The large- U Hubbard model for a semi-infinite crystal: a moment approach and an energy-dependent recursion method

The large-*U* Hubbard model for a semi-infinite crystal: a moment approach and an energy-dependent recursion method

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Abstract. Electron-correlation effects at metal surfaces can be studied qualitatively within the framework of the Hubbard model for a semi-infinite lattice. We propose a moment approach for an approximate determination of the local electronic self-energy that is applicable for systems with reduced translational symmetry. For the strong-correlation regime a one-pole *ansatz* for the self-energy can be motivated. All *a priori* unknown parameters in the *ansatz* for the self-energy are calculated self-consistently by exploiting the equality between two alternative but exact representations for the first four moments of the spectral density. With the resulting expression for the self-energy at hand, the many-body problem reduces to the problem of finding the local density of states (LDOS) for an energy-dependent effective one-particle Hamiltonian. We determine the LDOS for the semi-infinite system using a straightforward generalization of the standard tight-binding recursion method that is suitable for treating an energy-dependent Hamiltonian. The resulting energy dependence of the recursion coefficients is studied in detail for the (100) surface of a bcc crystal and an interpolation procedure for a numerically feasible evaluation of the theory is suggested.

1. Introduction

The Hubbard model [1–3] has evolved into one of the most extensively studied models in solid-state physics. Originally it was formulated to study the conditions for collective magnetic order, but nowadays quite generally contributes to the understanding of correlation effects among itinerant valence electrons. As the Hubbard model is a highly idealized subject for investigating the electronic structure of a solid, there is hardly a direct relation to experimental results. Nevertheless, much insight can be gained into the fundamental mechanisms responsible for spontaneous magnetism, for metal–insulator transitions and high-temperature superconductivity, for example. Moreover, the model serves as a reference for the development and comparison of different approaches to the problem of electron correlations.

The Hubbard model describes the complex interplay between the electrons' kinetic energy, their Coulomb interaction, the Pauli principle and, additionally, the lattice geometry. The latter is rather important because of the itinerant nature of the valence electrons; the electronic structure is expected to be a sensitive function of the local geometrical environment. The decisive role of the geometry shows up, for example, when comparing results for different lattice dimensions [4–8]. Sensitive dependencies on the lattice structure can be observed, e.g., in studies of band magnetism within the three-dimensional Hubbard model [9–11]. A typical situation where geometrical effects are of primary interest is

faced at the surface of a single crystal. The reduced coordination number of sites at the very surface is expected to have important consequences for the electronic structure. The intimate relation between electron-correlation and surface effects can be studied in detail within the Hubbard model for a semi-infinite crystal.

Using standard notation the Hubbard model reads

$$H = \sum_{ij\sigma}(T_{ij} - \mu\delta_{ij})c_{i\sigma}^{\dagger}c_{j\sigma} + \frac{1}{2}U\sum_{i\sigma}n_{i\sigma}n_{i-\sigma}. \tag{1}$$

Here $c_{i\sigma}^{\dagger}$ ($c_{i\sigma}$) creates (annihilates) an electron at the lattice site i and with spin direction σ. The T_{ij} are the hopping integrals, μ denotes the chemical potential, U is the on-site Coulomb interaction, and $n_{i\sigma} = c_{i\sigma}^{\dagger}c_{i\sigma}$ is the occupation-number operator. We consider a 'semi-infinite Hubbard model' that differs from the usual three-dimensional Hubbard model only with respect to the purely geometrical cut-off of the hopping at the surface: the sums over i and j thus extend over the sites of a semi-infinite lattice. Besides the cut-off of the hopping parameters there is a more implicit effect being introduced by the existence of the surface, namely an environmental dependence of the hopping [12] as well as of the Coulomb interaction [13, 14]. At the surface T_{ij} and U may differ significantly from their bulk values. For real systems this renormalization of the electronic parameters should be non-negligible. However, in the present case, studying a model system, it will be ignored for simplicity; a site-dependent Hubbard interaction U_i and an arbitrary dependence of the hopping parameters on the local geometric structure could easily be taken into account in principle.

The semi-infinite Hubbard model poses two major problems at least. The first one is the actual many-body problem. It can be formulated as the problem of finding the correct self-energy $\Sigma_{ij\sigma}(E)$ for the system of interacting electrons. Provided that the many-body problem has been solved in some way and an (approximate) expression for the self-energy has been derived, we can simplify the original model by introducing an effective one-particle Hamiltonian in the following way:

$$H_{\text{eff}} = \sum_{ij\sigma}(T_{ij} + \Sigma_{ij\sigma}(E) - \mu\delta_{ij})c_{i\sigma}^{\dagger}c_{j\sigma}. \tag{2}$$

It is easy to show that H and H_{eff} yield identical equations of motion for the one-particle Green function $G_{ij\sigma}(E) = \langle\langle c_{i\sigma}; c_{i\sigma}^{\dagger}\rangle\rangle_E$, from which all relevant information on the system can be obtained. With respect to $G_{ij\sigma}(E)$ we are thus allowed to replace H by H_{eff}.

The second major problem then consists of solving the equation of motion for the Green function for a semi-infinite crystal, i.e. solving the effective one-particle problem posed by H_{eff}. The second problem is surely non-trivial, but should probably allow for a numerically exact solution. For the first problem, however, we have to accept more or less drastic simplifications to cast it into a manageable form.

In a preceding study [15] we approximated the self-energy within a mean-field (Hartree–Fock) theory, $\Sigma_{ij\sigma}(E) = \delta_{ij}U\langle n_{i-\sigma}\rangle$, and solved the one-particle problem by means of the standard recursion method [16, 17]. The rather crude mean-field approximation provided a first insight into the problem of surface magnetism. Because of the typical shortcomings of mean-field theory, such as the overestimation of the possibility for collective magnetic order, however, an improved treatment for the many-body problem should be intended. For the conventional Hubbard model of an infinitely extended lattice with perfect translational symmetry there are well-established many-body approaches for the weak- [6, 18–21] as well as for the strong-correlation regime [10, 11, 22–29] which yield explicit and reliable expressions for the self-energy. Up to now, however, a generalization and application of

such many-body theories with respect to the Hubbard model for a crystal surface is an outstanding task. With the present paper we aim at a first step beyond mean-field theory to describe electron correlations at a crystal surface. For this purpose we will try to generalize the moment-equating spectral density approach (SDA) [10, 11, 22, 23] to systems with reduced translational symmetry.

For the usual three-dimensional ($d = 3$) Hubbard model the SDA has proven its usefulness in a number of previous applications [10, 11, 22, 23, 30–33]. It can be shown to be essentially equivalent to the Roth two-pole approximation for the one-particle Green function [24, 25] and to the Mori–Zwanzig projection method [26–29]. The main advantage of these methods rests on their simple concept and their non-perturbative character.

Fewer applications of the SDA or the Roth or Mori–Zwanzig method, respectively, are known for the case of the two-dimensional Hubbard model. Yet, there is interesting recent work: the quasi-particle band structure for different band-fillings obtained by the Roth method for the $d = 2$ case [25] has been compared with the results of quantum Monte Carlo simulations for the Hubbard model on a 12×12 square array of sites [34, 35]. Remarkable agreement has been found with respect to the dispersion of the quasi-particle bands. The results of the Mori–Zwanzig projection method for the $d = 2$ Hubbard model [29] have been compared with the results of an exact diagonalization study of the Hubbard model on a 4×4 array [36]. Qualitative and quantitative agreement is found with respect to the global features, such as the change of dispersion of the Hubbard bands and spectral weight transfer between them with varying band-filling. The SDA yields a real self-energy thereby predicting quasi-particles with infinite lifetime. This has to be considered as a serious drawback intrinsic to the method. However, as the comparison with the available rigorous results for small two-dimensional arrays shows [29], the δ-like quasi-particle peaks as predicted by the SDA almost exactly recover the average dispersion of the lower and of the upper Hubbard band.

In previous applications of the SDA the k-dependence of the self-energy has been neglected frequently. Much can be learned in this context from recent work on infinite-dimensional ($d = \infty$) lattice models and $1/d$ perturbation theory [4, 7, 8]. It is one of the most important results of these studies that for the infinite-dimensional ($d = \infty$) Hubbard model the self-energy is k-independent. This means a local self-energy $\Sigma_{ij\sigma}(E) = \delta_{ij}\Sigma_{i\sigma}(E)$ in Wannier representation. Within a perturbational approach the k-dependent self-energy for any finite-dimensional case can be obtained by successively including correction terms of the order $(1/d)^n$ for $n = 1, 2, \ldots$. In the Wannier representation for the self-energy this $1/d$ approach corresponds to starting from the local term and successively considering nearest-neighbour, next-nearest-neighbour, etc, correction terms. A convincing demonstration is given in [4] within the context of second-order perturbation theory in U for the periodic Anderson model: the $1/d$ expansion converges even for $d = 1$. Already for the $d = 2$ case corrections beyond nearest-neighbour terms are rather small, and for $d = 3$ the local approximation for the self-energy is an excellent starting point.

As a first approach we restrict ourselves to a local self-energy for the present study of the $d = 3$ semi-infinite Hubbard model. Retaining only the dominating local term of the self-energy considerably reduces the theoretical effort. We nevertheless believe that the method is able to give significant insight into the semi-infinite Hubbard model, at least for a band occupation not too close to half-filling. This is confirmed by comparison with numerically exact data for small systems again: according to [29, 37] the k-dependence of the self-energy is predominantly due to local antiferromagnetic correlations. Both an exact diagonalization study for a ten-site Hubbard ring [29] and the Mori–Zwanzig projection method or the SDA for the $d = 1$ Hubbard model [29, 37] show that these antiferromagnetic correlations are

only significant at and near half-filling in turn. The same is found qualitatively for the $d = 2$ case by the Roth method [25] and for $d = 3$ by the SDA [37], where compared with $d = 2$ and $d = 1$ a generally much weaker k-dependence of the self-energy is observed in addition.

A brief plan for the following work may be helpful. The first purpose of this paper is to generalize the SDA of [22] for systems without perfect translational invariance. Thereby we propose an approximate solution for the many-body problem in the strong-correlation regime that is applicable to the semi-infinite crystal (section 2). The energy dependence of the resulting self-energy implies an energy-dependent effective one-particle Hamiltonian, $H_{eff} = H_{eff}(E)$, and consequently introduces a major complication with respect to the one-particle problem. The second intention of the present study is thus to show up a possibility of treating this complication in a computationally efficient way. The recursion scheme that has been applied successfully in the mean-field study [15] is reformulated for the case of an energy-dependent Hamiltonian (section 3). We study the implied energy dependence of the recursion coefficients in detail to develop a numerically feasible interpolation technique (section 4). Finally, the main results are summarized in section 5.

2. The self-consistent moment approach

All interesting one-particle properties of a system of interacting electrons described within the framework of the semi-infinite Hubbard model are given in terms of the retarded one-particle Green function:

$$G_{ij\sigma}(E) = -i \int_0^\infty e^{(i/\hbar)E(t-t')} \langle [c_{i\sigma}(t), c_{j\sigma}^\dagger(t')]_+ \rangle \, d(t - t').$$ (3)

Here $[\cdots, \cdots]_+$ denotes the anticommutator, and $\langle \cdots \rangle$ is the grand canonical average. Since in the direction normal to the surface the translational symmetry is broken, we use a real-space rather than a k-space notation: i and j refer to one-particle states well localized at the respective sites of the semi-infinite lattice. Besides the Green function, the one-particle spectral density represents another basic quantity. It is given by

$$A_{ij\sigma}(E) = -\frac{1}{\pi} \text{Im} \, G_{ij\sigma}(E + i0^+).$$ (4)

The diagonal elements of the spectral density yield the spin- and temperature-dependent local quasi-particle density of states:

$$\rho_{i\sigma}(E) = \frac{1}{\hbar} A_{ii\sigma}(E - \mu).$$ (5)

From the Heisenberg equation of motion for the time-dependent operators in equation (3) we can easily derive the following equation of motion for the Green function:

$$E G_{ij\sigma}(E) = \hbar \delta_{ij} + \sum_k (T_{ik} - \mu \delta_{ik} + \Sigma_{ik\sigma}(E)) G_{kj\sigma}(E).$$ (6)

Hereby we have introduced the electronic self-energy $\Sigma_{ij\sigma}(E)$, which in general is a spin-, energy- and temperature-dependent complex quantity. All effects of electron correlations are incorporated in the self-energy. Since the equation of motion for the Green function is the same for both the original Hubbard Hamiltonian H (equation (1)) and the effective one-particle Hamiltonian H_{eff} (equation (2)), we can replace H by H_{eff} for the calculation of the Green function. Provided that the self-energy is known, we have to solve an effective one-particle problem only.

Our moment method provides an approximate expression for the self-energy. The method essentially consists of two steps. In the first step we try to find out the general structure of the self-energy guided by exactly solvable limiting cases, series expansions, sum rules and other physically plausible arguments, for example. From this we formulate an *ansatz* for the self-energy that will contain a certain number of *a priori* unknown parameters. The self-energy determines via equations (4) and (6) the spectral density and thereby the moments of the spectral density. The moments are defined by

$$M_{ij\sigma}^{(k)} = \frac{1}{\hbar} \int_{-\infty}^{\infty} E^k A_{ij\sigma}(E) \, \mathrm{d}E \qquad k = 0, 1, 2, \ldots. \tag{7}$$

In the second step the parameters in the *ansatz* for the self-energy are fixed by equating this expression for the moments of the spectral density with another exact but alternative representation:

$$M_{ij\sigma}^{(k)} = \langle [\mathcal{L}^k c_{i\sigma}, c_{j\sigma}^\dagger]_+ \rangle. \tag{8}$$

Here $\mathcal{L}^k \mathcal{O} = [\cdots [\mathcal{O}, H]_- \cdots, H]_-$ denotes the k-fold commutator of an operator $\mathcal{O}$ with the Hamiltonian H.

The main idea for this moment method is borrowed from the moment-equating SDA for an infinitely extended lattice with full translational invariance (see, e.g., [22]). In that case, Fourier transformation of the spectral density to k-space is possible and appropriate:

$$A_{ij\sigma}(E) = \frac{1}{N} \sum_k \mathrm{e}^{\mathrm{i}k \cdot (R_i - R_j)} A_{k\sigma}(E). \tag{9}$$

Guided by the atomic limit of vanishing Bloch-band width W, the following *ansatz* for the spectral density in k-space representation could be motivated in [22]:

$$A_{k\sigma}(E) = \hbar \sum_{j=1}^{2} \alpha_{j\sigma}(k) \delta(E - E_{j\sigma}(k) + \mu). \tag{10}$$

The quasi-particle energies $E_{j\sigma}(k)$ and the spectral weights $\alpha_{j\sigma}(k)$ $(\alpha_{1\sigma}(k) + \alpha_{2\sigma}(k) = 1)$ were treated as unknown parameters to be fixed by exploiting the equality between the two alternative expressions for the moments (7) and (8).

Because of the explicit use of translational symmetry and k-space representation, the usual SDA cannot be directly applied to systems with reduced symmetry. Moreover, it is by no means obvious how to formulate a plausible *ansatz* for the spectral density in a real-space representation. For the case of the semi-infinite Hubbard model we therefore turn to another basic quantity, the self-energy, and try to find a reasonable parametrization for it.

This *ansatz* is a key point of the theory. On the one hand is must be general enough to retain the essential physics of the model. On the other hand, an *ansatz* that includes more than a few unknown parameters cannot be handled in practice: the moments (8) needed to fix the unknowns will soon become very complex with increasing order k. Here we will choose the following parametrization for the self-energy:

$$\Sigma_{ij\sigma}(E) = \delta_{ij} \alpha_{i\sigma} \frac{E - \beta_{i\sigma}}{E - \gamma_{i\sigma}} \tag{11}$$

where the spin- and site-dependent parameters α, β and γ have to be treated as unknowns. These constants and thus the self-energy will turn out to be real, i.e. quasi-particle damping is neglected. Furthermore, we neglected off-diagonal terms in the *ansatz* for the self-energy (which corresponds to a k-independent self-energy in the case of an infinitely extended

periodic lattice). As discussed in the introduction, this implies that our *ansatz* is restricted to band-fillings that are not too close to half-filling.

With respect to the energy dependence of Σ, a look at the atomic Hubbard model ($W = 0$) may be helpful. In this case the self-energy can be calculated exactly since the hierarchy of equations of motion decouples automatically:

$$\Sigma_{ij\sigma}(E) = \delta_{ij} U \langle n_{i-\sigma} \rangle \frac{E + \mu - T_{ii}}{E + \mu - T_{ii} - U(1 - \langle n_{i-\sigma} \rangle)}. \tag{12}$$

The self-energy exhibits a first-order pole which is responsible for the splitting into the two Hubbard subbands. When the hopping T_{ij} is switched on ($W \neq 0$), additional satellites will appear. It can be shown exactly [33] that the spectral weight of these additional satellites is of the order $(W/U)^4$ or less, being therefore negligible in the strong-correlation regime $U \gg W$. Our one-pole *ansatz* for the self-energy is thus restricted to strongly correlated systems only.

As will become clear in the following, the *ansatz* (11) recovers exactly the results of the above-mentioned SDA [22] in the case of perfect translational invariance. For this reason we can state that the present formulation represents a straightforward generalization of the SDA to strongly correlated systems with reduced symmetry. Compared with those in other approaches [38], a rather simple form for the self-energy has to be assumed here. We would like to point out, however, that the following calculation is more or less exact. For the reasons mentioned in the introduction, we believe that this generalized SDA, while we are aware of its inherent restrictions, can give valuable insight into the semi-infinite Hubbard model.

To develop the theory up to the point where the numerical evaluation has to start, we first derive from equation (8) the moments that will be necessary to fix the parameters in the *ansatz* (11). The expression for the first moment ($k = 0$) only reflects the normalization of the spectral density. For the three unknowns α, β and γ we therefore need the first four moments ($k = 0, \ldots, 3$). Writing $\widetilde{T}_{ij} = T_{ij} - \mu \delta_{ij}$ for brevity, we obtain after a tedious but straightforward calculation:

$$M_{ij\sigma}^{(0)} = \delta_{ij}$$

$$M_{ij\sigma}^{(1)} = \widetilde{T}_{ij} + \delta_{ij} U \langle n_{i-\sigma} \rangle$$

$$M_{ij\sigma}^{(2)} = \sum_k \widetilde{T}_{ik} \widetilde{T}_{kj} + U \widetilde{T}_{ij}(\langle n_{i-\sigma} \rangle + \langle n_{j-\sigma} \rangle) + \delta_{ij} U^2 \langle n_{i-\sigma} \rangle + R_{ij-\sigma}^{(1)}$$

$$M_{ij\sigma}^{(3)} = \sum_{kl} \widetilde{T}_{ik} \widetilde{T}_{kl} \widetilde{T}_{lj} + U \sum_k \widetilde{T}_{ik} \widetilde{T}_{kj}(\langle n_{i-\sigma} \rangle + \langle n_{j-\sigma} \rangle + \langle n_{k-\sigma} \rangle) \tag{13}$$

$$+ U^2 \widetilde{T}_{ij}(\langle n_{i-\sigma} \rangle + \langle n_{j-\sigma} \rangle + \langle n_{i-\sigma} \rangle \langle n_{j-\sigma} \rangle)$$

$$+ U^2 \langle n_{i-\sigma} \rangle (1 - \langle n_{i-\sigma} \rangle) B_{ij-\sigma} + \delta_{ij} U^3 \langle n_{i-\sigma} \rangle + R_{ij-\sigma}^{(2)}.$$

The 'band correction' $B_{ij-\sigma}$ is a correlation function of higher order:

$$\langle n_{i-\sigma} \rangle (1 - \langle n_{i-\sigma} \rangle) B_{ij-\sigma} = \delta_{ij} B_{i-\sigma}^{(S)} + B_{ij-\sigma}^{(W)} + \delta_{ij} \widetilde{T}_{ii} \langle n_{i-\sigma} \rangle. \tag{14}$$

The 'band shift' $B_{i-\sigma}^{(S)}$ is most decisive, especially as regards the possibility of spontaneous magnetic order [22]:

$$B_{i-\sigma}^{(S)} = \sum_k (\widetilde{T}_{ik} \langle n_{i\sigma} c_{i-\sigma}^\dagger c_{k-\sigma} \rangle + \widetilde{T}_{ki} \langle n_{i\sigma} c_{k-\sigma}^\dagger c_{i-\sigma} \rangle - \widetilde{T}_{ki} \langle c_{k-\sigma}^\dagger c_{i-\sigma} \rangle). \tag{15}$$

The 'band-width correction'

$$B_{ij-\sigma}^{(W)} = \widetilde{T}_{ij}(\langle n_{i-\sigma} n_{j-\sigma} \rangle - \langle n_{i-\sigma} \rangle \langle n_{j-\sigma} \rangle - \langle c_{j\sigma}^\dagger c_{j-\sigma}^\dagger c_{i-\sigma} c_{i\sigma} \rangle - \langle c_{j\sigma}^\dagger c_{i-\sigma}^\dagger c_{j-\sigma} c_{i\sigma} \rangle) \tag{16}$$

splits up into four terms. The first two, which represent density correlations between two sites, obviously disappear within a mean-field approach. The third term describes double hopping from site to site and the fourth expresses spin exchange between electrons on different sites. Both the third and the fourth term are spin independent. With respect to the possibility of magnetic order, $B_{ij-\sigma}^{(W)}$ is not that important [22]. For simplicity we retain the local term of $B_{ij-\sigma}^{(W)}$ only:

$$B_{ij-\sigma}^{(W)} \approx \delta_{ij} B_{ii-\sigma}^{(W)}. \tag{17}$$

It should be mentioned that this approximation is necessary to be consistent with our local *ansatz* (11) for the self-energy. It is known that just the inclusion of off-diagonal elements in $B_{ij-\sigma}^{(W)}$ leads to non-local terms in the self-energy (which are small for band-fillings not too close to half-filling) [29, 37].

Apart from the band correction and from expectation values for the occupation-number operators $\langle n_{i-\sigma} \rangle$, there are some off-diagonal one-particle correlation functions which are all included in the following definitions:

$$R_{ij-\sigma}^{(1)} = \delta_{ij} U \sum_k (\widetilde{T}_{ik} \langle c_{i-\sigma}^\dagger c_{k-\sigma} \rangle - \widetilde{T}_{ki} \langle c_{k-\sigma}^\dagger c_{i-\sigma} \rangle)$$

$$R_{ij-\sigma}^{(2)} = U \widetilde{T}_{ij} \sum_k (\widetilde{T}_{ik} \langle c_{i-\sigma}^\dagger c_{k-\sigma} \rangle - \widetilde{T}_{ki} \langle c_{k-\sigma}^\dagger c_{i-\sigma} \rangle). \tag{18}$$

To simplify these expressions, we choose an orthonormal basis consisting of *real* functions $|i\sigma\rangle$ within the framework of second quantization. From this one-particle basis we can straightforwardly construct a real basis of the many-particle Fock space, in which the operators $c_{i\sigma}^\dagger$ and $c_{i\sigma}$ are represented by real matrices. We furthermore notice that the eigenstates of the Hamiltonian H can always be chosen to be real vectors in that basis since H is Hermitian. Remembering the definition of the grand canonical average, we can therefore take the matrix elements $\langle c_{i\sigma}^\dagger c_{j\sigma} \rangle$ to be real (even for $i \neq j$). We thus have

$$\langle c_{i\sigma}^\dagger c_{j\sigma} \rangle = \langle c_{i\sigma}^\dagger c_{j\sigma} \rangle^* = \langle c_{j\sigma}^\dagger c_{i\sigma} \rangle. \tag{19}$$

Furthermore, within the real basis $\{|i\sigma\rangle\}$ the hopping integrals are real: $T_{ij} = T_{ij}^* = T_{ji}$. This implies

$$R_{ij-\sigma}^{(1)} = R_{ij-\sigma}^{(2)} = 0. \tag{20}$$

The crucial point of our method is that all correlation functions that appear in the expression (8) for the moments can be derived exactly from the one-particle spectral density $A_{ij\sigma}(E)$. This guarantees a closed set of equations. Using the relation (19), we get from equations (14)–(17)

$$\langle n_{i-\sigma} \rangle (1 - \langle n_{i-\sigma} \rangle) B_{ij-\sigma} = \delta_{ij} \widetilde{T}_{ii} \langle n_{i-\sigma} \rangle (1 - \langle n_{i-\sigma} \rangle) + \delta_{ij} \sum_{k \neq i} \widetilde{T}_{ik} \langle c_{i-\sigma}^\dagger c_{k-\sigma} (2n_{i\sigma} - 1) \rangle. \tag{21}$$

All in all we thus have two types of correlation function that have to be determined:

$$\langle c_{i-\sigma}^\dagger c_{j-\sigma} \rangle$$
$$\langle c_{i-\sigma}^\dagger c_{j-\sigma} n_{i\sigma} \rangle. \tag{22}$$

Using the general spectral theorem [39], the one-particle correlation functions are given by

$$\langle c_{i-\sigma}^\dagger c_{j-\sigma} \rangle = \frac{1}{\hbar} \int_{-\infty}^{\infty} f(E) A_{ji-\sigma}(E - \mu) \, \mathrm{d}E \tag{23}$$

where $f(E)$ is the Fermi function:

$$f(E) = \frac{1}{e^{\beta(E-\mu)} + 1}.$$

(24)

In the following we show that the higher-order correlation function $B_{ij-\sigma}$ can also be expressed in terms of the spectral density. With the help of the commutator

$$[H, c^{\dagger}_{i-\sigma}]_{-} = \sum_{k} \widetilde{T}_{ki} c^{\dagger}_{k-\sigma} + U c^{\dagger}_{i-\sigma} n_{i\sigma}$$

(25)

the second expectation value in (22) can be written in the form

$$\langle c^{\dagger}_{i-\sigma} c_{j-\sigma} n_{i\sigma} \rangle = -\frac{1}{U} \sum_{k} \widetilde{T}_{ki} \langle c^{\dagger}_{k-\sigma} c_{j-\sigma} \rangle + \frac{1}{U} \langle [H, c^{\dagger}_{i-\sigma}]_{-} c_{j-\sigma} \rangle.$$

(26)

The first term, being a sum of one-particle correlation functions, can be handled by the spectral theorem (equation (23)). Applying once more the general spectral theorem, performing a Fourier transformation to time representation, using the Heisenberg equation of motion for time-dependent operators and integrating by parts, the following equation for the second term can be derived:

$$\langle [H, c^{\dagger}_{i-\sigma}]_{-} c_{j-\sigma} \rangle = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} f(E + \mu)$$

$$\times \int_{-\infty}^{\infty} e^{(i/\hbar)E(t-t')} \left(-i\hbar \frac{\partial}{\partial t'} \right) \langle [c_{j-\sigma}(t), c^{\dagger}_{i-\sigma}(t')]_{+} \rangle \, d(t - t') \, dE$$

$$= \frac{1}{\hbar} \int_{-\infty}^{\infty} f(E + \mu) E A_{ji-\sigma}(E) \, dE.$$

(27)

Combining the results, we have for the band correction

$$\langle n_{i-\sigma} \rangle (1 - \langle n_{i-\sigma} \rangle) B_{ij-\sigma} = \delta_{ij} \widetilde{T}_{ii} \langle n_{i-\sigma} \rangle (1 - \langle n_{i-\sigma} \rangle) + \delta_{ij} \frac{1}{\hbar} \int_{-\infty}^{\infty} f(E + \mu)$$

$$\times \sum_{k} (\widetilde{T}_{ik} - \delta_{ik} \widetilde{T}_{ii}) \sum_{l} \left(\frac{2}{U} [E\delta_{il} - \widetilde{T}_{il}] - \delta_{il} \right) A_{kl-\sigma}(E) \, dE.$$

(28)

This can be transformed into a more compact and elegant expression which also avoids the double lattice sum, when using the relation

$$\sum_{k} (E\delta_{ik} - \widetilde{T}_{ik} - \Sigma_{ik\sigma}(E)) A_{kj\sigma}(E) = 0$$

(29)

which is easily deduced from the equation of motion (6) and from (4) for a real energy E and a real self-energy $\Sigma_{ij\sigma}(E)$. Since the self-energy is site diagonal, we finally arrive at

$$\langle n_{i-\sigma} \rangle (1 - \langle n_{i-\sigma} \rangle) B_{ij-\sigma} = \delta_{ij} \widetilde{T}_{ii} \langle n_{i-\sigma} \rangle (1 - \langle n_{i-\sigma} \rangle) + \delta_{ij} \frac{1}{\hbar} \int_{-\infty}^{\infty} f(E + \mu)$$

$$\times (E - \Sigma_{ii-\sigma}(E) - \widetilde{T}_{ii}) \left(\frac{2}{U} \Sigma_{ii-\sigma}(E) - 1 \right) A_{ii-\sigma}(E) \, dE.$$

(30)

This completes the general theory, since now the parameters in the *ansatz* for the self-energy can be determined from the closed set of equations (4), (6), (7), (11), (13), (20), (23) and (30). Generally, an analytical solution is not possible, and the parameters have to be calculated numerically. This can be done, for example, by minimizing the following function with respect to $\alpha_{i\sigma}$, $\beta_{i\sigma}$ and $\gamma_{i\sigma}$:

$$G(\ldots, \alpha_{i\sigma}, \beta_{i\sigma}, \gamma_{i\sigma}, \ldots) = \sum_{i\sigma} \sum_{k=1}^{3} \left(\frac{1}{\hbar} \int_{-\infty}^{\infty} E^{k} A_{ii\sigma}(E) \, dE - \langle [\mathcal{L}^{k} c_{i\sigma}, c^{\dagger}_{i\sigma}]_{+} \rangle \right)^{2} \stackrel{!}{=} \min.$$

(31)

For the semi-infinite Hubbard model we can assume perfect translational symmetry *within* layers parallel to the surface. This implies spatially constant parameters within each layer (e.g. $\alpha_{i\sigma} = \alpha_{j\sigma}$ for sites i and j belonging to the same layer). For this reason it is sufficient to consider G as a function of the inequivalent parameters for different layers only. At a sufficiently large distance from the surface the parameters will tend to their bulk values. Therefore, only a finite number of non-equivalent parameters have to be determined, and the sum over i actually extends over the relevant surface layers only. Since the two alternative representations of moments are equivalent, the minimum of G should be zero. A different minimum value in the calculation would indicate that the *ansatz* for the self-energy was not sufficiently general to fulfil the constraints resulting from the equivalence between the moments' representations. It may also happen that there is more than one zero of G which indicates a solution to be not unique. Experience with the SDA for an infinitely extended system shows that different solutions can be obtained representing different magnetic structures (paramagnetism, ferromagnetism and antiferromagnetism). Moreover, in a certain range of the Coulomb interaction and the band-filling the existence of more than one ferromagnetic solution has been observed [22]. In such cases the most stable solution can be determined by calculating the respective internal energy $E_0 = \langle H \rangle$ or, for $T \neq 0$, the free energy $F(T)$, which both can be expressed in terms of the one-particle spectral density [15].

For the special case of an infinitely extended lattice the determination of the parameters can be performed analytically, and there is no need to introduce the function G. Following strictly along the lines of [10, 11, 22, 23, 29], we finally obtain the following result:

$$\alpha_{i\sigma} = U \langle n_{-\sigma} \rangle$$
$$\beta_{i\sigma} = B_{-\sigma} - \mu \qquad (32)$$
$$\gamma_{i\sigma} = B_{-\sigma} - \mu + U(1 - \langle n_{-\sigma} \rangle).$$

Due to translational invariance the expectation values become site independent: $\langle n_{i-\sigma} \rangle = \langle n_{-\sigma} \rangle$ and $B_{ii-\sigma} = B_{-\sigma}$. Inserting this result into equation (11) one exactly recovers the self-energy of the SDA. As mentioned above, we can therefore conclude that the moment method presented is a straightforward generalization of the SDA for systems with reduced (translational) symmetry.

Finally, we would like to present a somewhat simplified version of the theory, which yields an analytical expression for the self-energy also for the case of reduced symmetry: we think the semi-infinite crystal to be built up from layers parallel to the surface. For the explicit determination of the self-energy we assume the hopping between different layers to be switched off for the time being. This means that in a sense we treat the individual layers separately at this stage. Since each layer represents a subsystem with perfect (two-dimensional) translational invariance, we can apply the moment method to the rest of the Hamiltonian ending up with the result (32) holding separately for each layer. We do not exclude, however, variations of the parameters $\alpha_{i\sigma}$, $\beta_{i\sigma}$ and $\gamma_{i\sigma}$ from layer to layer:

$$\alpha_{i\sigma} = U \langle n_{i-\sigma} \rangle$$
$$\beta_{i\sigma} = B_{ii-\sigma} - \mu \qquad (33)$$
$$\gamma_{i\sigma} = B_{ii-\sigma} - \mu + U(1 - \langle n_{i-\sigma} \rangle).$$

Here i labels the different layers. Within each layer the parameters are site independent. Inserting into the *ansatz* (11) yields the final formula for the self-energy:

$$\Sigma_{ij\sigma}(E) = \delta_{ij} U \langle n_{i-\sigma} \rangle \frac{E + \mu - B_{ii-\sigma}}{E + \mu - B_{ii-\sigma} - U(1 - \langle n_{i-\sigma} \rangle)}. \qquad (34)$$

The crucial point of the procedure is that the expectation values $\langle n_{i-\sigma} \rangle$ and $B_{ii-\sigma}$ are to be determined within the *full* model (1), i.e. from the relations (23) and (30), whereby the inter-layer hopping is reintroduced. Since the local self-energy in the form (34) depends on the average occupation number at the same site and on the band correction at the same site only, the procedure described may be considered a 'local approximation'. The term refers to the local approximation frequently employed in weak-coupling theories (see [20] for a discussion). In the context of the SDA the local approximation has been tested and successfully applied for treating antiferromagnetic structures [11].

The most essential point of the moment method presented here is the *ansatz* for the self-energy, for which the motivation has been given above. The subsequent calculation, however, is practically exact. The local approximation is not a necessary part of the method but considerably reduces the effort required in the numerical evaluation. A major advantage of the method rests on the simplicity of the idea and of the final result which allows for investigating systems with a complex geometric or magnetic structure. The moment method yields a spin- and temperature-dependent self-energy for each layer parallel to the surface as well as spin-, temperature- and layer-dependent local occupation numbers. From these we can calculate the layer-dependent magnetization and the charge transfer between the layers and the dependencies of these quantities on the model parameters, namely the on-site Coulomb interaction U, the band-filling $\langle n \rangle$ and the temperature T. Effects of strong electron correlations can thus be studied in detail for a crystal surface. We have to bear in mind, however, that a self-consistent numerical evaluation of the theory inevitably requires an appropriate method for solving the equation of motion (6) for the Green function. This problem is tackled in the next section.

3. The energy-dependent recursion method

The conventional tight-binding recursion method provides a computationally efficient way to determine the Green function from its equation of motion within real-space representation. Therefore, the method is ideally suited for treating systems with reduced translational symmetry, such as solid surfaces, defects or clusters. The method and its applications to the electronic structure of solids are outlined in [16, 17]. Actually, the recursion method applies to a one-particle Hamiltonian and is commonly not used to deal with many-body interactions. In the present context, however, all correlation effects are incorporated in the self-energy. Within the framework of an independent-particle model, the self-energy can be interpreted as a non-local, energy-dependent and complex potential. As will be shown we can use the recursion scheme for the *effective* one-particle Hamiltonian in equation (2) that includes this generalized potential.

The essential points in the calculation are sketched briefly in the following. The idea is rather simple: the equation of motion (6) holds separately for each energy E. To obtain the Green function $G_{ij\sigma}(E)$ at a particular energy E, we have to apply the usual recursion method to the Hamiltonian that is given by evaluating the self-energy at energy E: $H_{\text{eff}} = H_{\text{eff}}(E)$. For each energy a transformation can be constructed so that $H_{\text{eff}}(E)$ becomes tridiagonal. Once the Hamiltonian is transformed into tridiagonal form, the diagonal elements of the Green function can be easily expressed as an infinite continued fraction:

$$G_{ii\sigma}(E) = G_{i\sigma}^{(0)}(E)$$

$$G_{i\sigma}^{(k)}(E) = \frac{\hbar}{E + \mathrm{i}\,0^+ - a_{i\sigma}^{(k)}(E) - (b_{i\sigma}^{(k+1)}(E))^2\, G_{i\sigma}^{(k+1)}(E)/\hbar} \qquad k = 0, 1, 2, \ldots. \tag{35}$$

According to equations (4) and (5), we then get the local quasi-particle density of states (LDOS) at the site i and for spin direction σ. The energy-dependent recursion coefficients $a_{i\sigma}^{(k)}(E)$ and $b_{i\sigma}^{(k)}(E)$ represent the diagonal and the first off-diagonal elements of the transformed Hamiltonian, respectively. For each energy E they can be calculated iteratively for a given site i and spin direction σ. Let $|i\sigma\rangle = c_{i\sigma}^{\dagger}|\text{vac}\rangle$ denote the local orbital at site i and with spin index σ. Choosing $|u_0, i\sigma\rangle = |w_0, i\sigma\rangle = |i\sigma\rangle$ for the starting orbital, the recursion coefficients are given by the following recurrence relations:

$$a_{i\sigma}^{(0)}(E) = \langle w_0, i\sigma| H_{\text{eff}}(E) |u_0, i\sigma\rangle$$

$$b_{i\sigma}^{(1)}(E)^2 = \langle w_0; i\sigma|(H_{\text{eff}}(E) - a_{i\sigma}^{(0)}(E))^2|u_0; i\sigma\rangle$$

$$|u_1; Ei\sigma\rangle = \frac{1}{b_{i\sigma}^{(1)}(E)}(H_{\text{eff}}(E) - a_{i\sigma}^{(0)}(E))|u_0; i\sigma\rangle \tag{36}$$

$$|w_1; Ei\sigma\rangle = \frac{1}{b_{i\sigma}^{(1)}(E)^*}(H_{\text{eff}}^{\dagger}(E) - a_{i\sigma}^{(0)}(E)^*)|w_0; i\sigma\rangle$$

and for $k \geqslant 1$:

$$a_{i\sigma}^{(k)}(E) = \langle w_k; Ei\sigma| H_{\text{eff}}(E) |u_k; Ei\sigma\rangle$$

$$b_{i\sigma}^{(k+1)}(E)^2 = [\langle w_k; Ei\sigma|(H_{\text{eff}}(E) - a_{i\sigma}^{(k)}(E)) - \langle w_{k-1}; Ei\sigma| b_{i\sigma}^{(k)}(E)]$$

$$\times [(H_{\text{eff}}(E) - a_{i\sigma}^{(k)}(E))|u_k; Ei\sigma\rangle - b_{i\sigma}^{(k)}(E) |u_{k-1}; Ei\sigma\rangle]$$

$$|u_{k+1}; Ei\sigma\rangle = \frac{1}{b_{i\sigma}^{(k+1)}(E)}((H_{\text{eff}}(E) - a_{i\sigma}^{(k)}(E))|u_k; Ei\sigma\rangle - b_{i\sigma}^{(k)}(E) |u_{k-1}; Ei\sigma\rangle) \tag{37}$$

$$|w_{k+1}; Ei\sigma\rangle = \frac{1}{b_{i\sigma}^{(k+1)}(E)^*}((H_{\text{eff}}^{\dagger}(E) - a_{i\sigma}^{(k)}(E)^*)|w_k; Ei\sigma\rangle - b_{i\sigma}^{(k)}(E)^* |w_{k-1}; Ei\sigma\rangle).$$

One easily verifies that the recurrence relations (36) and (37) lead to two sets of states $\{|u_k; Ei\sigma\rangle\}_{k=0,\dots,\infty}$ and $\{|w_k; Ei\sigma\rangle\}_{k=0,\dots,\infty}$ that are bi-orthonormal:

$$\langle w_k; Ei\sigma |u_l; Ei\sigma\rangle = \delta_{kl} \tag{38}$$

and satisfy the closure relation

$$\sum_k |u_k; Ei\sigma\rangle\langle w_k; Ei\sigma| = \mathbf{1} \tag{39}$$

for each energy E. Furthermore, with equations (36)–(39) we can prove $H_{\text{eff}}(E)$ to be tridiagonal, i.e.:

$$\langle w_k; Ei\sigma| H_{\text{eff}}(E) |u_k; Ei\sigma\rangle = a_{i\sigma}^{(k)}(E)$$

$$\langle w_{k+1}; Ei\sigma| H_{\text{eff}}(E) |u_k; Ei\sigma\rangle = \langle w_k; Ei\sigma| H_{\text{eff}}(E) |u_{k+1}; Ei\sigma\rangle = b_{i\sigma}^{(k)}(E) \tag{40}$$

for all $k \geqslant 0$ and all other matrix elements of $H_{\text{eff}}(E)$ to be zero. If the self-energy is real, as is the case for the moment method presented, the effective one-particle Hamiltonian $H_{\text{eff}}(E)$ is Hermitian, $H_{\text{eff}}^{\dagger}(E) = H_{\text{eff}}(E)$. This simplifies the calculation to some extent since we have $|u_k; Ei\sigma\rangle = |w_k; Ei\sigma\rangle$, and $a_{i\sigma}^{(k)}(E)$ and $b_{i\sigma}^{(k)}(E)$ are real numbers.

4. Results and discussion

To demonstrate its applicability, we have evaluated the theory for the (100) surface of a bcc crystal which serves as a model surface for the present study. Since the recursion scheme is most efficient in the case of a tight-binding model, we restrict ourselves to on-site and

nearest-neighbour hopping only: $T_0 = T_{ii}$ defines the energy zero, $T_1 = T_{ij}$ for nearest neighbours i and j is fixed at $T_1 = 1$ eV. This implies a width of $W = 2z_1^{(B)}T_1 = 16$ eV for the free bulk Bloch density of states. $z_1^{(B)} = 8$ is the bulk coordination number. For atoms within the topmost surface layer the coordination number is reduced to $z_1^{(S)} = 4$. We consider a strongly correlated paramagnetic electron system with $U = 2W$ at zero temperature, $T = 0$. The chemical potential μ will be chosen to yield a quarter-filled LDOS in the bulk, $\langle n \rangle = \langle n_{i\uparrow} \rangle + \langle n_{i\downarrow} \rangle = 0.5$.

The actual calculation proceeds as follows. Before solving the model for the crystal surface, we have to consider the bulk. Making use of translational symmetry, i.e. taking $\langle n_{i\sigma} \rangle = \langle n_\sigma \rangle = \langle n \rangle/2$ and $B_{ii\sigma} = B_\sigma = B_{-\sigma}$, equations (4), (23), (30), (34)–(37) are solved self-consistently for the expectation values $\langle n_\sigma \rangle$ and B_σ and the chemical potential μ. These quantities can be held constant for the subsequent calculation that includes the crystal surface. For the semi-infinite system we take the form (34) for the local self-energy, and translational symmetry is assumed to hold only within layers parallel to the (100) surface. The layer-dependent occupation numbers $\langle n_{i\sigma} \rangle$ and the layer-dependent band corrections $B_{ii\sigma}$ are determined self-consistently for L inequivalent layers parallel to the surface [40]. We take into account as many surface layers L as necessary to ensure that $\langle n_{i\sigma} \rangle$ and $B_{ii\sigma}$ approach their bulk values smoothly.

For the numerical evaluation of the theory we consider a cluster consisting of a finite number of sites N instead of the semi-infinite system. This implies a finite dimension of the one-particle Hilbert space and thus of the vectors and matrices in equations (36) and (37). The LDOS for each of the L inequivalent surface layers and the bulk LDOS are calculated at sites that have maximum distances from the cluster boundary. At these sites the cluster LDOS can be expected to resemble best the LDOS of the semi-infinite system. For the finite cluster the continued fraction (35) must terminate at some level $k = k_0 \leqslant N$, which results in a LDOS consisting of a finite number of weighted δ-peaks at different energies. To approximate the LDOS of the semi-infinite system, the cluster LDOS is convoluted with a Lorentzian and a Gaussian profile. Lorentz convolution is performed by replacing the infinitesimal $i0^+$ in equation (35) by $i\Gamma$ where Γ is a small positive number. This allows for using a discrete energy mesh in the calculation. After that the LDOS is smeared out by convoluting with a Gaussian profile with a full width at half-maximum α. A major advantage of this convolution procedure is that actually it is sufficient to determine only a rather small number of recursion coefficients up to $K \ll k_0$: taking into account more coefficients does not change the LDOS at all. It turns out that for the semi-infinite system the procedure yields the exact but smoothed LDOS of $H_{\text{eff}}(E)$ [15]. The following results have been calculated for $\Gamma = W/200$ and $\alpha = W/20$. For this choice a cluster of about $N = 7500$ sites and a recursion depth of $K = 40$ are sufficient. $L = 10$ inequivalent surface layers are taken into account. The energy-dependent recursion coefficients are calculated on a discrete energy mesh that is sufficiently fine with respect to convergence of the integrals in equations (23) and (30).

In the following we will discuss the results for the recursion coefficients that have been determined from a self-consistent calculation for the parameters given above. In particular, we focus on the energy dependence of the coefficients which is due to the energy dependence of the self-energy and thus due to correlation effects. Let us start with the zeroth-level ($k = 0$) coefficient $a_{i\sigma}^{(0)}(E)$ which is shown in figure 1 for the topmost surface layer and for the bulk. From equation (36) we immediately derive $a_{i\sigma}^{(0)}(E) = T_{ii} - \mu + \Sigma_{ii\sigma}(E)$: the zeroth recursion coefficient directly reflects the energy dependence of the local self-energy (34). It therefore exhibits a first-order pole at $E = B_{ii\sigma} - \mu + U(1 - \langle n_{i\sigma} \rangle)$. Due to the
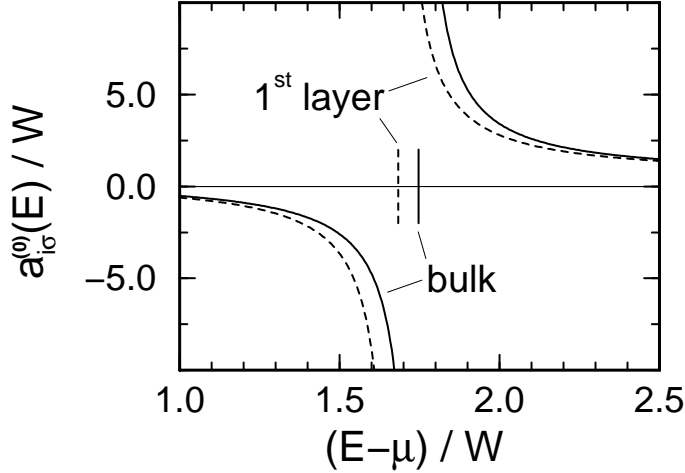
Figure 1. The zeroth-level ($k = 0$) recursion coefficient $a_{i\sigma}^{(0)}$ as a function of energy for the bulk and for the topmost surface layer of the (100) surface of a bcc crystal. The solid and the dashed vertical lines indicate the energetic position of the first-order pole of $a_{i\sigma}^{(0)}(E)$ for the bulk and the first layer, respectively. μ is the chemical potential and W the width of the free bulk Bloch density of states. The results are from a self-consistent calculation for a paramagnet with an on-site Coulomb interaction $U/W = 2$, and band-filling $\langle n \rangle = 0.5$ at zero temperature. Additional parameters of the calculation: $\Gamma = W/200$, $\alpha = W/20$, $L = 10$, $N \approx 7500$, $K = 40$ (see the text).

layer dependence of the expectation values $\langle n_{i\sigma} \rangle$ and $B_{ii\sigma}$, the energetic position of this pole varies from layer to layer. The strongest deviation from the bulk position has been found for the topmost surface layer. The deviation mainly results from the change of the band correction ($B_{ii\sigma}/W = 0.248$ in the bulk, $B_{ii\sigma}/W = 0.176$ in the first layer; see also figure 6 below).

The first-level recursion coefficient $b_{i\sigma}^{(1)}(E)$ is given by $b_{i\sigma}^{(1)}(E) = \sqrt{z_1^{(i)}} T_1$ where $z_1^{(i)}$ is the coordination number of the lattice site i. The coefficient is thus energetically constant and differs from its bulk value only for the sites of the topmost surface layer which have a reduced coordination number.

An easy analysis of the energy dependence of the recursion coefficients is also possible for those sites i that have a sufficiently large distance from the surface. In this case we can assume the expectation values $\langle n_{i\sigma} \rangle$ and $B_{ii\sigma}$ and thus the self-energy to be site independent. Expanding the states $|u_k; Ei\sigma\rangle$ in the local basis orbitals $|j\sigma\rangle = c_{j\sigma}^{\dagger}|0\rangle$,

$$|u_k; Ei\sigma\rangle = \sum_j \alpha_{j;Ei\sigma}^{(k)}|j\sigma\rangle \qquad \sum_j |\alpha_{j;Ei\sigma}^{(k)}|^2 = 1 \tag{41}$$

and inserting into equations (36) and (37), the recursion coefficient $a_{i\sigma}^{(k)}(E)$ is proven to have the form:

$$a_{i\sigma}^{(k)}(E) = \sum_j |\alpha_{j;Ei\sigma}^{(k)}|^2 (T_0 - \mu + \Sigma_{jj\sigma}(E)) + \sum_{j \neq j'} (\alpha_{j;Ei\sigma}^{(k)})^* T_{jj'} \alpha_{j';Ei\sigma}^{(k)}. \tag{42}$$

For $k = 0$ the operator $H_{\text{eff}}(E) - a_{i\sigma}^{(k)}(E)$ is energy independent in the bulk, since $a_{i\sigma}^{(0)}(E) = T_{ii} - \mu + \Sigma_{ii\sigma}(E) = T_0 - \mu + \Sigma_{\sigma}(E)$ exactly cancels the energy dependence of the diagonal elements of $H_{\text{eff}}(E)$, while due to the local *ansatz* (11) for the self-energy the

off-diagonal elements of $H_{\text{eff}}(E)$ are energy independent anyway. From equation (36) we then deduce that $b_{i\sigma}^{(1)}(E)$ and $|u_1; Ei\sigma\rangle$ and thus, following equation (41), all coefficients $\alpha_{j;Ei\sigma}^{(1)}$ are independent of energy, too. Using equation (37) and similar arguments, this can be shown by full induction to hold for all k: from the energy independence of $\alpha_{j;Ei\sigma}^{(k)}$ for a certain $k > 1$ we can conclude that $|u_k; Ei\sigma\rangle$ must be energy independent. Furthermore, equation (42) shows that $a_{i\sigma}^{(k)}(E) = T_0 - \mu + \Sigma_\sigma(E) + \text{constant}$ in the bulk, which implies that $H_{\text{eff}}(E) - a_{i\sigma}^{(k)}(E)$ does not depend on E. Therefore, $b_{i\sigma}^{(k+1)}(E)$ and $|u_{k+1}; Ei\sigma\rangle$ and thus all coefficients $\alpha_{j;Ei\sigma}^{(k+1)}$ are independent of energy. To conclude, for all sites i in the crystal volume, the energy dependence of the recursion coefficients $a_{i\sigma}^{(k)}(E)$ and $b_{i\sigma}^{(k)}(E)$ is rather simple: the energy dependence of $a_{i\sigma}^{(k)}(E)$ just reflects the energy dependence of the self-energy for all k, while $b_{i\sigma}^{(k)}(E)$ is a constant for each k.
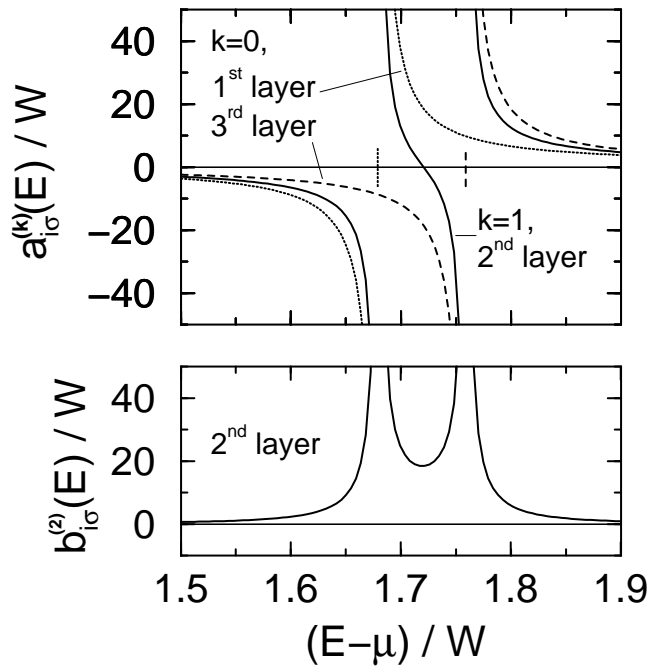
Figure 2. Zeroth-level recursion coefficients $a_{i\sigma}^{(0)}$ for the first (dotted line) and the third layer (dashed line) from the surface and first-level coefficients $a_{i\sigma}^{(1)}$ (solid line) and $b_{i\sigma}^{(2)}$ (solid line, second panel) for the second layer from the surface as functions of energy.

For the surface layers, however, the energy dependence of the recursion coefficients is not that simple. The upper panel of figure 2 shows the zeroth-level recursion coefficient $a_{i\sigma}^{(0)}(E)$ for the first and for the third layer from the surface and the first-level coefficient $a_{i\sigma}^{(1)}(E)$ for the second layer. As has been discussed above, the energy dependence of the zeroth-level coefficients is simply given by the energy dependence of the local self-energy. Due to the layer-by-layer variations of $\langle n_{i\sigma} \rangle$ and $B_{ii\sigma}$, the location of the pole of $a_{i\sigma}^{(0)}(E)$ is different comparing the first with the third layer. The first-level coefficient for the second layer from the surface, however, exhibits a more complicated energy dependence (see figure 2). It shows up two poles, the energetic positions of which coincide with the positions of the poles of the zeroth-order coefficients for the first and the third layer. This

can be explained by considering once more equations (36) and (37). If i denotes a site within the second layer, we have

$$|u_1, Ei\sigma\rangle = \frac{1}{\sqrt{8}} \sum_j |j\sigma\rangle \tag{43}$$

where the sum extends over all nearest-neighbour sites j, i.e. over four sites within the first and over four sites within the third layer. This implies

$$a_{i\sigma}^{(1)}(E) = \frac{1}{8} \sum_j \langle j\sigma | H_{\text{eff}}(E) | j\sigma \rangle = \frac{1}{8} \sum_j (T_0 - \mu + \Sigma_{jj\sigma}(E)). \tag{44}$$

The first-level coefficient $a_{i\sigma}^{(1)}(E)$ for the second layer is thus given by the arithmetic mean of the zeroth-level coefficients for the first and the third layer. As a consequence of the two-pole structure of $a_{i\sigma}^{(1)}(E)$, the second-level coefficient $b_{i\sigma}^{(2)}(E)$ for the second layer shows up two singularities at the related energetic positions (see figure 2, lower panel).
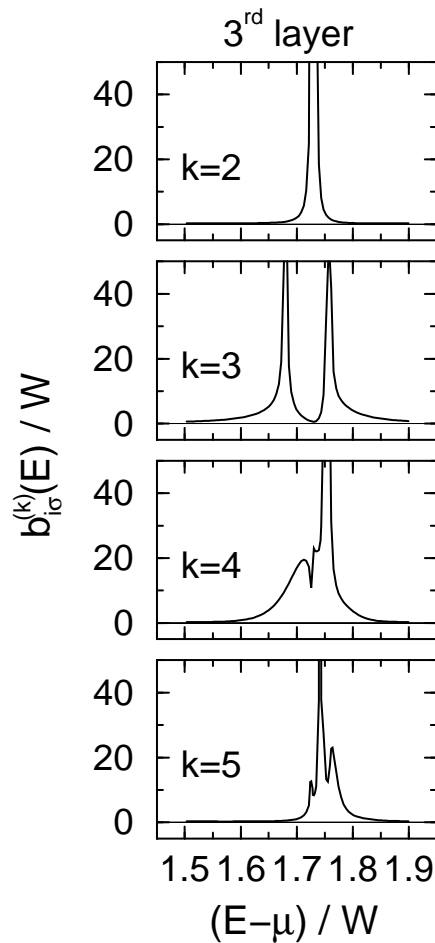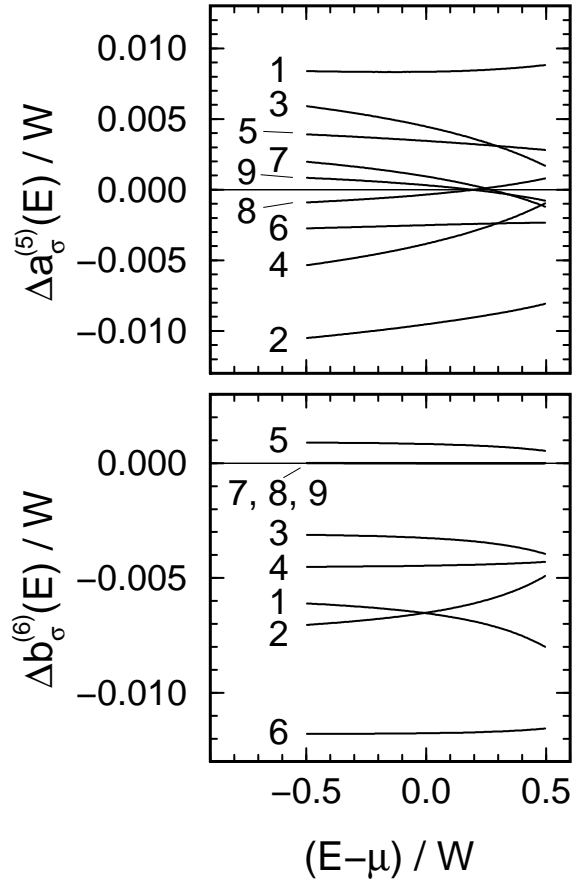

Figure 3. Recursion coefficients $b_{i\sigma}^{(k)}$ for the third layer from the surface and for $k = 2, \dots, 5$ as functions of energy.

The example discussed above indicates that in the vicinity of the surface the energy dependence of the recursion coefficients tends to become more and more complicated when higher levels k are considered. This is corroborated by figure 3, where the coefficients $b_{i\sigma}^{(k)}(E)$ for the third layer from the surface are shown for $k = 2, \ldots, 5$. The first-level coefficient is constant, $b_{i\sigma}^{(1)}(E) = \sqrt{8}T_1$. The energetic positions of the poles of the local self-energies for the second and the fourth layer differ very slightly from each other. Therefore, contrasting with the case for the second layer, the second coefficient ($k = 2$) for the third layer shows only one strong maximum. For the higher recursion levels, however, rather complex peak structures and singularities come into existence. We notice that the main peaks are located in the energy range between $(E - \mu)/W = 1.6$ and $(E - \mu)/W = 1.9$. On the other hand, due to the form of the self-energy (34), the quasi-particle density of states is expected to split up into two parts for the strongly correlated system ($U/W = 2.0$): for $\langle n \rangle = 0.5$ the lower Hubbard band lies around the Fermi level while the upper Hubbard band is located at energies $\sim U/W$ above the Fermi level. The main peaks will thus be located in the Hubbard gap.

In figure 4 we take a closer look at the recursion coefficients in an energy range where a non-vanishing quasi-particle density of states is expected. Between $(E - \mu)/W = -0.5$ and $(E - \mu)/W = 0.5$ the recursion coefficients do not differ very much from their bulk values. In figure 4 we have thus shown the differences between the coefficients for a given layer and the corresponding bulk coefficients. The differences between the fifth-level coefficients $\Delta a_{i\sigma}^{(5)}(E)$ for surface and bulk and the related differences between surface and bulk sixth-level coefficients $\Delta b_{i\sigma}^{(6)}(E)$ are given for the first nine layers from the surface as functions of energy. Let us concentrate on the coefficients $a_{i\sigma}^{(5)}(E)$ first. For all surface layers considered, the energy dependence slightly differs from the E^{-1}-behaviour of the bulk coefficient. The largest differences are observed for the topmost surface layer and the second layer. The differences from the bulk coefficient become smaller and smaller with increasing distance to the surface. In the bulk the coefficient $b_{i\sigma}^{(6)}(E)$ is energetically constant. Therefore, the differences $\Delta b_{i\sigma}^{(6)}(E)$ shown in the lower panel of figure 4 reflect the true energy dependence of the coefficients. The energy dependence is most pronounced for the first and the second layer, and becomes weaker and weaker with increasing distance to the surface. Already for the fourth and all subsequent layers there is hardly any energy dependence. However, for the first six layers from the surface there are significant differences from the bulk value. While the energy dependence exclusively results from correlation effects, this layer dependence is also observed for the 'free' ($U = 0$) system. It reflects the effects of the reduced coordination number of sites at the very surface on the electronic structure. Equations (36) and (37) show that for the calculation of $b_{i\sigma}^{(6)}(E)$ only those local basis orbitals $|j\sigma\rangle$ need to be considered that belong to a cluster of sites j that can be reached by six or fewer nearest-neighbour hoppings from site i. For this reason there is no direct influence of the surface on the sixth-level coefficient $b_{i\sigma}^{(6)}(E)$ for the seventh and all subsequent layers, and apart from a very slight energy dependence (which is not visible on this scale) the coefficient has approached its bulk value. The example given by figure 4 shows that it is possible to distinguish between effects of electron correlations and effects due to the presence of the surface in the analysis of the recursion coefficients.
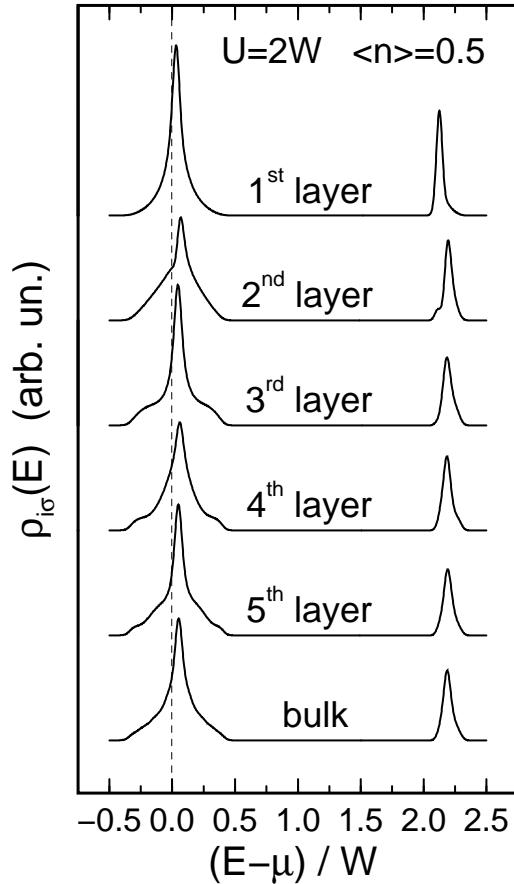
Figure 5 shows the layer-dependent quasi-particle density of states (LDOS) for the first five layers from the surface and the bulk quasi-particle density of states. We first discuss the bulk LDOS. Due to the first-order pole of the self-energy (34), the free Bloch band splits up into two quasi-particle subbands in the strong-correlation regime. Both the lower and the upper Hubbard band show themselves in the LDOS. The separation between the lower and

Figure 4. The difference between a recursion coefficient $a_{i\sigma}^{(k)}$ $(b_{i\sigma}^{(k)})$ for the ith layer from the surface and the recursion coefficient $a_{\sigma}^{(k)}$ $(b_{\sigma}^{(k)})$ for the bulk as a function of energy. Results for the recursion depth $k = 5$ $(k = 6)$ and for the first nine layers $i = 1, \ldots, 9$ are indicated in the figure.

the upper part of the LDOS is approximately given by U. For quarter-filling ($\langle n \rangle = 0.5$) the main part of the spectral weight is concentrated in the lower part around the Fermi energy; the upper part has to be interpreted as a correlation satellite. The electron correlation results in a band narrowing; the width of the lower part amounts to $W_l/W \approx 0.85$. Because of the slight Gaussian and Lorentzian broadening of the LDOS, a more exact determination of the band edges is difficult.

The shape of the LDOS for the surface layers significantly differs from the shape of the bulk LDOS. For each surface layer the LDOS splits up into a lower and an upper Hubbard part. As discussed above, the energetic position of the first-order pole of the local self-energy varies from layer to layer. This layer dependence, however, does not manifest itself in a rigid shift of the LDOS for each of the surface layers. Instead, the layer dependence affects the shape of the LDOS and results in a transfer of spectral weight. The rather large energetic difference between the pole positions for the first and the second layer, for example, leads to different centres of gravity of the upper parts of the LDOS for the first and the second layer. The edges of each surface-layer LDOS coincide with the related edges of

Figure 5. The local quasi-particle density of states for the first five layers from the (100) surface of a bcc crystal and bulk quasi-particle density of states as functions of energy. For the parameters of the calculation, see figure 1.

the bulk LDOS; the layer-by-layer variations are not so pronounced as to result in split-off states. Therefore, we also observe the same above-mentioned narrowing of the lower part of the LDOS at the surface. For the first layer, however, there is an additional effective narrowing of the lower (and of the upper) Hubbard part of the LDOS. Compared with the case for the bulk, the mean deviation from the centre of gravity is strongly reduced for the lower part of the top-layer LDOS; the lower part of the LDOS is much more 'compressed'. This effective narrowing is due to the reduced coordination number for sites in the topmost layer (cf. [15]). Compared with the bulk LDOS, the LDOS for the layers near the surface is considerably distorted. The shape of the top-layer LDOS exhibits the most significant changes with respect to the bulk. In the calculation ten surface layers have been included. It turns out that already the LDOS for the fifth and for all subsequent surface layers resemble the bulk LDOS rather well. The LDOS of the tenth layer can no longer be distinguished from the LDOS in the bulk within numerical accuracy.

The convergence of the surface-layer LDOS to the bulk LDOS with increasing distance from the surface implies the convergence of all integral quantities that are derived from the LDOS. This is demonstrated in figure 6 where the expectation values $\langle n_{i\sigma} \rangle$ and
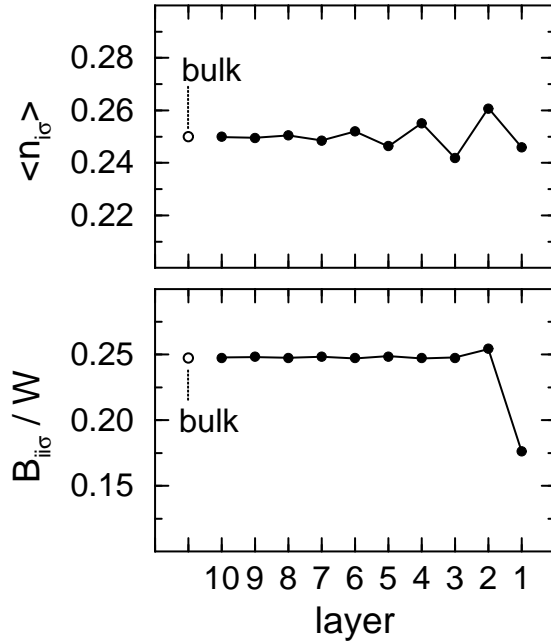
Figure 6. The local average occupation number $\langle n_{i\sigma} \rangle$ and local band correction $B_{ii\sigma}$ for the first ten layers parallel to the (100) surface of a bcc crystal (layer 1 means the topmost surface layer). The bulk values $\langle n_\sigma \rangle$ and B_σ are shown additionally. For the parameters of the calculation, see figure 1.

$B_{ii\sigma}$ are shown for each of the ten surface layers and for the bulk. We notice that near the surface the average occupation number $\langle n_{i\sigma} \rangle$ oscillates around its bulk value $\langle n_\sigma \rangle = 0.25$. With increasing distance to the surface the damping of the oscillations becomes stronger, and eventually the layer-dependent occupation number becomes constant and reaches its bulk value. Generally, the charge transfer associated with the oscillations in $\langle n_{i\sigma} \rangle$ is rather small: the strongest charge transfer is observed for the second layer, where $2\langle n_{i\sigma} \rangle - 2\langle n_\sigma \rangle = \langle n_i \rangle - \langle n \rangle = 0.022$. Also the band correction $B_{ii\sigma}$ slightly oscillates around and finally converges to its bulk value (see figure 6). For the topmost surface layer, however, the band correction is strongly reduced. The result indicates that the band correction is rather sensitive to surface correlation effects. This may have interesting consequences for surface magnetism in the semi-infinite Hubbard model, since the band correction is very decisive as regards the possibility of spontaneous magnetic order.

At this point we would like to stop discussing of the results. A detailed and more systematic analysis of surface correlation effects and surface magnetism is beyond the scope of this study and will appear in a forthcoming paper. Our main intention was to demonstrate that a numerical evaluation of the theory is possible. Finally, we thus turn to the question of a computationally efficient evaluation once more. The main idea as regards tackling the one-particle problem posed by H_{eff} was to apply the recursion technique, since the method is ideally suited for treating systems with reduced translational symmetry. The energy dependence of the self-energy, however, implies an energy-dependent effective Hamiltonian $H_{\mathrm{eff}} = H_{\mathrm{eff}}(E)$, and thus it seems that the recursion scheme must be applied for each energy E out of an energy mesh that is sufficiently fine to guarantee the necessary convergence

of energy integrals that involve the LDOS. The results presented in figures 2 and 3 and their discussion have shown that the layer-by-layer variations of the energetic location of the first-order pole in the layer-dependent self-energy may lead to a rather complex energy dependence of the recursion coefficients. In particular, this holds for the higher levels and in the vicinity of the surface. The complicated structures in the energy-dependent recursion coefficients, however, are confined in the Hubbard gap. Therefore, they are not significant at all as regards the calculation of the imaginary part of the local Green function and thus of the LDOS. In that energetic range where there is a non-vanishing LDOS, a quite smooth and monotonic energy dependence of the recursion coefficients has been observed (see figure 4 for the lower Hubbard part of the LDOS; for the upper part we obtained similar results). For this reason an interpolation of the energy dependence of the recursion coefficients within that energy range is worth the effort to circumvent the computationally rather time-consuming application of the recursion scheme for each energy. We have tested this idea and applied a simple third-order spline interpolation technique. In the relevant energy ranges (at sufficiently large energetic distances from the poles of the layer-dependent self-energy) all recursion coefficients $a_{i\sigma}^{(k)}(E)$ and $b_{i\sigma}^{(k+1)}(E)$ for $k = 0, \ldots, 40$ have been determined on a very sparse energy mesh only. After that the energy dependence of the coefficients has been interpolated to yield smooth functions of energy which are inserted in the continued-fraction representation (35) of the Green function to determine the LDOS. To give an example, about ten energy points in the sparse mesh within the range of the upper and the lower Hubbard band each are completely sufficient for recovering the exact results obtained without interpolation. A spline interpolation of the coefficients is thus very profitable from the numerical point of view. Indeed, it seems to be inevitable for future systematic studies of the dependencies of the results on important model parameters, such as the on-site Coulomb interaction U, the band-filling $\langle n \rangle$ and the temperature T.

5. Concluding remarks

We have presented a moment approach and an energy-dependent recursion method for investigating effects of electron correlations in the semi-infinite Hubbard model. Neglecting a possible quasi-particle damping, a local *ansatz* for the layer-dependent electronic self-energy could be motivated for the strong-correlation regime $U/W \gg 1$. The *a priori* unknown layer-dependent parameters in the *ansatz* have been determined by equating two different but exact representations of the first four moments of the spectral density. Within a local approximation, we could derive a compact form for the self-energy which includes the average local occupation numbers $\langle n_{i\sigma} \rangle$ and a higher-order equal-time correlation function: the band correction $B_{ii\sigma}$. Both expectation values can be calculated self-consistently from the one-electron spectral density. The main advantages of our moment approach rest on the rather simple concept, on its non-perturbative character and on the fact that no restrictions need to be imposed as regards the geometry of the underlying lattice. In the special case of an infinitely extended lattice with perfect translational symmetry, our approach reduces to the spectral density approach, which has proven its usefulness in a number of previous applications.

For the determination of the occupation numbers $\langle n_{i\sigma} \rangle$ and the band correction $B_{ii\sigma}$, the local density of states has to be calculated from the one-particle Green function. With the formal result for the self-energy at hand, we can replace the original Hubbard Hamiltonian in the equation of motion for the Green function by an effective one-particle Hamiltonian. Due to the energy dependence of the self-energy, the effective Hamiltonian itself becomes energy dependent. It has been shown that the equation of motion can be solved numerically for

the semi-infinite system by the standard tight-binding recursion method when performing a straightforward generalization for the case of an energy-dependent Hamiltonian. The advantages of the recursion method show up for tight-binding systems with reduced (translational) symmetry, such as solid surfaces, defects or clusters. For those systems the moment approach for the many-electron problem is thus ideally complemented by the energy-dependent recursion method which provides a solution for the remaining one-particle problem.

The theory has been applied to the (100) surface of a bcc single crystal. We have considered a strongly correlated, paramagnetic electron system with $U = 2W$ at quarter-filling $\langle n \rangle = 0.5$ and temperature $T = 0$. The self-consistent results for the energy dependence of the recursion coefficients have been analysed in detail. Only the low-level and the bulk recursion coefficients allow for a simple interpretation. The energy dependence of the coefficients $a_{i\sigma}^{(k)}(E)$ for the zeroth level $k = 0$ at all sites i as well as for all levels k at sites in the bulk directly reflect the energy dependence of the local self-energy. On the other hand, the coefficient $b_{i\sigma}^{(k)}(E)$ is a constant for $k = 1$ at all sites and in the bulk even for all levels k. In all other cases and in particular for high-level coefficients in the vicinity of the surface, we have observed a rather complex energy dependence. In those energy ranges where there is a non-vanishing local quasi-particle density of states (LDOS), however, the energy dependence of the coefficients is smooth. This allows for an interpolation of the energy dependence of the recursion coefficients which drastically reduces the computational effort.

With the interpolation of the recursion coefficients the numerical problem remains tractable also for a systematic study of the dependencies of the results on the model parameters U, $\langle n \rangle$ and T. Such work is in progress. Furthermore, improvements are intended for the future that take into account non-local terms within a refined *ansatz* for the self-energy as well as quasi-particle damping along the direction shown in [41]. The semi-infinite Hubbard model can serve as a prototype model for studying itinerant surface magnetism. A further application of the theory will therefore concern the question of spontaneous magnetic order at the surface.

Acknowledgment

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