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EXACT DIAGONALIZATION OF MANY-FERMION HAMILTONIAN COMBINED WITH WAVE-FUNCTION READJUSTMENT: APPLICATION TO ONE-DIMENSIONAL SYSTEMS*

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We describe briefly a new method of approach to the interacting fermion and boson systems. Namely, we determine the explicit form of the single-particle wave functions $\{w_i(\boldsymbol{r})\}$ appearing in the microscopic parameters of models in the second-quantization representation. The method is illustrated on the examples of H_2 molecule and He atom, the Hubbard chain, and a ring of $N \leq 10$ atoms.

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1. Introduction

Current discussion of properties of the lattice *correlated fermion systems* relies heavily on parametrized models such as the Hubbard [1], t–J [2], Kondo-impurity [3], as well as the impurity and the lattice Anderson models [4]. In all these models the microscopic parameters such as the hopping integral t (or hybridization), the intraatomic Coulomb U, and the nearest-neighbor Coulomb and exchange integrals (K and J, respectively) are taken as parameters, in terms of which we express the ground state energy and other physical properties including the *quantum phase transitions*. In such

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discussion we utilize the exact solutions in zero- and one- dimensions [5], exact diagonalization for finite systems [6], (usually combined with the density-matrix renormalization group technique [7]), as well as various approximate solutions using slave bosons [8], dynamic mean field concept [9], perturbation techniques, *etc.*, to name a few. In this extensive analysis the most important factor is the nonperturbative influence of the interaction on the single-particle states, since their magnitude is comparable or even substantially larger than the Fermi energy, *i.e.* the systems are those of *strongly correlated particles*.

A direct comparison of the solutions with the experiment is not always possible as the microscopic parameters are mostly *not* directly measurable. However, the full solution would require their explicit determination, since they contain single-particle (Wannier) wave functions. In connection with this one usually starts with a single-particle solution (such as LDA), determines the single-particle states and band energies $\{\varepsilon_{\boldsymbol{k}}\}$ and then introduces local corrections. In this manner approaches such as LDA+U [10] or SIC [11] have been devised. They require a very subtle discussion of the interaction part, as it is included twice, at the band-structure calculation stage, as well as at that including the local corrections. Apart from that it is impossible to know a priori, in which systems the method would work, particularly when we consider the system of low dimensionality.

We have proposed [12] a *new* method of approach to the correlated systems which combines the *exact diagonalization* of many fermion Hamiltonian in the Fock space with a readjustment of the single-particle wave functions (in Hilbert space), in the correlated state (the application to the approximate solutions is discussed briefly at the end). Our method is based on an elementary but yet fundamental question: Should one not readjust the single-particle wave function to the situation when the interaction plays such a crucial role in determining the character of the nontrivial quantum macro state? In other words, we include the interaction processes in the Fock space first and thus obtained ground state energy of the interacting particles optimize with respect to the wave functions contained in the microscopic parameters. This wave function relaxation in the interacting state is simply possible, since the single-particle basis $\{w_i(\boldsymbol{r})\}$ defining the field operators $\hat{\Psi}_\sigma(\boldsymbol{r})$ and $\hat{\Psi}^\dagger_\sigma(\boldsymbol{r})$ is completely arbitrary if only it is complete and (possibly) orthonormal [13]. From the theoretical side, such a readjustment of the wave function leads to the *renormalized wave equation* which represents the Euler equation obtained from the ground state energy, which is regarded as a functional of the single-particle wave functions and their gradients. The wave-function determination *completes* the solution of the second-quantized models if only their rigorous treatment in the Fock space is possible.

Few features of this new approach should be mentioned at the outset. First, the method is free in a natural manner from counting the interaction twice, since the wave function is obtained only after constructing the ground (or equilibrium) state of the interacting system. Second, it provides the solution as a function of lattice parameter. In particular, the solution provides the equilibrium lattice constant if the considered model has this property. Third, the approach represents probably the only possibility of determining in a consistent way the single-particle wave function in rather strongly interacting (correlated) system. However, the method has one disadvantage, namely, it can be applied rigorously only to either exactly soluble model systems or small systems containing $N \leq 10$–20 atoms, depending on the system dimensionality. It should certainly be applicable to the discussion of quantum states of correlated quantum dots and other quantum cluster systems. The construction of systematic analysis based on an approximate solution is yet to be resolved. Therefore, we review here only our recent results [12, 14, 15] and provide a brief overview of the subject on this early stage of development.

2. Method of approach

In describing the system of interacting particles one usually starts from the concept of the field operator $\hat{\Psi}_\sigma(\boldsymbol{r})$, which is defined in a complete orthonormal basis of single-particle basis $\{w_i(\boldsymbol{r})\chi_\sigma\}$ in the following manner:

$$\hat{\Psi}_\sigma(\boldsymbol{r}) = \sum_i w_i(\boldsymbol{r})\chi_\sigma a_{i\sigma} \,, \tag{1}$$

where $a_{i\sigma}$ is the annihilation operator of a particle in a single-particle state $|i\sigma\rangle$. One should note that the basis $\{w_i(\boldsymbol{r})\chi_\sigma\}$ is completely arbitrary in this definition. As already noted above, the natural (and fundamental) question one may ask immediately is: Can one find an optimal way of determination the wave function $\{w_i(\boldsymbol{r})\}$ and solve the corresponding Hamiltonian

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

in the Fock space exactly? Such a procedure is perfectly well defined as the operators $H_1(\boldsymbol{r})$ and $V(\boldsymbol{r}_1 - \boldsymbol{r}_2) \equiv V_{12}$, representing respectively the single-particle and two-particle operators, act only in the coordinate (Hilbert) space, whereas the creation and annihilation operators act in the occupation-number (Fock) space. In the present section we combine those two *complementary* steps, which will be then implemented explicitly in some model situations in the next sections.

A remark is in order before presenting the formalism. Namely, starting from the diagonalization in the Fock space we obtain the expression for *e.g.* the ground state energy, which is still a functional of the single-particle wave functions $\{w_i(\boldsymbol{r})\}$ via the parameters

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

and

$$V_{ijkl} \equiv \langle w_i w_j | V | w_k w_l \rangle \equiv \int d^3 r d^3 r' w_i^\star(\boldsymbol{r}) w_j^\star(\boldsymbol{r}') V(\boldsymbol{r} - \boldsymbol{r}') w_k(\boldsymbol{r}) w_l(\boldsymbol{r}'), \tag{4}$$

which describe respectively the atomic part of energy (t_{ii}), the hopping integrals (t_{ij} for $i \neq j$), and the interaction matrix elements in the basis $\{w_i(\boldsymbol{r})\}$. The minimization of the ground state energy with respect to the choice of the basis functions $\{w_i(\boldsymbol{r})\}$(appearing only under integrals) will lead to the Euler equation for those wave functions that plays the role of the *renormalized wave equation.*

Explicitly, we start from the model of interacting fermions on a lattice for which the Hamiltonian (2) after substituting into it expression (1) has the following form in the real-space representation

$$H = \sum_{ij\sigma} t_{ij} a_{i\sigma}^\dagger a_{j\sigma} + \frac{1}{2} \sum_{ijkl\sigma\sigma'} V_{ijkl} a_{i\sigma}^\dagger a_{j\sigma'}^\dagger a_{l\sigma'} a_{k\sigma} \equiv E_1 + E_2. \tag{5}$$

The solution of this model involves calculation of the ground-state energy

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

Introducing the correlation functions

$$C_{ij} \equiv \sum_{\sigma} \left\langle a_{i\sigma}^\dagger a_{j\sigma} \right\rangle , \qquad \text{and} \quad C_{ijlk} \equiv \sum_{\sigma\sigma'} \left\langle a_{i\sigma}^\dagger a_{j\sigma'}^\dagger a_{l\sigma'} a_{k\sigma} \right\rangle , \tag{7}$$

we see that the diagonalization of the Hamiltonian (6) requires determination of the above correlation functions as a function of parameters t_{ij} and V_{ijkl}.

In the standard treatment of correlated model systems t_{ij} and V_{ijkl} are regarded as constants, *i.e.* the solution is analyzed as a function of those parameters dividing the whole situation roughly into two limiting situations: (a) the metallic limit when $|E_1| \gg E_2$, and (b) the strong-correlation limit when $|E_1| \ll E_2$ (this limit may correspond also the so-called Mott or Mott–Hubbard insulator limit when the number of electrons N_e is equal to the number of sites N. The regime when the two terms in (5) of comparable magnitude ($|E_1| \simeq E_2$) is regarded as a separate limit (c) in which the Mott–Hubbard (metal-insulator) transition takes place. In the situation (a) the band theoretical or perturbation techniques [11, 12] provide the electronic states, at least at temperature $T = 0$, with a sufficient degree of accuracy. Therefore, the most interesting are the limits (b) and (c) when the single-particle part is not dominant. In those limits the interaction part determines the nature of the quantum ground state, *e.g.* induces the crystallization of the electron gas on the parent ions (the Mott–Hubbard transition), as well as leads to the strong spin correlations among the electrons (exemplified by the kinetic exchange interaction) or even introduces pairing which may lead (for $N_e \neq N$) to the superconductivity [16].

The nontrivial effects of interaction are particularly strong for low-dimensional systems, where *e.g.* the electrons are localized for arbitrarily small magnitude of the interaction if only short-range part of both t_{ij} (i, j are the nearest neighbors) and V_{ijkl} ($i = j = k = l$) are taken into account [5]. In the same manner, the principal assumptions of the Fermi-liquid theory [7] may be broken and the system may form (again for $N_e = N$) a Tomonaga–Luttinger fermionic liquid [18].

In view of the above discussion stressing the strongly nonperturbative nature of the interactions one should ask again: Should one not optimize the single-particle basis $\{w_i(\boldsymbol{r})\}$ *together* with the determination of the correlation functions $C_{ij} \equiv C_1(\boldsymbol{R}_i - \boldsymbol{R}_j)$ and $C_{ijkl} \equiv C_2(\boldsymbol{R}_i - \boldsymbol{R}_k, \boldsymbol{R}_j - \boldsymbol{R}_l, \ldots)$? This is particularly so because the contributions $E_1 < 0$ (for bound states) and $E_2 > 0$ (for repulsive interactions) compete with each other in determining the resultant state (metallic or insulating) of the system. Such question can be inferred from those posed long time ago by Peierls, Mott, Anderson and others [19] about the principal role played by the electron correlations, which have a nontrivial (*e.g.* non Hartree–Fock) character.

As the answer to the posed question we have proposed [12, 14, 15] to close the analysis of the correlated states by taking $C_{ij} = C_{ij}\{t_{ij}, V_{ijkl}\}$ and $C_{ijkl} = C_{ijkl}\{t_{ij}, V_{ijkl}\}$ and determining the renormalized wave equation for $\{w_j(\boldsymbol{r})\}$ by treating E_{G} as a functional of $\{w_i(\boldsymbol{r})\}$ and their derivatives, since $H_1(\boldsymbol{r}) = -(\hbar/2m)\nabla^2 + V(\boldsymbol{r})$, with $V(\boldsymbol{r})$ being the single-particle potential. In such a situation $w_i(\boldsymbol{r})$ is determined from an Euler equation for the functional

$$F\{w_i(\boldsymbol{r})\} = E_{\mathrm{G}}\{w_i(\boldsymbol{r})\} - \sum_i \lambda_i \left(\int d^3r |w_i(\boldsymbol{r})|^2 - 1 \right) , \tag{8}$$

where λ_i is the Lagrange multiplier introduced for the function $w_i(\boldsymbol{r})$, which is required to be normalized (*i.e.* represents a bound state). The general form of this equation is

$$\frac{\delta E_{\mathrm{G}}}{\delta w_i^{\star}(\boldsymbol{r})} - \nabla \frac{\delta E_{\mathrm{G}}}{\delta \nabla w_i^{\star}(\boldsymbol{r})} - \lambda_i w_i(\boldsymbol{r}) = 0\,, \tag{9}$$

or explicitly

$$\left[\frac{\delta E_{\mathrm{G}}}{\delta w_i^{\star}(\boldsymbol{r})} - \nabla \frac{\delta E_{\mathrm{G}}}{\delta \nabla w_i^{\star}(\boldsymbol{r})}\right] \left(\sum_{j(i)} t_{ij} C_{ij} + \frac{1}{2}\sum_{jkl} V_{ijkl} C_{ijlk}\right) - \lambda_i w_i(\boldsymbol{r}) = 0\,. \tag{10}$$

Defining this *renormalized wave equation* in the form $(\tilde{H}_i - \lambda_i) w_i(\boldsymbol{r}) = 0$, we obtain the explicit form of the *renormalized* single-particle Hamiltonian $\tilde{H}_i = \tilde{H}_1$, which has the same form at each lattice site if the lattice is translationally invariant (H_1 is its *bare* counterpart). In the next section we will write the explicit form of this equation for concrete examples. Note that λ_i does not necessarily plays the role of the eigenvalue, as *e.g.* the atomic energy is defined as $\varepsilon_a = \langle w_i | H_1 | w_i \rangle = t_{ii}$. Also, if the functions $\{w_i(\boldsymbol{r})\}$ are orthogonalized first, then in Eqs. (8)–(10) one has to put $\lambda_i \equiv 0$, and then Eqs. (9) and (10) correspond to a variational minimization of $E_{\mathrm{G}} = E_{\mathrm{G}}\{w_i(\boldsymbol{r})\}$.

3. Simple examples: $\mathbf{H_2}$ molecule and He atom

We start with the most general Hamiltonian in the Fock space for a two-site system [20] for the case, each site contributing a single s-type orbital:

$$\begin{aligned} H \; = \; & \varepsilon_a (n_1 + n_2) + t \sum_{\sigma} (a_{1\sigma}^{\dagger} a_{2\sigma} + a_{2\sigma}^{\dagger} a_{1\sigma}) + U\Big(n_{1\uparrow} n_{1\downarrow} + n_{2\uparrow} n_{2\downarrow}\Big) \\ & -2J\left(\boldsymbol{S}_1 \cdot \boldsymbol{S}_2 - \frac{1}{4} n_1 n_2\right) + K n_1 n_2 + J(a_{1\uparrow}^{\dagger} a_{1\downarrow}^{\dagger} a_{2\downarrow} a_{2\uparrow} + \text{h.c.}) \\ & + V \sum_{\sigma} (n_{1\sigma} + n_{2\sigma})(a_{1\bar{\sigma}}^{\dagger} a_{2\bar{\sigma}} + a_{2\bar{\sigma}}^{\dagger} a_{1\bar{\sigma}}). \end{aligned} \tag{11}$$

The first term determines the atomic location (ε_a) of the electrons on the two sites, t describes the hopping (resonance) integral, U is the magnitude of the intraatomic Coulomb interaction (the Hubbard interaction), J is the Heisenberg exchange integral, K is the intersite Coulomb interaction, and V represents the so-called correlated hopping term. For the sake of completeness we will write the explicit expressions for those quantities (in atomic units, Ry), namely

$$\varepsilon_a = \int d^3 r w_i^\star(\boldsymbol{r}) \Big[-\nabla^2 + \sum_j V(\boldsymbol{r} - \boldsymbol{R}_j) \Big] w_i(\mathbf{r}) \equiv \langle w_i \mid H_1 \mid w_i \rangle \,, \tag{12}$$

$$\begin{aligned} t &\equiv t_{12} \equiv t_{ij} = \int d^3 r w_i^\star(\boldsymbol{r}) \Big[-\nabla^2 + \sum_j V(\boldsymbol{r} - \boldsymbol{R}_j) \Big] w_j(\boldsymbol{r}) \\ &\equiv \langle w_i \mid H_1 \mid w_j \rangle \,, \end{aligned} \tag{13}$$

$$U = \int d^3 r d^3 r' \mid w_i(\boldsymbol{r}) \mid^2 \frac{2}{\mid \boldsymbol{r} - \boldsymbol{r}' \mid} \mid w_i(\boldsymbol{r}') \mid^2 \equiv \langle w_i w_i \mid V_{12} \mid w_i w_i \rangle \,, \tag{14}$$

$$J_{ij} = \int d^3 r d^3 r' w_i^\star(\boldsymbol{r}) w_j(\boldsymbol{r}') \frac{2}{\mid \boldsymbol{r} - \boldsymbol{r}' \mid} w_j^\star(\boldsymbol{r}) w_i(\boldsymbol{r}') \equiv \langle w_i w_j \mid V_{12} \mid w_j w_i \rangle \,, \tag{15}$$

$$\begin{aligned} K &\equiv K_{12} \equiv K_{ij} = \int d^3 r d^3 r' \mid w_i(\boldsymbol{r}) \mid^2 \frac{2}{\mid \boldsymbol{r} - \boldsymbol{r}' \mid} \mid w_j(\boldsymbol{r}') \mid^2 \\ &\equiv \langle w_i w_j \mid V_{12} \mid w_i w_j \rangle \,, \end{aligned} \tag{16}$$

$$\begin{aligned} V &\equiv V_{12} \equiv V_{ij} = \int d^3 r d^3 r' \mid w_i(\boldsymbol{r}) \mid^2 \frac{2}{\mid \boldsymbol{r} - \boldsymbol{r}' \mid} w_i(\boldsymbol{r}') w_j^\star(\boldsymbol{r}') \\ &\equiv \langle w_i w_j \mid V_{12} \mid w_i w_i \rangle \,. \end{aligned} \tag{17}$$

The two-site Hamiltonian (11) may be easily diagonalized for $N_e = 2$ electrons. Namely, since the total spin (S) and its z component (S^z) are the integrals of motion, one can write the trial basis for triplet ($S = 1$) and singlet ($S = 0$) states. Namely, there are six such states

$$|1\rangle = a^\dagger_{1\uparrow} a^\dagger_{2\uparrow} |0\rangle \quad (S = S^z = 1) \,, \tag{18}$$

$$|2\rangle = a^\dagger_{1\downarrow} a^\dagger_{2\downarrow} |0\rangle \quad (S = 1, \ S^z = -1) \,, \tag{19}$$

$$|3\rangle = \frac{1}{\sqrt{2}} \left(a^\dagger_{1\uparrow} a^\dagger_{2\downarrow} + a^\dagger_{1\downarrow} a^\dagger_{2\uparrow} \right) |0\rangle \quad (S = 1, \ S^z = 0) \,, \tag{20}$$

$$|4\rangle = \frac{1}{\sqrt{2}} \left(a^\dagger_{1\uparrow} a^\dagger_{2\downarrow} - a^\dagger_{1\downarrow} a^\dagger_{2\uparrow} \right) |0\rangle \quad (S = 0) \,, \tag{21}$$

$$|5\rangle = \frac{1}{\sqrt{2}} \left(a^\dagger_{1\uparrow} a^\dagger_{1\downarrow} + a^\dagger_{2\uparrow} a^\dagger_{2\downarrow} \right) |0\rangle \quad (S = 0) \,, \tag{22}$$

$$|6\rangle = \frac{1}{\sqrt{2}} \left(a^\dagger_{1\uparrow} a^\dagger_{1\downarrow} - a^\dagger_{2\uparrow} a^\dagger_{2\downarrow} \right) |0\rangle \quad (S = 0) \,. \tag{23}$$

The triplet state have eigenvalues $\lambda_1 = \lambda_2 = \lambda_3 = 2\,\varepsilon_a + K - J$, which separate from the singlet states, for which we have (3×3) Hamiltonian matrix $\langle i \mid H \mid j\rangle$ in such chosen basis, namely

$$(H)_{ij} = \left(\begin{array}{ccc} 2\varepsilon_a + K + J, & 2(t+V), & 0 \\ 2(t+V), & 2\varepsilon_a + J + U, & 0 \\ 0, & 0, & 2\varepsilon_a + U - J \end{array} \right). \tag{24}$$

This matrix has the eigenvalues

$$\lambda_{4,5} = 2\varepsilon_a + \tfrac{1}{2}(K+U) + J \pm \tfrac{1}{2}\left[(U-K)^2 + 16(t+V)^2\right]^{1/2}, \tag{25}$$

$$\lambda_6 = 2\varepsilon_a + U - J\,. \tag{26}$$

The corresponding eigenstates are also easy to obtain. The most important feature is that λ_5 is the lowest eigenvalue. Therefore, according to our proposal we have still to minimize λ_5 with respect to $\{w_i(\boldsymbol{r})\} = \{w_1(\boldsymbol{r}),\, w_2(\boldsymbol{r})\}$. The corresponding renormalized wave equation will take the form

$$\begin{aligned} \lambda_i w_i(\boldsymbol{r}) = {} & [-\nabla^2 + V(\boldsymbol{r} - \boldsymbol{R}_1)]w_i(\boldsymbol{r}) + V(\boldsymbol{r} - \boldsymbol{R}_2)w_j(\boldsymbol{r}) \\ & + \frac{1}{2}\frac{\delta}{\delta w_i^\star}(U + K + 2J) - \frac{1}{2}\frac{1}{\left[(U-K)^2 + 16(t+V)^2\right]^{1/2}} \\ & \times \left[(U-K)\frac{\delta(U-K)}{\delta w_i^\star} + 16(t+V)\frac{\delta(t+V)}{\delta w_i^\star}\right]. \end{aligned} \tag{27}$$

The first term represents atomic energy for the particle located on i-th site, the second reflects the attraction to the j-th site, whereas the remaining terms describe nonlinear nonlocal influence of the Coulomb interaction between the particles. To solve this equation in a simplified way we compose the orthogonalized atomic wave functions $\{w_i(\boldsymbol{r})\}$ of the (nonorthogonal) atomic $1s$ functions

$$\psi_i(\boldsymbol{r}) \equiv \psi(\boldsymbol{r} - \boldsymbol{R}_i) = \sqrt{\frac{a^3}{\pi}}\exp(- \mid \boldsymbol{r} - \boldsymbol{R}_i \mid \alpha)\,.$$

Then, imposing the orthonormality conditions $\langle w_i \mid w_j\rangle = \delta_{ij}$ on the function taken in the form

$$w_i(\boldsymbol{r}) = \beta[\psi_i(\boldsymbol{r}) - \gamma\psi_j(\boldsymbol{r})]\,, \tag{28}$$

with $i \neq j$, and $S = \langle \psi_1 \mid \psi_2\rangle$, we obtain that

$$\beta = \frac{1}{\sqrt{2}}\left[\frac{1}{1-S^2} + \frac{1}{(1-S^2)^{1/2}}\right]^{1/2}, \quad \gamma = \frac{S}{1+\sqrt{1-S^2}}\,. \tag{29}$$

The parameters ε_a, t, U, K, J, and V must be now redefined in the atomic basis using (28). In effect, one obtains the expressions for those parameters in terms of the Slater integrals [21]. Those expressions are provided in the original paper [12]. Substituting those to the expression (25) for λ_5 we will obtain the expression for the lowest eigenenergy as a function of interatomic distance (bond length) R and the size of the atomic functions α^{-1}, *i.e.* $\lambda_5 = \lambda_5(R, \alpha)$. Minimizing this expression, as well as all excited-state energies (λ_i for $i \neq 5$), we will obtain the scheme of the energy levels depicted in Fig. 1 as a function of R. The optimal bond length is $l_B = 0.757\,\text{Å}$ and the optimal ground state energy is $E_{\rm G} = -2.296\,\text{Ry}$, which

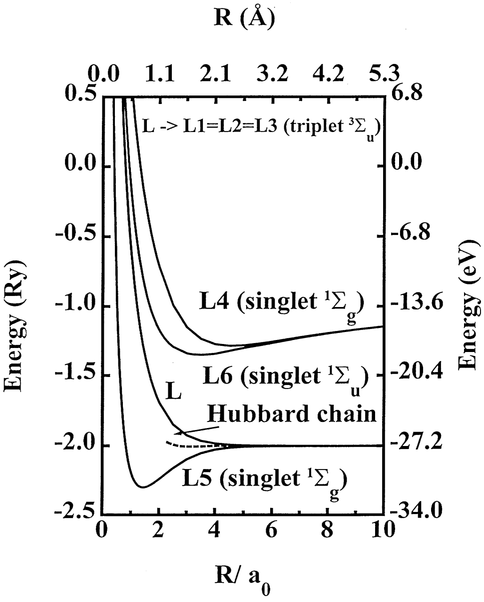

Fig. 1. The lowest six energy levels for H_2 molecule (solid lines) calculated to the same degree of accuracy as for the Hubbard chain (see main text), for which the ground state energy of which (per two sites) is shown as the dashed line.

differ by about 2.5% of Kołos and Wolniewicz [22]. The optimized size of the orbitals for each eigenvalue is provided in Fig. 2. Finally, the corresponding orthogonalized atomic wave function centered on the corresponding nucleus is shown in Fig. 3. Note that we do not have to construct any molecular wave functions or construct the Heitler–London determinantal wave function; the only simplifying assumption is the choice of a simple basis. Obviously, the present approach can be extended to include the states $2s$, $2p$, *etc.*, but this would go beyond the main purpose of this section — the illustration of our method of approach to the interacting systems. The influence of the higher excited atomic states is important to reach the quantitative description of

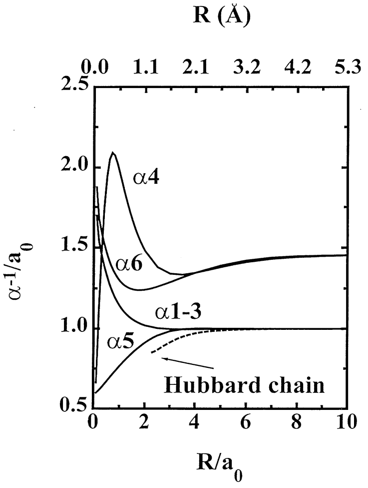

Fig. 2. Optimal size of atomic functions for the first six states of the H_2 molecule (solid lines), as compared to that for the Hubbard chain (dashed line).

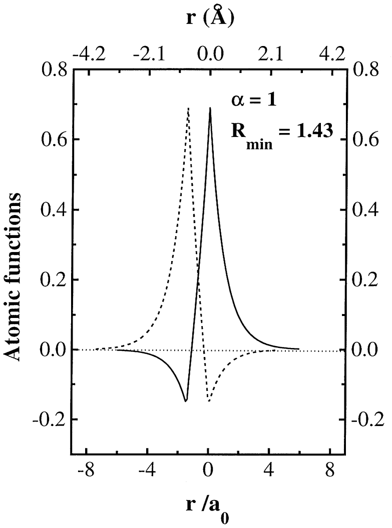

Fig. 3. Renormalized and orthogonalized atomic orbitals (the Wannier functions) for H_2 molecule in the equilibrium configuration ($R = R_{\mathrm{min}} = 1.43\,a_0$).

H_2 molecule, since for example the magnitude U is of the order of the value for $1s \to 2s$ atomic transitions. One methodological remark is in order. In constructing Fig. 2 we have optimized the size α^{-1} of the orbitals for each eigenvalue λ_i separately. Strictly speaking, when the transitions between the states are fast, then we should optimize the size of the atomic orbital only in the ground state (for eigenvalue λ_5) and then substitute this optimal size to those representing the excited states. Otherwise, the eigenstates are not orthogonal to each other.

In Fig. 4 we display the distance dependence of the model parameters.

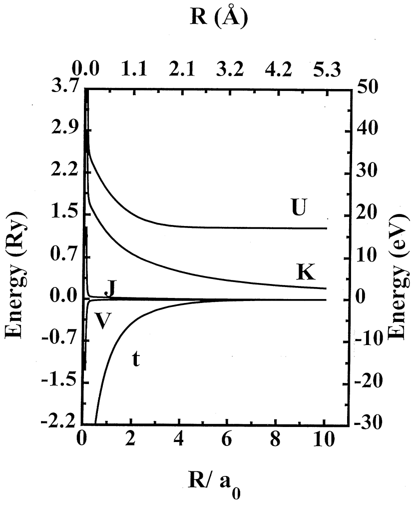

Fig. 4. The microscopic parameters of the two-site Hamiltonian calculated for the H_2 molecule as a function of the bond length (in units of Bohr radius).

Ground state of helium atom

The He atom is the simplest system with interacting electrons. The single-electron Hamiltonian is $H_1 = -\nabla^2 - 4/r$. Taking the electron wave function in the 1s form $\psi(\boldsymbol{r}) = (\alpha^3/\pi)^{1/2} \exp(-\alpha r)$, we can write down the system ground-state energy in one-state approximation $E = 2\varepsilon_a + U$ in the form

$$E = 2(\alpha^2 - 4\alpha) + \frac{5}{4}\alpha = 2\alpha^2 - \frac{27}{4}\alpha\,. \tag{30}$$

Minimizing λ with respect to α we obtain that $\alpha = 27/16$, and that $E = \lambda_{\min} = -5.695\,\mathrm{Ry}$, the well known value [23]. It is interesting to write the full renormalized wave equation, which has the form

$$\left(-\nabla^2 - \frac{4}{r}\right) w(\boldsymbol{r}) + w(\boldsymbol{r}) \int d^3r \frac{2}{\mid \boldsymbol{r} - \boldsymbol{r}' \mid} \mid w(\boldsymbol{r}') \mid^2 = \lambda w(\boldsymbol{r})\,. \tag{31}$$

This equation coincides with the Hartree equation for the single-particle wave function. It would be interesting to calculate $\lambda_{\min}$ taking explicitly the solution of (31).

4. Hubbard chain

The Hubbard model is based on a drastic simplification of the Hamiltonian (6) in the following sense: *(i)* From all the matrix element only the interaction term $V_{iii} \equiv U$ is retained, and *(ii)* the hopping matrix element t_{ij} for $i \neq j$ is taken only if i and j represent the nearest neighboring sites, *i.e.* $t_{\langle ij\rangle} = t < 0$. In effect, the model Hamiltonian with an inclusion of the atomic part is of the form

$$H = \varepsilon_a \sum_{i\sigma} n_{i\sigma} + t \sum_{\langle ij\rangle\sigma} a^{\dagger}_{i\sigma} a_{j\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow} \, . \tag{32}$$

This model in one dimension was solved by Lieb and Wu [5] and the expression for the ground state energy in the half-filled band ($N_e = N$) case is

$$\frac{E_{\mathrm{G}}}{N} = E_0 + 4t \int\limits_0^{\infty} d\omega \frac{J_1(\omega) J_0(\omega)}{\omega \left[1 + \exp\left(\frac{\omega U}{2t}\right)\right]} \, , \tag{33}$$

where E_0 contains both the atomic (ε_a) and the lattice contributions, and $J_n(x)$ is the Bessel function with $n = 0$ or 1. The model parameters t and U are defined as before

$$t = \int d^3 r w_i^*(\boldsymbol{r}) H_1(\boldsymbol{r}) w_{i\pm 1}(\boldsymbol{r}) = \langle w_i \mid H_1 \mid w_{i\pm 1}\rangle, \tag{34}$$

and

$$U = \int d^3 r d^3 r' \mid w_i(\boldsymbol{r}) \mid^2 \frac{2}{\mid \boldsymbol{r} - \boldsymbol{r}' \mid} \mid w_i(\boldsymbol{r}') \mid^2 \, . \tag{35}$$

Similarly,

$$\varepsilon_a = \langle w_i \mid H_1(\boldsymbol{r}) \mid w_i \rangle \, . \tag{36}$$

Finally, the lattice contribution will be taken in the simplest classical form, which written in the atomic unit has the form $\sum_i \mid \boldsymbol{R}_i - \boldsymbol{R}_{i+1} \mid^{-1}$.

As the solution of this model provides the ground-state energy in the form of (33), we have to determine the single-particle basis. We start from the atomic 1s-type functions $\{\Psi_i(\boldsymbol{r})\}$, which are orthogonalized in the tight-binding approximation, which defined through

$$w_i(\boldsymbol{r}) = \beta \Psi_i(\boldsymbol{r}) + \gamma[\Psi_{i+1}(\boldsymbol{r}) + \Psi_{i-1}(\boldsymbol{r})] \, , \tag{37}$$

where the coefficients β and γ are obtained from the conditions $\langle w_i \mid w_i \rangle = 1$ and $\langle w_i \mid w_{i\pm 1}\rangle = 0$. Hence

$$\beta = \frac{1 + \sqrt{1 - 3S^2}}{\sqrt{2 - 5S^2 + 2(1 - 2S^2)\sqrt{1 - 3S^2}}} \, ,$$

$$\gamma = \frac{-S}{\sqrt{2-5S^2+2(1-2S^2)\sqrt{1-3S^2}}}\,. \tag{38}$$

With the help of the Wannier functions $\{w_i(\boldsymbol{r})\}$ we can define the parameters t and U as follows:

$$\begin{aligned} \varepsilon_a &= \left(\beta^2+2\gamma^2\right)\varepsilon'_a + 4\beta\gamma t'\,, & (39)\\ t &= \left(\beta^2+3\gamma^2\right)t' + 2\beta\gamma\varepsilon'_a\,, & (40) \end{aligned}$$

and

$$U = \left(\beta^4+2\gamma^4\right)U' + 8\beta^3\gamma V' + 8\beta\gamma^3 V' + 4\beta^2\gamma^2 K' + 8\beta^2\gamma^2 J'\,, \tag{41}$$

where the primed parameters are the Slater integrals calculated for the s-type atomic wave functions; they depend on both the size (α^{-1}) of the atomic orbitals and the interatomic distance R. Also, one has to include the atomic part ε_a, as it varies with R.

The simplified atomic basis optimization is carried through the minimization of the functional E_{G} with respect to α (for given R) after substitution of the expressions (39)–(41) to (33). The ground-state energy (per atom) obtained in this manner (with the ion–ion repulsion included to the fourth neighbor) is displayed in Fig. 5. The energy approaches the atomic

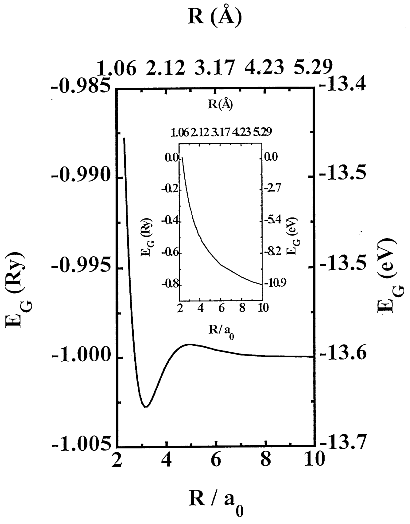

Fig. 5. Ground-state energy E_{G} of the Hubbard chains as a function of relative interatomic distance R/a_0. The atomic part of the energy and the interionic Coulomb repulsion (to the fourth neighbor) is included. The inset provides E_{G} with inclusion of nearest neighbor Coulomb interaction $\sim K$ in the Hartree–Fock approximation.

value ($-1\,\mathrm{Ry}$) per site for $R/a_0 > 6$, where $a_0 = 0.539\,\text{Å}$ is the Bohr radius. The optimal distance is $R_{\mathrm{min}} = 3.15a_0 \approx 1.6\,\text{Å}$ and the minimum of $E_{\mathrm{G}}/N \approx -1.03\,\mathrm{Ry}$, *i.e.* the cohesive energy is $\approx 0.4\,\mathrm{eV/atom}$. One should note that the chain collapses if the repulsion between the ions is taken only between the nearest or the second nearest neighbors. In the inset we show the result for E_{G} when the nearest neighbor Coulomb interaction $K\sum_i n_i n_{i+1}$ is also included in the Hartree–Fock approximation (the chain is again instable then).

The interatomic distance dependence of the size of the optimized atomic orbital size (in units of a_0) is shown in Fig. 6 (the bare orbitals have the size $\alpha^{-1}/a_0 = 1$). The orbitals in the correlated state shrink under the influence of the Coulomb interaction. In the inset we display the R dependence of the nearest neighbor overlap integral S. Even for the chain spacing $R = R_{\mathrm{min}}$ (marked by the vertical dotted line) the overlap $S < 0.3$, making our version of the tight-binding approximation (37) applicable for $R \geq R_{\mathrm{min}}$.

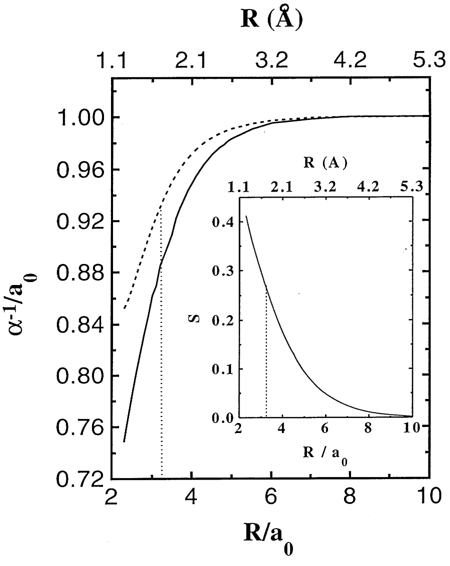

Fig. 6. Optimal size of atomic 1s orbital (including correlations) in units of the atomic Bohr radius as a function of interatomic distance (the dashed line, with the nearest-neighbor Coulomb interaction, as in Fig. 5). In the inset the overlap integral is displayed. The vertical dotted line marks the position, at which E_{G} has a minimum.

In Fig. 7 we have plotted the distance dependence of the microscopic parameters based on our solution for the Hubbard model in the tight-binding approximation (the dashed lines include in the solution the Kn^2 coming from the Hartree–Fock approximation for the intersite Coulomb interaction). We see that in the atomic limit $U \sim 15\,\mathrm{eV}$ for the renormalized $1s$ orbitals. The hopping parameter decreases strongly with the increasing distance. This means that for the distance $R \simeq 3a_0 \simeq 1.5\,\text{Å}$ the situation $U = W$ is achieved, where $W = 2z \mid t \mid = 4 \mid t \mid$is the band-width of the single-particle states.

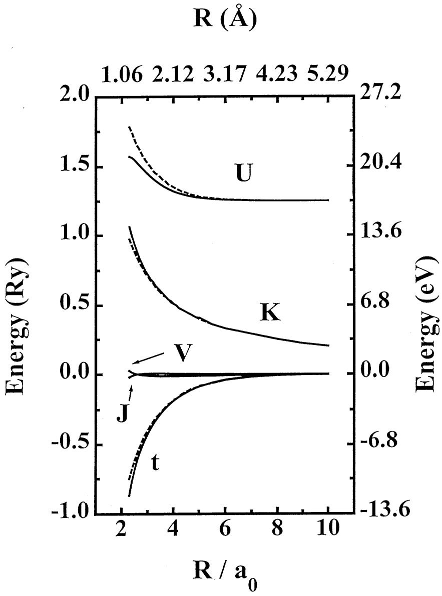

Fig. 7. The microscopic parameters calculated for the optimized Wannier function obtained for the Hubbard chain (solid lines), and with the Kn^2 term in E_{G} (dashed lines).

5. One-dimensional quantum dots (rings)

Our method can be applied also to one-dimensional rings up to $N = 12$ atoms, for which a careful treatment of both two-site interactions and more distant hopping processes (and the wave function overlaps) is possible.The Hamiltonian has the same formal structure as (11) except that now we include *all* pair interactions between the pair of sites $\langle i, j\rangle$ along the ring. Such a Hamiltonian is diagonalized numerically in the Fock space and the parameters are calculated with the help of *exact* one-band Wannier functions defined as

$$w_i(\boldsymbol{r}) = \sum_{j=0}^{N-1} \beta_{i-j}\psi_j(\boldsymbol{r})\,. \tag{42}$$

The coefficients β_{ij} can be calculated starting from the representation of the Bloch function in the tight-binding approximation

$$\Phi_{\boldsymbol{q}}(\boldsymbol{r}) = N_{\boldsymbol{q}} \sum_j \mathrm{e}^{i\boldsymbol{q}\cdot \boldsymbol{R}_j} \psi_j(\boldsymbol{r}) \,, \tag{43}$$

where the normalization factor is determined via the overlap S_{ij} between the corresponding atomic wave functions, *i.e.* has the form

$$N_{\boldsymbol{q}} = \Big(N \sum_j \mathrm{e}^{i\boldsymbol{q}\cdot(\boldsymbol{R}_j - \boldsymbol{R}_i)} S_{ij} \Big)^{-1/2} . \tag{44}$$

The coefficients β_{ij} are defined through

$$\beta_{ij} = \frac{1}{\sqrt{N}} \sum_{\boldsymbol{q}} \mathrm{e}^{i\boldsymbol{q}\cdot(\boldsymbol{R}_i - \boldsymbol{R}_j)} N_{\boldsymbol{q}} \,. \tag{45}$$

The Hamiltonian and the microscopic parameters have a complicate form and therefore will not be written down here [14]. Additionally, if we include the interactions and the overlaps beyond the nearest-neighbor 3-site integrals appear which are dealt with in spheroidal coordinates. Here we discuss only the final results obtained from detailed numerical analysis.

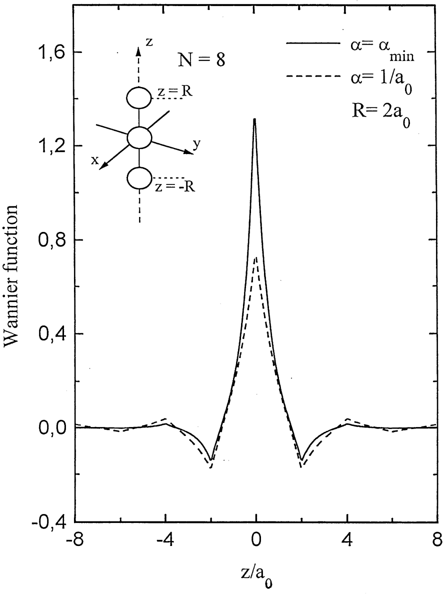

Fig. 8. Renormalized (solid line) and bare (dashed line) Wannier functions for the ring of $N = 8$ atoms and the interatomic distance $R/a_0 = 2$.

The bare and renormalized Wannier functions, the latter obtained for diagonalized exactly chain of $N = 8$ atoms, are depicted in Fig. 8 for the distance $R = 2a_0$. The repulsive interaction shrinks then even to the large extent when compared to the case of Hubbard chain. The values of the microscopic parameters for different R values (together with their asymptotic form) are presented in Table I. We note two basic features of these results: *(i)* the atomic energy ε_a depends rather strongly on the distance, and *(ii)* the intersite Coulomb interaction $\sim K_{ij}$ falls off slowly with the distance and has the asymptotic form $K_{ij} \approx 2/R_{ij}$ (in Ry). The Heisenberg exchange integral (J_1) and the correlated hopping (V_1) are of at least two orders of magnitude smaller than either U or K_1. The renormalized hopping parameter t_1 is almost an order of magnitude larger than either t_2 and t_3, making the tight-binding approximation realistic (t_p is obviously the hopping integral between the p-th neighbors).

TABLE I

Microscopic parameters (in Rydbergs) as a function of interatomic distance R for different neighbors $p = 1, 2, 3$.

R/a_0	ε_a	t_1	$10^3 t_2$	$10^3 t_3$	U	K_1	K_2	K_3	$10^3 J_1$	$10^3 V_1$	$10^3 V_2$
2.0	−4.043	−0.585	89.6	−98.3	2.301	1.077	0.676	0.450	9.54	−18.07	33.58
2.5	−3.734	−0.331	45.5	−45.0	1.949	0.843	0.499	0.331	7.39	−17.45	19.58
3.0	−3.422	−0.200	24.4	−21.9	1.717	0.692	0.391	0.259	5.59	−16.08	11.95
4.0	−2.916	−0.083	7.4	−5.3	1.452	0.508	0.269	0.179	2.90	−12.92	4.49
5.0	−2.558	−0.037	4.2	−2.7	1.327	0.403	0.206	0.138	1.26	−9.64	1.56

Probably the most spectacular R dependence is that of statistical distribution function $n_{\boldsymbol{k}\sigma} = \langle 0 \mid a^\dagger_{\boldsymbol{k}\sigma} a_{\boldsymbol{k}\sigma} \mid 0 \rangle$ in the momentum space, as shown in Fig. 9 for $N = 10$ atoms. For small lattice constant ($R/a_0 = 2$) a clear sign of the Fermi wave vector $k_F = \pi R/2$ (corresponding to one electron per atom) can be seen, whereas for $R \geq 5a_0$ this distribution is smeared out throughout the first Brillouin zone meaning that the electrons are practically localized for that distance. This point is elaborated in detail elsewhere. The ground state $\mid 0 \rangle$ of the system is a true spin singlet, *i.e.* with $\langle 0 \mid \sum_{i=1}^{N} \boldsymbol{S}_i \mid 0 \rangle = 0$. The calculation of the wave function allows for determination of experimentally measurable quantities such as spin–spin correlation function or exchange integrals. Also, by extending the results to the situation with $N_e < N$ one can study the dynamics of the holes in this strongly correlated mesoscopic system. The results will be presented elsewhere.

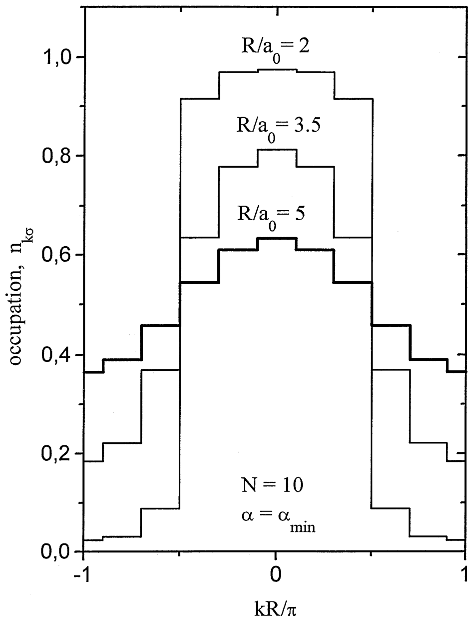

Fig. 9. Momentum distribution $n_{\boldsymbol{k}\sigma}$ for electrons in the first Brillouin zone for ring of $N = 10$ atoms and the interatomic distances specified.

6. Conclusions

We have reviewed briefly a new method of calculations of the electronic states in correlated low-dimensional and small systems. The method is based on diagonalizing first the many-particle Hamiltonian in the Fock space followed by the readjustment of the single-particle wave function. Therefore, the present two-step procedure *in a reverse order* is thus, strictly speaking, possible only in the situation when the exact solution of the many-particle aspect of a model is available or executable numerically. The obtained solutions provide the physical properties of the considered system as a function of lattice parameter, *not* only as a function of the microscopic parameters.

One may ask if the application of the method to the systems with an approximate treatment of the correlations is possible. Such approach was outlined some time ago [24], where the electronic correlations have been treated within the Gutzwiller approach. We believe that our method can be also used starting from the dynamic mean-field theory (DMFT) [9]. The implementation of DMFT combined with the wave-function optimization would provide a possibility of testing the predictions of the Hubbard model, as the variations of the properties with changing lattice constant can be carried out experimentally by applying the pressure.

On the theoretical side one should incorporate the density-matrix renormalization group technique [7] to extend the size of the system (number of atoms N), particularly for $N_e < N$, when one can study carefully the hole states and their pairing induced by the kinetic exchange interaction and/or paramagnons.

Extension of our method to two-dimensional systems would be also important, but that would involve more advanced numerical procedures.

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