Density-matrix functional theory of the Hubbard model: An exact numerical study

R. López-Sandoval
Laboratoire de Physique Quantique, Unité Mixte de Recherche 5626 du CNRS, Université Paul Sabatier, 118 route de Narbonne, F-31062 Toulouse Cedex, France

G. M. Pastor
Laboratoire de Physique Quantique, Unité Mixte de Recherche 5626 du CNRS, Université Paul Sabatier, 118 route de Narbonne, F-31062 Toulouse Cedex, France
and Institut für Theoretische Physik, Freie Universität Berlin, Arnimallee 14, D-14195 Berlin, Germany
(Received 19 July 1999)

A density-functional theory for many-body lattice models is considered in which the single-particle density matrix γ_{ij} is the basic variable. Eigenvalue equations are derived for solving Levy's constrained search of the interaction energy functional $W[\gamma_{ij}]$. $W[\gamma_{ij}]$ is expressed as the sum of Hartree-Fock energy $E_{\mathrm{HF}}[\gamma_{ij}]$ and the correlation energy $E_C[\gamma_{ij}]$. Exact results are obtained for $E_C(\gamma_{12})$ of the Hubbard model on various periodic lattices, where $\gamma_{ij}=\gamma_{12}$ for all nearest neighbors i and j. The functional dependence of $E_C(\gamma_{12})$ is analyzed by varying the number of sites N_a, band filling N_e, and lattice structure. The infinite one-dimensional chain and one-, two-, or three-dimensional finite clusters with periodic boundary conditions are considered. The properties of $E_C(\gamma_{12})$ are discussed in the limits of weak ($\gamma_{12}\simeq\gamma_{12}^0$) and strong ($\gamma_{12}\simeq\gamma_{12}^\infty$) electronic correlations, and in the crossover region ($\gamma_{12}^\infty\leqslant\gamma_{12}\leqslant\gamma_{12}^0$). Using an appropriate scaling we observe that $\varepsilon_C(g_{12})=E_C/E_{\mathrm{HF}}$ has a pseudo-universal behavior as a function of $g_{12}=(\gamma_{12}-\gamma_{12}^\infty)/(\gamma_{12}^0-\gamma_{12}^\infty)$. The fact that $\varepsilon_C(g_{12})$ depends weakly on N_a, N_e, and lattice structure suggests that the correlation energy of extended systems could be obtained quite accurately from finite-cluster calculations. Finally, the behaviors of $E_C(\gamma_{12})$ for repulsive ($U>0$) and attractive ($U<0$) interactions are contrasted.

I. INTRODUCTION

Density-functional theory (DFT) has been the subject of remarkable developments since its original formulation by Hohenberg and Kohn.[1,2] After formal improvements, extensions, and an uncountable number of applications to a wide variety of physical problems, this theoretical approach has become the most efficient, albeit not infallible, method of determining the electronic properties of matter from first principles.[3,4] The most important innovation of DFT, which is actually at the origin of its breakthrough, is to replace the wave function by the electronic density $\rho(\vec{r})$ as the fundamental variable of the many-body problem. In practice, density-functional (DF) calculations are largely based on the Kohn-Sham (KS) scheme that reduces the many-body N-particle problem to the solution of a set of self-consistent single-particle equations.[2] Although this transformation is formally exact, the implementations always require approximations, since the KS equations involve functional derivatives of the unknown interaction energy $W[\rho(\vec{r})]$, usually expressed in terms of the exchange and correlation (XC) energy $E_{\mathrm{XC}}[\rho(\vec{r})]$. Therefore, understanding the functional dependence of $E_{\mathrm{XC}}[\rho(\vec{r})]$ and improving its approximations are central to the development of DF methods. The currently most widespread *Ansätze* for $E_{\mathrm{XC}}[\rho(\vec{r})]$—the local-density approximation[2] with spin-polarized[5] and gradient-corrected extensions[6]—were originally derived from exact results for the homogeneous electron gas. It is one of the purposes of this paper to investigate the properties of the interaction-energy functional from an intrinsically inhomogeneous point of view, namely, by considering exactly solvable many-body lattice models.

Despite the remarkable success of the local-spin-density approximation, present DFT fails systematically in accounting for phenomena where strong electron correlations play a central role, for example, in heavy-fermion materials or high-T_c superconductors. These systems are usually described by simplifying the low-energy electron dynamics using parametrized lattice models such as Pariser-Parr-Pople,[7] Hubbard,[8] or Anderson[9] models and related Hamiltonians.[10] Being in principle an exact theory, the limitations of the DF approach have to be ascribed to the approximations used for exchange and correlation and not to the underlying Hohenberg-Kohn-Sham (HKS) formalism. It would be therefore very interesting to extend the range of applicability of DFT to strongly correlated systems and to characterize the properties E_{XC} in the limit of strong correlations. Studies of the XC functional on simple models should provide useful insights for future extensions to realistic Hamiltonians. Moreover, taking into account the demonstrated power of the DF approach in *ab initio* calculations, one may also expect that a DFT with an appropriate E_{XC} could become an efficient tool for studying many-body models, a subject of theoretical interest on its own.

Several properties of DFT on lattice models have been already studied in previous works.[11–13] Gunnarsson and Schönhammer were, to our knowledge, the first to propose a DF approach on a semiconductor model in order to study the band-gap problem.[11] In this case the local site occupancies were treated as the basic variables. Some years later Schindlmayr and Godby[12] provided a different formulation of DFT

on a lattice by considering as basic variables both diagonal elements γ_{ii} and off-diagonal elements γ_{ij} of the single-particle density matrix (see also Refs. 14–16). Schönhammer *et al.* then derived a more general framework that unifies the two previous approaches.[13] Using Levy's constrained search method[17] they showed that different basic variables and different W functionals can be considered depending on the type of model or perturbation under study. Site occupations alone may be used as basic variables, if only the orbital energies are varied (i.e., if all hopping integrals t_{ij} are kept constant for $i \neq j$). However, off-diagonal elements of the single-particle density matrix must be included explicitly if the functional W is intended to be applied to more general situations involving different values of t_{ij}, for example, the Hubbard model on various lattice structures or for different interaction regimes, i.e., different U/t.

In this paper we investigate the properties of Levy's interaction-energy functional W as a function of γ_{ij} by solving the constrained search minimization problem exactly. In Sec. II the basic formalism of density-matrix functional theory (DMFT) on lattice models is recalled and the equations for determining $W[\gamma_{ij}]$ are derived. Section III presents and discusses exact results for the correlation energy E_C of the Hubbard model, which is given by the difference between W and the Hartree-Fock (HF) energy E_{HF}. These are obtained, either numerically for finite clusters with different lattice structures, or from the Bethe-Ansatz solution for the one-dimensional chain. Finally, Sec. IV summarizes our conclusions and points out some relevant extensions.

II. THEORY

In Sec. II A the main results of Levy's formulation of DMFT are presented in a form that is appropriate for the study of model Hamiltonians such as the Hubbard model. Here the hopping integrals t_{ij} between sites (or orbitals) i and j play the role given in conventional DFT to the external potential $V_{\mathrm{ext}}(\vec{r})$. Consequently, the single-particle density matrix γ_{ij} replaces the density $\rho(\vec{r})$ as the basic variable.[12–16] In Sec. II B, we derive equations that allow to determine Levy's interaction-energy functional $W[\gamma_{ij}]$ in terms of the ground-state energy of a many-body Hamiltonian with effective hopping integrals λ_{ij} that depend implicitly on γ_{ij}.

A. DMFT of lattice models

We consider the many-body Hamiltonian

$$H=\sum_{ij\sigma} t_{ij}\hat{c}^{\dagger}_{i\sigma}\hat{c}_{j\sigma}+\frac{1}{2}\sum_{\substack{ijkl\\ \sigma\sigma'}} V_{ijkl}\hat{c}^{\dagger}_{i\sigma}\hat{c}^{\dagger}_{k\sigma'}\hat{c}_{l\sigma'}\hat{c}_{j\sigma}, \quad (2.1)$$

where $\hat{c}^{\dagger}_{i\sigma}$ ($\hat{c}_{i\sigma}$) is the usual creation (annihilation) operator for an electron with spin σ at site (or orbital) i. H can be regarded as the second quantization of Schrödinger's equation on a basis.[18] However, in the present paper, the hopping integrals t_{ij} and the interaction matrix elements V_{ijkl} are taken as parameters to be varied independently. The matrix t_{ij} defines the lattice (e.g., one-dimensional chains, square or triangular two-dimensional lattices) and the range of single-particle interactions (e.g., up to first or second neighbors). From the *ab initio* perspective t_{ij} is given by the external potential and by the choice of the basis.[18] V_{ijkl} defines the type of many-body interactions which may be repulsive (Coulomb like) or attractive (in order to simulate electronic pairing) and which are usually approximated as short ranged (e.g., intra-atomic). Equation (2.1) is mainly used in this section to derive general results which can then be applied to various specific models by simplifying the interactions. A particularly relevant example, to be considered in some detail in Sec. III, is the single-band Hubbard model with nearest-neighbor (NN) hoppings,[8] which can be obtained from Eq. (2.1) by setting $t_{ij}=-t$ for i and j NN's, $t_{ij}=0$ otherwise, and $V_{ijkl}=U\delta_{ij}\delta_{kl}\delta_{ik}$.[7,10]

In order to apply DMFT to model Hamiltonians of form (2.1) we follow Levy's constrained search procedure[17] as proposed by Schindlmayr and Godby.[12] The ground-state energy is determined by minimizing the functional

$$E[\gamma_{ij}]=E_K[\gamma_{ij}]+W[\gamma_{ij}] \quad (2.2)$$

with respect to the single-particle density matrix γ_{ij}. $E[\gamma_{ij}]$ is physically defined for all density matrices that can be written as

$$\gamma_{ij}=\sum_{\sigma}\gamma_{ij\sigma}=\sum_{\sigma}\langle\Psi|c^{\dagger}_{i\sigma}c_{j\sigma}|\Psi\rangle \quad (2.3)$$

for all i and j, where $|\Psi\rangle$ is an N-particle state. In other words, γ_{ij} must derive from a physical state. It is then said to be pure-state N representable.[19,20] The first term in Eq. (2.2) is given by

$$E_K=\sum_{ij} t_{ij}\gamma_{ij}. \quad (2.4)$$

It includes all single-particle contributions and is usually regarded as the kinetic energy associated with the electronic motion in the lattice. Notice that Eq. (2.4) yields the exact kinetic energy for a given γ_{ij}. There are no corrections on E_K to be included in other parts of the functional as in the KS approach. The second term in Eq. (2.2) is the interaction-energy functional given by[17]

$$W[\gamma_{ij}]=\min\left[\frac{1}{2}\sum_{\substack{nmkl\\ \sigma\sigma'}} V_{nmkl}\langle\Psi[\gamma_{ij}]|\hat{c}^{\dagger}_{n\sigma}\hat{c}^{\dagger}_{k\sigma'}\hat{c}_{l\sigma'}\hat{c}_{m\sigma}|\Psi[\gamma_{ij}]\rangle\right]. \quad (2.5)$$

The minimization in Eq. (2.5) implies a search over all N-particles states $|\Psi[\gamma_{ij}]\rangle$ that satisfy $\langle\Psi[\gamma_{ij}]|\Sigma_{\sigma}\hat{c}^{\dagger}_{i\sigma}\hat{c}_{j\sigma}|\Psi[\gamma_{ij}]\rangle=\gamma_{ij}$ for all i and j. Therefore, $W[\gamma_{ij}]$ represents the minimum value of the interaction energy compatible with a given density matrix γ_{ij}. W is usually expressed in terms of the Hartree-Fock energy

$$E_{\mathrm{HF}}[\gamma_{ij}]=\frac{1}{2}\sum_{\substack{ijkl\\ \sigma\sigma'}} V_{ijkl}(\gamma_{ij\sigma}\gamma_{kl\sigma'}-\delta_{\sigma\sigma'}\gamma_{il\sigma}\gamma_{kj\sigma}) \quad (2.6)$$

and the correlation energy $E_C[\gamma_{ij}]$ as

$$W[\gamma_{ij}]=E_{\rm HF}[\gamma_{ij}]+E_C[\gamma_{ij}]. \tag{2.7}$$

W and E_C are universal functionals of γ_{ij} in the sense that they are independent of t_{ij}, i.e., of the system under study. They depend on the considered interactions or model, as defined by V_{ijkl}, on the number of electrons N_e, and on the structure of the many-body Hilbert space, as given by N_e and the number of orbitals or sites N_a. Notice that E_C in Eq. (2.7) does not include any exchange contributions. Given γ_{ij} ($\gamma_{ij\sigma}=\gamma_{ij}/2$ in nonmagnetic cases) there is no need to approximate the exchange term, which is taken into account exactly by $E_{\rm HF}$ [Eq. (2.6)]. Nevertheless, if useful in practice, it is of course possible to split W in the Hartree energy E_H and the exchange and correlation energy $E_{\rm XC}$ is a similar way as in the KS approach.

The variational principle results from the relations[17]

$$E_{gs}\leqslant\sum_{ij}\ t_{ij}\gamma_{ij}+W[\gamma_{ij}] \tag{2.8}$$

for all pure-state N-representable γ_{ij},[19] and

$$E_{gs}=\sum_{ij}\ t_{ij}\gamma_{ij}^{gs}+W[\gamma_{ij}^{gs}], \tag{2.9}$$

where $E_{gs}=\langle\Psi_{gs}|H|\Psi_{gs}\rangle$ refers to the ground-state energy and $\gamma_{ij}^{gs}=\langle\Psi_{gs}|\Sigma_\sigma\hat{c}_{i\sigma}^\dagger\hat{c}_{j\sigma}|\Psi_{gs}\rangle$ to the ground-state single-particle density matrix.

As already pointed out in previous works,[12,13] W and E_C depend in general on both diagonal elements γ_{ii} and off-diagonal elements γ_{ij} of the density matrix, since the hopping integrals t_{ij} are nonlocal in the sites. The situation is similar to the DF approach proposed by Gilbert for the study of non-local potentials $V_{ext}(\vec{r},\vec{r}')$ as those appearing in the theory of pseudo-potentials.[14–16] A formulation of DFT on a lattice only in terms of γ_{ii} would be possible if one would restrict oneself to a family of models with constant t_{ij} for $i\neq j$. However, in this case the functional $W[\gamma_{ii}]$ would depend on the actual value of t_{ij} for $i\neq j$.[13]

The functional $W[\gamma_{ij}]$, valid for all lattice structures and for all types of hybridizations, can be simplified at the expense of universality if the hopping integrals are short ranged. For example, if only NN hoppings are considered, the kinetic energy E_K is independent of the density-matrix elements between sites that are not NN's. Therefore, the constrained search in Eq. (2.5) may restricted to the $|\Psi[\gamma_{ij}]\rangle$ that satisfy $\langle\Psi[\gamma_{ij}]|\Sigma_\sigma\hat{c}_{i\sigma}^\dagger\hat{c}_{j\sigma}|\Psi[\gamma_{ij}]\rangle=\gamma_{ij}$ only for $i=j$ and for NN ij. In this way the number of variables in $W[\gamma_{ij}]$ is reduced significantly, rendering the interpretation of the functional dependence far simpler. While this is a great practical advantage, it also implies that W and E_C lose their universal character since the dependence on the NN γ_{ij} is now different for different lattices. In Sec. III results for one-, two-, and three-dimensional lattices with NN hoppings are compared in order to quantify this effect.

For the applications in Sec. III we shall consider the single-band Hubbard model with NN hoppings, which in the usual notation is given by[8]

$$H=-t\sum_{\langle i,j\rangle\sigma}\ \hat{c}_{i\sigma}^\dagger\hat{c}_{j\sigma}+U\sum_i\ \hat{n}_{i\downarrow}\hat{n}_{i\uparrow}. \tag{2.10}$$

In this case the interaction energy functional reads

$$W[\gamma_{ij}]=\min\left[U\sum_l\ \langle\Psi[\gamma_{ij}]|\hat{n}_{l\uparrow}\hat{n}_{l\downarrow}|\Psi[\gamma_{ij}]\rangle\right], \tag{2.11}$$

where the minimization is performed with respect to all N-particle $|\Psi[\gamma_{ij}]\rangle$, satisfying $\langle\Psi[\gamma_{ij}]|\Sigma_\sigma\hat{c}_{i\sigma}^\dagger\hat{c}_{j\sigma}|\Psi[\gamma_{ij}]\rangle=\gamma_{ij}$ for i and j NN's. If the interactions are repulsive ($U>0$) $W[\gamma_{ij}]$ represents the minimum average number of double occupations which can be obtained for a given degree of electron delocalization, i.e., for a given value of γ_{ij}. For attractive interactions ($U<0$) double occupations are favored, and $W[\gamma_{ij}]$ corresponds to the maximum of $\Sigma_l\langle\hat{n}_{l\uparrow}\hat{n}_{l\downarrow}\rangle$ for a given γ_{ij}.

B. Exact interaction energy functional

In order to determine $E_C[\gamma_{ij}]$ and $W[\gamma_{ij}]$, we look for the extremes of

$$F=\sum_{\substack{ijkl\\\sigma\sigma'}}\ [V_{ijkl}\langle\Psi|\hat{c}_{i\sigma}^\dagger\hat{c}_{k\sigma'}^\dagger\hat{c}_{l\sigma}\hat{c}_{j\sigma}|\Psi\rangle]+\varepsilon(1-\langle\Psi|\Psi\rangle)+\sum_{i,j}\ \lambda_{ij}\left(\langle\Psi|\sum_\sigma\ \hat{c}_{i\sigma}^\dagger\hat{c}_{j\sigma}|\Psi\rangle-\gamma_{ij}\right) \tag{2.12}$$

with respect to $|\Psi\rangle$. Lagrange multipliers ε and λ_{ij} have been introduced to enforce the normalization of $|\Psi\rangle$ and the conditions on the representability of γ_{ij}. Derivation with respect to $\langle\Psi|$, ε and λ_{ij} yields the eigenvalue equations

$$\sum_{ij\sigma}\ \lambda_{ij}\hat{c}_{i\sigma}^\dagger\hat{c}_{j\sigma}|\Psi\rangle+\sum_{\substack{ijkl\\\sigma\sigma'}}\ V_{ijkl}\hat{c}_{i\sigma}^\dagger\hat{c}_{k\sigma'}^\dagger\hat{c}_{l\sigma}\hat{c}_{j\sigma}|\Psi\rangle=\varepsilon|\Psi\rangle \tag{2.13}$$

and the auxiliary conditions $\langle\Psi|\Psi\rangle=1$ and $\gamma_{ij}=\langle\Psi|\Sigma_\sigma\hat{c}_{i\sigma}^\dagger\hat{c}_{j\sigma}|\Psi\rangle$. The Lagrange multipliers λ_{ij} play the role of hopping integrals to be chosen in order that $|\Psi\rangle$ yields the given γ_{ij}. The pure-state representability of γ_{ij} ensures that there is always a solution.[19] In practice, however, one usually varies λ_{ij} in order to scan the domain of representability of γ_{ij}. For given λ_{ij}, the eigenstate $|\Psi_0\rangle$ corresponding to the lowest eigenvalue of Eq. (2.13) yields the minimum $W[\gamma_{ij}]$ for $\gamma_{ij}=\langle\Psi_0|\Sigma_\sigma\hat{c}_{i\sigma}^\dagger\hat{c}_{j\sigma}|\Psi_0\rangle$. Any other $|\Psi\rangle$ satisfying $\gamma_{ij}=\langle\Psi|\Sigma_\sigma\hat{c}_{i\sigma}^\dagger\hat{c}_{j\sigma}|\Psi\rangle$ would have higher ε and thus higher W. The subset of γ_{ij} which are representable by a ground state of Eq. (2.13) is the physically relevant one, since it necessarily includes the absolute minimum γ_{ij}^{gs} of $E[\gamma_{ij}]$. Nevertheless, it should be noted that pure-state representable γ_{ij} may be considered that can only be represented by excited states or by linear combinations of eigenstates of Eq. (2.13). In the later case, $\lambda_{ij}=0\forall ij$, and $|\Psi_0\rangle$ is an eigenstate of the interaction term with lowest eigenvalue. Examples shall be discussed in Sec. III.

For the Hubbard model Eq. (2.13) reduces to

$$\sum_{\substack{\langle ij\rangle\\\sigma}}\ \lambda_{ij}\hat{c}_{i\sigma}^\dagger\hat{c}_{j\sigma}|\Psi\rangle+U\sum_i\ \hat{n}_{i\uparrow}\hat{n}_{i\downarrow}|\Psi\rangle=\varepsilon|\Psi\rangle. \tag{2.14}$$

This eigenvalue problem can be solved numerically for clusters with different lattice structures and periodic boundary conditions. In this case we expand $|\Psi[\gamma_{ij}]\rangle$ in a complete set of basis states $|\Phi_m\rangle$ which have definite occupation numbers $\nu_{i\sigma}^m$ at all orbitals $i\sigma$ ($\hat{n}_{i\sigma}|\Phi_m\rangle=\nu_{i\sigma}^m|\Phi_m\rangle$ with $\nu_{i\sigma}^m=0$ or 1). The values of $\nu_{i\sigma}^m$ satisfy the usual conservation of the number of electrons $N_e=N_{e\uparrow}+N_{e\downarrow}$ and of the z component of the total spin $S_z=(N_{e\uparrow}-N_{e\downarrow})/2$, where $N_{e\sigma}=\Sigma_i\nu_{i\sigma}^m$. For not too large clusters, the lowest energy $|\Psi_0[\gamma_{ij}]\rangle$—the ground state of Eq. (2.14)—can be determined by sparse-matrix diagonalization procedures, for example, by using the Lanczos iterative method.[21] $|\Psi_0[\gamma_{ij}]\rangle$ is calculated in the subspace of minimal S_z, since this ensures that there are no *a priori* restrictions on the total spin S. In addition, spin-projector operators may be used to study the dependence of $E_C(\gamma_{12})$ on S.

For a one-dimensional (1D) chain with NN hoppings $t_{ij}=t$, translational symmetry implies equal density-matrix elements γ_{ij} between NN's. Therefore, one may set $\lambda_{ij}=\lambda$ for all NN's ij, and then Eq. (2.14) has the same form as the 1D Hubbard model for which Lieb and Wu's exact solution is available.[22] In this case the lowest eigenvalue ε is determined following the work by Shiba.[23] The coupled Bethe-Ansatz equations are solved as a function of λ, band-filling $n=N_e/N_a$, and for positive and negative U, by means of a simple iterative procedure.

III. RESULTS AND DISCUSSION

In this section we present and discuss exact results for the correlation energy functional $E_C[\gamma_{ij}]$ of the single-band Hubbard Hamiltonian with nearest neighbor hoppings.[8] Given the lattice structures, N_a and N_e, the model is characterized by the dimensionless parameter U/t which measures the competition between kinetic and interaction energies [see Eq. (2.10)]. $U>0$ corresponds to the usual intra-atomic repulsive Coulomb interaction, while the attractive case ($U<0$) simulates intra-atomic pairing of electrons.

A. Repulsive interaction $U>0$

In Fig. 1 the correlation energy E_C of the 1D Hubbard model is shown for half-band filling ($N_e=N_a$) as a function of the density-matrix element or bond order γ_{12} between NN's. $\gamma_{ij}=\gamma_{12}$ for all NN's i and j. Results are given for rings of finite length N_a as well as for the infinite chain. Several general qualitative features may be identified. First of all we observe that on bipartite lattices $E_C(\gamma_{12})=E_C(-\gamma_{12})$, since the sign of the NN bond order can be changed without affecting the interaction energy $W(\gamma_{12})$ by changing the phase of the local orbitals at one of the sublattices ($c_{i\sigma}\rightarrow -c_{i\sigma}$ for $i\in A$ and $c_{j\sigma}$ unchanged for $j\in B$, where A and B refer to the sublattices).[24,25] Let us recall that the domain of definition of $E_C(\gamma_{12})$ is limited by the pure-state representability of γ_{ij}. The upper bound γ_{12}^{0+} and the lower bound γ_{12}^{0-} for γ_{12} ($\gamma_{12}^{0+}=-\gamma_{12}^{0-}=\gamma_{12}^0$ on bipartite lattices) are the extreme values of the bond order between NN's on a given lattice and for given N_a and N_e ($\gamma_{ij}=\gamma_{12}$ for all NN's ij). They represent the maximum degree of electron delocalization. γ_{12}^{0+} and γ_{12}^{0-} correspond to the extremes of the kinetic energy E_K ($E_K=\Sigma_{\langle ij\rangle}t_{ij}\gamma_{ij}=zN_a/2\gamma_{12}$, where z is the coordination number) and thus to the ground state of the Hubbard model for $U=0$ [γ_{12}^{0+} for $t>0$ and γ_{12}^{0-} for $t<0$; see Eq. (2.10)]. For $\gamma_{12}=\gamma_{12}^0$ the underlying electronic state $|\Psi_0\rangle$ is usually a single Slater determinant, and therefore $E_C(\gamma_{12}^0)=0$. In other words, the correlation energy vanishes as expected in the fully delocalized limit.[26] As $|\gamma_{12}|$ decreases E_C decreases ($E_C<0$), since correlations can reduce the Coulomb energy more and more efficiently as the electrons localize. E_C is minimum in the strongly correlated limit $\gamma_{12}=\gamma_{12}^\infty$. For half-band filling this corresponds to a fully localized electronic state ($\gamma_{12}^\infty=0$). Here E_C cancels out the Hartree-Fock energy $E_{\rm HF}$ and the Coulomb energy W vanishes ($E_C^\infty=-E_{\rm HF}$).[27] The ground-state values of γ_{12}^{gs} and E_{gs} for a given U/t result from the competition between lowering E_C by decreasing γ_{12} and lowering E_K by increasing it ($t>0$). The divergence of $\partial E_C/\partial\gamma_{12}$ for $\gamma_{12}=\gamma_{12}^0$ is a necessary condition in order that $\gamma_{12}^{gs}<\gamma_{12}^0$ for arbitrarily small $U>0$. On the other side, for small γ_{12}, we observe that $(E_C+E_{\rm HF})\propto\gamma_{12}^2$. This implies that for $U/t\gg 1$, $\gamma_{12}^{gs}\propto t/U$ and $E_{gs}\propto t^2/U$, a well-known result in the Heisenberg limit of the Hubbard model ($N_e=N_a$).[10]

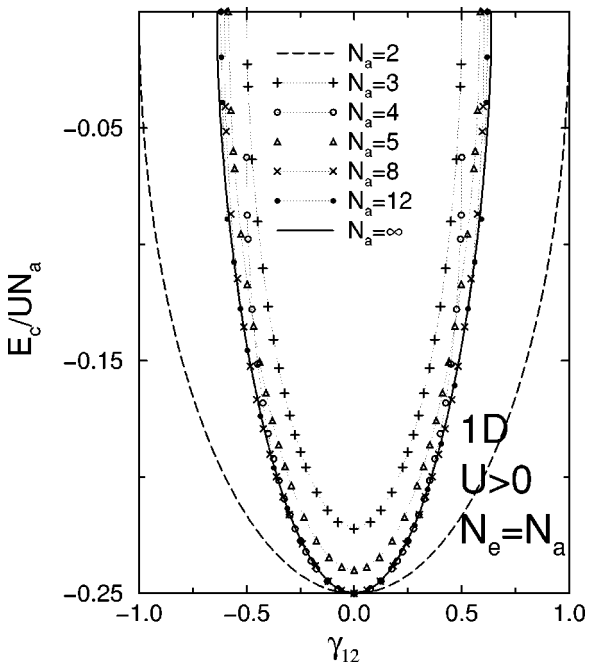

FIG. 1. Correlation energy E_C of the Hubbard model on one-dimensional rings with N_a sites and $N_e=N_a$ electrons as a function of the density-matrix element or bond order γ_{12} between nearest neighbors (NN). $\gamma_{ij}=\gamma_{12}$ for all NN's ij. U refers to the intra-atomic Coulomb repulsion [$U>0$, see Eq. (2.10)] (Ref. 24).

A more quantitative analysis of $E_C(\gamma_{12})$, and in particular the comparison of results for different N_a, is complicated by the size dependence of γ_{12}^0 and $E_{\rm HF}$. It is therefore useful to measure E_C in units of the Hartree-Fock energy and to bring the domains of representability to a common range by considering $\varepsilon_C=E_C/E_{\rm HF}$ as a function of $g_{12}=\gamma_{12}/\gamma_{12}^0$. Figure 2 shows that $\varepsilon_C(g_{12})$ has approximately the same behavior for all considered N_a. Finite-size effects are small except for the very small sizes. The largest deviations from the common trend are found for $N_a=N_e=4$. Here we observe a

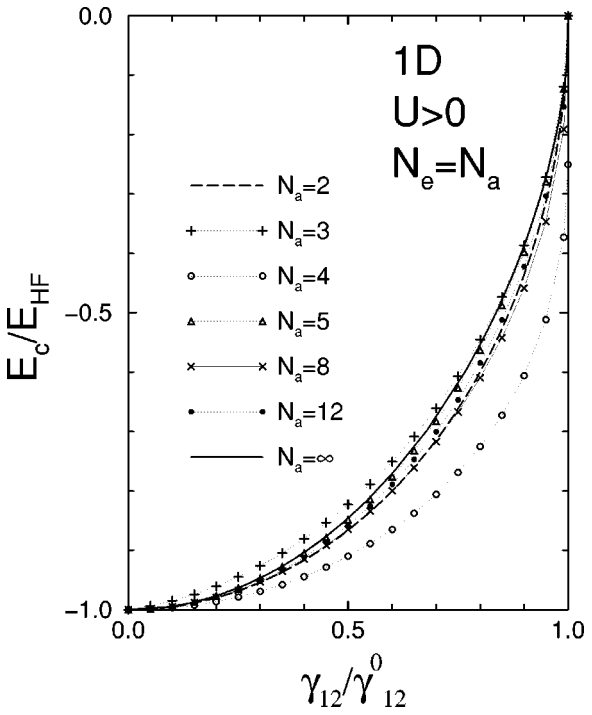

FIG. 2. Correlation energy E_C in units of the Hartree-Fock energy E_{HF} (Ref. 27) for the Hubbard model on one-dimensional rings. Results are given as a function of $\gamma_{12}/\gamma_{12}^0$, where γ_{12}^0 is the NN ground-state bond order in the uncorrelated limit ($U=0$). $\gamma_{ij}=\gamma_{12}$ for all NN's ij. N_a refers to the number of sites, and $N_e=N_a$ to the number of electrons. $E_C(\gamma_{12})=E_C(-\gamma_{12})$; see Fig. 1.

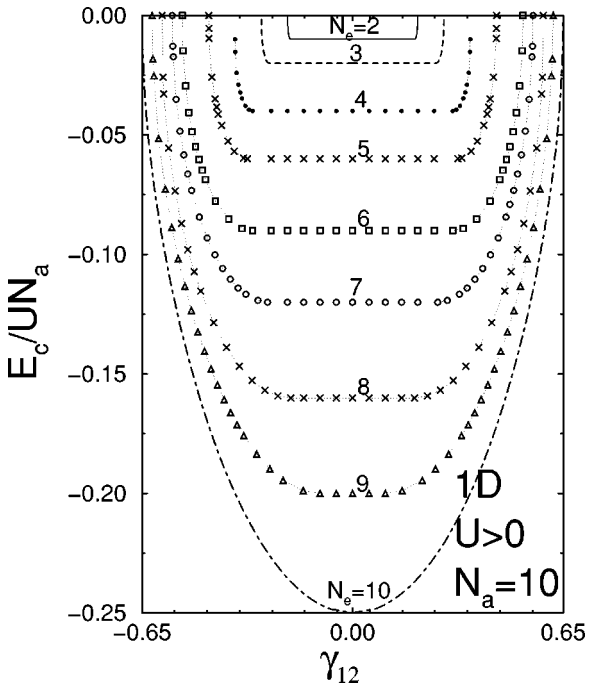

FIG. 3. Band-filling dependence of the correlation energy $E_C(\gamma_{12})$ of the one-dimensional Hubbard model for $N_a=10$ sites. $\gamma_{ij}=\gamma_{12}$ for all NN's ij. N_e refers to the number of electrons, and U to the intra-atomic Coulomb repulsion. On bipartite lattices $E_C(\gamma_{12},N_e)=E_C(-\gamma_{12},N_e)=E_C(\gamma_{12},2N_a-N_e)$ (Ref. 24).

discontinuous drop of ε_C for $g_{12}=1$ ($g_{12}<1$) which is due to the degeneracy of the single-particle spectrum. In fact in this case two of the four electrons occupy a doubly degenerate state in the uncorrelated limit and the minimum interaction energy $W(\gamma_{12})$ does not correspond to a single-Slater-determinant state even for $\gamma_{12}=\gamma_{12}^0$.[28] As N_a increases, $\varepsilon_C(g_{12})$ approaches the infinite-length limit with alternations around the $N_a=\infty$ curve. The strong similarity between $\varepsilon_C(g_{12})$ for small N_a and for $N_a=\infty$ is a remarkable result. It suggests that good approximations for $E_C(\gamma_{12})$ in extended systems could be derived from finite cluster calculations.

Figure 3 shows the band-filling dependence of $E_C(\gamma_{12})$ in a ten-site 1D Hubbard ring. Results are given for $N_e\leqslant N_a$, since for $N_e\geqslant N_a$, $E_C(\gamma_{ij},N_e)=E_C(-\gamma_{ij},2N_a-N_e)$ as a result of electron-hole symmetry.[24] Although $E_C(\gamma_{12})$ depends strongly on N_e, several qualitative properties are shared by all band fillings: (i) As in the half-filled band case, the domain of representability of γ_{12} is bound by the bond orders in the uncorrelated limits. In fact, $\gamma_{12}^{0-}\leqslant\gamma_{12}\leqslant\gamma_{12}^{0+}$, where γ_{12}^{0+} (γ_{12}^{0-}) corresponds to the ground state of the $U=0$ tight-binding model for $t>0$ ($t<0$). On bipartite lattices $\gamma_{12}^{0+}=-\gamma_{12}^{0-}=\gamma_{12}^0$. Notice that γ_{12}^0 increases monotonously with N_e as the single-particle band is filled up. This is an important contribution to the band-filling dependence of E_C (see Fig. 3). (ii) In the delocalized limit, $E_C(\gamma_{12}^0)=0$ for all the N_e for which $W(\gamma_{12}^0)$ derives from a single Slater determinant.[26] Moreover, the divergence of $\partial E_C/\partial\gamma_{12}$ for $\gamma_{12}=\gamma_{12}^0$ indicates that $\gamma_{12}^{gs}<\gamma_{12}^0$ for arbitrarily small $U>0$, as expected from perturbation theory. (iii) Starting from $\gamma_{12}=\gamma_{12}^0$, $E_C(\gamma_{12})$ decreases with decreasing γ_{12}, reaching its lowest possible value $E_C^\infty=-E_{\mathrm{HF}}$ for $\gamma_{12}=\gamma_{12}^{\infty+}$ ($N_e\leqslant N_a$). The same behavior is of course observed for $\gamma_{12}<0$. In particular, $E_C=-E_{\mathrm{HF}}$ also for $\gamma_{12}=\gamma_{12}^{\infty-}$. As shown in Fig. 3, E_C^∞ decreases rapidly with increasing N_e, since E_{HF} increases quadratically with the electron density.[27] (iv) On bipartite lattices $\gamma_{12}^{\infty+}=-\gamma_{12}^{\infty-}=\gamma_{12}^\infty$, while on nonbipartite structures one generally has $|\gamma_{12}^{\infty+}|\neq|\gamma_{12}^{\infty-}|$, since the single-particle spectrum is different for positive and negative energies. The decrease of E_C with decreasing $|\gamma_{12}|$ shows that the reduction of the Coulomb energy due to correlations is done at the expense of kinetic energy or electron delocalization, as already discussed for $N_e=N_a$ (Fig. 1). (v) $\gamma_{12}^\infty>0$ for all $N_e<N_a$ ($\gamma_{12}^\infty=0$ for $N_e=N_a$). γ_{12}^∞ represents the largest NN bond order that can be constructed under the constraint of vanishing Coulomb repulsion energy. A lower bound for γ_{12}^∞ is given by the bond order $\gamma_{12}^{\mathrm{FM}}$ in the fully polarized ferromagnetic state ($\gamma_{12}^\infty\geqslant\gamma_{12}^{\mathrm{FM}}$). This is obtained by occupying the lowest single-particle states with all electrons of the same spin ($N_e\leqslant N_a$). Therefore, $\gamma_{12}^{\mathrm{FM}}$ increases with N_e for $N_e\leqslant N_a/2$, and then decreases for $N_a/2<N_e\leqslant N_a$ reaching $\gamma_{12}^{\mathrm{FM}}=0$ at half-band filling ($\gamma_{12}^{\mathrm{FM}}>0$ for $N_e<N_a$). In this way the nonmonotonous dependence of γ_{12}^∞ on N_e can be explained (see Fig. 3). (vi) The correlation energy is constant and equal to $-E_{\mathrm{HF}}$ for $\gamma_{12}^{\infty-}\leqslant\gamma_{12}\leqslant\gamma_{12}^{\infty+}$. These values of γ_{12} can never correspond to the ground state of the Hubbard model, since in this range increasing γ_{12} always lowers the kinetic energy ($t>0$) without increasing the Coulomb repulsion ($\gamma_{12}^\infty\leqslant\gamma_{12}^{gs}\leqslant\gamma_{12}^0$). For $\gamma_{12}^{\infty-}<\gamma_{12}<\gamma_{12}^{\infty+}$, γ_{12} cannot be represented by a ground state of Eq. (2.14). In this range γ_{12} can be derived from a linear combination of states having minimal Coulomb repulsion.[29]

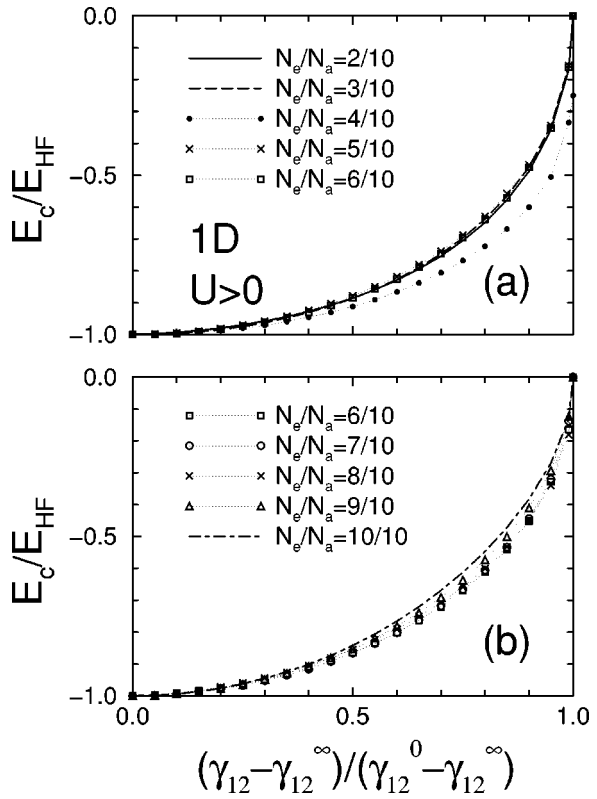

FIG. 4. Correlation energy E_C in units of the Hartree-Fock energy E_{HF} (Ref. 27) for the one-dimensional Hubbard model on a 1D ten-site ring. Results are given as a function of the degree of delocalization $g_{12}=(\gamma_{12}-\gamma_{12}^{\infty})/(\gamma_{12}^{0}-\gamma_{12}^{\infty})$, where γ_{12}^{0} refers to the NN bond order in the uncorrelated ground state ($U=0$), and γ_{12}^{∞} to the NN bond order in the strongly correlated limit ($U/t\rightarrow\infty$). As in Fig. 3, different band fillings N_e/N_a are considered: (a) $N_e\leqslant 6$ and (b) $N_e\geqslant 6$.

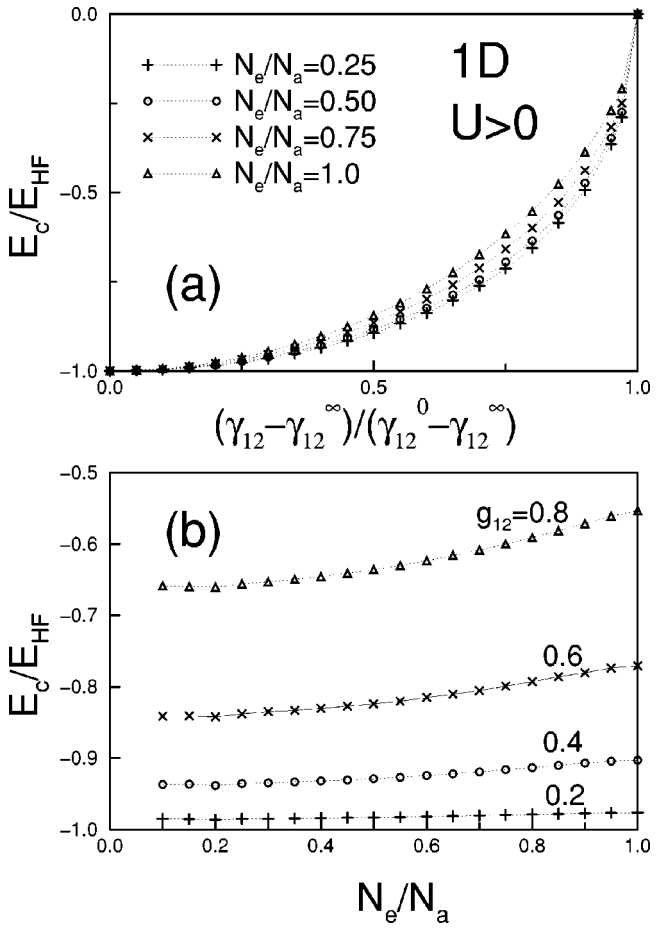

FIG. 5. Correlation energy E_C of the Hubbard model on the infinite one-dimensional chain. Results are given for $\varepsilon_C=E_C/E_{\mathrm{HF}}$ (E_{HF} is the Hartree-Fock energy) as a function of (a) $g_{12}=(\gamma_{12}-\gamma_{12}^{\infty})/(\gamma_{12}^{0}-\gamma_{12}^{\infty})$, and (b) band filling N_e/N_a (see the caption of Fig. 4).

In order to compare the functional dependences of the correlation energy for different band fillings, it is useful to scale E_C in units of the Hartree-Fock energy and to bring the relevant domains $\gamma_{12}^{\infty}\leqslant\gamma_{12}\leqslant\gamma_{12}^{0}$ of different N_e to a common range. In Fig. 4, $\varepsilon_C=E_C/E_{\mathrm{HF}}$ is shown as a function of $g_{12}=(\gamma_{12}-\gamma_{12}^{\infty})/(\gamma_{12}^{0}-\gamma_{12}^{\infty})$. We observe that the results for $\varepsilon_C(g_{12})$ are remarkably similar for all band fillings. The largest deviations from the common trend are found for $N_e=4$. As already discussed for $N_a=N_e=4$, this anomalous behavior is related to the degeneracy of the single-particle spectrum and to the finite size of system. Figure 4 shows that for the Hubbard model the largest part of the dependence of $E_C(\gamma_{12})$ on band filling comes from E_{HF}, γ_{12}^{0}, and γ_{12}^{∞}. Similar conclusions are drawn from the results for the infinite 1D chain presented in Fig. 5. For a given g_{12}, $\varepsilon_C(g_{12})$ depends weakly on N_e/N_a if the carrier density is low ($N_e/N_a\leqslant 0.4$), and tends to increase as we approach half-band filling [see Fig. 5(b)]. For high carrier densities it becomes comparatively more difficult to reduce the Coulomb energy for a given degree of delocalization g_{12}. The effect is most pronounced for $g_{12}\simeq 0.8$–0.9, i.e., close to the uncorrelated limit. As we approach the strongly correlated limit ($g_{12}\leqslant 0.4$), the dependence of ε_C on N_e/N_a is very weak even for $N_e/N_a\approx 1$. One concludes that $\varepsilon_C(g_{12})$ is a useful basis for introducing practical approximations on more complex systems.

The correlation energy E_C is a universal functional of the complete single-particle density matrix γ_{ij}. $E_C[\gamma_{ij}]$ and $W[\gamma_{ij}]$ may depend on N_a and N_e but are independent of t_{ij}, and in particular of the lattice structure. The functional $E_C(\gamma_{12})$ considered in this paper depends by definition on the type of lattice, since the constraints imposed in the minimization only apply to NN bonds. In order to investigate this problem we have determined $E_C(\gamma_{12})$ for 2D and 3D finite clusters having $N_a\leqslant 12$ sites and periodic boundary conditions. In Fig. 6 we compare these results with those of the 1D 12-site periodic ring. As shown in the inset figure, the qualitative behavior is in all cases very similar. The main quantitative differences come from the domain of representability of γ_{12}, i.e., from the values of γ_{12}^{0+} and γ_{12}^{0-} ($\gamma_{12}^{0-}\leqslant\gamma_{12}\leqslant\gamma_{12}^{0+}$). Once scaled as a function of $\gamma_{12}/\gamma_{12}^{0}$, E_C depends rather weakly on the lattice structure. Notice that the Hartree-Fock energy $E_{\mathrm{HF}}=(U/4)N_a$ is the same for all structures. However, for the bcc structure we obtain $W(\gamma_{12}^{0})<E_{\mathrm{HF}}$, i.e., $E_C(\gamma_{12}^{0})<0$, due to degeneracies in the single-particle spectrum of the considered finite cluster [see the inset of Fig. 6(b)]. In order to correct for this finite size effect it is here more appropriate to consider $\varepsilon_C=[E_C(\gamma_{12})-E_C(\gamma_{12}^{0})]/W(\gamma_{12}^{0})$. Still, the differences in ε_C between bcc and fcc structures appear to be more important than between square

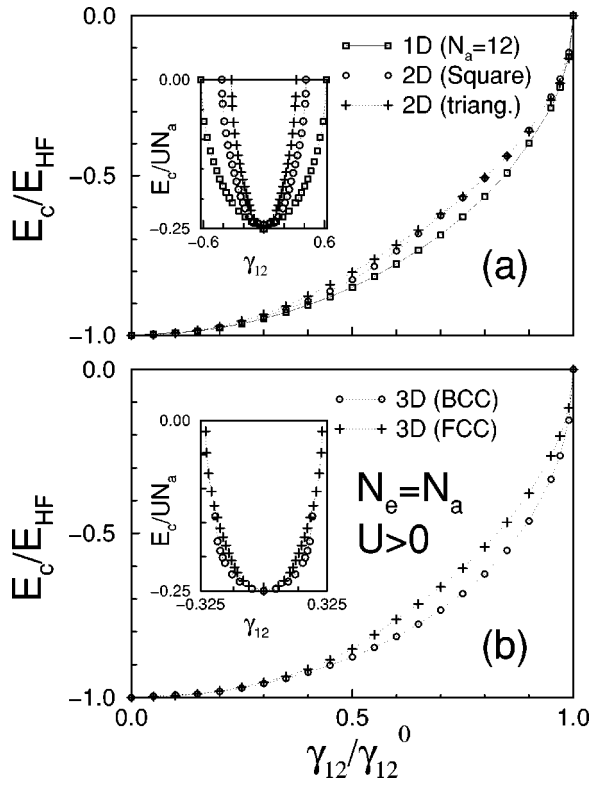

FIG. 6. Correlation energy $E_C(\gamma_{12})$ of the Hubbard model on different lattice structures. Finite clusters with periodic boundary conditions are considered at half-band filling: (a) a one-dimensional (1D) ring ($N_a=12$), 2D square and triangular lattices (3×4 clusters), and (b) 3D fcc and bcc lattices (two-tetrahedron cluster with $N_a=8$) (Ref. 28). U refers to the intra-atomic Coulomb repulsion ($U>0$). Notice the effect of scaling γ_{12} with the uncorrelated γ_{12}^0 by comparing main and inset figures.

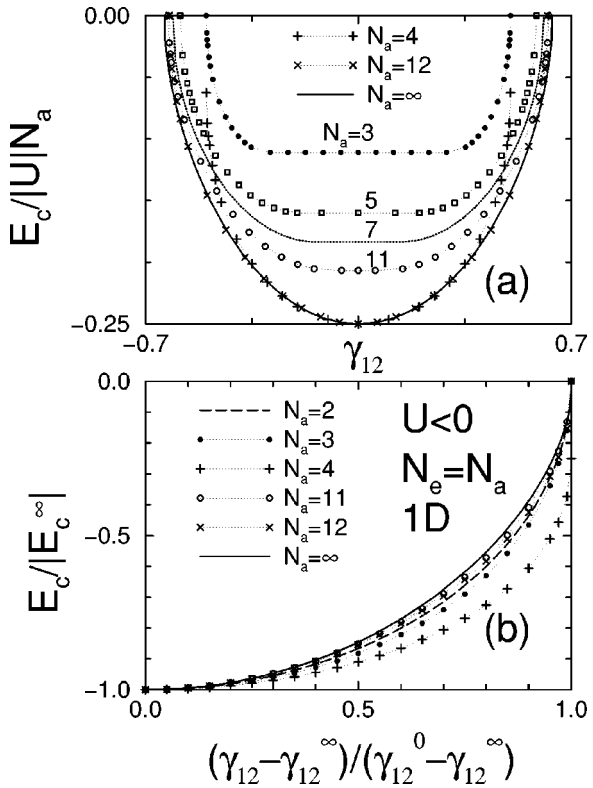

FIG. 7. Correlation energy E_C of the attractive Hubbard model ($U<0$) on one-dimensional rings with N_a sites and $N_e=N_a$ electrons. In (a) E_C is shown as a function of the density-matrix element γ_{12} between nearest neighbors (NN), $\gamma_{ij}=\gamma_{12}$ for all NN ij. In (b) $E_C/|E_C^\infty|$ is given as a function of the degree of delocalization $g_{12}=(\gamma_{12}-\gamma_{12}^\infty)/(\gamma_{12}^0-\gamma_{12}^\infty)$. See the caption of Fig. 4.

and triangular 2D lattices. This is probably related to the degeneracies in the spectrum of the bcc cluster, as already observed for rings with $N_e=4m$ [Figs. 2 and 4(a)].

The largest changes in ε_C for different lattice structures are observed for intermediate degree of delocalization ($g_{12}\simeq0.7$–0.9; see Fig. 6). Note that there is no monotonic trend as a function of the lattice dimension. For example, for $g_{12}=0.7$–0.9, ε_C first increases somewhat as we go from 1D to 2D lattices, but it then decreases coming close to the 1D curve for the 3D fcc lattice [$\varepsilon_C(\text{2D})>\varepsilon_C(\text{fcc})>\varepsilon_C(\text{1D})>\varepsilon_C(\text{bcc})$ for $0.7\leqslant g_{12}\leqslant0.9$]. Finally, it is worth noting that in the strongly correlated limit ($g_{12}\leqslant0.3$) the results for $\varepsilon_C(g_{12})$ are nearly the same for all considered lattice structures (see Fig. 6). This should be useful in order to develop simple general approximations to $E_C(\gamma_{12})$ in this limit.

B. Attractive interaction $U<0$

The attractive Hubbard model describes itinerant electrons with local intra-atomic pairing ($U<0$). The electronic correlations are very different from those found in the repulsive case discussed so far. In particular Levy's interaction energy functional $W[\gamma_{ij}]$ now corresponds to the maximum average number of double occupations for a given γ_{ij} [see Eq. (2.11)]. Therefore, it is also very interesting to investigate the properties of the correlation energy functional $E_C[\gamma_{ij}]$ for $U<0$, and to contrast them with the results of Sec. III A.

In Fig. 7 the correlation energy $E_C(\gamma_{12})$ of the attractive Hubbard model is given at half-band filling for various finite rings ($N_a\leqslant12$) and for the infinite 1D chain ($N_e=N_a$). The band-filling dependence of $E_C(\gamma_{12})$ is shown in Fig. 8 for a 12-site ring ($N_e\leqslant N_a=12$). As in the repulsive case, $\gamma_{12}^{0-}\leqslant\gamma_{12}\leqslant\gamma_{12}^{0+}$, since the domain of representability of γ_{12} is independent of the form or type of the interaction. Moreover, $E_C(\gamma_{12})=E_C(-\gamma_{12})$ due to the electron-hole symmetry of bipartite lattices.[24] Starting from γ_{12}^{0+} or γ_{12}^{0-} ($\gamma_{12}^{0+}=-\gamma_{12}^{0-}=\gamma_{12}^0$ on bipartite lattices), $E_C(\gamma_{12})$ decreases with decreasing $|\gamma_{12}|$ reaching the minimum E_C^∞ for $\gamma_{12}=\gamma_{12}^\infty$ and for $\gamma_{12}=\gamma_{12}^{\infty-}$ ($\gamma_{12}^{\infty+}=-\gamma_{12}^{\infty-}=\gamma_{12}^\infty$ in this case). For N_e even, $W(\gamma_{12}^\infty)=N_eU/2$, and for N_e odd, $W(\gamma_{12}^\infty)=(N_e-1)U/2$, which correspond to the maximum number of electron pairs that can be formed. For N_e even, the minimum $E_C^\infty=U(N_e/2)[1-N_e/(2N_a)]$ is achieved only for a complete electron localization (i.e, $\gamma_{12}^\infty=0$). In contrast, for odd N_e a finite-size effect is observed. In this case, one of the electrons remains unpaired even in the limit of strong electron correlations and the minimum of E_C is $E_C^\infty=U[(N_e-1)/2][1-(N_e+1)/(2N_a)]$. Moreover, nonvanishing γ_{12}^∞ are obtained as a result of the delocalization of the unpaired electron. γ_{12}^∞ represents the maximum bond order that can be obtained when $(N_e-1)/2$ electron pairs are formed (γ_{12}^∞

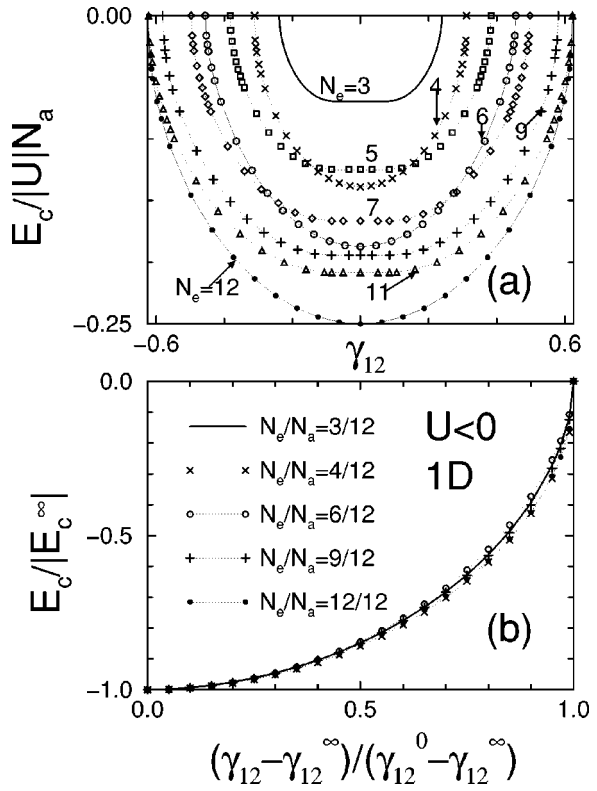

FIG. 8. Band-filling dependence of the correlation energy $E_C(\gamma_{12})$ of the one-dimensional attractive Hubbard model ($U<0$). The number of sites is $N_a=12$, and the number of electrons N_e is indicated. In (a) E_C is shown as a function of γ_{12} and in (b) $E_C/|E_C^\infty|$ is given as a function of the degree of delocalization $g_{12}=(\gamma_{12}-\gamma_{12}^\infty)/(\gamma_{12}^0-\gamma_{12}^\infty)$. Notice, $E_C(\gamma_{12},N_e)=E_C(-\gamma_{12},N_e)=E_C(\gamma_{12},2N_a-N_e)$ (Ref. 24).

$\to 0$ for $N_a\to\infty$, N_e odd). Notice that in all cases the ground state γ_{12}^{gs} is found in the interval $\gamma_{12}^\infty \leqslant \gamma_{12}^{gs} \leqslant \gamma_{12}^0$.

It is interesting to observe that $E_C(\gamma_{12})$ can be appropriately scaled in a similar way as for $U>0$. In Fig. 8(b), $\varepsilon_C(g_{12})=E_C/|E_C^\infty|$ is shown as a function of the degree of delocalization $g_{12}=(\gamma_{12}-\gamma_{12}^\infty)/(\gamma_{12}^0-\gamma_{12}^\infty)$. $\varepsilon_C(g_{12})$ presents a pseudouniversal behavior in the sense that it depends weakly on N_a and N_e. The main deviations from the common trend are found for $N_e=N_a=4$. As already discussed for $U>0$, this is a consequence of degeneracies in the single-particle spectrum. In this case, the wave function corresponding to the minimum in Levy's functional for $\gamma_{12}\to\gamma_{12}^0$ [Eq. (2.11)] cannot be described by a single Slater determinant, and $W(\gamma_{12}\to\gamma_{12}^0)<E_{\rm HF}$.

IV. CONCLUSION

Density-matrix functional theory has been applied to lattice Hamiltonians taking the Hubbard model as a particularly relevant example. In this framework the basic variable is the single-particle density matrix γ_{ij}, and the key unknown is the correlation energy functional $E_C[\gamma_{ij}]$. The challenge is therefore to determine $E_C[\gamma_{ij}]$ or to provide with useful accurate approximations for it. In this paper we presented a systematic study of the functional dependence of $E_C(\gamma_{12})$ on periodic lattices, where γ_{12} is the density-matrix element between nearest neighbors ($\gamma_{ij}=\gamma_{12}$ for all NN's ij). Based on finite-cluster exact diagonalizations and on the Bethe-Ansatz solution of the 1D chain, we derived rigorous results for $E_C(\gamma_{12})$ of the Hubbard model as a function of the number of sites N_a, band filling N_e/N_a, and lattice structure. A basis for applications of density-matrix functional theory to many-body lattice models is thereby provided. The observed pseudouniversal behavior of $\varepsilon_C(g_{12})=E_C/E_{\rm HF}$ as a function of $g_{12}=(\gamma_{12}-\gamma_{12}^\infty)/(\gamma_{12}^0-\gamma_{12}^\infty)$ encourages transferring $\varepsilon_C(g_{12})$ from finite-size systems to infinite lattices or even to different lattice geometries. In fact, the exact $E_C(\gamma_{12})$ of the Hubbard dimer has been recently used to infer a simple general *Ansatz* for $E_C(\gamma_{12})$.[30] With this approximation to $E_C(\gamma_{12})$ the ground-state energies and charge-excitation gaps of 1D and 2D lattices have been determined successfully in the whole range of U/t. Further investigations, for example, by considering magnetic impurity models or more complex multiband Hamiltonians, are certainly worthwhile.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the support of CONACyT-Mexico (R.L.S.) and the Alexander von Humboldt Foundation (G.M.P.), as well as computer resources provided by IDRIS (CNRS, France).

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[18] Given a basis set $\{\phi_i\}$, the hopping integrals are expressed as

$$t_{ij}=\int d^3r\phi_i^*(\vec{r})\left[-\frac{\hbar^2}{2m}\nabla^2+V_{\rm ext}(\vec{r})\right]\phi_j(\vec{r}),$$

and the matrix elements of the Coulomb interaction as

$$V_{ijkl}=e^2\int d^3r d^3r'\,\phi_i^*(\vec{r})\phi_k^*(\vec{r}')\frac{1}{|\vec{r}-\vec{r}'|}\phi_l(\vec{r}')\phi_j(\vec{r}).$$

[19] A single-particle density matrix γ_{ij} is said to be pure-state N representable if an N-particle state $|\Psi\rangle$ exists such that $\gamma_{ij}=\langle\Psi|\Sigma_\sigma\hat{c}_{i\sigma}^\dagger\hat{c}_{j\sigma}|\Psi\rangle$ for all i and j.

[20] An extension of the definition domain of $E[\gamma_{ij}]$ to ensemble-representable density matrices Γ_{ij} is straightforward following the work by Valone (see Ref. 16). Ensemble density matrices are written as $\Gamma_{ij}=\Sigma_n w_n\langle\Psi_n|\Sigma_\sigma\hat{c}_{i\sigma}^\dagger\hat{c}_{j\sigma}|\Psi_n\rangle$ with $w_n\geqslant 0$ and $\Sigma_n w_n=1$. In practice, Γ_{ij} are much easier to characterize than pure-state density matrices.

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[24] The electron-hole transformation $\hat{h}_{i\sigma}^\dagger=\hat{c}_{i\sigma}$ leaves the Hubbard Hamiltonian and Eq. (2.14) formally unchanged, except for an additive constant and a change of sign in the hopping integrals t_{ij} [or of λ_{ij} in Eq. (2.14)]. $E_C(\gamma_{12},N_e)=E_C(-\gamma_{12},2N_a-N_e)$, since the form of the interaction term is unaffected by changing electrons to holes, and since the density matrix for holes satisfies $\gamma_{ij}^h=\Sigma_\sigma\langle\hat{h}_{i\sigma}^\dagger\hat{h}_{j\sigma}\rangle=-\gamma_{ji}$. Moreover, on bipartite lattices with only NN hoppings $E_C(\gamma_{12},N_e)=E_C(-\gamma_{12},N_e)$, since the sign of the NN bond order may be changed by changing the sign of $\hat{c}_{i\sigma}$ on one of the sublattices.

[25] A lattice is *bipartite* if two distinct subsets of lattice sites A and B can be defined such that every lattice site belongs either to A or to B, and that there is no pair of NN's belonging to the same subset. All NN bonds (or hoppings) connect a site in A with a site in B.

[26] In the presence of degeneracies in the single-particle spectrum of finite systems one may find that the minimum of $W[\gamma_{ij}]$ does not correspond to a single Slater determinant, and that $W(\gamma_{12}\rightarrow\gamma_{12}^0)<E_{\rm HF}$. Such a behavior is observed, for example, in rings with $N_a=N_e=4$ m. This is a finite-size effect which importance decreases with increasing N_a: $W(\gamma_{12}^0)/(UN_a)=0.19$, 0.23, and 0.24 for rings with $N_e=N_a=4$, 8 and 12, respectively. $E_{\rm HF}/(UN_a)=0.25$.

[27] In the nonmagnetic case the Hartree-Fock energy of the Hubbard model is $E_{\rm HF}/N_a=(U/4)(N_e/N_a)^2$ for N_e even and $E_{\rm HF}/N_a=(U/4)(N_e/N_a)^2[1-(1/N_e)^2]$ for N_e odd. Notice that in this model the difference between $E_{\rm HF}$ and the Hartree energy $E_H/N_a=(U/2)(N_e/N_a)^2$ is only the self interaction.

[28] If $W(\gamma_{12}^0)<E_{\rm HF}$, i.e., $E_C(\gamma_{12}^0)<0$, it is more appropriate to consider $\varepsilon_C=[E_C(\gamma_{12})-E_C(\gamma_{12}^0)]/W(\gamma_{12}^0)$ in order to correct for this finite-size effect. In this way $\varepsilon_C(g_{12})$ is less sensitive to the details of the lattice structure or cluster size.

[29] Using a linear combination $|\Psi\rangle$ between two N-particles states $|\Psi_a\rangle$ and $|\Psi_b\rangle$ satisfying $\langle\Psi_a|\Psi_b\rangle=0$ and $\langle\Psi_a|\Sigma_\sigma\hat{c}_{i\sigma}^\dagger\hat{c}_{j\sigma}|\Psi_b\rangle=0$ (for instance, two states with different total spin S or S_z), one may represent the NN matrix elements $\gamma_{12}=\gamma_{ij}=\langle\Psi|\Sigma_\sigma\hat{c}_{i\sigma}^\dagger\hat{c}_{j\sigma}|\Psi\rangle$ in the interval $\gamma_{12}^a\leqslant\gamma_{12}\leqslant\gamma_{12}^b$, where γ_{12}^a and γ_{12}^b are the bond orders corresponding to $|\Psi_a\rangle$ and $|\Psi_b\rangle$ ($\gamma_{12}^a<\gamma_{12}^b$). For example, one may take $|\Psi_a\rangle$ as a fully localized state with maximal S_z ($\gamma_{ij}^a=0$, $\forall ij$) and $|\Psi_b\rangle$ as the state representing γ_{12}^∞ for $S_z=0$.

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