see main text.
The combined exact diagonalization-\textit{ab initio} approach involves calculations of the ground-state energy with a simultaneous self-consistent determination of the sublattice magnetization $m = \langle n_{i\uparrow} - n_{i\downarrow} \rangle$ and of the hopping correlation function $\langle a_{i\sigma}^\dagger a_{j\sigma} \rangle$, which will not be discussed in detail here (obviously, $\langle \delta n_i \rangle = 0$).

The most spectacular are the spin-spin correlations in the collective spin-singlet ($\sum_{i=1}^N \mathbf{S}_i \equiv 0$) state. In Fig. 15a we display the corresponding spin-spin correlation function $\langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle$ as a function of the distance $|i-j|$ for $N = 10$ and several values of $R$. We observe Néel-like state correlations in this spin singlet state as it oscillates through the whole system length. For $N = 11$ these quasi oscillatory correlations are strongly suppressed due to the spin-frustration effects, as shown explicitly in Fig. 15b. Changing the lattice constant $R$ does not alter the picture qualitatively. This long-range feature of spin-spin correlations will have profound consequences on the single-particle spectrum, as we discuss below. Here the boundary conditions discussed below (cf. Sec. 4.5) have been considered, although the difference between the cases a and b survives even for the periodic boundary conditions. Additional features of the $N$ dependence of $\langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle$ have been discussed in [26].

4.2. Momentum distribution in the ground state: Fermi or Luttinger nano liquid localization?

We now introduce the particle quasimomentum distribution $n_{k\sigma}$ in the ground state for the situation with one electron per atom; this is displayed in Fig. 16 for the number of atoms $N = 6 \div 14$. We observe a very universal character of the curves provided the periodic boundary conditions are taken for the chains of $N = 4n + 2$ atoms, whereas the antiperiodic boundary conditions are taken for $N = 4n$ atoms, with $n$ being a natural number. It is very tempting to regard the distributions for $R/a_0 \leq 3.5$ as modified Fermi-Dirac function characterizing the Fermi liquid even for such short chains for which we have discrete momentum states. However, for $R/a_0 \to 4$ the distributions becomes...
The combined exact diagonalization- ab initio approach

Figure 16. Momentum distribution $\pi_{k\sigma}$ for the number of atoms $N = 6 \div 14$ as it evolves with the increasing lattice constant $R$.

Figure 17. Statistical distribution $n_{k\sigma}$ for electrons in a chain of $N = 6 \div 14$ atoms with periodic boundary conditions. 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 $k < k_F$. 
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Figure 18. The critical behavior of the quasiparticle mass at the Fermi level; for details see main text.

Figure 19. Luttinger–liquid scaling for a half–filled one–dimensional chain of \( N = 6 \div 14 \) atoms. Interatomic distance \( R \) is specified in the units of \( a_0 \).
Table 9. Optimized inverse orbital size, microscopic parameters and the ground-state energy for \( N = 10 \) atoms calculated in Slater–type basis, as a function of interatomic distance. Intersite Coulomb repulsion \( K_1 \) is included on the mean–field level in \( \epsilon^{eff}_a \), Hubbard \( U \) term is treated exactly. Single–particle potential contains six Coulomb wells.

| \( R/a_0 \) | \( \alpha_{\text{min}}a_0 \) | \( \epsilon^{eff}_a \) | \( t \) | \( U \) | \( K \) | \( E_G/N \) |
|------|------|------|------|------|------|--------|
| 1.5  | 1.806| 0.9103| -1.0405| 2.399| 1.695| 0.0665  |
| 2.0  | 1.491| -0.1901| -0.5339| 1.985| 1.172| -0.5179 |
| 2.5  | 1.303| -0.6242| -0.3076| 1.722| 0.889| -0.7627 |
| 3.0  | 1.189| -0.8180| -0.1904| 1.553| 0.713| -0.8800 |
| 3.5  | 1.116| -0.9104| -0.1230| 1.440| 0.596| -0.9391 |
| 4.0  | 1.069| -0.9559| -0.0815| 1.365| 0.513| -0.9693 |
| 4.5  | 1.039| -0.9784| -0.0546| 1.317| 0.451| -0.9848 |
| 5.0  | 1.022| -0.9896| -0.0370| 1.288| 0.403| -0.9926 |
| 6.0  | 1.013| -0.9977| -0.0165| 1.269| 0.334| -0.9982 |
| 7.0  | 1.001| -0.9995| -0.0072| 1.252| 0.286| -0.9996 |
| 8.0  | 1.001| -0.9999| -0.0031| 1.251| 0.250| -0.9999 |
| 10.0 | 1.000| -1.0000| 0.0003| 1.250| 0.200| -1.0000 |

Figure 20. Spectral functions \( A(k, \omega) \) for \( N = 10 \) (a) and \( N = 12 \) atoms, with periodic boundary conditions. A clear dispersion of the states is observed for \( R = 1.5a_0 \), which transform into the atomic peaks with the increasing \( R \), through an incoherent regime for \( R/a_0 \approx 3 \).
The combined exact diagonalization-\textit{ab initio} approach

Figure 21. Density of single-particle states for $N = 10$ atoms. Note a pronounced incoherent spectrum for $R$ in the range $3 \div 5a_0$.

Figure 22. Spectral-density-peak positions for the nanochain of $N = 10$ (left panel) and $N = 11$ (right panel) atoms with generalized boundary conditions. The Hartree–Fock (solid line) and noninteracting system (dashed line) dispersion relations are shown for comparison.
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continuous, i.e. without an apparent Fermi ridge at Fermi momentum $k_F = \pi/(2R)$, in rough agreement with the preliminary results for the case with the Slater-type orbitals \[13\]. So, a crossover with the increasing interatomic distance from the Fermi liquid-like behavior to the chain of atomic-like states is clearly seen. It should be noted that the Luttinger liquid-like scaling fitting to the points displayed in Fig. \[15\] is equally convincing, at least for this half-filled band configuration, as discussed next.

4.3. Single-particle spectral density function evolution

The state of a nanochain viewed through the statistical distribution of momentum states can be discussed as follows. The ideal Mott localized state, as is seen in the bulk systems, is not possible for finite system. This is simply because the length of the system is finite and therefore, the probability of the electron tunneling from an atomic state on one chain end to the other end is \textit{nonzero}. The quantitative question is, whether it is of the order $e^{-N\alpha R}$ or larger. Due to the fact that the overlap integral is $\sim \frac{1}{3}(\alpha R)^2 e^{-\alpha R}$, the probability is enhanced by a nonzero hopping amplitude between more distant neighbors. Having in mind this circumstance, it is at least imaginable, that the distribution function displayed in Fig. \[16\] is Fermi-Dirac like for $\alpha R \sim 1$. One can thus try to formalize this observation further. Namely, in Fig. \[17\] we plot $n_{k\sigma}$ for a half filled band system containing up to $N = 14$ electrons. The continuous lines represent the parabolic parametrization:

$$n_{k\sigma} = \frac{1}{2} sgn(k - k_F) \left[ \alpha (k - k_F)^2 + \beta |k - k_F| + \gamma \right],$$ \hspace{1cm} (73)

| $R/a_0$ | $\alpha_{\text{min}} a_0$ | $e_{\text{max}}^{\text{eff}}$ | $t$ | $U$ | $K$ | $E_G/N$ |
|-------|----------------|----------------|-------|-----|-----|---------|
| 1.5   | 1.309          | 0.1311         | -0.8643 | 2.002 | 1.154 | -0.5684 |
| 2.0   | 1.205          | -0.5342        | -0.4595 | 1.718 | 0.908 | -0.8154 |
| 2.5   | 1.120          | -0.7893        | -0.2750 | 1.530 | 0.750 | -0.9139 |
| 3.0   | 1.067          | -0.8975        | -0.1776 | 1.412 | 0.639 | -0.9567 |
| 3.5   | 1.038          | -0.9465        | -0.1197 | 1.342 | 0.558 | -0.9756 |
| 4.0   | 1.020          | -0.9698        | -0.0820 | 1.299 | 0.494 | -0.9841 |
| 4.5   | 1.013          | -0.9812        | -0.0562 | 1.276 | 0.442 | -0.9881 |
| 5.0   | 1.005          | -0.9868        | -0.0382 | 1.260 | 0.399 | -0.9901 |
| 6.0   | 1.003          | -0.9908        | -0.0170 | 1.251 | 0.333 | -0.9914 |
| 7.0   | 1.000          | -0.9915        | -0.0072 | 1.247 | 0.286 | -0.9917 |
| 8.0   | 1.000          | -0.9917        | -0.0027 | 1.246 | 0.250 | -0.9917 |
| 10.0  | 1.000          | -0.9917        | -0.0003 | 1.246 | 0.200 | -0.9917 |

Table 10. Same as in Table\[9\] calculated in Gaussian–type STO–3G basis.
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for both $k < k_F$ and $k > k_F$ (note that the Fermi point is not occupied for $N$ even). This parametrization, in fact implies a discontinuous distribution, allows us to interpret the distribution discontinuity $\Delta n_{k_F} \equiv n_{k_F-0} - n_{k_F+0}$ in terms effective mass enhancement at the Fermi point.

$$m_F^*/m_{\text{BAND}} = (\Delta n_{k_F})^{-1} \equiv Z^{-1},$$

where $Z^{-1}$ is the usual Fermi-liquid enhancement factor. The corresponding enhancement factor determined in that manner is plotted in Fig. 18 (squares), whereas the solid line represents the finite-size scaling with interatomic distance, $m_F^*/m_{\text{BAND}} = A|R - R_C|^{-\gamma}$, with $A \simeq 10.2$, the localization threshold is $R_C a_0 = 3.92$, and the critical exponent has the approximate value $\gamma = 4/3$. This behavior emulates a quantum critical behavior and should not be taken literally. Nonetheless, the value of $R_C$ distinguishes qualitatively between the nanometallic state $R < R_C$ (for which the distribution (73) has a jump at $k_F$) and the Mott insulating (semiconducting) state ($R > R_C$, the distribution function is a continuous function of $k$).

However, the situation is not that simple. One can ask the question whether this short one-dimensional system is not rather resembling the Luttinger liquid-like behavior. This task has been undertaken seriously and in Fig. 19 we plot the fitting of the data displayed in Fig. 16 to the corresponding dependence for the Tomanaga-Luttinger liquid, with the logarithmic correction included, namely [27]

$$\ln |n_{k_F} - n_{k_0}| = -\Theta \ln z + b \ln \ln z + c + \theta(1/\ln z),$$

where $z = \pi/|k_F - \pi/R|, \Theta, b$, and $c$ are constants. The parameters depend on the distance $R$, as shown elsewhere [27]. This fitting provides also the localization threshold $R_C \simeq 2.60a_B$, which is reduced by 50% from the value for the Fermi liquid interpretation of $n_{k_0}$. One should also note that the present interpretation of the exact solution displayed in Fig. 16 does not admit a discontinuity at $k = k_F$. However, it is quite amazing that both the Fermi- and Luttinger-liquid interpretations can provide satisfying interpretation of $n_{k_0}$ to an equal degree. This means that there must be an underlying universal behavior of a new type, incorporating Fermi- and Luttinger-liquid concepts, at least semiquantitatively. Nonetheless, for the not too large $R$ the Fermi-Dirac-like distribution fits better the $k$ dependence. The situation for odd $N$ requires an explicit discussion of boundary conditions and is provided below.

To characterize the spectrum of single-particle excitations we use the definition of the spectral-density function

$$A(k, \omega) = \sum_n \left| \langle \Phi_{n+1}^{N} | a_{k \sigma}^{\dagger} | \Phi_{0}^{N} \rangle \right|^2 \delta \left[ \omega - (E_{n+1}^{N} - E_{0}^{N}) \right],$$

where upper(lower) sign corresponds to the energies with $\omega > \mu$ ($\omega < \mu$), respectively, $|\Phi_{n}^{N}\rangle$ is the $n$-th eigenstate of the system containing $N$ particles, $E_{n}^{N}$ is the corresponding eigenenergy, and $< .. >$ is the matrix element are calculated within the Lanczos algorithm [32]. In Fig. 20 we present the panel of $A(k, \omega)$ for three distances $R$. For small $R$, a clear two-peak structure appears at the Fermi momenta $k_F = \pm \pi/(2R)$ for
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$N = 12$; an artificial broadening of the peaks appears because we use the approximate expression for the $\delta(x)$ function: $\delta(x) \approx (1/\pi)\epsilon/(x^2 + \epsilon^2)$, with $\epsilon = 10^{-2}\text{Ry}$.

The splitting is caused by the antiferromagnetic correlations depicted in Fig. 15a. In the range $R/a_0 \leq 2$ the quasiparticles are well defined, but an incoherent part grows with the increasing $R$. For $R/a_0 \sim 3 \div 4$ the \textit{Hubbard subbands} are formed and evolve continuously into atomic levels located respectively at $\omega = \epsilon_a$ and $\omega = \epsilon_a + U$ for $R \to \infty$. Those two limiting peak positions correspond to the ground $H^0$ and excited $H^-$ states, respectively.

Combining the last results with the corresponding discussion for the $H_N$ clusters one sees that \textit{the Hubbard subband structure represents a universal feature of nanoscopic systems}. In the limit of larger interatomic separation this structure is clearly distinguishable from the discrete level structure coming from geometric quantization of this confined system.

To demonstrate the importance of \textit{incoherent} part of the spectrum we have calculated the density of states $N(\omega) = \sum_k A(k, \omega)$, displayed in Fig. 21 for $N = 10$ atoms, for the interatomic distances specified. In the regime $R = 3 \div 5a_0$ well resolved quasiparticle peaks coalesce into a complicated random-like (incoherent) spectrum, out of which clean atomic peaks emerge for larger $R$. Note that the intermediate regime corresponds to the situation for which the bare bandwidth $W = 4|t|$ of the single particle states fulfills the condition $W \sim U$, i.e. the electronic system switches from the weak- to the rather strong-correlations regime, corresponding to the delocalization-localization crossover of the Mott-Hubbard type taking place. For one electron per atom the lower energy manifold is filled with electrons, whereas the upper is empty. The presence of the incoherent spectrum for $R \approx 3 \div 5a_0$ seems to represent also a universal feature, as it appears also for larger values of $N$.

4.4. Slater vs. Gaussian trial basis

We now compare the results obtained within EDABI when either the adjustable Slater or the STO-3G functions are used. Probably, most interesting is to compare the results for the Hubbard model with intersite Coulomb interactions taken in the Hartree-Fock approximation (only then the results for the Slater 1s-like basis are energetically stable. In Table 9 we list the results for the Slater basis containing both $E_G$ and microscopic parameters for a ring of $N = 10$ atoms. The same for the case of STO-3G basis is shown in Table 10. One sees that the Gaussian basis provides a lower value of $E_G$. This is because in the Slater case we have neglected 3- and 4-site interactions in the atomic basis that represents a rather crude approximation. On the contrary, the results for $E_G$ obtained for the STO-3G basis for $N = 10$ atoms are very close (within $10^{-2}\text{Ry}$) to those obtained for an exact solution for an infinite chain \cite{30} and the values of the microscopic parameters within $10^{-3}$ \cite{28}. Because of the good accuracy of the results for the Gaussian basis we have also provided in Table 11 the results for the chain of $N = 10$ atoms when the long-range part of the Coulomb interactions $\sim K_{ij}$ are included. These results provide the range of variation of the microscopic parameters when compared to either $H_2$ (cf. Table 2) or $U_1$ value for He atom (cf. Table 3).
4.5. The role of boundary-conditions: parity effects

It is believed that system properties in the thermodynamic limit \((N \to \infty)\) are the same regardless of the boundary conditions used. This claim has been tested on many model systems. However, for finite clusters the boundary conditions are crucial. For the chains studied here when \(N = 4n + 2\) (where \(n\) is a natural number) the periodic boundary conditions (PBC) are used, whereas for \(N = 4n\) the antiperiodic boundary conditions (ABC) lead to a lower-energy state. Namely, the terminal-atomic annihilation operators should be defined as follows

\[
\begin{align*}
    a_{N+1,\sigma} &\to a_{1\sigma} \quad \text{for PBC}, \\
    a_{N+1,\sigma} &\to -a_{1\sigma} \quad \text{for ABC}.
\end{align*}
\]

Therefore, the terminal hopping term involving the end atoms changes sign for ABC, while the interaction terms \(\sim n_i^\uparrow n_i^\downarrow, n_i n_j\) and \(S_i \cdot S_j\) remain unaltered. Obviously, the periodic boundary conditions are proper for any \(N\), when we have a ring geometry. The situation becomes more involved when \(N\) is an odd number. Namely, we write down the Hamiltonian (68) in the form

\[
H = \epsilon_a \sum_{i\sigma} n_{i\sigma} + t \sum_{j\sigma} e^{-i\Phi/N} a_{j\sigma}^\dagger a_{j+1\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow} + \sum_{i<j} K_{ij} \delta n_i \delta n_j,
\]

where \(\Phi\) is the fictitious (dimensionless) flux through the ring. One can show that the unitary transformation \(c_{j\sigma} \to e^{-i\Phi/N} c_{j\sigma}\) allows for accumulation of complex phase factor in the terminal hopping term, which then takes the form \(t(e^{-i\Phi} a_{N\sigma}^\dagger a_{1\sigma} + h.c.)\) and this can be regarded as generalized boundary condition \(a_{N+1,\sigma} \to e^{i\Phi/N} a_{1\sigma}\). We do not distinguish between the system with a fictitious flux and the generalized boundary conditions. The presence of the flux can be regarded as an accumulation of the Berry phase during the motion of individual electron in the milieu of all other electrons. With such interpretation the boundary conditions apply also to linear chain.

The electron momentum for nanochains with such boundary conditions is displayed in Fig. 23. The discrete momenta, corresponding to the solution of the single particle part of (78) for a finite \(N\), are given by

\[
k_n = \frac{2\pi n - \Phi}{N}, 0 \leq n \leq N
\]

The optimal BCs, corresponding to the minimal ground-state energy \(E_G\), with respect to \(\Phi\), are realized for \(\Phi = 0\) when \(N = 6, 10, 14, \ldots\) (periodic BCs), \(\Phi = \pi\) when \(N = 4, 8, 12, \ldots\) (antiperiodic BCs), and \(\Phi = \pi/2, 3/2\pi\) when \(N\) is odd. A basic analysis of Eq. (78) shows, that for the optimal BCs, the Fermi momentum value \(k_F = \pi/(2R)\) is never reached for even \(N\), whereas for odd \(N\) it happens for a single value of \(n\). This circumstance has important implication for the nanochain electronic structure, however, almost does not affect its transport properties, as discussed below. The exact meaning of the averaging procedure when drawing Fig. 23 is elaborated elsewhere. Analogously, the effect of BCs on the spin-spin correlation function \(< S_i \cdot S_j >\) is also touched upon there.
An explicit form of the dispersion relation derived from the spectral density functions with inclusion of the generalized boundary conditions, is shown in Fig. 22. We see again, that the spin splitting is present. Also, one can see the difference between either dispersion relation for noninteracting particles or with that calculated in the Hartree-Fock approximation for the Slater antiferromagnetic chain.

5. Transport in nanosystems

In this Section we complement the discussion of nanochains by providing the values of Drude weight (charge stiffness) and optical gap. We also show, how the EDABI method can be used to calculate the conductance of an open system: a quantum dot attached to the leads.

5.1. Drude weight for nanochains

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 \[ \sigma(\omega) = D \delta(\omega) + \sigma_{\text{reg}}(\omega), \] where the regular part is

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

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

\[
D = -\frac{\pi}{N} \langle \Psi_0 | T | \Psi_0 \rangle - \frac{2\pi}{N} \sum_{n \neq 0} \frac{|\langle \Psi_n | j_p | \Psi_0 \rangle|^2}{E_n - E_0},
\]

where the kinetic–energy term \( T \) is the same as the second term in Eq. (78), and the diamagnetic current operator is defined as usual: \( j_p = i t \sum_{j \sigma} (a_{j \sigma}^\dagger a_{j+1 \sigma} - \text{h.c.}) \). Here the states \( | \Psi_n \rangle \) in Eqs. (80) and (81) are the eigenstates of the Hamiltonian (78) corresponding to the eigenenergies \( E_n \), again with boundary conditions which minimize the ground–state energy for a given system size \( N \) (see previous Section). We calculate matrix elements \( \langle \Psi_n | j_p | \Psi_0 \rangle \) numerically by adapting the method developed by Dagotto [32], which is stable for even number of electrons only. Namely, we diagonalize the Hamiltonian (78) in the Fock space with the help of Davidson technique [33], and then repeat the procedure starting from a specially prepared initial state \( j_p | \Psi_0 \rangle \). Replacing the Lanczos scheme, utilized in Ref. [32], by the Davidson one provides an excellent accuracy for either even or odd number of electrons. The evolution of Drude weight with \( N \) and \( R \) is shown in Fig. 24. In the half–filled case \( N_e = N \) (cf. Fig. 24a) Drude weight gradually decrease with \( N \), as we have shown for even \( N \) [34]. The most interesting feature of these results is, that the curves for odd \( N \) fits smoothly between those for even \( N \), with very weak parity effect, totally incomparable with that present in the charge gap and electron momentum distribution [35]. This observation can be understood when we take into account, that the Drude weight defined by Eq. (81) is the integral quantity, involving the summation over all the excited states of the Hamiltonian.
The parity effect on Drude weight disappears for the system with a single hole \((N_e = N - 1, \text{ cf. Fig. } 24b)\), in which the magnetic frustration is absent. For this case, the Drude weight evolution with \(R\) is very interesting. In the weak–correlation range \((R/a_0 \lesssim 2)\) the chain shows a highly–conducting behavior for each \(N\). Next, in the intermediate range \((R/a_0 = 4 \div 5)\) the Drude weight decrease rapidly with \(N\), indicating an insulating (Mott–Hubbard) state in the large–\(N\) limit. In the strongly–correlated range \((R/a_0 \sim 10)\) the Drude weight approaches again its maximal value \(D = 1\). Such a behavior can be explained, when we analyze the situation in two steps: First, for low

\[\text{Eq. (78), so it cannot be determined only by the electronic structure near the Fermi points, particularly for a small system.}\]

Figure 23. Electron momentum distribution for chains of \(N = 8 \div 13\) atoms: \((a)\) datapoints for optimal boundary conditions (BCs) and the sample \(n(k)\) curves averaged over BCs (solid lines); \((b)\) the original \(n(k_q(\phi))\) functions used for the averaging.
values of $R$, the bandwidth–to–interaction ratio is small, and the system with a single hole does not differ significantly from a half–filled one. This is why in both cases Drude weight decreases gradually with both $N$ and $R$, as the tunneling amplitude through the barrier of a finite width. Second, for the largest values of $R$, the system can be described by an effective $t – J$ model \[36\] with a coupling constant $J = 4t^2/(U – K) \ll |t|$ (where $K \equiv K_{j,j+1}$ denotes the nearest neighbor Coulomb repulsion), which corresponds to an asymptotically–free hole motion. Then, it become clear that in the intermediate range the Drude weight has to suppressed, what can be interpreted in terms of a partially localized spin–ordered state. It would be very interesting to test experimentally this

Figure 24. Normalized Drude weight for nanochains in the half–filled case (a), and for a system with a single hole (b). The optimal boundary conditions are specified for each dataset.
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result, possibly for a mesoscopic atomic ring.

The smooth behavior of the system transport properties with \( N \) is illustrated in Fig. 25 on the example of other relevant quantity, the optical gap \( \Delta E_{\text{opt}} = E_i - E_0 \) (where \( E_i \) is the energy lowest-lying excited level \( |\Psi_i\rangle \), for which \( \langle \Psi_i | j | \Psi_0 \rangle \neq 0 \)). Again, adding a single hole totally removes the weak parity effect (not shown). The large-\( R \) behavior of \( \Delta E_{\text{opt}} \) could be explained by the value for an insulating limit \( \Delta E_{\text{opt}} \approx U - K \), whereas small \( R \) we have a strong \( N \) dependence similar to those observed for \( D \). The later shows, that the contribution of the state \( |\Psi_i\rangle \) to the sum (81) is dominating for such a partly-localized quantum nanoliquid [34].

5.2. \( H_2 \) molecule as a quantum dot

We have recently shown, that EDABI method is useful to investigate the zero-temperature conductance of diatomic molecule, modeled as a correlated double quantum dot attached to noninteracting leads [4]. This became possible when utilizing the Rejec–Ramšak formulas, relating the linear–response conductance to the ground–state energy dependence on magnetic flux [37]. Here we complement the discussion with the stability analysis showing, that large coupling between molecule and the leads may provide the possibility for interatomic distance manipulation in an experiment.

We start with the Hamiltonian which is a generalization of the Anderson impurity model [38], and can be written as

\[
H = H_L + V_L + H_C + V_R + H_R; 
\]

(82)

where \( H_C \) models the central region, \( H_{L(R)} \) describes the left (right) lead, and \( V_{L(R)} \) is the coupling between the lead and the central region. Both \( H_{L(R)} \) and \( V_{L(R)} \) terms have

\[
\text{Figure 25. Optical gap for nanochains in the half-filled case.}
\]
The combined exact diagonalization-\textit{ab initio} approach

\begin{figure}
\centering
\includegraphics[width=0.5\textwidth]{fig26}
\caption{Diatomic molecule as a double quantum dot.}
\end{figure}

a tight–binding form, with the hopping $t$ and the tunneling amplitude $V$

$$
H_{L(R)} = t \sum_{j \neq L(R), \sigma} (a_{j \sigma}^\dagger a_{j+1, \sigma} + \text{h.c.).}
$$

(83)

$$
V_{L(R)} = V \sum_{\sigma} (a_{L(R) \sigma}^\dagger a_{1(2) \sigma} + \text{h.c.),}
$$

(84)

as depicted schematically in Fig. 26. The index $j = L(R)$ corresponds to the last atom of the left (right) lead. The central–region term $H_C$ is a version of Hamiltonian (68) for two atoms, and describes a double quantum dot with electron–electron interaction

$$
H_C = (\epsilon_a - eV_G) \sum_{j=1,2} n_i - t' \sum_{\sigma=\uparrow, \downarrow} (a_{1 \sigma}^\dagger a_{2 \sigma} + \text{h.c.)})
$$

$$
+ U \sum_{j=1,2} n_{i\uparrow} n_{i\downarrow} + Kn_1 n_2 + (Ze)^2/R,
$$

(85)

where $\epsilon_a$ is atomic energy, $V_G$ is an external gate voltage, $t'$ is the internal hopping integral, $U$ and $K$ represents the intra– and inter–site Coulomb interactions, respectively, and the last term describes the Coulomb repulsion of the two ions at the distance $R$. Here we put $Z = 1$ and calculate all the parameters $\epsilon_a$, $t'$, $U$, and $K$ as the Slater integrals \[39\] for 1$s$–like hydrogenic orbitals $\Psi_{1s}(r) = \sqrt{\alpha^3/\pi} \exp(-\alpha |r|)$, where $\alpha^{-1}$ is the orbital size (cf. Fig. 26). The parameter $\alpha$ is optimized to get a minimal ground state energy for whole the system described by the Hamiltonian \[82\]. Thus, following the idea of EDABI method \[34\], we reduce the number of physical parameters of the problem to just a three: the interatomic distance $R$, the gate voltage $V_G$, and the lead–molecule coupling $V$ (we put the lead hopping $t = 1$ Ry = 13.6 eV to work in the wide–bandwidth limit).

We discuss now the molecule conductivity calculated from the Rejec–Ramšak two–point formula \[37\]:

$$
G = G_0 \sin^2 \pi [E(\pi) - E(0)]/2\Delta
$$

(86)

where $G_0 = 2e^2/h$ is the conductance quantum, $\Delta = 1/N\rho(\epsilon_F)$ is the average level spacing at Fermi energy, determined by the density of states in an infinite lead $\rho(\epsilon_F)$, $E(\pi)$ and $E(0)$ are the ground–state energies of the system with periodic and
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Table 11. Same as in Table 9, calculated in Gaussian–type STO–3G basis, with the inclusion of the long–range Coulomb interactions.

| $a/a_0$ | $\alpha_{\min}a_0$ | $\epsilon^f$ | $t$ | $U$ | $K$ | $E_G/N$ |
|--------|-----------------|--------|-----|-----|-----|--------|
| 1.5    | 1.322           | 0.1340 | -0.8684 | 2.014 | 1.156 | -0.7691 |
| 2.0    | 1.208           | -0.5338 | -0.4603 | 1.721 | 0.909 | -0.9377 |
| 2.5    | 1.119           | -0.7894 | -0.2748 | 1.528 | 0.749 | -0.9824 |
| 3.0    | 1.063           | -0.8977 | -0.1770 | 1.407 | 0.639 | -0.9924 |
| 3.5    | 1.030           | -0.9466 | -0.1192 | 1.334 | 0.557 | -0.9932 |
| 4.0    | 1.011           | -0.9697 | -0.0817 | 1.288 | 0.493 | -0.9922 |
| 4.5    | 1.006           | -0.9812 | -0.0562 | 1.269 | 0.442 | -0.9917 |
| 5.0    | 1.006           | -0.9868 | -0.0382 | 1.260 | 0.399 | -0.9915 |
| 6.0    | 1.002           | -0.9908 | -0.0170 | 1.250 | 0.333 | -0.9917 |
| 7.0    | 1.000           | -0.9915 | -0.0072 | 1.247 | 0.286 | -0.9917 |
| 8.0    | 1.000           | -0.9917 | -0.0027 | 1.246 | 0.250 | -0.9917 |
| 10.0   | 1.000           | -0.9917 | -0.0003 | 1.246 | 0.200 | -0.9917 |

Figure 27. Zero–temperature conductance of the system in Fig. 26 as a function of the gate voltage $V_G$ and interatomic distance $R$. 1s orbital size $\alpha^{-1}$ is optimized variationally. The lead parameters are $t = 1$Ry and $V = 0.5t$. 

\[ G / G_0 \]

\[ G / V_G \]

\[ G / BZ \]

\[ G / BZ / BZ \]

\[ G / BP / CP \]

\[ G / BC \]

\[ G / BM \]

\[ G / BH \]

\[ G / BE \]

\[ G / BM \]

\[ G / BC \]

\[ G / BF \]

\[ G / BM \]

\[ G / BC \]
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Figure 28. The optimized inverse inverse orbital size (a) and average central region occupancy (b) for the diatomic molecule attached to noninteracting leads characterized by the parameters \( t = 1 \text{Ry} \) and \( V = 0.5t \).

antiperiodic boundary conditions, respectively. \( E(\phi) \) is calculated for \( \phi = 0, \pi \) within the Rejec–Ramšak variational method \cite{37}, complemented by the inverse orbital size \( \alpha \) optimization, as mentioned above. We use typically \( N = 10^2 \div 10^3 \) sites to reach the convergence.

In Fig. 27 we show the conductivity for \( V = 0.5t \), and different values of the interatomic distance \( R \). The conductance spectrum evolves from the situation well-separated peaks corresponding to the independent filling of bonding and antibonding molecular orbitals \( (R \lesssim 2a_0, \text{where} \ a_0 \text{is the Bohr radius}) \), to the single peak in the intermediate range \( (R \approx 3a_0) \), which decays when \( t' \ll V \) for large \( R \).

Probably, the most interesting feature of the conductance depicted in Fig. 27 is their strong asymmetry for small \( R \). Namely, the low–\( V \) conductance peak, corresponding to the system filling \( \langle n_1 + n_2 \rangle \approx 1 \) (one hole) is significantly wider than the high–\( V \) peak for \( \langle n_1 + n_2 \rangle \approx 3 \) (one extra electron). Such a particle–hole symmetry breaking is the novel feature, observed when including the correlation–induced basis optimization, and absent in the parametrized–model approach \cite{37,40}. It is also a new feature of a nanosystem, do not observed in mesoscopic double quantum dots \cite{41}, where the particle–hole symmetry holds.

The relation between the observed asymmetry, basis renormalization, and electron correlations can be clarified as follows. \textit{First}, one can observe that the optimal values of the variational parameter \( \alpha \), provided in Fig. 28a, decrease dramatically for high \( V_G \), corresponding to the overdoped situation \( \langle n_1 + n_2 \rangle > 2 \) (cf. Fig. 28b). This is because the system minimize energy of double occupancies, which is of the order \( U \sim \alpha \) \cite{39}. \textit{Then}, we focus on an small \( R \) limit, in which the well separation of molecular orbitals allows one to approximate the expression for a single impurity at zero temperature \cite{42}

\begin{equation}
G = G_0 \sin^2(\pi \langle n_k \rangle / 2),
\end{equation}

where \( \langle n_k \rangle \) is the bonding \( (k = 0) \) or antibonding \( (k = \pi) \) orbital occupancy. Expanding
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Table 12. The binding energy $\Delta E$ and the bond length $R_{\text{min}}$ for different coupling to the lead $V$. The conductance at the energy minimum is also provided.

| $V/t$ | $\Delta E$ | $R_{\text{min}}/a_0$ | $G_{\text{min}}^V/G_0$ |
|-------|------------|----------------------|----------------------|
| 0.0   | -0.296     | 1.43                 | 0                    |
| 0.1   | -0.293     | 1.44                 | $10^{-4}$            |
| 0.2   | -0.282     | 1.46                 | 0.004                |
| 0.3   | -0.180     | 1.52                 | 0.023                |
| 0.4   | -0.040     | 1.59                 | 0.093                |
| 0.5   | +0.074     | 1.93                 | 0.422                |

around the maximum we have $G(V_G) - G(V_G^{*,k}) \approx -G_0(\chi_c \pi/2)^2(V_G - V_G^{*,k})$, where $V_G^{*,k}$ ($k = 0, \pi$) is the low/high voltage peak position and $\chi_c$ is the charge susceptibility, which may be approximated as $\chi_c \approx \partial \langle n_1 + n_2 \rangle / \partial V_G$, since the orbitals are filled separately. Values of the later derivative read from Fig. 28, around the low and high voltage peak positions ($\langle n_1 + n_2 \rangle \approx 1$ and $\approx 3$, respectively) provides a clear asymmetry. Moreover, the expansion of $G(V_G)$ allows one to roughly estimate the peak width as $\Delta V_G \approx \chi_c^{-1} \approx (U + K)/2 \sim \alpha$, what provides an indirect correspondence between the spectrum asymmetry and basis renormalization.

The practical possibility of the conductance measurement involving atoms manipulation (changing of $R$) were also explored in terms of the system stability. Namely, the binding energies $\Delta E \equiv E_{R_{\text{min}}} - E_{\infty}$ (where $R_{\text{min}}$ is the bond length), listed in Table 12 shows that the system become metastable around $V = 0.5t$ ($\Delta E > 0$ indicates a \textit{local} energy minimum). Therefore, the binding of the atoms to the lead become stronger than interaction between the atoms, that may allow individual atoms manipulation.

We would like to stress here, that \textit{ab initio} analysis have never been performed for the \textit{open} system with strong electron correlation.Apart from simplifying the discussion (the model parameters are calculated as a function of interatomic distance), such an approach leads to new physical effects, since the particle–hole symmetry is broken, as exemplified on the example of the conductivity calculations.

6. Concluding remarks

In this paper we have provided a detailed discussion of the method based on the diagonalization in the Fock space, when combined with with an \textit{ab initio} adjustment of single-particle wave functions in the interacting state of N-particle system (\textit{the EDABI method}). The method can be improved upon by systematically increasing the number of wave functions in the basis $[\psi_i(\mathbf{r})]$ when defining the field operator for the system (thus enriching the model). We have illustrated our method with the discussion of several nanoscopic systems ranging from atoms to nanochains and quantum dots.
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The method is useful when the exact solution of a model is available in the Fock space. Such situation happens also for one dimensional atomic chain represented by the Lieb-Wu solution of the Hubbard model \[30\]. In that situation, exact Wannier or Bloch wave functions can be constructed. Other applications such as solving the magnetic impurity in a nonmetallic environment are also possible, although not carried out explicitly as yet.

The importance of our approach is, among others, in showing explicitly that the concept of the statistical distribution of particles with quasimomentum, as a good quantum number, is feasible for a relatively small interatomic distances. This means, that the corresponding N-electron states form a quantum nanoliquid for not too-large inter-distance in nanowire. In connection with this, in replying the question how small a piece of metal can be, we can say that the nanoliquid exhibits metallic conductivity for \(eV \geq \Delta E(N, R)\), where \(V\) is the voltage applied to the system and \(\Delta E(N, R)\) is the energy difference between the highest occupied and the lowest unoccupied state, i.e. that the momentum is a good quantum number then. For an intermediate interatomic distance, we have a gradual transition to a Mott insulator, above which the monoatomic (quantum) nanowire is useless for electronic applications.

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See e.g. R.P. Feynman, *Statistical Mechanics: A Set of Lectures* (W.A. Benjamin, Menlo Park, CA, 1972) ch. 6.7. In the case of fermions we use the spinor notation for the field operators, e.g. \( \Psi_i^\dagger(\mathbf{r}) \equiv (\Psi_\uparrow_i^\dagger(\mathbf{r}), \Psi_\downarrow_i^\dagger(\mathbf{r})) \), \( a_i^\dagger \equiv (a_{i\uparrow}^\dagger, a_{i\downarrow}^\dagger) \), and \( \Phi_i(\mathbf{r}) \equiv (\Phi_{i\uparrow}(\mathbf{r}), \Phi_{i\downarrow}(\mathbf{r})) \equiv \Phi_i(\chi_{i\uparrow}, \chi_{i\downarrow}). \)

One could obtain a complete solution of (1) directly by determining the field operator from the Heisenberg equation of motion for \( \Psi \) or for the Green function related to it. However, this is usually not feasible if one has to go beyond the Hartree-Fock approximation or the interaction part must be treated nonperturbatively.

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Note that the parameters \( t_{ij} \) and \( v_{ijkl} \) contain the functions \( \{w_i(\mathbf{r})\} \) under the integral expressions (8) and (2.2), so \( E_G \) is indeed a functional of \( \{w_i(\mathbf{r})\} \) an \( \{\nabla w_i(\mathbf{r})\} \).

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The notion of the self-adjusted state differs from the concept of quasiparticle state invoked by Landau in his theory of Fermi liquids. Landau quasiparticle results from an adiabatic switching of the interaction and therefore , the quasiparticle states are in one-to-one correspondence with the states of an ideal quantum gas forming the liquid. Here, the self-adjusted states can be either localized or itinerant as the interparticle interaction cannot be treated perturbationally. The statistical distribution of correlated state can differ from the Fermi-Dirac distribution (cf. Ref. 8), as quasimomentum may not be a good quantum number.

In the context of the orbit-size relaxation one can talk about wave-function renormalization. The statistical distribution is determined by dynamics in the Fock space.

Note that the atomic orbitals 1s and 2s are not orthogonal to each other for arbitrary values of their spatial extents \( 1/\alpha \). The 2p orbitals are orthogonal to each other and to s orbitals, since they contain a nontrivial angular dependence expressed via spherical harmonics \( Y^m_l(\theta, \phi) \).

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