Vol. 32 (2001) *ACTA PHYSICA POLONICA B* No 10 Special Issue

EXACT DIAGONALIZATION OF MANY-FERMION HAMILTONIAN COMBINED WITH WAVE-FUNCTION READJUSTMENT

II. METALLICITY AND ELECTRON LOCALIZATION IN NANOSCOPIC SYSTEMS*

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(Received June 21, 2001)

We apply our new method of approach to electronic states in correlated systems [for a brief review, Part I, see: *Acta Phys. Pol.* **B31**, 2879 (2000)] to the analysis of the states and electron localization in nanoscopic chains containing up to $N = 12$ atoms. The Mott and the Hubbard criteria of localization are explicitly evaluated and the importance of the former is stressed. We also define the many-particle wave function and calculate it explicitly for the hydrogen molecule. Further applications of our method are listed at the end.

PACS numbers: 71.10.Fd, 71.15.Fv, 31.25.Nj

1. Introduction

A combined first- and second-quantization scheme

It is generally perceived that the wave mechanics [1] (hereinafter called the first-quantization scheme) describes the matter-wave aspect of the system behavior, whereas the second-quantization scheme [2] restores the particle language as it operates with the particle transitions (creations and annihilations) between the states with well defined quantum numbers appropriate

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[*] Presented at the XII School of Modern Physics on Phase Transitions and Critical Phenomena, Lądek Zdrój, Poland, June 21–24, 2001.

for a complete set of single particle states [3]. Obviously, a complete description of the physical system relies on *the complementarity* of both descriptions of the quantum states. The question we have addressed [4–7] in this respect is whether one can combine both first- and the second-quantization schemes in approaching the many-particle systems, possibly in a systematic manner, which would represent a nonperturbational description of many-body aspects of N-particle states.

Such an approach has a number of advantages. First of them is that wave and particle aspects of the states converge into a single scheme. Second, we can treat the so-called *correlated fermion systems*, for which the interaction part is comparable (if not *prevalent*) to the single-particle part of the system energy. As an extra bonus from such a treatment we obtain the explicit form of the many-particle wave function starting from a single-particle scheme, as will be illustrated at the and of this paper on the simple examples of H_2 molecule.

The method has been applied so far to the simple systems [4–6]: H_2 molecule, He atom, Hubbard chain, and linear chain with *all* pair-site interactions. So, it requires further development. Below we discuss a nanoscopic system of linear chain configuration with periodic boundary conditions and discuss the electron localization for this case as an example of a *quantum phase transition* [7]. At the end, we return to some general features of our approach (*cf.* Section 2) by defining the many-particle wave function and making a suggestion about the *iterative* aspects of the description of quantum states in interacting many-particle systems, *i.e.* describe the *feedback effect* between the first- and second-quantization aspects of the states. But first, we summarize briefly the method of approach (*cf.* Section 2) and present the results for nanoscopic systems (Sections 3 and 4).

It is worth summarizing the method in a few words. We start with the many-body Hamiltonian in the Fock-space, in which the single-particle wave functions are contained in the microscopic parameters of the model. The creation and annihilation operators describe the transitions between the single-particle states selected to define the field operators. Therefore, the Fock-space aspect of the problem accounts for redistribution of particles (dynamic processes) induced by the interaction amongst them. Once the dynamic processes have been accounted for *i.e.* the Hamiltonian has been diagonalized in the Fock space (rigorously or otherwise), we optimize the ground-state energy with respect to the single-particle orbitals contained in the microscopic parameters of the Hamiltonian. The second procedure closes the solution of the many-body problem in the sense that the system properties can be discussed as a function of the mean interparticle distance, *not* only as a function of the parameters, as is usually the case. The solution is nonperturbational in the sense, in which the interaction terms are included in the diagonalization procedure of the Hamiltonian. In what follows we implement this methodology to the *correlated nanoscopic chain* (*cf.* Sections 3 and 4) and return subsequently to some general aspects of the method in Section 5.

2. Method combining first- and second-quantizations

We start with the Hamiltonian in the Fock space of the form [8, 9]

$$\begin{aligned} H &= \sum_{\sigma} \int d^3\boldsymbol{r} \widehat{\Psi}^{\dagger}_{\sigma}(\boldsymbol{r}) H_1(\boldsymbol{r}) \widehat{\Psi}_{\sigma}(\boldsymbol{r}) \\ &+ \frac{1}{2} \sum_{\sigma_1\sigma_2} \iint d^3\boldsymbol{r}_1 d^3\boldsymbol{r}_2 \widehat{\Psi}^{\dagger}_{\sigma_1}(\boldsymbol{r}_1) \widehat{\Psi}^{\dagger}_{\sigma_2}(\boldsymbol{r}_2) V(\boldsymbol{r}_1 - \boldsymbol{r}_2) \widehat{\Psi}_{\sigma_2}(\boldsymbol{r}_2) \widehat{\Psi}_{\sigma_1}(\boldsymbol{r}_1) \,, \end{aligned} \tag{1}$$

where $H_1(\boldsymbol{r})$ and $V_{12} \equiv V(\boldsymbol{r}_1 - \boldsymbol{r}_2)$ are, respectively, the Hamiltonians for a single particle and a single pair of particles in the coordinate (Schrödinger) representation, and $\widehat{\Psi}_{\sigma}(\boldsymbol{r})$ is the field operator defined through

$$\widehat{\Psi}_{\sigma}(\boldsymbol{r}) = \sum_i w_i(\boldsymbol{r}) \chi_{\sigma} a_{i\sigma} \,, \tag{2}$$

where $a_{i\sigma}$ is the annihilation operator of a particle in a single-particle state $w_i(\boldsymbol{r})\chi_{\sigma}$. One should note that the basis $\{w_i(\boldsymbol{r})\chi_{\sigma}\}$ is completely arbitrary in this definition. By inserting (2) into (1) we obtain the usual form of the Hamiltonian

$$H = \sum_{ij\sigma} t_{ij} a^{\dagger}_{i\sigma} a_{j\sigma} + \frac{1}{2} \sum_{ijkl\sigma\sigma'} V_{ijkl} a^{\dagger}_{i\sigma} a^{\dagger}_{j\sigma'} a_{l\sigma'} a_{k\sigma} \,, \tag{3}$$

with the microscopic parameters defined by

$$t_{ij} \equiv \langle w_i | H_1 | w_j \rangle = \int d^3 r w_i^*(\boldsymbol{r}) H_1(\boldsymbol{r}) w_j(\boldsymbol{r}) \,, \tag{4}$$

and

$$V_{ijkl} \equiv \langle w_i w_j | V_{12} | w_k w_l \rangle = \int d^3 r_1 d^3 r_2 w_i^*(\boldsymbol{r}_1) w_j^*(\boldsymbol{r}_2) V(\boldsymbol{r}_1 - \boldsymbol{r}_2) w_k(\boldsymbol{r}_1) w_l(\boldsymbol{r}_2) \,. \tag{5}$$

Thus in the form (3) of the many-particle Hamiltonian the single- and many-particle aspects of the problem are separated in the sense that calculation of the parameters t_{ij} and V_{ijkl} is separated from the diagonalization of the

Hamiltonian in the Fock space. This can be seen explicitly when we calculate the ground state energy

$$E_{\mathrm{G}} \equiv \langle H \rangle = \sum_{ij\sigma} t_{ij} \langle a^{\dagger}_{i\sigma} a_{j\sigma} \rangle + \frac{1}{2} \sum_{ijkl\sigma\sigma'} V_{ijkl} \langle a^{\dagger}_{i\sigma} a^{\dagger}_{j\sigma'} a_{l\sigma'} a_{k\sigma} \rangle, \tag{6}$$

where the averaging $\langle ... \rangle$ takes place over *all* feasible occupancies of *given* single particle states $|i\sigma_1\rangle$, $|j\sigma_2\rangle$, $|k\sigma_3\rangle$, and $|k\sigma_4\rangle$ (compatible with the total number of particles).

So far, the approach is standard [8,9]. We have proposed [4–6] to close the solution with optimization of the single-particle basis $\{w_i(\boldsymbol{r})\}$ by treating the E_{G} expression (6) as a functional of $\{w_i(\boldsymbol{r})\}$ and their gradients, which are contained in the microscopic parameters. In such situation the *renormalized* wave function is determined from the Euler equation for the functional

$$F\{w_i(\boldsymbol{r})\} = E_{\mathrm{G}}\{w_i(\boldsymbol{r})\} - \sum_{i \geq j} \lambda_{ij} \left(\int d^3 r w^*_i(\boldsymbol{r}) w_j(\boldsymbol{r}) - \delta_{ij} \right), \tag{7}$$

where λ_{ij} are the Lagrange multipliers, which appear in the general case, when the single-particle basis is nonorthonormal (otherwise and usually, the basis is chosen as orthonormal and then $\lambda_{ij} \equiv 0$ and we have the customary Lagrange–Euler problem). The general form of this equation in the stationary case is:

$$\frac{\delta E_{\mathrm{G}}}{\delta w^*_i(\boldsymbol{r})} - \nabla \cdot \frac{\delta E_{\mathrm{G}}}{\delta \nabla w^*_i(\boldsymbol{r})} - \sum_{j \geq i} \lambda_{ij} w_j(\boldsymbol{r}) = 0. \tag{8}$$

We will work here with fermions (electrons) on the lattice and the wave functions $\{w_i(\boldsymbol{r})\}$ will be taken in the form of the (orthonormal) Wannier functions. Additionally, as is implicit in the treatment above, we define one global spin quantization axis for *all* single particle states used to define $\widehat{\Psi}_{\sigma}(\boldsymbol{r})$.

3. Nanoscopic chain of correlated electrons

We consider a chain of N atoms, with one valence electron per atom in $1s$ state and apply periodic boundary conditions. The Hamiltonian (3) containing *all* two-site terms is of the form

$$\begin{aligned} H \;=\; & \sum_{i=0}^{N-1} \Bigg\{ \varepsilon_a n_i + U n_{i\uparrow} n_{i\downarrow} + \sum_{j=0}^{i-1} \Big\{ \left(K_{ij} - \tfrac{1}{2} J_{ij}\right) n_i n_j - 2 J_{ij} \boldsymbol{S}_i \cdot \boldsymbol{S}_j \\ & + \sum_{\sigma} \left[t_{ij} + V_{ij} (n_{i\bar{\sigma}} + n_{j\bar{\sigma}}) \right] \left(a^{\dagger}_{i\sigma} a_{j\sigma} + a^{\dagger}_{j\sigma} a_{i\sigma} \right) + J_{ij} \left(a^{\dagger}_{i\uparrow} a^{\dagger}_{i\downarrow} a_{j\downarrow} a_{j\uparrow} \right. \\ & \left. + a^{\dagger}_{j\uparrow} a^{\dagger}_{j\downarrow} a_{i\downarrow} a_{i\uparrow} \right) \Big\} \Bigg\}, \end{aligned} \tag{9}$$

where, respectively, the first two terms express the atomic part of the single-particle ($\varepsilon_a \equiv t_{ii}$) and two-particle ($U \equiv V_{iiii}$) energies, the next two represent the intersite Coulomb ($K_{ij} \equiv V_{ijij}$) and exchange ($J_{ij} \equiv V_{ijji}$) energies, the following two describe the intersite particle hopping (t_{ij}) and so-called correlated hopping ($V_{ij} \equiv V_{iiij}$) for $i \neq j$, whereas the last part is responsible for two-electron hopping between the sites i and j. In such notation the Wannier functions are chosen as real functions.

The Wannier functions are defined through the atomic 1s functions in the following manner

$$w_i(\boldsymbol{r}) = \sum_{j=0}^{N-1} \beta_{i-j} \psi_j(\boldsymbol{r}), \tag{10}$$

where the 1s functions of the (adjustable) size α^{-1} centered on the j-the site are

$$\psi_j(\boldsymbol{r}) = \left(\frac{\alpha^3}{\pi}\right)^{1/2} \exp\left(-\alpha|\boldsymbol{r} - \boldsymbol{R}_j|\right) , \tag{11}$$

and the expansion coefficients $\beta_{i-j} \equiv \beta_p$ are determined from [4, 5]

$$\beta_p = N^{-1} \sum_{\boldsymbol{k}} \left\{ \sum_{p'} S_{p'} \cos(\boldsymbol{k} \cdot \boldsymbol{R}_{p'}) \right\}^{-1/2} \cos(\boldsymbol{k} \cdot \boldsymbol{R}_p) . \tag{12}$$

The overlap integrals S_p are defined as

$$S_p \equiv \langle \psi_i \mid \psi_{i+p} \rangle = \int d^3r \psi^*(\boldsymbol{r} - \boldsymbol{R}_i) \psi(\boldsymbol{r} - \boldsymbol{R}_{i+p}) ,$$

and the summation over the wave vectors $\{\boldsymbol{k}\}$ runs over the first Brillouin zone.

The whole solution procedure consists of the following steps. First, we transform the parameters ε_a, U, t_p, K_p, J_p, and V_p (for $p = |i - j|$) to the atomic basis $\{\psi_i(\boldsymbol{r})\}$, where they can be explicitly calculated [5]. These calculation include three-site terms contained in the expression for t_{ij}. In this manner, the parameters for all the values of $p = 1, ..., N-1$ have been included. Second, we diagonalize numerically the Hamiltonian (9) for given values of the parameters by calculating the ground state energy E_{G}. This energy is subsequently optimized with respect to the orbital size α^{-1} for given interatomic distance R. The obtained earlier eigenvectors in the occupation number representation and the Wannier functions for the optimal size $\alpha^{-1} = \alpha_{\mathrm{min}}^{-1}$ allow us to calculate explicitly not only $E_{\mathrm{G}} = E_{\mathrm{G}}(R)$, but also the relevant correlation functions such as the momentum distribution function $n_{\boldsymbol{k}\sigma}$ for the electrons and spin–spin correlation functions, as well as the microscopic parameters $t_p = t_p(R)$, $U = U(R)$, *etc.* Below we analyze only the results important for a characterization of the transition from itinerant to localized states of electrons, which represents a quantum transformation of the metallic state into the atomic configuration of localized spins. The discussion of these results will carry us out to the natural question: How small a metal can be?

4. Transformation of a nanoscopic metal into a spin system

The explicit analysis can be performed only numerically. We will discuss results for $N \leq 12$ atoms with one electron per atom. Strictly speaking, we model a chain of hydrogenic-like states, as the screening of internal shells and their polarizability are not included. In Fig. 1 we display the electron momentum distribution $n_{\boldsymbol{k}\sigma} = \langle a^{\dagger}_{\boldsymbol{k}\sigma} a_{\boldsymbol{k}\sigma} \rangle$ for $N = 10$ atoms and the two interatomic distances $R = 3a_0$ and $R = R_{\mathrm{c}} = 3.929\, a_0$, where a_0 is $1s$ Bohr radius. The points represent the result of numerical computation described in the preceding section, whereas the continuous lines represent the interpolation

$$n_{\boldsymbol{k}\sigma} = \tfrac{1}{2} + \mathrm{sgn}(k - k_{\mathrm{F}}) \left(\alpha |k - k_{\mathrm{F}}|^2 + \beta |k - k_{\mathrm{F}}| - \gamma \right), \tag{13}$$

where α, β, and γ represent the fitted parameters and k_{F} is the Fermi wave vector, $k_{\mathrm{F}} = \pi/(2R)$. This form of the distribution function can be

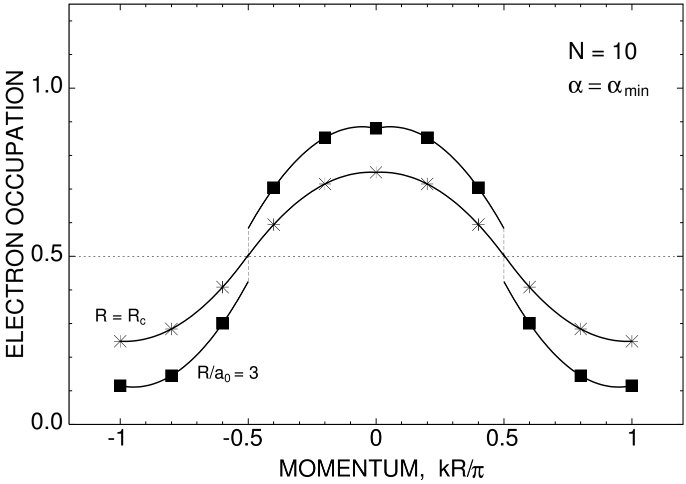

Fig. 1. Momentum distribution $n_{k\sigma}$ for electrons in the linear chain of $N = 10$ atoms; the interatomic distance R is specified in units of $1s$ Bohr radius a_0. The continuous line represents the parabolic interpolation discussed in main text, which is of the same type for both $k > k_{\mathrm{F}}$ and $k < k_{\mathrm{F}}$ (k_{F} is the Fermi wave vector).

understood by representing it via its Fourier transform, which contains the correlation functions $\langle a^\dagger_{i\sigma} a_{i+p\sigma}\rangle$, namely we have

$$n_{\boldsymbol{k}\sigma} = \tfrac{1}{2} + \sum_{j(i)} \mathrm{e}^{i\boldsymbol{k}\cdot(\boldsymbol{R}_i - \boldsymbol{R}_j)} \langle a^\dagger_{i\sigma} a_{j\sigma}\rangle \,. \tag{14}$$

From Fig. 1 one clearly sees that there exists a critical interatomic distance $R = R_\mathrm{c}$, at which the distribution function is continuous. Note that the interpolation formula (13), with k as a continuous variable, emulates a large system with the same statistical properties. The localization threshold is defined as the distance at which the value of the discontinuity at the Fermi level $\Delta n_{k_\mathrm{F}} \equiv n_{k=k_\mathrm{F}-0} - n_{k=k_\mathrm{F}+0}$, disappears. Having determined this quantity, one can use the Fermi-liquid relation for the quasiparticle mass enhancement at the Fermi level [10]

$$\frac{m^*}{m_\mathrm{B}} = \left(\Delta n_{k_\mathrm{F}}\right)^{-1}, \tag{15}$$

where m_B is the effective band mass at the Fermi level, which must be calculated separately [10]. In effect, in Fig. 2 we display this enhancement as a function of R. The computed points can be fitted with the continuous line

$$m^*_\mathrm{F} = A|R - R_\mathrm{c}|^{-\gamma'}, \tag{16}$$

with $A \simeq 10,2$, $R_\mathrm{c} \simeq 3.92a_0$, and $\gamma' \simeq 4/3$. This infinite effective mass means that the quasiparticles are localized on atoms to minimize the atomic part of the energy. Obviously, m^*_F represents the effective mass for a translational motion throughout the crystal and as such is unrelated to that the electron has when moving in the atom. To clarify this situation we have plotted in Fig. 4 the quantity $n_\mathrm{c}a_\mathrm{H}$, where $N_\mathrm{c} = 1/R$ is the carrier concentration (number of electrons per unit length of the chain), and $a_\mathrm{H} = \alpha^{-1}_\mathrm{min}$ is the optimal size of the atomic orbit for given interatomic distance R. The dotted line marks the value 0.2 corresponding to the Mott criterion in bulk systems.

In order to relate our criterion of the electron localization in this nanoscopic system to the well known criteria due to Hubbard [11] and Mott [12] we proceed as follows. We calculate first the ratio $W/(U - K_1)$, where W is the width of the band states $W = 4|\sum_{j(i)} t_{ij}|$, as a function of the lattice parameter R. The result is displayed in Fig. 3 (in the inset we present the R dependence of the orbital size α^{-1} in units of a_0). The dot-dashed line marks the Hubbard localization threshold defined through the condition $W/(U - K_1) = 1$. This condition is met for $R \sim 2.7a_0$, well below R_c. So, the two criteria of localization are incompatible for the nanoscopic system of small number of atoms $N \sim 10$.

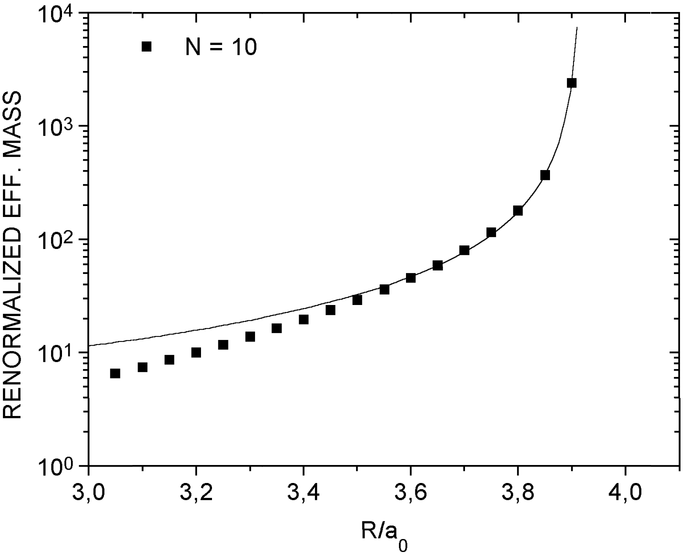

Fig. 2. The quantum critical behavior of the quasiparticle mass at the Fermi level: The computed points for $N = 10$ atoms are fitted with the curve $m^* \sim |R - R_c|^{-4/3}$, with $R_c \simeq 4.3a_0$. Note the logarithmic scale for the effective mass.

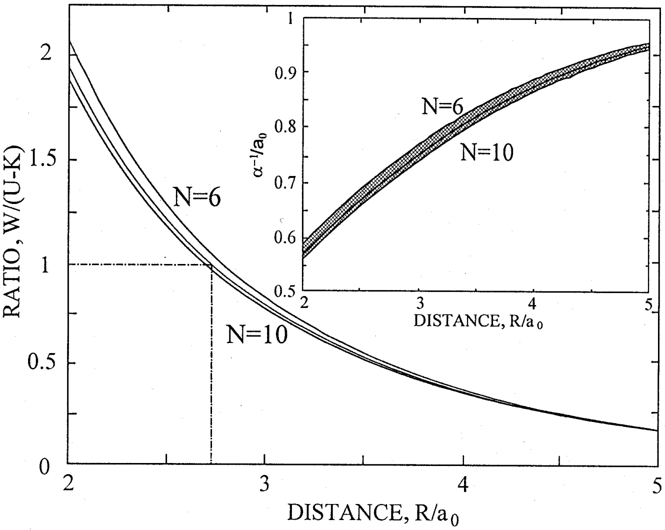

Fig. 3. The bare bandwidth-to-interaction ratio *versus* R; the Hubbard criterion for localization is marked (see main text). The inset provides the optimal size $\alpha^{-1} = \alpha_{\min}^{-1}$ (in units of a_0) of the atomic orbitals composing the *optimized* Wannier functions.

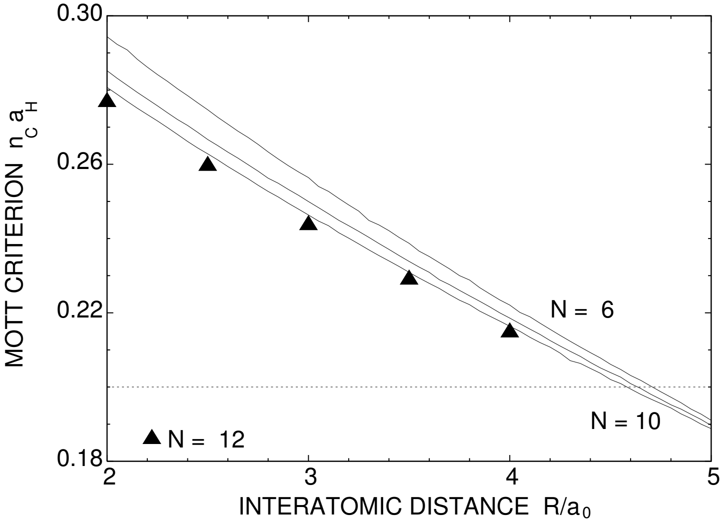

Fig. 4. The Mott criterion value $n_c a_H$ vs. R and for different number of atoms $N = 6 \div 12$. The horizontal dotted line marks the Mott criterion for the bulk 3-dimensional systems.

One can notice a good agreement with the value of R_c if one writes the Mott criterion for the localization in the form $n_c a_H \simeq 0.22$. One may say that the Mott-criterion applicability even in the one-dimensional case originates from the long-range nature of the Coulomb interaction we take into account and which, in turn, imitates the higher-lattice dimensionality. Hence, the long-standing conclusion [13] about the universality of the insulating state for the *Hubbard chain* does not extend to the $1s$ models with a realistic account of the electronic structure. This conclusion is very important also because it removes one of the main objections against using the itinerant (or even effective mass) states in low dimensional metals (wires) and quantum dots. In Fig. 5 we display an exemplary evolution with increasing R of the band structure of the linear chain with periodic boundary conditions. The continuity of the wave vector k is obtained by using the following expression for the band energy

$$\varepsilon_k = \varepsilon_a + 2 \sum_{p=1}^{N-1} t_p \cos(kR_p)\,, \tag{17}$$

where t_p represent the calculated hopping integrals using the optimized Wannier functions in the correlated state. The horizontal plane marks the position of the Fermi level, which is localized always in the middle of the band when the shift of the atomic level ε_a is accounted for with the increasing distance R. Obviously, the band flattens out with increasing R but is always nonzero, since the bandwidth characterizes the wave function overlap between the neighboring sites. The true localization ($W \to 0$ or equivalently) $m^* \to \infty$, is achieved only when the interparticle interactions are properly included.

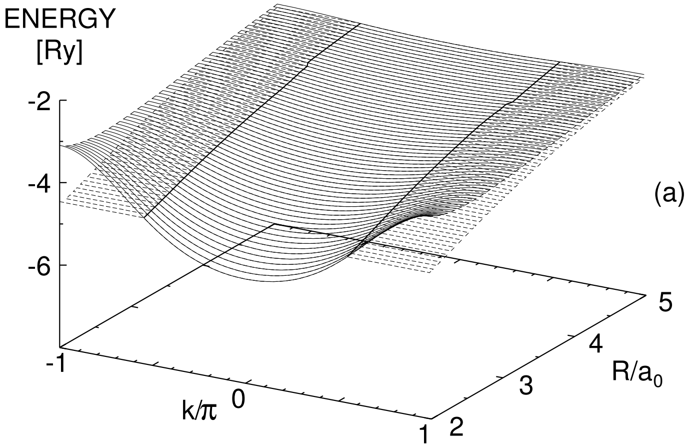

Fig. 5. The space profile of the band shape for $N = 10$ atoms versus R, taking into account the calculated hopping integrals $\{t_p\}_{p=1\ldots5}$. The horizontal plane intersecting the band marks the Fermi level position for one electron per atom.

From the foregoing discussion it follows that the system evolves with the increasing interatomic distance from a metal (as visualized by the existence of the Fermi ridge in Fig. 1) towards the Mott insulating state with one (nonpaired) electron per atom. The system possesses a *quantum critical point* for metal–insulator transition at $R = R_{\rm c}$ only if we extrapolate our results to the large N limit. Such an extrapolation procedure here relies on regarding the quasimoment $\hbar k$ as a quasicontinuous variable, so we can interpolate between the discrete computed points the properties such as $n_{k\sigma}$, m^*, and ε_k. The electronic properties of the system for $R > R_{\rm c}$ are close to those of a Mott–Heisenberg magnetic insulator, as discussed in detail elsewhere [8]. For the sake of completness we display in Fig. 6 the basic characteristics (as a function of R), which are well defined in both itinerant and atomic states. Those comprise: *(i)* the site spin magnitude $\Theta_{\rm M} = (4/3)\langle \boldsymbol{S}_i^2\rangle$, where $\boldsymbol{S}_i \equiv (S_i^\dagger, S_i^-, S_i^z) = (a_{i\uparrow}^\dagger a_{i\downarrow}, a_{i\downarrow}^\dagger a_{i\uparrow}, 1/2(n_{i\uparrow} - n_{i\downarrow}))$ is the electron spin on site i, *(ii)* the spin–spin correlation function $\Theta_{\rm AF} \equiv -\langle \boldsymbol{S}_i \cdot \boldsymbol{S}_{i+1}\rangle$, and *(iii)* $\Theta_{\rm MI} = 4\sigma^2\{n_{k\sigma}\}$, where $\sigma^2\{n_{k\sigma}\}$ is the dispersion of the statistical distribution defined as

$$\sigma^2\{n_{k\sigma}\} = \frac{1}{2N}\sum_{k\sigma} n_{k\sigma}^2 - \left(\frac{1}{2N}\sum_{k\sigma} n_{k\sigma}\right)^2 . \tag{18}$$

The averages are for the ground state, and are determined via the exact diagonalization in the occupation-number representation. The quantity $\Theta_{\rm M}(= 1 - 2\langle n_{i\uparrow} n_{i\downarrow}\rangle)$ takes the value (1/2) in the ideal gas limit and approaches unity in the atomic limit, where we have a Pauli spin $(\tau/2)$ on each atom. $\Theta_{\rm AF}$ approaches the value (3/4) for the singlet configuration of the atomic spins, whereas $\sigma^2\{n_{k\sigma}\}$ acquires the value 1 in the ideal gas limit $(n_{k\sigma} = \Theta(\mu - \varepsilon_k))$ and vanishes for an even momentum distribution $(n_k = 1/2)$, when the particle position is sharply defined on atom. Thus, the quantity $\Theta_{\rm MI}$ plays the role of the *order parameter* for this *crossover behavior*, since it clearly distinguishes between the complementary momentum and position representations for the system quantum states. From Fig. 6 it follows that for $R/a_0 \simeq 5a_0$ all three parameters *(i)–(iii)* acquire (with 5% margin) their asymptotic values for purely atomic states.

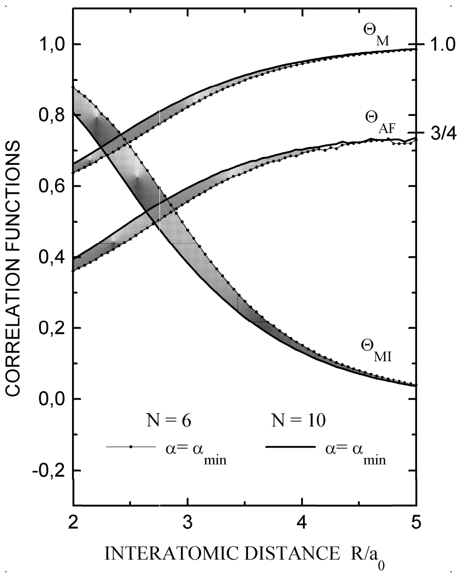

Fig. 6. Correlation functions defined in the text versus interatomic distance R, depicting the *crossover* from itinerant to localized state, for $N = 6 \div 10$ atoms. The shaded areas are drawn to emphasize the convergence of the results in the large R (atomic) limit.

5. Remark on the many-particle wave function from the combined first- and second-quantization scheme

We have started from the Hamiltonian (1) in the second-quantization formalism. The single-particle wave function is contained in the field-operator definition (2). It is well known [13] that the general N-particle state in the Fock space is defined as follows

$$|\Phi_\alpha\rangle = \frac{1}{\sqrt{N!}} \int d^3r_1 ... d^3r_N \Psi_\alpha(\boldsymbol{r}_1 ... \boldsymbol{r}_N) \widehat{\Psi}^\dagger(\boldsymbol{r}_1) ... \widehat{\Psi}^\dagger(\boldsymbol{r}_N)|0\rangle, \tag{19}$$

where $\Psi_\alpha(\boldsymbol{r}_1 ... \boldsymbol{r}_N)$ is the N-particle wave function and $|0\rangle$ is the vacuum state. In effect, we have that

$$\Psi_\alpha(\boldsymbol{r}_1 ... \boldsymbol{r}_N) = \frac{1}{\sqrt{N!}} \langle 0|\widehat{\Psi}(\boldsymbol{r}_N) ... \widehat{\Psi}(\boldsymbol{r}_1)|\Phi_\alpha\rangle, \tag{20}$$

where $\widehat{\Psi}(\boldsymbol{r}_i)$ is the field operator (2) summed up over the spin index σ. In our method, we diagonalize the Hamiltonian in the Fock space first. So, we determine first explicitly the ground state $|\Phi_\alpha\rangle \equiv |\Phi_0\rangle$. Hence, we can determine explicitly the many-particle wave function $\Psi_0(\boldsymbol{r}_1 ... \boldsymbol{r}_N)$. Here we present the results for the elementary example of the states for H_2 molecule, which were obtained in an analytic form in Part I, leaving more complicated cases to a separate publication. Namely, the ground state for H_2 molecule is of the form [4]

$$|\Phi_0\rangle = \frac{1}{\sqrt{2D(D-U+K)}} \left\{ 4(t+V)|4\rangle - (D-U+K)|5\rangle \right\}. \tag{21}$$

In this formula $D \equiv [(U-K)^2 + 16(t+V)^2]^{1/2}$, and the states $|4\rangle$ and $|5\rangle$ are, respectively

$$\left\{ \begin{array}{l} |4\rangle = \frac{1}{\sqrt{2}} \left(a^\dagger_{1\uparrow} a^\dagger_{2\downarrow} - a^\dagger_{1\downarrow} a^\dagger_{2\uparrow} \right) |0\rangle \\ |5\rangle = \frac{1}{\sqrt{2}} \left(a^\dagger_{1\uparrow} a^\dagger_{1\downarrow} + a^\dagger_{2\uparrow} a^\dagger_{2\downarrow} \right) |0\rangle. \end{array} \right. \tag{22}$$

Taking the field operator for these two-site system ($i = 1, 2$) in the form (note the summation over spin indices)

$$\widehat{\Psi}^\dagger(\boldsymbol{r}) = \sum_\sigma \left(a^\dagger_{1\sigma} w_1(\boldsymbol{r}) \chi_\sigma(\boldsymbol{r}) + a^\dagger_{2\sigma} w_2(\boldsymbol{r}) \chi_\sigma(\boldsymbol{r}) \right), \tag{23}$$

we obtain the wave function of the ground state singlet in the form

$$\Psi_0(\boldsymbol{r}_1 \boldsymbol{r}_2) = \frac{2(t+V)}{\sqrt{2D(D-U+K)}} \Phi_{\rm c}(\boldsymbol{r}_1 \boldsymbol{r}_2) - \frac{1}{2} \sqrt{\frac{D-U+K}{2D}} \Phi_i(\boldsymbol{r}_1 \boldsymbol{r}_2), \tag{24}$$

where the covalent part $\Phi_{\rm c}$ has the usual form

$$\Phi_{\rm c}(\boldsymbol{r}_1\boldsymbol{r}_2) = [w_1(\boldsymbol{r}_1)w_2(\boldsymbol{r}_2) + w_1(\boldsymbol{r}_2)w_2(\boldsymbol{r}_1)][\chi_\uparrow(\boldsymbol{r}_1)\chi_\downarrow(\boldsymbol{r}_2) - \chi_\downarrow(\boldsymbol{r}_1)\chi_\uparrow(\boldsymbol{r}_2)], \tag{25}$$

with $w_i(\boldsymbol{r}_1)$ being the Wannier function (molecular orbital) centered on the i-th atom. The ionic part has a slightly different form

$$\Phi_i(\boldsymbol{r}_1\boldsymbol{r}_2) = [w_1(\boldsymbol{r}_1)w_1(\boldsymbol{r}_2) + w_2(\boldsymbol{r}_1)w_2(\boldsymbol{r}_2)][\chi_\uparrow(\boldsymbol{r}_1)\chi_\downarrow(\boldsymbol{r}_2) - \chi_\downarrow(\boldsymbol{r}_1)\chi_\uparrow(\boldsymbol{r}_2)]. \tag{26}$$

Note that these are the exact expressions within the subspace spanned by the $1s$ orbitals on the two atoms. The space part is symmetric while the spin part is antisymmetric, as it should be. A further increase in accuracy of our calculation would require the inclusion of $2s, 2p$, *etc.* states in definition (23). Such procedure can be devised in a systematic way.

In a similar manner, one can obtain the wave functions for the first excited triplet states with $S = 2$ and $S^z = +1, -1, 0$.

At the end of this remark we would to mention an *iterative* aspect of our approach. We start from a single-particle basis $\{w_i(\boldsymbol{r})\}$ which defines the field operator and the Hamiltonian in the Fock space which we diagonalize subsequently in that space. The ground state energy obtained in this manner is regarded as a functional of the single-particle wave function. In other words, $E_{\rm G}\{w_i(\boldsymbol{r})\} = \langle \tilde{H}_1 \rangle$, where $\tilde{H}_1$ represents the renormalized single-particle Hamiltonian [4, 5]. $\tilde{H}_1$ determines the *readjusted (renormalized)* wave functions $\{w_i(\boldsymbol{r})\}$. With the help of those functions we define again the field operator (23) which in turn defines the many-particle wave function (20). The last step terminates the iteractive procedure and provides an explicit form of the many-particle wave function. A detailed analysis of this point will be discussed elsewhere.

6. Conclusions

The present method bases on the exact diagonalization in the Fock space, which is performed first and is followed by the single-particle optimization of the wave functions contained in the expression for the field operator. The exact diagonalization can be performed only for simple systems such as those discussed in the present paper. However, the method can be implemented also to approximate solutions for the correlated systems such as the dynamic mean field approach [14] or Gutzwiller approximation [15]. Also, one can include more complicated atomic structure involving heavier atoms, which would require inclusion of the core electrons and polarization effects. We should be able to see a progress along these lines soon, since our method allows for a systematic analysis of interaction and single-particle aspects of the electronic states in a nonperturbational manner.

The work was supported by the Polish State Committee for Scientific Research (KBN) of Poland, Grant No. 2P03B 092 18.

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