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Optimization of single-particle basis for exactly soluble models of correlated electrons

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We determine the explicit form of the single-particle wave functions $\{w_i(\mathbf{r})\}$ appearing in the microscopic parameters of models in the second-quantization representation. Namely, the general form of the *renormalized wave equation* is derived from the *Lagrange-Euler principle* by treating the system ground-state energy of an exact correlated state as a functional of $\{w_i(\mathbf{r})\}$ and their derivatives. The method is applied to three model situations with one orbital per atom. For the first example—the Hubbard chain—the optimized basis is obtained only *after* the electronic correlation has been included in the rigorous Lieb-Wu solution for the ground-state energy. The renormalized Wannier wave functions are obtained variationally starting from the atomic basis for the *s*-type wave functions. The principal characteristics such as the ground-state energy and the model parameters are calculated as a function of interatomic distance. Second, the atomic systems such as the H_2 molecule or He atom can be treated in the same manner and the optimized orbitals are obtained to illustrate the method further. Finally, we illustrate the method by solving exactly correlated quantum dots of $N \leqslant 8$ atoms with the subsequent optimization of the orbitals. Our method may be regarded as the *next step* in analyzing exactly soluble many-body models that provides properties as a function of the lattice parameter and defines at the same time the renormalized wave function for a single particle.

I. INTRODUCTION

The physics of correlated electronic 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[4] models. In all these models the microscopic parameters such as the hopping integral t (or hybridization V), the intra-atomic Coulomb U, and the nearest-neighbor Coulomb and exchange integrals (K and J, respectively) are taken as parameters, which contain single-particle (Wannier) wave functions. Those single-particle wave functions appear as a complete but otherwise arbitrary basis to define the field operators in the Fock space, and are usually left intact when discussing the solution, for e.g., ground-state energy as a function of the parameters. In this manner, the exact solutions for the one-dimensional Hubbard,[5] Kondo and Anderson impurities,[6] or periodic Kondo-lattice[7] models have been obtained and unveil the essential role of the local part of the Coulomb and exchange interactions in inducing long-range correlations and in turn, a highly nontrivial nature of the quantum macroscopic ground state, even in the situation when there is no spontaneous symmetry breaking. For example, features such as the insulating nature of the ground state of the Hubbard chain for an arbitrarily small amplitude U of the Coulomb interaction or the completely compensated nature of the impurity magnetic moment in the ground state cannot be obtained within any straightforward perturbation scheme.

The solution is customarily analyzed as a function of model parameters. In view of the above one can ask 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? This question is particularly acute if one wants to interpret the many-body state also in the single-particle terms or to calculate the physical properties of the correlated state as a function of, e.g., lattice constant (the analysis of experiment in terms of the model parameters is usually not feasible). From the theoretical side, such a readjustment of the wave function leads to the *renormalized wave equation*, an example of which we propose in this paper in some exactly soluble cases. In brief, we combine the rigorous solution of a parametrized model in the Fock space with the consistent determination of the single-particle wave functions in the Hilbert space introduced concommitantly with the model, as they are necessary to define the field operators. The wave function is determined by an additional Lagrange-Euler procedure completes the solution of the second-quantized models if only their rigorous treatment is possible.

In connection with this fundamental question one should remark that whereas the local-density approximation with on-site Coulomb interaction[8] (LDA+U) or *GW* (Ref. 9) band-theoretical schemes provide a qualitatively correct picture of the Mott localization induced by the electron-electron interaction in some of the three-dimensional narrow-band systems, one has to devise a different approach for low-dimensional systems, in which the normal metallic state is

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not stable even for small U/W ratio, where W is the width of the bare band states. A simple discussion of this particular point is the main aim of this paper. Thus we combine the analysis of the second-quantized model, for which a systematic analysis of correlation is possible with the method of wave-function determination. Namely, in our approach the single-particle wave function is determined *a posteriori*, after the correlations have been taken into account, *not before*. An implementation of this principle carries, in our view, a new ingredient: The wave function of the particle in such an effective medium has the properties of the renormalized atomic or Wannier function, which is treated on the same footing as the electronic correlations. Its Fourier transform provides a renormalized Bloch function for infinite systems. The method is illustrated also with an exact solution for the $N\leqslant 8$ atom system with $N_e=N$ electrons and a simultaneous determination of their single-particle functions. We think that the method may be particularly useful in determining the properties of small systems such as *correlated quantum dots*, for which methods based on the band theory may be inapplicable. On the other hand, the approach may supplement also the quantum-chemical calculations as it incorporates an exact treatment of electronic correlations in selected model situations.

The structure of the paper is as follows. In the next section we present the method of combining an exact solution in the Fock space with the correlation-induced readjustment of the single-particle wave function contained in the microscopic parameters of the model. In Sec. III we determine the renormalized wave equation for the Hubbard chain and solve it variationally. In Sec. IV we consider the H_2 molecule in the same manner and compare the results with those for the Hubbard chain. In Sec. V we apply the method to the small systems—*correlated quantum dots* involving $N\leqslant 8$ atoms. We diagonalize there the Hamiltonian in the Fock space involving *all* pair interactions and subsequently optimize the orbitals providing the system energy versus interatomic distance. The Appendices A–D provide some of the technical details of the calculations.

II. METHOD

In approaching the system of interacting electrons we start from the concept of the field operator $\hat{\Psi}_\sigma(\mathbf{r})$, which is customarily defined in a complete orthonormal basis of single-particle wave functions $\{w_i(\mathbf{r})\chi_\sigma\}$ in the following manner:

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

where $a_{i\sigma}$ is the annihilation operator of a particle in a state $|i\sigma\rangle$. One should note that the basis $\{w_i(\mathbf{r})\chi_\sigma\}$ is completely arbitrary in this definition. The fundamental question is: Can one find a method of unique way of determination of the wave functions $\{w_i(\mathbf{r})\chi_\sigma\}$ and solve the corresponding Hamiltonian

$$\begin{aligned}H=&\sum_\sigma \int d^3\mathbf{r}\hat{\Psi}^\dagger_\sigma(\mathbf{r})H_1(\mathbf{r})\hat{\Psi}_\sigma(\mathbf{r})\\&+\frac{1}{2}\sum_{\sigma_1\sigma_2}\int\int d^3\mathbf{r}_1d^3\mathbf{r}_2\hat{\Psi}^\dagger_{\sigma_1}(\mathbf{r}_1)\hat{\Psi}^\dagger_{\sigma_2}(\mathbf{r}_2)\\&\times V(\mathbf{r}_1-\mathbf{r}_2)\hat{\Psi}_{\sigma_2}(\mathbf{r}_2)\hat{\Psi}_{\sigma_1}(\mathbf{r}_1)\end{aligned} \tag{2}$$

in the Fock space exactly? Such a procedure involving the two separate steps, if it exists, is perfectly well defined as the operators $H_1(\mathbf{r})\equiv H_1$ and $V(\mathbf{r}_1-\mathbf{r}_2)\equiv V_{12}$ act *only* in the coordinate representation (for one and two particles, respectively) in the Hilbert space, whereas the creation and annihilation operators act in the occupation-number (Fock) space. In the present paper we discuss three model systems when this method of two-step approach is explicitly implemented.

Namely, we start from the model of interacting electrons on a lattice for which the Hamiltonian (2) has the following form in the real-space representation

$$\begin{aligned}H=&\sum_{ij\sigma}t_{ij}a^\dagger_{i\sigma}a_{j\sigma}+\frac{1}{2N}\sum_{ijkl\sigma\sigma'}V_{ijkl}a^\dagger_{i\sigma}a^\dagger_{j\sigma'}a_{l\sigma'}a_{k\sigma}\\=&E_1+E_2,\end{aligned} \tag{3}$$

where $t_{ij}=\langle w_i|H_1|w_j\rangle$ is the hopping (Bloch) integral for the single electron with Hamiltonian H_1, involving two sites i and j, $w_i(\mathbf{r})$ is the Wannier function centered on the site $i\equiv\mathbf{R}_i$, and $V_{ijkl}=\langle w_iw_j|V_{12}|w_kw_l\rangle$ is the matrix element of the interaction V_{12} between two particles. The solution of this model involves calculation of the ground-state energy

$$\begin{aligned}E_G=\langle H\rangle=&\sum_{ij\sigma}t_{ij}\langle a^\dagger_{i\sigma}a_{j\sigma}\rangle\\&+\frac{1}{2N}\sum_{ijkl\sigma\sigma'}V_{ijkl}\langle a^\dagger_{i\sigma}a^\dagger_{j\sigma'}a_{l\sigma'}a_{k\sigma}\rangle,\end{aligned} \tag{4}$$

i.e., an explicit determination of the correlation functions $C_{ij}\equiv\langle a^\dagger_{i\sigma}a_{j\sigma}\rangle$ and $C_{ijlk}\equiv\langle a^\dagger_{i\sigma}a^\dagger_{j\sigma'}a_{l\sigma'}a_{k\sigma}\rangle$ as a function of parameters t_{ij} and V_{ijkl}.

In the usual 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 into two limiting situations: (a) the metallic limit when $|E_1|\gg E_2$, and (b) the strong-correlation (or insulating limit for $N_e=N$) when $|E_1|\ll E_2$. The regime $|E_1|\simeq E_2$ is regarded as a situation (c) in which the Mott-Hubbard (metal-insulator) phase transition takes place. The most interesting are the limits (b) and (c) when the single-particle part is not dominant. One should ask then: Should one not optimize the single-particle basis $\{w_i(\mathbf{r})\}$ together with determination of the correlation function, as the contributions $E_1\leqslant 0$ and $E_2>0$ compete with each other in determining the resultant state (metallic or insulating) of this system? This question has been posed long time ago by Peierls, Mott, Anderson, Hubbard, and others.[10] The analysis provided by them underlines the principal role played by the electron correlations, which in the present context means that the correlation functions C_{ij} and C_{ijkl} have a nontrivial (e.g., non-Hartree-Fock) character.

In the present paper we propose to close this analysis by taking $C_{ij}=C_{ij}\{t_{ij},V_{ijkl}\}$ and $C_{ijlk}=C_{ijlk}\{t_{ij},V_{ijkl}\}$ and determining the renormalized wave equation for $\{w_i(\mathbf{r})\}$ by treating E_G as a functional of $\{w_i(\mathbf{r})\}$ and their derivatives, since $H_1=-(\hbar^2/2m)\nabla^2+V(\mathbf{r})$, with $V(\mathbf{r})$ being the single-particle potential. In such a situation $w_i(\mathbf{r})$ is determined from a Lagrange-Euler equation for the functional

$$\mathcal{F}\{w_i(\mathbf{r})\}=E_G\{w_i(\mathbf{r})\}-\sum_i \lambda_i\left(\int d^3r|w_i(\mathbf{r})|^2-1\right), \quad (5)$$

where λ_i is the Lagrange multiplier introduced for the function $w_i(\mathbf{r})$, which is normalized (i.e., represents a bound state). Generally, this equation reads

$$\frac{\delta E_G}{\delta w_i(\mathbf{r})}-\boldsymbol{\nabla}\cdot\frac{\delta E_G}{\delta \boldsymbol{\nabla} w_i(\mathbf{r})}-\lambda_i w_i(\mathbf{r})=0, \quad (6)$$

or more explicitly

$$(\tilde{H}_1-\lambda_i)w_i\equiv\left[\frac{\delta}{\delta w_i(\mathbf{r})}-\boldsymbol{\nabla}\cdot\frac{\delta}{\delta\boldsymbol{\nabla} w_i(\mathbf{r})}\right]\left(\sum_{j\sigma} t_{ij}C_{ij}^{\sigma}+\frac{1}{2}\sum_{jkl\sigma\sigma'} V_{ijkl}C_{ijlk}^{\sigma\sigma'}\right)-\lambda_i w_i(\mathbf{r})=0, \quad (7)$$

where $\tilde{H}_1$ represents a renormalized single-particle Hamiltonian (H_1 is its *bare* counterpart). This system of equations for $\{w_i(\mathbf{r})\}$ may seem hopeless to solve and this is the reason why the band-theoretical approach is almost always used and usually successful. However, in the remaining part of the paper we show that in some exactly soluble cases this new approach is perfectly feasible and leads to reliable results in the limit of *strong correlations*, albeit in simple situations for the moment (the discussion of this paper is expanded at the end of the paper).

In the following analysis we will make use of the *tight-binding approximation* (TBA). In the present context this method may be briefly summarized for a periodic system as follows. The Bloch function $\Phi_{\mathbf{q}}(\mathbf{r})$ defined as

$$\Phi_{\mathbf{q}}(\mathbf{r})=N_{\mathbf{q}}\sum_j e^{i\mathbf{q}\cdot\mathbf{R}_j}\Psi_j(\mathbf{r}), \quad (8)$$

where $\Psi_j(\mathbf{r})$ are atomic functions [here taken in the form of s function, $\Psi_j(\mathbf{r})=(\pi a^3)^{-1/2}\exp(-|\mathbf{r}-\mathbf{R}_j|/a)$, with an adjustable Bohr radius $a\equiv\alpha^{-1}$], and $N_{\mathbf{q}}$ is the normalized factor

$$N_{\mathbf{q}}=\left(N\sum_j e^{i\mathbf{q}\cdot(\mathbf{R}_j-\mathbf{R}_i)}S_{ij}\right)^{-1/2}, \quad (9)$$

whereas $S_{ij}=\langle\Psi_i|\Psi_j\rangle$ is the overlap integral. The Wannnier function is defined as $w_i(\mathbf{r})\equiv\Sigma_l\beta_{li}\Psi_l(\mathbf{r})$, where in the periodic system

$$\beta_{li}=\frac{1}{\sqrt{N}}\sum_{\mathbf{q}} e^{i\mathbf{q}\cdot(\mathbf{R}_l-\mathbf{R}_i)}N_{\mathbf{q}}. \quad (10)$$

In the extreme version of the approach we take into account only the overlap between the nearest neighbors $\langle ij\rangle$. In the case of a small system β_{li} are calculated explicitly, without referring to Eq. (10). The simple variational solution of Eq. (7) we analyze here relies on the minimization of $\langle w_i|\tilde{H}_1|w_i\rangle$ with respect to the adjustable Bohr radius a. In the next three sections we consider three concrete situations with adjusted wave functions: the Hubbard chain, H_2 molecule, and the exact solution for small system up to $N=8$ atoms. In Appendix D we consider briefly the He and H^- atomic systems within the same scheme.

III. HUBBARD CHAIN

A. General features

We start with our first example: the insulating solution for the Hubbard chain. The ground state energy expression obtained by Lieb and Wu[5] for the Hubbard chain containing N atoms, when written down in physical units, has the form (cf. Appendix A)

$$\frac{E_G}{N}=E_0+4t\int_0^\infty d\omega\frac{J_1(\omega)J_0(\omega)}{\omega[1+\exp(\omega U/2t)]}, \quad (11)$$

where E_0 contains both the atomic (ϵ_a) and the lattice contributions, t is the nearest-neighbor (NN) hopping, U is the intra-atomic part of the Coulomb interaction, and $J_n(x)$ is the Bessel function with $n=0$ or 1. The detailed discussion of this solution as a function of t/U is provided in Ref. 11.

The parameters t and U are defined with the help of the orthonormal basis $\{w_i(\mathbf{r})\equiv w(\mathbf{r}-\mathbf{R}_i)\}$ of Wannier functions, through which they are defined in the following manner:

$$t=\left\langle w_i\left|-\frac{\hbar^2}{2m}\nabla^2+V(\mathbf{r})\right|w_{i\pm1}\right\rangle\equiv\int d^3r\, w_i^*(\mathbf{r})T(\mathbf{r})w_{i\pm1}(\mathbf{r}) \quad (12)$$

and

$$U=\int d^3r\, d^3r'|w_i(\mathbf{r})|^2\frac{e^2}{|\mathbf{r}-\mathbf{r}'|}|w_i(\mathbf{r}')|^2. \quad (13)$$

Similarly,

$$\epsilon_a=\langle w_i|T(\mathbf{r})|w_i\rangle \quad (14)$$

is the atomic part of the electron energy in the crystalline medium. Finally, the lattice part will be taken in the simplest classical form as $\approx e^2\Sigma_i|\mathbf{R}_i-\mathbf{R}_{i+1}|^{-1}$, i.e., to the fourth neighbor [it is regarded as a constant when optimizing the basis $\{w_i(\mathbf{r})\}$].

From above it follows that E_G is regarded as a functional of the basis $\{w_i(\mathbf{r})\}$, i.e., $E_G\equiv E_G\{w_i(\mathbf{r}),\boldsymbol{\nabla} w_i(\mathbf{r})\}$. Therefore, the corresponding *renormalized* wave equation is obtained by setting, as before, the Lagrange-Euler equation under the constraint that each wave function w_i should be normalized. Thus, the functional to be minimized is $\mathcal{F}\{w_i,\boldsymbol{\nabla} w_i\}\equiv E_G\{w_i,\boldsymbol{\nabla} w_i\}-\Sigma_i\lambda_i[\int d^dr|w_i(\mathbf{r})|^2-1]$, where $\{\lambda_i\}$ are the Lagrange multipliers. The renormalized wave equation for the function w_i has then the form

$$\frac{\delta E_G}{\delta w_i}-\boldsymbol{\nabla}\cdot\frac{\delta E_G}{\delta\boldsymbol{\nabla} w_i}-\lambda w_i=0 \quad (15)$$

with the eigenvalue λ site independent in this case. The explicit solution of this quite complicated equation is not the purpose of this paper, as it requires a development of quite involved numerical procedures. Ultimately, the solution of Eq. (15) must contain the physical features, which we discuss next.

B. Optimization of the atomic orbitals

The Hubbard model is a single narrow-band model with $1s$ type of orthogonalized single-particle basis. The optimized basis is obtained as follows. We start from the atomic functions $\{\Psi_i(\mathbf{r})\}$, where $\Psi_i(\mathbf{r}) = (\pi/\alpha^3)^{-1/2} \exp(-\alpha|\mathbf{r}-\mathbf{R}_i|)$, with $\alpha = 1/a$. Next, the orthogonalized atomic wave functions are defined through

$$w_i(\mathbf{r}) \equiv \beta\Psi_i(\mathbf{r}) + \gamma[\Psi_{i+1}(\mathbf{r}) + \Psi_{i-1}(\mathbf{r})], \tag{16}$$

where the coefficients β and γ are obtained from the conditions $\langle w_i|w_i\rangle \equiv \int d^3r\, w_i(\mathbf{r})^2 = 1$ and $\langle w_i|w_{i\pm1}\rangle = 0$. Hence

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

$$\gamma = \frac{-S}{\sqrt{2-5S^2+2(1-2S^2)\sqrt{1-3S^2}}}. \tag{17}$$

Note that TBA is defined in the range of interatomic distance R, where the overlap integral $S = \langle\Psi_i|\Psi_{i\pm1}\rangle$ is substantially smaller than unity, i.e., for R not too small, as checked *a posteriori*, after the whole optimization of the orbital size has been carried out.

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

$$\epsilon_a = (\beta^2 + 2\gamma^2)\epsilon_a' + 4\beta\gamma t', \tag{18}$$

$$t \equiv \langle w_i|T|w_{i+1}\rangle = (\beta^2 + 3\gamma^2)t' + 2\beta\gamma\epsilon_a', \tag{19}$$

and

$$U = (\beta^4 + 2\gamma^4)U' + 8\beta^3\gamma V' + 8\beta\gamma^3 V' + 4\beta^2\gamma^2 K' + 8\beta^2\gamma^2 J', \tag{20}$$

where the parameters t', ϵ_a', U', K', V', and J' are the Slater integrals calculated in Ref. 12 for the s-type *atomic* wave functions. For the sake of notation consistency and their subsequent interpretation in Sec. IV, we list them in Appendix B. We see that all the primed parameters, defined for the atomic basis $\{\Psi_i(\mathbf{r})\}$, depend on both the size $\{a \equiv \alpha^{-1}\}$ of the atomic orbitals and the interatomic distance R. Therefore, one has to include the atomic part ϵ_a, as it varies with R. Note also that the parameters t and U contain *all* pair-interaction parameters in the nonorthogonal basis $\{\Psi_i\}$; this point will be discussed in detail in the next section.

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 (12)–(14) to the ground-state energy (11). The ground-state energy (per atom) obtained in this manner (with the ion-ion repulsion and the atomic parts included) is displayed in Fig. 1 as a function of R, which supplements the corresponding results[13] for E_G versus $U/|t|$. The energy approaches the atomic value (-1 Ry) for $R/a_0 > 6$. The optimal distance is $R_{min} \simeq 3.15a_0 \approx 1.6$ Å and the minimum of $E_G/N \approx -1.03$ Ry, i.e. the cohesive energy is ≈ 0.4 eV/atom. The inset shows the result for E_G obtained when the nearest-neighbor Coulomb interaction $K = \langle w_i w_{i\pm1}|V_{12}|w_i w_{i\pm1}\rangle$ is also included in the Hartree-Fock approximation (for meaning of these results see discussion below). The ion-ion repulsion energy was taken approximately up to the fourth neighbors, when it takes the form (in atomic units) $4/R$ (cf. also the discussion below).

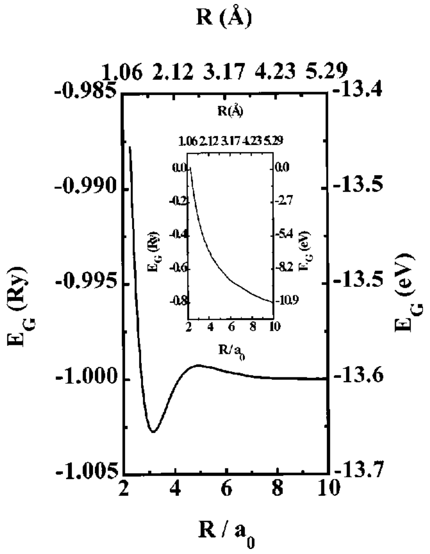

FIG. 1. Ground-state energy E_G of the Hubbard chain (per site) as a function of relative interatomic distance R/a_0. The atomic energy and the interionic Coulomb repulsion (to the fourth neighbor) is included. The inset provides E_G with inclusion of nearest-neighbor Coulomb interaction in the Hartree-Fock approximation.

The interatomic distance dependence of the size of the optimized atomic orbital (in units of the Bohr radius a_0) is shown in Fig. 2 (the bare orbitals have the size $\alpha^{-1}/a_0 = 1$). In the inset we display the R dependence of the NN overlap integral. Even for the chain spacing $R = R_{min}$ (marked by the vertical dotted line) the overlap $S < 0.3$, making our version of TBA applicable for $R \geqslant R_{min}$. The electronic correlations diminish the orbital size (and the overlap) remarkably, whereas the dominant hopping processes should increase it. This means that the correlations make the tight-binding approach applicable even for relatively small interatomic distances. Because of the diminution of α^{-1} the role played by the atomic energy is increased and, effectively, this decreases the $|t|/U$ ratio. The atomic limit ($E_G/N \simeq -1$ Ry, $\alpha^{-1} \simeq a_0$) is practically achieved for $R > R_c = 7a_0 \sim 3.5$ Å. In effect, the $|t|/U$ ratio falls off rapidly as R exceeds R_c. The situation with $U = W$ is achieved already for $R \approx 3a_0 \simeq 1.5$ Å. To check the validity of the Hubbard model calculations we have also repeated the whole calculations by including the NN Coulomb interaction term $K\Sigma_i n_i n_{i+1}$, which has been treated in the Hartree-Fock approximation, when it reduces to KNn^2. The dashed line in Fig. 2 provides the correction to the optimized orbital size

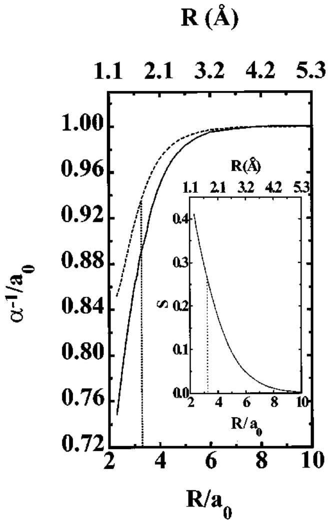

FIG. 2. Optimal size of atomic 1*s* orbit (including correlations) in units of the atomic Bohr radius as a function of interatomic distance (the dashed line, with NN Coulomb interaction, as in Fig. 1). In the inset the overlap integral is displayed. The vertical dotted line marks the position at which E_G has a minimum.

due to the presence of the Kn^2 term in E_G; the change is not negligible and the results for E_G in that case displayed in the inset of Fig. 1 reflect this.

From Fig. 1 we can draw the conclusion that the linear chain (*not* the Hubbard chain) is unstable if the intersite interactions are included in the Hartree-Fock approximation. In connection with this problem one should note that the quantum correction to E_G due to the ion zero-point motion destabilizes the linear chain further (see below). The same effect would have inclusion of the interionic repulsion between more distant neighbors. This instability is in accordance with the well-known fact that a nondimerized polimer composed of atomic hydrogen atoms does not exist. This instability is also discussed in Sec. V, where we present the exact results for a finite chain. The remedy for this is also pointed out there.

One can also see another important feature of the Hubbard chain stability. For that purpose we show in Fig. 3(a) the ground-state energy as a function of *R*. We observe a steady decrease of E_G with diminishing R if only the nearest-neighbor ion-ion repulsion is included (the lower curve). The upper curve is obtained when additionally the nearest-neighbor electron-electron interaction is included in the Hartree-Fock approximation (see also the inset in Fig. 1). Thus, the total-energy value is very sensitive to the range of the interactions included. In plotting of Fig. 3(a) we have also included zero-point motion estimated in Appendix C.

To show the atomic wave-function compression we plotted in Fig. 3(b) the atomic orbit compression induced by the electronic correlations. The result is not much different from that plotted in Fig. 2 (the case without intersite interaction).

In Fig. 4 we have plotted the renormalized Wannier functions $w_0(\mathbf{r})$ at R_{min} and for both the optimal ($\alpha \simeq 1.08 a_0^{-1}$, solid line) and the bare ($\alpha = a_0^{-1}$, dotted line) values of α. The main difference is around $r=0$.

The above results containing first-principles calculations for the Hubbard chain will be compared with the corresponding analysis performed for the H_2 molecule, which we discuss next. Such a comparison is necessary to grasp qualitatively the role of chain dimerization.

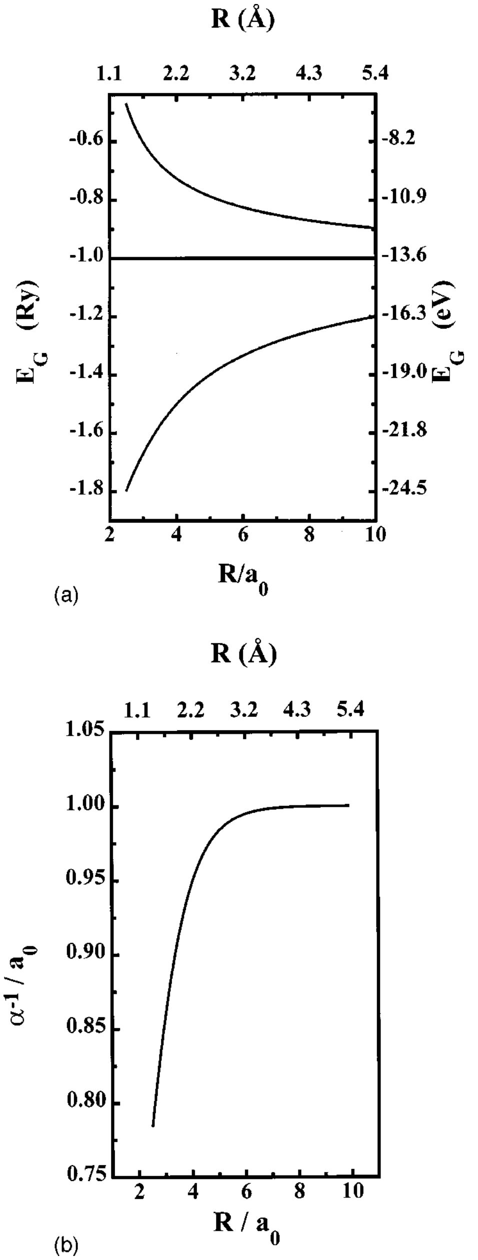

FIG. 3. (a) Ground-state energy as a function of both the interatomic distance when only the nearest-neighbor interionic repulsion is included (the lower curve), and also the nearest-neighbor Coulomb repulsion is taken into account (the upper curve). The zero-point motion of ions (estimated in Appendix C) is also included. (b) The optimized size of the orbitals for the calculations depicted in (a) as a function of interatomic distance.

IV. H_2 SYSTEM AND COMPARISON WITH THE HUBBARD CHAIN

A. H_2 molecular states

We analyze the H_2 molecule in the same manner as the Hubbard chain. To achieve that we start with the most general Hamiltonian for a two-site system,[14] each site contributing a single *s*-type orbital:

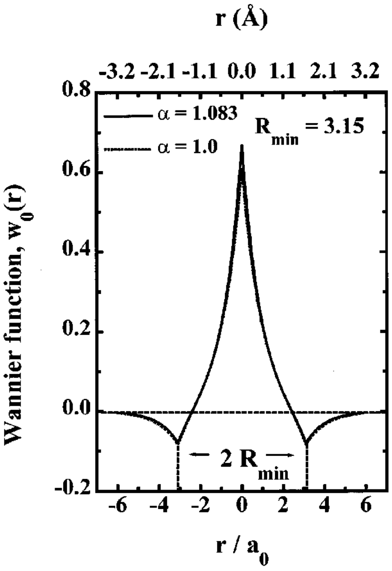

FIG. 4. The renormalized (solid line) and bare (dotted line) Wannier function profile $w_0(\mathbf{r})$ for $R=R_{min}$.

$$H=\epsilon_1 n_1+\epsilon_2 n_2+t\sum_{\sigma}\left(a_{1\sigma}^{\dagger}a_{2\sigma}+a_{2\sigma}^{\dagger}a_{1\sigma}\right)+U_1 n_{1\uparrow}n_{1\downarrow}+U_2 n_{2\uparrow}n_{2\downarrow}-2J\mathbf{S}_1\cdot\mathbf{S}_2+\left(K+\frac{1}{2}J\right)n_1 n_2+J(a_{1\uparrow}^{\dagger}a_{1\downarrow}^{\dagger}a_{2\downarrow}a_{2\uparrow}+\text{H.c.})+V\sum_{\sigma}\left[(n_{1\sigma}+n_{2\sigma})(a_{1\bar{\sigma}}^{\dagger}a_{2\bar{\sigma}}+a_{2\bar{\sigma}}^{\dagger}a_{1\bar{\sigma}})\right]. \tag{21}$$

Here, for the sake of generality, we have assumed that both the atomic level positions and the intra-atomic Coulomb interactions are different $(\epsilon_1\neq\epsilon_2, U_1\neq U_2)$. The remaining terms represent respectively the hopping between the atoms, the interatomic (Heisenberg) exchange, the pair hopping, and the so-called correlated hopping. All the terms come from the Coulomb interaction between the electrons. Note that in the case of the Hubbard chain all the terms J, K, and V appeared explicitly after expressing the Wannier functions through the nonorthogonal atomic functions. Here those terms appear already in the Wannier representation.

This Hamiltonian can be easily diagonalized for $N_e=1$ electron (H_2^+ state), since then the two eigenvalues $\lambda_\pm$, each degenerate with respect to spin $\sigma=\pm 1$, are

$$\lambda_\pm=\frac{1}{2}(\epsilon_1+\epsilon_2)\pm\left[\left(\frac{\epsilon_1-\epsilon_2}{2}\right)^2+t^2\right]^{1/2}. \tag{22}$$

The corresponding eigenstates are $|\lambda_{\pm\sigma}\rangle\equiv a_{1\pm}a_{1\sigma}^{\dagger}|0\rangle+a_{2\pm}a_{2\sigma}^{\dagger}|0\rangle$, with $a_{1\pm}/a_{2\pm}=[(\epsilon_2-\lambda_\pm)/(\epsilon_1-\lambda_\pm)]^{1/2}$ and

$$|a_2|=\pm\left(\frac{\epsilon_1-\lambda_\pm}{\epsilon_1+\epsilon_2-2\lambda_\pm}\right)^{1/2}. \tag{23}$$

These states reduce in the limit $\epsilon_1=\epsilon_2$ to the ordinary bonding and antibonding states: $|\lambda_{\pm\sigma}\rangle=(1/\sqrt{2})(a_{1\sigma}^{\dagger}\pm a_{2\sigma}^{\dagger})|0\rangle$.

For $N_e=2$ electrons we have six states: three triplet $(S=1)$ and three singlet $(\mathrm{S}=0)$ states. The triplet states are

$$|1\rangle=a_{1\uparrow}^{\dagger}a_{2\uparrow}^{\dagger}|0\rangle,\quad |2\rangle=a_{1\downarrow}^{\dagger}a_{2\downarrow}^{\dagger}|0\rangle,$$

$$|3\rangle=\frac{1}{\sqrt{2}}(a_{1\uparrow}^{\dagger}a_{2\downarrow}^{\dagger}+a_{1\downarrow}^{\dagger}a_{2\uparrow}^{\dagger})|0\rangle, \tag{24}$$

and have eigenvalues $\lambda_1=\lambda_2=\lambda_3=\epsilon_1+\epsilon_2+K-J$. The three singlet states are mixtures of the three trial states:

$$|4\rangle=\frac{1}{\sqrt{2}}(a_{1\uparrow}^{\dagger}a_{2\downarrow}^{\dagger}-a_{1\downarrow}^{\dagger}a_{2\uparrow}^{\dagger})|0\rangle,$$

$$|5\rangle=\frac{1}{\sqrt{2}}(a_{1\uparrow}^{\dagger}a_{1\downarrow}^{\dagger}+a_{2\uparrow}^{\dagger}a_{2\downarrow}^{\dagger})|0\rangle,$$

$$|6\rangle=\frac{1}{\sqrt{2}}(a_{1\uparrow}^{\dagger}a_{1\downarrow}^{\dagger}-a_{2\uparrow}^{\dagger}a_{2\downarrow}^{\dagger})|0\rangle, \tag{25}$$

and lead to the (3×3) Hamiltonian matrix $\langle i|H|j\rangle$ for these states of the form

$$(H)_{ij}=\begin{pmatrix} 2\epsilon+K+J & 2(t+V) & 0\\ 2(t+V) & 2\epsilon+J+U & \frac{1}{2}(U_1-U_2)\\ 0 & \frac{1}{2}(U_1-U_2) & 2\epsilon+U-J \end{pmatrix}, \tag{26}$$

where $\epsilon_a=(\epsilon_1+\epsilon_2)/2$ and $U=(U_1+U_2)/2$. We consider here explicitly a simple situation with $U_1=U_2=U$. Then, the eigenvalues are

$$\lambda_{4,5}=2\epsilon_a+\frac{1}{2}(K+U)+J\pm\frac{1}{2}[(U-K)^2+16(t+V)^2]^{1/2}, \tag{27}$$

$$\lambda_6=2\epsilon+U-J. \tag{28}$$

In the limit $U-K\gg 4|t+V|$ we have approximately that $\lambda_{4,5}=2\epsilon_a+U+K+J\pm 4(t+V)^2/(U-K)$. For $J>0$ we have in λ_5 a competition between the direct and kinetic exchange interactions. The eigenstates $|\lambda_{4,5}\rangle\equiv|\tilde{\lambda}_\pm\rangle$ take the form for $\epsilon_1=\epsilon_2=\epsilon=0$, and $U_1=U_2=U$:

$$|\tilde{\lambda}_\pm\rangle=[2D(D\pm U\mp K)]^{-1/2}\{4(t+V)|4\rangle\pm(D\pm U\mp K)|5\rangle\}, \tag{29}$$

with $D=[(U-K)^2+16(t+V)^2]^{1/2}$. We see that these eigenstates have an admixture of symmetric ionic state $|5\rangle$. Finally, the eigenstate $|\lambda_6\rangle$ has the form $|\lambda_6\rangle=(1/\sqrt{2})(a_{1\uparrow}^{\dagger}a_{1\downarrow}^{\dagger}-a_{2\uparrow}^{\dagger}a_{2\downarrow}^{\dagger})|0\rangle$. To illustrate our method of approach we set first the variational minimization of the wave functions w_1 and w_2.

B. Renormalized wave equation for H_2

Within the second-quantization scheme the relevant Wannier functions $w_1(\mathbf{r})$ and $w_2(\mathbf{r})$ are obviously not determined. In other words, the eigenvalues λ_i are expressed in terms of the parameters ϵ_a, t, U, K, J, and V, as one sees from Eq.s (27), (28). We fix them again by employing the same type of variational principle as before, under the condition that they are normalized. Such procedure means physically that the original atomic orbitals readjust themselves in each eigenstate. This will certainly happen when the interaction energy is comparable or even larger than its single-particle counterpart.

For one electron ($N_e=1$) we obtain the Schrödinger equation for bonding and antibonding states in the form

$$E_i^{\pm} w_i(\mathbf{r}) = \left[-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r}-\mathbf{R}_i) + V(\mathbf{r}-\mathbf{R}_j) \right] \times [w_i(\mathbf{r}) \pm w_j(\mathbf{r})]. \tag{30}$$

This is not a strange result, since in that case there is no electron-electron interaction.

The simplest nontrivial situation occurs for triplet states for which the wave equation takes the form

$$\begin{aligned} E_i^{\pm} w_i(\mathbf{r}) = {} & \left[-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r}-\mathbf{R}_1) + V(\mathbf{r}-\mathbf{R}_2) \right] w_i(\mathbf{r}) \\ & + w_i(\mathbf{r}) \int d^3\mathbf{r}' V_{12}(\mathbf{r}-\mathbf{r}') |w_i(\mathbf{r}')|^2 \\ & + w_i(\mathbf{r}) \int d^3\mathbf{r}' V_{12}(\mathbf{r}-\mathbf{r}') |w_j(\mathbf{r}')|^2 \\ & - w_j(\mathbf{r}) \int d^3\mathbf{r}' V_{12}(\mathbf{r}-\mathbf{r}') w_j(\mathbf{r}') w_i(\mathbf{r}'). \end{aligned} \tag{31}$$

Here $V(\mathbf{r}-\mathbf{R}_i) = -e^2/|\mathbf{r}-\mathbf{R}_i|$ is the atomic potential and $V_{12}(\mathbf{r}-\mathbf{r}') = e^2/|\mathbf{r}-\mathbf{r}'|$ is the Coulomb repulsion between electrons. The interaction part contains both $i=j$ and the intersite ($i \neq j$) Coulomb contributions, as well as the attractive exchange contribution. One can say that the readjusted orbitals obey the wave equation of the Hartree-Fock type. This case illustrates a general rule that if the eigenvalues contain only linear combination of the parameters, then the renormalized wave equation is equivalent to that introduced by Slater by taking the two-particle wave function in the form of the Slater determinant. One should note that here this equation is derived in a systematic manner.

A true nontrivial situation appears when we discuss a renormalized equation for the singlet states, among them for the lowest eigenstate $\tilde{\lambda}_-$, when the eigenvalue is not a linear function of the microscopic parameters. In that situation, the general equation for, e.g., $\tilde{\lambda}_-$ has the form

$$E_i w_i = \frac{\delta \lambda_5}{\delta w_i} - \boldsymbol{\nabla} \cdot \frac{\delta \lambda_5}{\delta \boldsymbol{\nabla} w_i} \tag{32}$$

or, more explicitly,

$$\begin{aligned} E_i w_i(\mathbf{r}) = {} & \left[-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r}-\mathbf{R}_1) + V(\mathbf{r}-\mathbf{R}_2) \right] w_i(\mathbf{r}) \\ & + \frac{1}{2} \frac{\delta}{\delta w_i^*}(U+K+2J) \\ & - \frac{1}{2} \frac{1}{[(U-K)^2 + 16(t+V)^2]^{1/2}} \left[(U-K)\frac{\delta(U-K)}{\delta w_i^*} \right. \\ & \left. + 16(t+V)\frac{\delta(t+V)}{\delta w_i^*} \right]. \end{aligned} \tag{33}$$

In essence, apart from the usual Hartree-Fock corrections (second term), the contribution from the kinetic exchange interaction is also present. One should note that this renormalized wave equation is *exact* within the given subspace of single-particle states selected to define the field operator. Furthermore, within this combined scheme containing first and second quantizations, one can calculate to the same degree of accuracy the ground and excited states, as we set the wave equation separate for each eigenstate.

The system of renormalized wave equations (33) for w_1 and w_2 is quite difficult to solve. The solution requires involved numerical procedures, which will not be dealt with here. Instead, in order to illustrate the results we have performed again the analytic calculations for the H_2 molecule. Also, in this example we see that by devising the renormalized wave equation we include easily the dynamic processes considered in the Fock space as a part of the *nonlocal contribution* to the effective potential. We demonstrate the importance of these contributions by considering the H_2 molecule in the simplest approximation for $w_i(\mathbf{r})$. A similar renormalized wave equation for H^- ion ground state is discussed in Appendix D.

C. Orbital size readjustment for H_2 and comparison with the Hubbard chain

Taking two $1s$ atomic functions $\Psi_i(\mathbf{r}) \equiv \Psi(\mathbf{r}-\mathbf{R}_i)$ we can form in the case of the H_2 molecule the corresponding orthogonalized functions $w_i(\mathbf{r})$:

$$w_i(\mathbf{r}) = \beta[\Psi_i(\mathbf{r}) - \gamma \Psi_j(\mathbf{r})], \tag{34}$$

with $j \neq i$, $S = \langle \Psi_1 | \Psi_2 \rangle$, and

$$\beta = \frac{1}{\sqrt{2}} \left[\frac{1}{1-S^2} + \frac{1}{(1-S^2)^{1/2}} \right]^{1/2}, \quad \gamma = \frac{S}{1+\sqrt{1-S^2}}. \tag{35}$$

The parameters ϵ_i, t, U_i, etc., are defined in Appendix B. Substituting the explicit form (34) of the wave function, we obtain the parameters in the following form:

$$\epsilon_a = \beta^2(1+\gamma^2)\epsilon_a' - 2\beta^2\gamma t', \tag{36}$$

$$t = \beta^2(1+\gamma^2)t' - 2\beta^2\gamma\epsilon_a', \tag{37}$$

$$U = \beta^4[(1+\gamma^4)U' + 2\gamma^2K' - 4\gamma(1+\gamma^2)V' + 4\gamma^2J'], \tag{38}$$

$$K = \beta^4[2\gamma^2U' + (1+\gamma^2)K' - 4\gamma(1+\gamma^2)V' + 4\gamma^2J'], \tag{39}$$

$$J = \beta^4[2\gamma^2U' + 2\gamma^2K' - 4\gamma(1+\gamma^2)V' + (1+\gamma^2)^2J'], \tag{40}$$

$$\begin{aligned} V = \beta^4[& -\gamma(1+\gamma^2)U' - \gamma(1+\gamma^2)K' + (1+6\gamma^2+\gamma^4)V' \\ & - 2\gamma(1+\gamma^2J')], \end{aligned} \tag{41}$$

where the primed integrals are also provided in Appendix B. We see that the nonorthogonality of the atomic wave functions leads to various combinations of the microscopic parameters. All of them are the functions of the orbital size (α^{-1}) and the interionic distance R.

Substituting the expressions (36)–(41) to the expressions for eigenvalues, adding the internuclear repulsion (e^2/R),

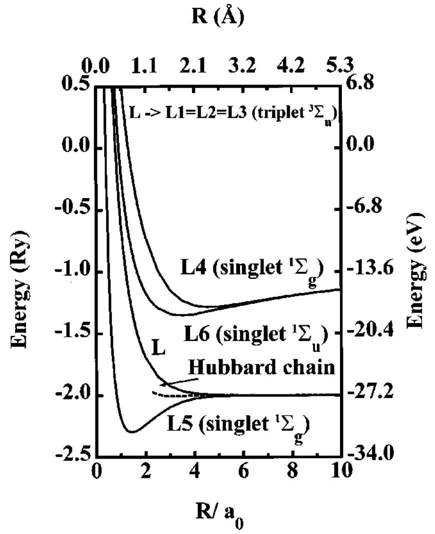

FIG. 5. The lowest six energy levels for H_2 molecule (solid lines) calculated to the same degree of accuracy as for the Hubbard chain, ground-state energy of which (per two sites) is shown as the dashed line. For detailed discussion see main text.

and optimizing each of λ_i with respect to α, we reach the expression for $\lambda_i = \lambda_i(R)$ drawn in Fig. 5, whereas the optimized orbital radii α^{-1} (in units of the Bohr radius a_0) are shown in Fig. 6(a). The ground-state energy of the hydrogen molecule is $E_G = -2.296$ Ry and the bond length is $l_B = 0.757$ Å, and misses the values obtained by Kołos and Wolniewicz[15] by about 2.5%, which are $E_G = -2.349$ Ry, and $l_B = 0.74$ Å. The experimental value is[16] $l_B = 0.746$ Å. For the sake of completeness we have displayed the ground-state energy for the Hubbard chain (per two sites), as well as the orbital size in that case [both dependences are marked by the dashed lines in Figs. 5 and 6(a), respectively]. Also, the value of $R_{min} = 1.57$ Å is vastly different from the corresponding value $l_B = 0.74$ Å here.

The important feature of our approach is that the interelectronic correlations are treated exactly (within the model with one orbital per atom). Therefore, we do not need to construct approximate molecular orbitals, as one proceeds when starting from either Heitler-London or Mulliken-Slater approaches.[17] Instead, we obtain *renormalized* atomic orbitals (corresponding to the Wannier functions depicted in Fig. 4 in the spatially extended system) drawn in Fig. 6(b). Their sum would provide a *renormalized* molecular orbital. The meaning of this renormalized picture becomes evident if one refers to the physical interpretation of the chemical bond provided some time ago by Ruedenberg.[18] Namely, the secondary minimum at the position of the neighboring proton provides a potential energy decrease (‘‘electron promotion’’). The corresponding kinetic energy increase can be seen only numerically by noting that the orbit shrinks ($\alpha^{-1} a_0 < 1$); in effect, the results are in accordance with the virial theorem. However, we must stress that our method includes exactly *all* interactions between the 1s electrons in this two-atom system.

The stability of the molecular states speaks for dimerization in the case of the linear chain, i.e., the stability of the broken symmetry ground state against the translationally invariant Lieb-Wu state, if the interionic interaction is included. The intersite Coulomb interaction K does not change the situation. The magnitude of this interaction is demonstrated explicitly in Fig. 7, where the values of all parameters are collected and displayed as a function of internuclear distance for H_2 molecule [Fig. 7(a)] and of the spacing for the Hubbard chain [Fig. 7(b) for the situation depicted in Fig. 1]. The solid curves displayed in Fig. 7(b) contain the wave functions obtained for the Hubbard model, whereas the dashed lines include additionally in the solution the Kn^2 term (see discussion in Sec. III B). The values of the parameters displayed in Fig. 7(a) are unrealistic for $R < a_0$, as then the excited states 2s, 2p, etc. also become important and have not been included here. The corresponding parameters values are different in the two situations (a) and (b). Therefore, their estimates based on bare atomic functions will differ importantly from those displayed here.

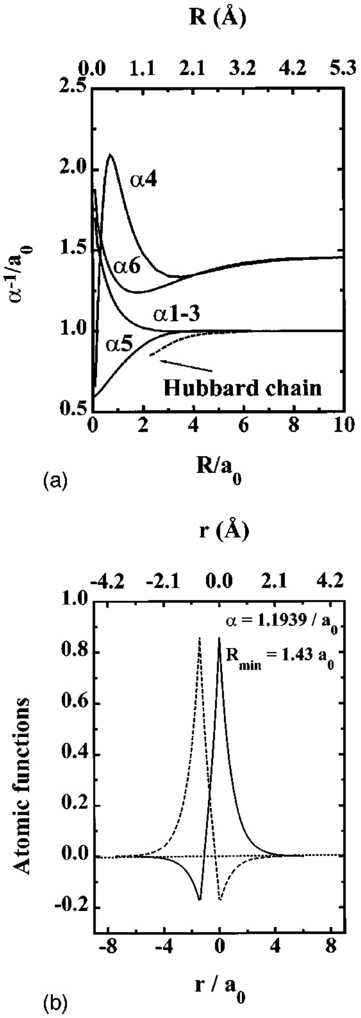

FIG. 6. (a) Optimal size of the atomic function (including correlations) for the first six states of the H_2 molecule (solid line), as compared to that calculated to the same degree of accuracy for the Hubbard chain (dashed line). (b) Renormalized atomic 1s orbitals in the H_2 molecule for the equilibrium configuration ($R_{min} = 1.43 a_0$).

V. CORRELATED QUANTUM DOT

As the third and final example we discuss briefly the system of $N \leqslant 8$ atoms, each contributing with one orbital to the

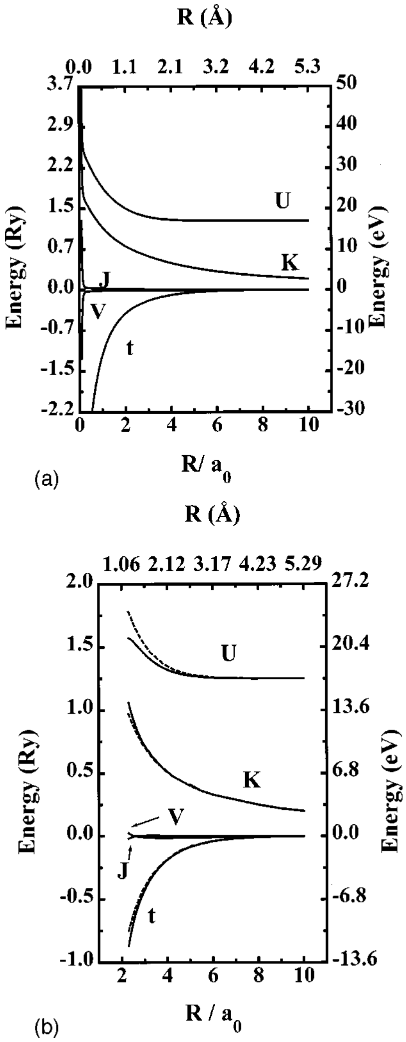

FIG. 7. (a) The parameters of the Hamiltonian for H_2 molecule, all as a function of distance; (b) the same for the Hubbard model (solid line), and with the Kn^2 term in E_G (dashed lines).

system. We diagonalize the Hamiltonian (3) numerically by taking submatrices of the total number 4^N of available states in the Fock space and subsequently adjust the orthogonalized orbital size as a function of interatomic distance.

The N-atom $(N_e = N)$-electron system we consider is closed on a ring (i.e., the periodic boundary conditions are imposed). The Hamiltonian has the form (21) except we include the pair interactions between *all* equally spaced neighbors. Additionally, in the single-particle part $H_1(\mathbf{r})$ we include the potential of the parent atom $(i=j)$ and of all $(i \neq j)$ neighbors $[V(\mathbf{r}) = \Sigma_j V(\mathbf{r}-\mathbf{R}_j)]$, as well as take the *exact* Wannier functions [i.e., include *all* β_{li} coefficients in Eq. (10)] and determine *all possible* hopping integrals t_{ij} for those small systems. The results for the lowest eigenvalue providing the system ground-state energy as a function of interatomic distance is shown in Fig. 8. The result for $N=2$ (the H_2 molecule) obtained with the help of the same numerical procedure provides the test of the method accuracy and is drawn for comparison as the solid line (it agrees exactly with the results of the preceding section). As in the infinite-Hubbard-chain case, the results for $N>2$ do not have an optimal interatomic distance if interatomic interactions are included. However, in practice such quantum dots are deposited on the substrate, which enforces their structural stability. The interatomic distance has then the meaning of the lattice constant mismatch with the substrate material. The one-dimensional dot configuration is achieved by taking the periodic boundary conditions.

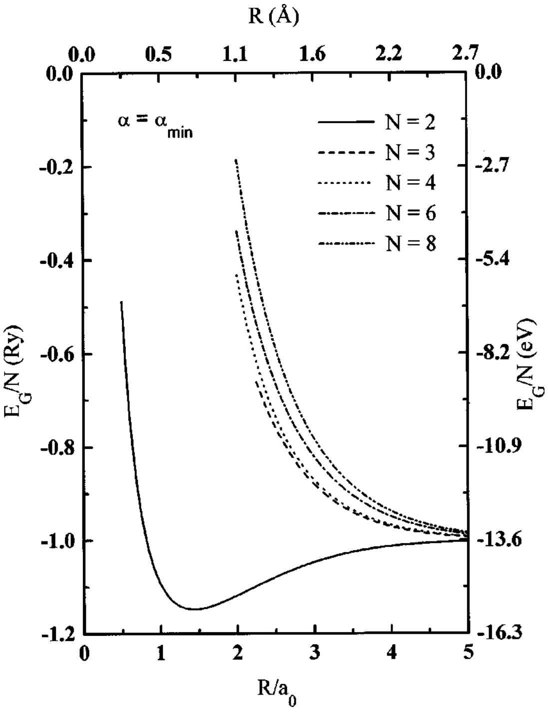

FIG. 8. Ground-state energy for short chains with $N \leq 8$ atoms closed in a ring, as a function of interatomic distance. The results for $N=2$ (H_2 molecule—solid line) are drawn for comparison.

In Fig. 9 we exhibit the optimal orbital size obtained from

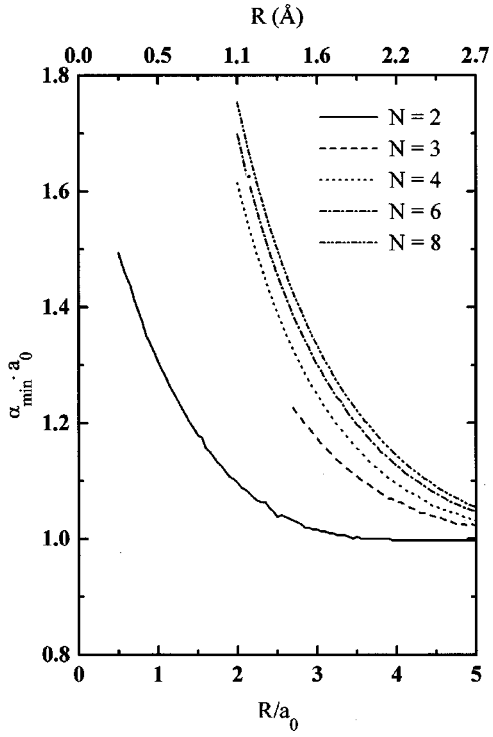

FIG. 9. The optimal size of atomic orbitals for $N \leq 8$ sites, as a function of interatomic distance.

the minimization of E_G with respect to $\alpha=a^{-1}$. We see that the renormalized orbital size a approaches gradually the Bohr-orbital size a_0 when $R\gg a_0$. The larger value of a for $N\geqslant 3$ with respect to the bond length l_B for the $N=2$ (H_2) case is caused by the circumstance that in the former case each atom has a neighbor from each side.

One should note that based on the present results one can extend the method to larger values of N with the help of the density-matrix renormalization group (DMRG) method.[19] The implementation of this method is not the purpose of the present paper. Instead, we try to emphasize with the help of analytic and numerical arguments the feasibility of combining first- and second-quantization formalisms, particularly in the situation when the corresponding problem in the Fock space is exactly soluble and the corresponding wave-function optimization (in the Hilbert space) by variational means leads to convergent results for E_G and α.

VI. A BRIEF OVERVIEW

In this paper we have proposed a renormalized wave equation for a single electron in an interacting medium as an example of simple systems with a nonperturbative ground state as well as discussed its simple variational solution. The wave equation is obtained explicitly by regarding the system ground-state energy as a functional, which contains the renormalized wave function in the expressions for the microscopic parameters. The variational solution of this equation provides in Secs. III and IV the parameters (and hence of the total energy) as a function of the lattice parameter. In essence, we supplement the rigorous treatment of the electronic correlations formulated in the Fock space with a natural idea of *a posteriori* readjustment of the wave function in the correlated state.

The simplicity of the present method proves important when applying it to the more complex problems. For example, one supplements the small-cluster calculations of correlated systems with our single-particle basis optimization, as was illustrated in Sec. V. Such a procedure may be particularly important for *correlated quantum dots*. Also, the renormalized wave functions can be used to determine the matrix elements for optical transitions in the systems, where the perturbative approach fails. Finally, one can incorporate the single-particle basis optimization for approximate solutions of models for correlated systems such as the Gutzwiller solution of the Mott-Hubbard localization. A simple approach in this direction has been proposed some time ago.[20] A treatment of some of the above problems is under way and will be published separately.

It is also straightforward to extend the present approach from Sec. III to the Anderson Hamiltonian taking the exact solution of Kawakami and Okiji.[6(d)] More importantly, one can apply the present method to other exactly soluble models, an extensive list of which may be found in Ref. 21.

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APPENDIX A: HUBBARD MODEL IN PHYSICAL UNITS

The Lieb-Wu solution is obtained for the Hubbard Hamiltonian

$$H=\epsilon_a\sum_{i\sigma} n_{i\sigma}+t\sum_{\langle ij\rangle\sigma} a^{\dagger}_{i\sigma}a_{j\sigma}+U\sum_{i} n_{i\uparrow}n_{i\downarrow} \tag{A1}$$

when one sets $\epsilon_a=0$ and $t=-1$. This solution can be adopted to the general case if one notices that (i) the first term provides an additive constant $\epsilon_a N_e$, where N_e is the number of electrons in the system, and (ii) we can divide Eq. (A1) by $|t|$ and in this manner obtain exactly the situation considered in Ref. 5 with the mapping $U\rightarrow U/|t|$, and $E_G\rightarrow E_G/|t|$, to transform Eq. (20) in Ref. 5 into Eq. (11) in this paper. One should emphasize again that both ϵ_a and t should be included explicitly when optimizing the model parameters in Sec. III B, as both quantities contain renormalized Wannier single-particle function $w_i(\mathbf{r})$ and thus are dependent on the interatomic distance R.

APPENDIX B: SLATER INTEGRALS FOR *s*-TYPE WAVE FUNCTIONS

The microscopic parameters for both the Hubbard model and two-site system such as the H_2 molecule contain at most two-site integrals of the same type. In the orthogonalized basis and in the atomic units they are

$$\epsilon_a=\int d^3r\, w_i^*(\mathbf{r})\left[-\nabla^2+\sum_j V(\mathbf{r}-\mathbf{R}_j)\right]w_i(\mathbf{r})\equiv\langle w_i|T|w_i\rangle, \tag{B1}$$

$$t_{ij}=\int d^3r\, w_i^*(\mathbf{r})\left[-\nabla^2+\sum_j V(\mathbf{r}-\mathbf{R}_j)\right]w_j(\mathbf{r})\equiv\langle w_i|T|w_j\rangle, \tag{B2}$$

$$U_i=\int d^3r\, d^3r'\,|w_i(\mathbf{r})|^2\frac{2}{|\mathbf{r}-\mathbf{r}'|}|w_i(\mathbf{r}')|^2 \equiv\langle w_iw_i|V_{12}|w_iw_i\rangle, \tag{B3}$$

$$K_{ij}=\int d^3r\, d^3r'\,|w_i(\mathbf{r})|^2\frac{2}{|\mathbf{r}-\mathbf{r}'|}|w_j(\mathbf{r}')|^2 \equiv\langle w_iw_i|V_{12}|w_jw_j\rangle, \tag{B4}$$

$$J_{ij}=\int d^3r\, d^3r'\,w_i^*(\mathbf{r})w_j(\mathbf{r}')\frac{2}{|\mathbf{r}-\mathbf{r}'|}w_j^*(\mathbf{r})w_i(\mathbf{r}') \equiv\langle w_iw_j|V_{12}|w_jw_i\rangle, \tag{B5}$$

$$V_{ij}=\int d^3r\, d^3r'\,|w_i(\mathbf{r})|^2\frac{2}{|\mathbf{r}-\mathbf{r}'|}w_i(\mathbf{r})w_j^*(\mathbf{r}') \equiv\langle w_iw_i|V_{12}|w_iw_j\rangle. \tag{B6}$$

In the present paper only the values for the nearest neighbors ij for t, K, J, and V appear. The primed quantities ϵ_i',

t', U', etc., have the form (B1)–(B6), but with the functions $w_i(\mathbf{r})$ replaced by $1s$-type functions $\Psi_i(\mathbf{r})$. The expressions (B1)–(B6) of the quantities through the primed parameters is provided by Eqs. (18)–(20) for the Hubbard chain, and by Eqs. (36)–(41) for the H_2 case. Therefore, it remains to write down, following Slater,[12] the expressions (B1)–(B6) for the primed quantities. In our notation (and in the atomic units) they have the form

$$\epsilon_a' = \alpha^2 - 2\alpha - \frac{2}{R} + 2\left(\alpha + \frac{1}{R}\right)\exp(-2\alpha R), \tag{B7}$$

$$\begin{aligned} t' = {} & \alpha^2 \exp(-\alpha R)\left(1 + \alpha R + \frac{1}{3}\alpha^2 R^2\right) - 4\alpha \exp(-\alpha R) \\ & \times (1 + \alpha R), \end{aligned} \tag{B8}$$

$$U' = \frac{5}{4}\alpha, \tag{B9}$$

$$K' = \frac{2}{R} - \alpha \exp(-2\alpha R)\left[\frac{2}{\alpha R} + \frac{3}{2}\alpha R + \frac{1}{3}(\alpha R)^2 + \frac{11}{4}\right], \tag{B10}$$

$$\begin{aligned} V' = \alpha\Bigg\{ & \exp(-\alpha R)\left[2\alpha R + \frac{1}{4} + \frac{5}{8\alpha R}\right] - \frac{1}{4}\exp(-3\alpha R) \\ & \times \left(1 + \frac{5}{2\alpha R}\right)\Bigg\}, \end{aligned} \tag{B11}$$

$$\begin{aligned} J' = {} & \frac{12}{5R}[S^2 C + S^2 \ln(\alpha R) - 2SS' \,\mathrm{Ei}(-2\alpha R) \\ & + (S')^2 \,\mathrm{Ei}(-4\alpha R)] + \alpha \exp(-2\alpha R) \\ & \times \left[\frac{5}{4} - \frac{23}{10}\alpha R - \frac{6}{5}\alpha^2 R^2 - \frac{2}{15}\alpha^3 R^3\right], \end{aligned} \tag{B12}$$

where

$$\mathrm{Ei}(-x) \equiv -\int_x^\infty \frac{dt}{t}\exp(-t), \tag{B13}$$

$C = 0.577\,22$ is the Euler constant, and

$$S = \exp(-\alpha R)\left(1 + \alpha R + \frac{1}{3}\alpha^2 R^2\right),$$

$$S' = \exp(\alpha R)\left(1 - \alpha R + \frac{1}{3}\alpha^2 R^2\right). \tag{B14}$$

The quantity S is the overlap integral. Equations (B7)–(B14) are used when optimizing the energies with respect to α (and R, if a minimum appears).

APPENDIX C: ZERO-POINT MOTION OF IONS

The quantum correction to static configuration of ions (protons in the cases of the H_2 molecule or the Hubbard chain of H atoms) relies on estimating their zero-point oscillations. This can be done relatively simply if one introduces the momentum (δP) and position (δR) uncertainties so that the energy of such oscillations per ion is

$$\Delta E = \frac{(\delta P)^2}{2M} + \frac{1}{2}\left(\frac{e^2}{R + \delta R} + \frac{e^2}{R - \delta R}\right). \tag{C1}$$

For $\delta R \ll R$ we can write

$$\Delta E = \frac{(\delta P)^2}{2M} + \frac{e^2}{R} + 2\frac{e^2}{R}\left(\frac{\delta R}{R}\right)^2. \tag{C2}$$

Introducing the uncertainty relation $(\delta P)^2(\delta R)^2 \geqslant \frac{3}{4}\hbar^2$, we will have in the minimal situation

$$\Delta E = \frac{e^2}{R} + \frac{1}{2M}\frac{3\hbar^2}{4(\delta R)^2} + \frac{k}{2}(\delta R)^2, \tag{C3}$$

with the elastic constant $k = 4e^2/R^3$. Minimizing this expression with respect to δR we obtain $\delta R = [3\hbar^2/(2Mk)]^{1/4}$, and the energy

$$\Delta E = \frac{e^2}{R} + \hbar\left(\frac{3k}{2M}\right)^{1/2}. \tag{C4}$$

The first term provides the classical Coulomb repulsion between nearest neighbors, while the second represents zero-point contribution with frequency $\omega = (6e^2/MR^3)^{1/2}$. In atomic units this contribution amounts to the energy

$$\Delta E = 2\sqrt{6}\left[\frac{m}{M}\left(\frac{a_0}{R}\right)^3\right]^{1/2} \approx \frac{1.1}{15}\left(\frac{a_0}{R}\right)^{3/2}, \tag{C5}$$

if the mass of the proton is taken for M and m is the electron mass. This contribution is small if $R > a_0$, but may be significant for obtaining the detailed energy balance. A better estimate for the Hubbard chain would be to take into account the phonons, as well as the change in the electron-ion attraction.

APPENDIX D: RENORMALIZED WAVE EQUATION FOR THE He ATOM AND H^- ION

The renormalized wave equation for other two-electron systems, the H^- ion and He atom, can be obtained relatively easily for the ground state, since it involves two electrons on the same lattice. In the He atom case the eigenvalue of the $1s^2$ state is $\lambda_1 = 2\epsilon_a + U$, and the renormalized wave equation reduces to the usual Hartree equation

$$\left(\nabla^2 - \frac{Ze^2}{r}\right)\Psi(\mathbf{r}) + \Psi(\mathbf{r})\int d^3r' \frac{e^2}{|\mathbf{r} - \mathbf{r}'|}|\Psi(\mathbf{r}')|^2 = E\Psi(\mathbf{r}), \tag{D1}$$

where $Z = 2$. Taking $1s$-type wave functions for both electrons, we obtain the ground-state energy in the atomic units in the form $E = 2\alpha^2 - \frac{27}{4}\alpha$, the standard value of $\alpha = 27/16$, and the corresponding energy $E = -5.695$ Ry.[17]

The same type of treatment of H^- (with $Z = 1$) does not provide a stable H^- state. The reason is the assumption that both electrons are in a $1s^2$-like state. However, this circumstance does not invalidate the whole approach in this test case.

Namely, to overcome the problem for the H^- ion one needs to resort to a more involved approach going beyond the scope of the present paper. Let us only note that one can understand the nature of the problem in the following physical way. The first electron occupies the $1s$ state with $\Psi(\mathbf{r}) = (\alpha^3/\pi)^{1/2}\exp(-\alpha r)$. Substituting this into the integral appearing in Eq. (D1) one obtains the effective wave equation for the second electron in the form (in the atomic units):

$$\left(-\nabla^2 - \frac{2}{r}\right)\Psi(\mathbf{r}) + \left[\frac{2}{r} - 2\alpha\exp(-2\alpha r)\left(1+\frac{1}{\alpha r}\right)\right]\Psi(\mathbf{r}) = E\Psi(\mathbf{r}). \tag{D2}$$

Note that the *e-e* repulsion *cancels out completely* the attraction to the nucleus. However, what is left is an attractive potential so that its renormalized wave equation reads

$$-\nabla^2\Psi(\mathbf{r}) - 2\alpha\left(1+\frac{1}{\alpha r}\right)\exp(-2\alpha r)\Psi(\mathbf{r}) = E\Psi(\mathbf{r}). \tag{D3}$$

For $r \ll 1$ the effective potential has the Yukawa form and for $r \gg 1$ the exponential form. This central potential has always bound states. So, the second electron is indeed bound and the whole H^- system is stable. Subsequently, one should antisymmetrize the product of the two functions. Nonetheless, the numerical discussion requires a more detailed treatment and will be presented elsewhere.

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