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Two-site Hubbard model, the Bardeen-Cooper-Schrieffer model, and the concept of correlation entropy

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Exactly solvable models (the two-electron two-site Hubbard model and the Bardeen-Cooper-Schrieffer model) are revisited in terms of their natural occupation numbers (eigenvalues of the true, i.e., correlated, one-particle density matrix). Entropylike expressions that may serve as measures of the correlation strength are related to possible reference states for the definition of correlation and discussed as functions of the system parameters. [S0163-1829(97)03015-4]

I. INTRODUCTION

Many-electron systems such as atoms, molecules, clusters, solids, and models of it such as jellium, Hubbard, and Bardeen-Cooper-Schrieffer (BCS) show the complex phenomenon of ''electron correlation,'' caused by the Coulomb interaction. Often weak and strong correlations are distinguished. The question is obvious, whether these qualitative terms can be made quantitatively precise. Indeed there are recent attempts to define (in addition to the correlation energy and the correlation and Coulomb hole, respectively) quantum-kinematic measures of the correlation strength.[1–11] To define such measures, in Refs. 1 and 2 fluctuations, in Refs. 3 and 4 the coefficients of the configuration-interaction (CI) expansion, and in Ref. 5 the order of converged many-body perturbation theory are used. In Refs. 4 and 6–11 it is studied to what extent the one-particle density matrix (1PDM) $\gamma(x,x')=\langle\Psi|\psi^+(x')\psi(x)|\Psi\rangle$ of a state $|\Psi\rangle$ displays the correlation present in that state [ψ^+,ψ are Fermi operators and $x=(\mathbf{r},\sigma)$]. The idea is to use the eigenvalues n_κ of the 1PDM for that purpose. The deviations of these natural occupation numbers (NON's) n_κ from 1 or 0 (these are the only values in the limit of ''no correlation,'' or, more precisely, in the case of only a single Slater determinant) describe the phenomenon correlation on the 1P level. So the q-order nonidempotency $C(q)=N-\Sigma_\kappa(n_\kappa)^q$, the Tsallis entropy $S(q)=C(q)/(q-1)$,[12] and the correlation ''entropy'' $S=S(1)=C'(1)$ or

$$S=\sum_\kappa n_\kappa(-\ln n_\kappa),\quad \sum_\kappa n_\kappa=N \tag{1.1}$$

are zero for no correlation and increase with increasing correlation. Increasing correlation can be achieved (i) for the state (e.g., the ground state $|0\rangle$) of a system with given parameters by going from a not as good description of the correlation to a better one (e.g., better basis set and more Slater determinants in the CI expansion) or (ii) for a ''perfect'' description of a correlated many-electron state by changing system parameters (e.g., geometry parameters and coupling constants). In Ref. 6 the entropylike expression S is conjectured to be proportional to the correlation energy. Of course S is not the only quantity that indicates correlation. Other quantities obtained from the NON's n_κ (with values $n_{\kappa'}$ near and below 1 and a ''jump'' to values $n_{\kappa''}$ near and above 0) are (i) the difference between the lowest value of the $n_{\kappa'}$ and the highest value of the $n_{\kappa''}$ (it generalizes the renormalization constant or quasiparticle weight z_F of the electron-gas momentum distribution); (ii) the sum of all $n_{\kappa''}$ (correlation tail); and (iii) the second-order nonidempotency $C=C(2)$, which is simultaneously the normalization of the Coulomb hole $u_C(x_1;x_2)=\rho(x_1)\rho(x_2)-|\gamma(x_1,x_2)|^2-n(x_1;x_2)$, where $\rho(x)=\gamma(x,x)$ and $n(x_1;x_2)$ is the pair distribution function. It may be that these quantities and others (e.g., those obtained from the spin-traced 1PDM, see below) behave differently when changing different system parameters. So not only a single quantity, but rather a certain set of quantities [and for a given parameter value λ_0 not only $S(\lambda_0)$, etc., but also the derivatives $S'(\lambda_0)$, etc.] would be necessary to characterize the correlation sufficiently precisely (on a 1P level).

The correlation entropy itself [with Eq. (1.1) or modifications of it or with higher-order entropies obtained from higher-order reduced density matrices] is still in its infancy. The ultimate applications are unknown, but may include tests of the quality of the approximate correlated many-electron wave functions[13–15] and constructions of quantum states with the maximum-entropy method.[16,17] Obviously a reasonable definition of a quantitative correlation measure [i.e., a possible modification of Eq. (1.1)] depends on the choice of a reasonable reference state (which is not always a single Slater determinant). In the case a system has more than one control parameter, one may not exclude that it is reasonable to let each parameter have its own correlation strength. For these questions see the following remarks.

The correlation entropy (1.1) is based on the nonidempotency of the NON's n_κ and proves to be an appropriate measure of the correlation strength (on the 1P level) if the reference state defining correlation is a single Slater determinant. The latter is not always the case. Indeed the situation is more complicated when the symmetry of the problem (angular momenta as conserved quantities, dissociation limit of a molecule, etc.) requires more than a single Slater determinant even in the absence of Coulomb repulsion (e.g., spin conservation alone mixes Slater determinants in the noninteracting wave function[10]). Then Eq. (1.1) would indicate a correlation, although there is no correlation. So modifications of formula (1.1) are necessary.

In addition to the eigenvalues n_κ of the ''full'' (spin-dependent) 1PDM $\gamma(x,x')$ it seems reasonable to consider also the eigenvalues n_k of the spin-traced 1PDM $\gamma(\mathbf{r},\mathbf{r}')=\Sigma_\sigma\gamma(x,x')|_{\sigma'=\sigma}$. These spatial NON's n_k vary between 0 and 2 and for the definition of the other correlation entropies the following nonidempotencies can be used. (i) Among all the n_k there is a certain number N_0 $(<N)$ of NON's n_{k_0} with values between 1 and 2. Then the reduced NON's $n_{k_0}-1$ are between 0 and 1 and all the other N_1 $(=N-N_0)$ NON's n_{k_1} also have values between 0 and 1. (ii) All the $n_k/2$ have values between 0 and 1. So possible measures of the correlation strength are

$$S_1=-\sum_{k_0}(n_{k_0}-1)\ln(n_{k_0}-1)-\sum_{k_1}n_{k_1}\ln n_{k_1}, \quad (1.2)$$

$$S_2=-\sum_k\frac{n_k}{2}\ln\frac{n_k}{2}. \quad (1.3)$$

They have in common to measure deviations of the NON's from 0 and 2, but in particular NON's with values approximately equal to 1 are treated differently: They almost do not contribute to S_1, whereas each such NON contributes approximately $\frac{1}{2}\ln 2$ to S_2. (Note that $S_2=\frac{1}{2}S$ if $n_\kappa=\frac{1}{2}n_k$, where κ includes s, and note that for $N=2$ and for a singlet the spatial wave function is a sum of permanents (a permanent is defined like a determinant but with all plus signs); $n_{k_0}\approx 1$ and $n_{k_1}\approx 1$ mean the dominance of that permanent where two different natural states are singly occupied.)

Application of Eqs. (1.2) and (1.3) to the ground state (singlet) of the molecule $H_2(R)$ shows,[10] that $S_1(R)$ has a maximum where n_{k_0} passes through 1.5 and vanishes asymptotically for $R\rightarrow\infty$; it corresponds to a reference state that shows a smooth transition from a Hartree-Fock (HF) description for small R to a Heitler-London (HL) description for large R. (Note that HF means a spatial permanent with $n_{k_0}=2$ and $n_{k_1}=0$, from which follows a single Slater determinant of spin orbitals, and that HL means a spatial permanent with $n_{k_0}=n_{k_1}=1$, from which follow two Slater determinants of spin orbitals.) $S_2(R)$, on the other hand, approaches ln2 asymptotically for $R\rightarrow\infty$ and corresponds to an understanding of the correlation with the HF approximation as a reference state for all separations R, although the HF approximation (with a single determinant) fails in the dissociation limit and hence must be strongly corrected (strong correlation). So which correlation entropy (S_1 or S_2) is more appropriate depends on the more or less reasonable reference state. Yet to be studied is the question whether Eqs. (1.2) or (1.3) or even other constructions are more appropriate to display the correlation for a fixed separation R but varying, in particular, the increasing coupling constant λ of the electron-electron repulsion $\lambda\epsilon^2/r_{12}$. An appropriate correlation measure should increase with λ. Also the question is open whether ''static and dynamic correlations''[18] can be characterized by different correlation measures (e.g., in cases where near degeneracies exist, Be as an example requires at least four Slater determinants of spin orbitals as a reasonable reference state or starting point).

The concept of correlation entropy has been applied so far to the uniform electron gas with the density parameter r_s,[7] to half-space jellium,[8] to the isoelectronic series He(Z) and the Hooke law model with the oscillator frequency ω,[4,9] to the molecule $H_2(R)$,[4,10] and to other atoms and molecules.[11] While Refs. 4 and 7–10 investigate how S,S_1,S_2 depend on the system parameters r_s,Z,ω,R, in Ref. 11 the basis set dependence of the entropy expression $-\Sigma_k n_k\ln n_k$ is considered and Collins' conjecture[6] is checked; note that this entropy is $2S_2-N\ln 2$ for $n_\kappa=\frac{1}{2}n_k$ and it consists of positive and negative terms, so it is or can be totally negative and is nonzero $(=-N\ln 2)$ in the no-correlation case of $N/2$ NON's $n_{k_0}=2$. In the present work exactly solvable models, namely, the two-site two-electron Hubbard model (Sec. II) and the BCS model (Sec. III), are studied in terms of correlation entropies.

II. THE TWO-ELECTRON TWO-SITE HUBBARD MODEL

In the Hamiltonian

$$\hat{H}=-\frac{t}{2}\sum_{i,\sigma}c^\dagger_{i\sigma}c_{\bar{i}\sigma}+2U\sum_i\hat{n}_{i\uparrow}\hat{n}_{i\downarrow} \quad (2.1)$$

the prefactors $-t/2$ and $2U$ are, contrary to the usual notation t and U, chosen to make the following expressions as simple as possible. The first term ($\hat{T}$) describes the hopping between the two sites $i=1$ and 2 ($\bar{1}=2$, $\bar{2}=1$), with $c^\dagger_{i\sigma}$, $c_{i\sigma}$ the Fermi creation and annihilation operators (at site i and with spin $\sigma=\uparrow,\downarrow$), and the second term ($\hat{V}$) describes the on-site interaction (repulsion for $U>0$, attraction for $U<0$) between the two electrons with the spin-dependent site occupancy operator $\hat{n}_{i\sigma}=c^\dagger_{i\sigma}c_{i\sigma}$. Equation (2.1) may be considered as a simplified version of a tight-binding description of the H_2 molecule. For papers treating molecules within the Hubbard model see Refs. 19 and 20 and for a recent paper dealing with the attractive Hubbard model (with the transition from the weak-coupling limit with BCS properties to the strong-coupling limit with Bose-Einstein condensation) see Ref. 21.

The eigenstates of $\hat{H}$ are characterized by their energies E, by the eigenvalues S (= 0 or 1) and M_S (= 0 or 0,±1) of the total spin, and by the eigenvalues p (= ± 1) of the site permutation operator. The four 1P states $|i\sigma\rangle = c^{\dagger}_{i\sigma}|\mathrm{vac}\rangle$ with $c_{i\sigma}|\mathrm{vac}\rangle = 0$ form the basis set to construct $\binom{4}{2} = 6$ two-particle (or geminal) states $|E,S,M_S,p\rangle$, namely, three triplet states with $p=-1$, one singlet state with $p=-1$, and two other singlet states with $p=+1$; see the following.

In the triplet three states ($M_S = 0, \pm 1$) there is no interaction (because the spins are parallel) and no hopping (because of the Pauli principle), so they are (uninteresting) eigenstates of $\hat{T}$ and $\hat{V}$ with the eigenvalues 0: $|0,1,M_S,-1\rangle$. The singlet state

$$|\, 2U,\, 0,\, 0, -1\rangle = \frac{1}{\sqrt{2}}(c^{\dagger}_{1\uparrow}c^{\dagger}_{1\downarrow} - c^{\dagger}_{2\uparrow}c^{\dagger}_{2\downarrow})|\mathrm{vac}\rangle \tag{2.2}$$

does not depend on t and U and is an eigenstate of $\hat{T}$ and $\hat{V}$ with eigenvalues 0 and $2U$, respectively; it is a purely ionic state. The two other singlet states arise from the mixing of the ionic and nonionic geminals, respectively:

$$|A\rangle = \frac{1}{\sqrt{2}}(c^{\dagger}_{1\uparrow}c^{\dagger}_{1\downarrow} + c^{\dagger}_{2\uparrow}c^{\dagger}_{2\downarrow})|\mathrm{vac}\rangle, \tag{2.3}$$

$$|B\rangle = \frac{1}{\sqrt{2}}(c^{\dagger}_{1\uparrow}c^{\dagger}_{2\downarrow} + c^{\dagger}_{2\uparrow}c^{\dagger}_{1\downarrow})|\mathrm{vac}\rangle.$$

With $|E,\, 0,\, 0, +1\rangle = \alpha|A\rangle + \beta|B\rangle$ and

$$\hat{H}|A\rangle = 2U|A\rangle - t|B\rangle, \tag{2.4}$$

$$\hat{H}|B\rangle = -t|A\rangle,$$

the diagonalization of $\hat{H}$ yields $E^{*} = \sqrt{t^2+U^2} + U$ for the excited state $|E^{*},\, 0,\, 0, +1\rangle$ and

$$E = -\sqrt{t^2+U^2} + U \tag{2.5}$$

for the ground state (GS) $|E,\, 0,\, 0, +1\rangle \equiv |0\rangle$ (see Fig. 1).

The GS coefficients

$$\alpha = \frac{1}{\sqrt{2}}\sqrt{1 - \frac{x}{\sqrt{1+x^2}}}, \quad \beta = \frac{1}{\sqrt{2}}\sqrt{1 + \frac{x}{\sqrt{1+x^2}}} \tag{2.6}$$

depend only on the dimensionless parameter combination $x = U/t$. Note that $2\alpha\beta = 1/\sqrt{1+x^2}$.

Knowing the GS $|0\rangle$, the following expectation values can be constructed: the spin-dependent and spin-summed site occupancies $n_{i\sigma}$ and $n_i = \Sigma_\sigma n_{i\sigma}$, respectively, the spin-traced 1PDM $\gamma_{ii'} = \langle 0|\Sigma_\sigma c^{\dagger}_{i'\sigma} c_{i\sigma}|0\rangle$, the spin-summed pair occupancy $n_{ij} = n_i n_j - \delta_{ij} n_i$ (on-site for $j=i$ and off-site for $j=i$), and the hopping and interaction energies T and V, respectively.

For the 1PDM of the GS

$$\gamma_{ii'} = \begin{pmatrix} 1 & 2\alpha\beta \\ 2\alpha\beta & 1 \end{pmatrix} \tag{2.7}$$

results. Thus the site occupancy $n_i = \gamma_{ii}$ is $n_i = 1$ and the hopping energy $T = -(t/2)\Sigma_i \gamma_{i\bar{i}}$ is $T = -2\alpha\beta t$ or

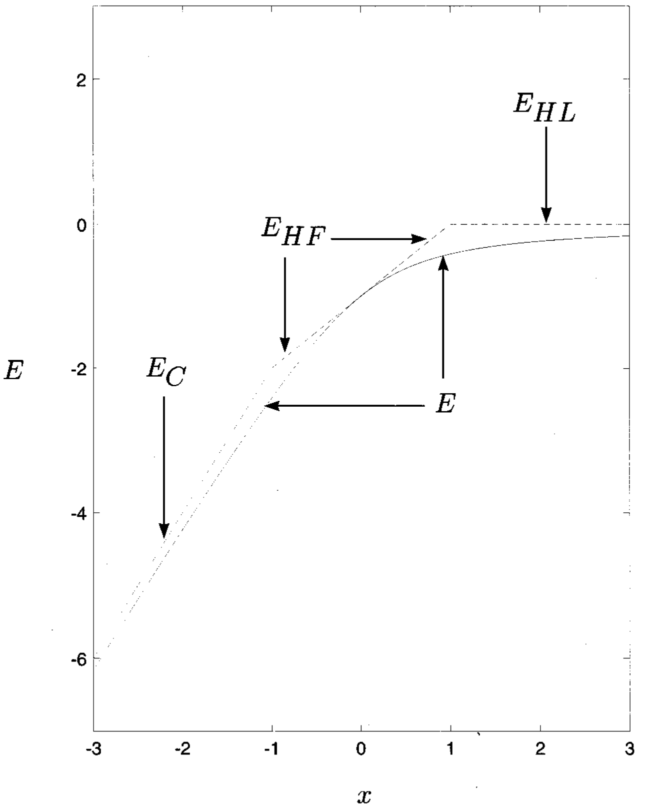

FIG. 1. Hubbard model (2.1): GS energy (2.5) vs $x = U/t$. The dashed lines are reasonable reference energies: $E_C = 2U$ [cf. Eq. (2.2)] for $x \leqslant -1$, $E_{\mathrm{HF}} = -t + U$ for $|x| \leqslant 1$, and $E_{\mathrm{HL}} = 0$ for $x \geqslant 1$. Energy is in units of t.

$$T = -\frac{t}{\sqrt{1+x^2}}, \tag{2.8}$$

with $T = -t$ for $U = 0$ and $T \to 0$ for $U \to \pm\infty$. [The same result (2.8) arises from $T = t\partial E/\partial t$ according to the Hellmann-Feynman theorem.[22]] Diagonalization of $\gamma_{ii'}$ yields the site NON's

$$n_{\pm} = 1 \pm \frac{1}{\sqrt{1+x^2}} \tag{2.9}$$

(see Fig. 2) (the site and spin NON's are $n_{\pm,\sigma} = n_\sigma n_\pm$ with $n_\sigma = \frac{1}{2}$) and the binding (+) and antibinding (−) molecular natural orbitals (NO's), respectively,

$$|\pm\sigma\rangle = \frac{1}{\sqrt{2}}(|\, 1\sigma\rangle \pm |\, 2\sigma\rangle) = \frac{1}{\sqrt{2}}(c^{\dagger}_{1\sigma} \pm c^{\dagger}_{2\sigma})|\rangle \equiv c^{\dagger}_{\pm\sigma}|\rangle. \tag{2.10}$$

Electron pairs are described by the on-site and off-site pair occupancies, respectively,

$$n_{ii} = \frac{1}{2}\left(1 - \frac{x}{\sqrt{1+x^2}}\right), \tag{2.11}$$

$$n_{i\bar{i}} = \frac{1}{2}\left(1 + \frac{x}{\sqrt{1+x^2}}\right)$$

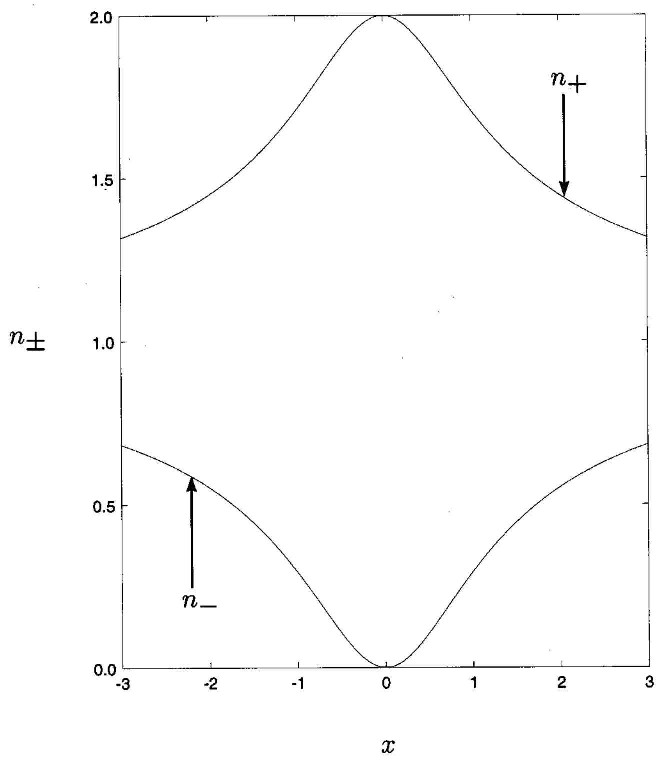

FIG. 2. Hubbard model (2.1): natural occupation numbers $n_\pm$ of the GS $|0\rangle$ (cf. Eqs. (2.13) or (2.14)], vs $x=U/t$ according to Eq. (2.9). n_+ and n_- describe the occupation of the binding and antibinding natural orbitals (2.10), respectively.

(see Fig. 3). Thus the interaction energy $V=U\Sigma_i n_{ii}$ is

$$V=\left(1-\frac{x}{\sqrt{1+x^2}}\right)U, \tag{2.12}$$

with $V=U$ for $x=0$, $V\rightarrow 0$ for $x\rightarrow +\infty$, and $V\rightarrow 2U$ for $x\rightarrow -\infty$. (The same result arises from $V=U\partial E/\partial U$ due to the Hellmann-Feynman theorem.) For $n_\pm$ vs the scaled Hubbard parameter x see Fig. 1.

A comparison of Eqs. (2.6) and (2.11) shows $n_{ii}=\alpha^2$ and $n_{i\bar{i}}=\beta^2$ or

$$|0\rangle=\sqrt{n_{ii}}|A\rangle+\sqrt{n_{i\bar{i}}}|B\rangle. \tag{2.13}$$

Thus on-site and off-site pair occupancies determine the weight of the ionic geminal $|A\rangle$ and the nonionic geminal $|B\rangle$ in the GS $|0\rangle$. For $x=0$ they are mixed with equal weights; see $|0\rangle=(1/\sqrt{2})(|A\rangle+|B\rangle)$. The increasing Hubbard repulsion U (>0) suppresses the ionic contribution or double occupancy of a single site and vanishes asymptotically for $x\rightarrow +\infty$; see $|0\rangle\rightarrow|B\rangle$. The increasing Hubbard attraction $|U|$ suppresses the nonionic contribution or single occupancy and vanishes asymptotically for $x\rightarrow -\infty$; see $|0\rangle\rightarrow|A\rangle$.

The CI expression of the GS $|0\rangle$ in terms of the NO's (2.10) yields

$$|0\rangle=\sqrt{\frac{n_+}{2}}|++\rangle-\mathrm{sgn}U\sqrt{\frac{n_-}{2}}|--\rangle, \tag{2.14}$$

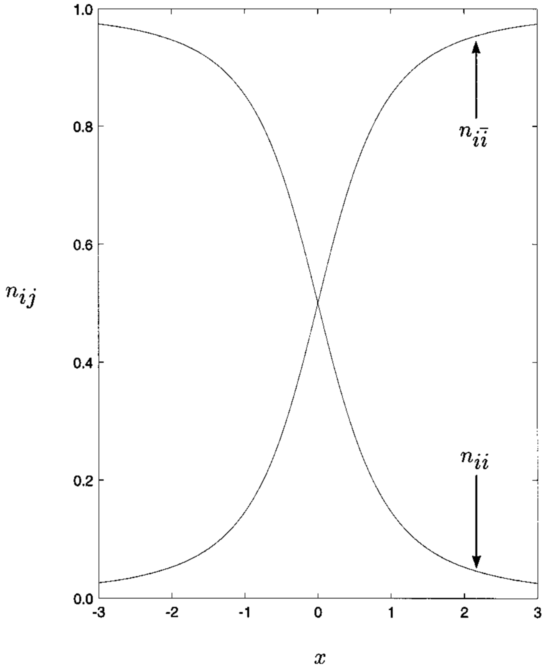

FIG. 3. Hubbard model (2.1): on-site and off-site pair occupancy of the GS $|0\rangle$ vs $x=U/t$ according to Eqs. (2.11).

where the geminals $|\pm\pm\rangle=c^\dagger_{\pm\uparrow}c^\dagger_{\pm\downarrow}|\rangle$ are introduced and $\alpha+\beta=\sqrt{n_+}$ and $\alpha-\beta=-\mathrm{sgn}U\sqrt{n_-}$ have been used. So the NON's $n_\pm$ determine the weights of the geminals $|++\rangle$ and $|--\rangle$ in the GS $|0\rangle$. For $x=0$ it is $|0\rangle=|++\rangle$. With the increasing Hubbard repulsion U (>0) or attraction $|U|$ the weights of $|++\rangle$ and $|--\rangle$ decrease and increase, respectively, and for $x\rightarrow\pm\infty$ they become equally weighted; see $|0\rangle\rightarrow(1/\sqrt{2})(|++\rangle\mp|--\rangle)$. This discussion of the GS $|0\rangle$ in terms of the NO's (2.10) shows simultaneously that $|0\rangle$ is given for $x=0$ by a single Slater determinant, whereas $|0\rangle$ is given for $x\rightarrow\pm\infty$ by those mixings of two Slater determinants in each case that asymptotically degenerate with the triplet state $|0,1,0,-1\rangle$ and the singlet state $|2U,0,0,-1\rangle$ of Eq. (2.2), respectively.

In the HF approximation the GS is given by $|\mathrm{HF}\rangle=|++\rangle$ and $E_{\mathrm{HF}}=-t+U$. This is a reasonable approximation only for small $|x|(\lesssim 1)$. For large $|x|$ the correlation energy $E_{\mathrm{corr}}=-\sqrt{t^2+U^2}+t$ approaches $-|U|+t$; see Fig. 4. This unreasonable diverging behavior results from not suppressing the ionic state $|A\rangle$ in $|\mathrm{HF}\rangle=1/\sqrt{2}(|A\rangle+|B\rangle)$.

If one considers alternatively for $x\geqslant 1$ the HL approximation $|\mathrm{HL}\rangle\equiv|B\rangle$ of Eq. (2.3) with $E_{\mathrm{HL}}=0$ [see Eq. (2.4)] as a reasonable reference state and for $x\leqslant -1$ the state $|C\rangle\equiv|2U,0,0,-1\rangle$ of Eq. (2.2) with $E_C=2U$ as a reasonable reference state, i.e., altogether $|\tilde{\Psi}\rangle=|C\rangle|\Theta(-x-1)+|\mathrm{HF}\rangle\Theta(1-|x|)+|\mathrm{HL}\rangle\Theta(x-1)$ [with $\Theta(x)$ a step function], then the difference between the true energy (2.5) and the reference energy $\tilde{E}=E_C\Theta(-x-1)+E_{\mathrm{HF}}\Theta(1-|x|)+E_{\mathrm{HL}}\Theta(x-1)$, i.e.,

$$\Delta E=\begin{cases}-\sqrt{U^2+t^2}-U & \text{for } U<-t\\ -\sqrt{t^2+U^2}+t & \text{for } -t<U<t\\ -\sqrt{U^2+t^2}+U & \text{for } U>t\end{cases} \tag{2.15}$$

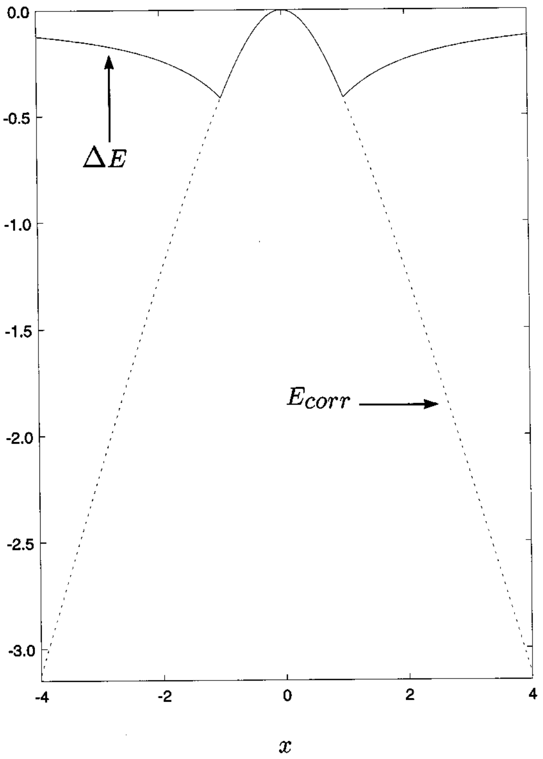

FIG. 4. Hubbard model (2.1): energy differences of the GS $|0\rangle$ vs $x=U/t$. The full line $\Delta E=E-\tilde{E}$ [cf. Eq. (2.15)] and the dashed line $E_{\text{corr}}=E-E_{\text{HF}}$. Energy is in units of t.

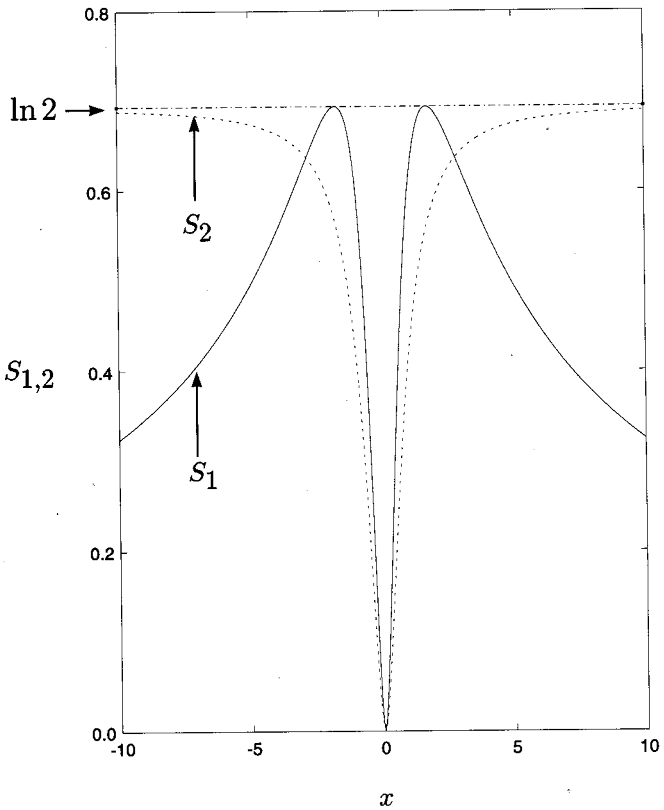

FIG. 5. Hubbard model (2.1): correlation entropy of the GS $|0\rangle$ vs $x=U/t$. The full line is S_1 of Eq. (2.18) and the dashed line S_2 of Eq. (2.19).

vanishes for $x\to 0$ (where $|\text{HF}\rangle$ is good), and $x\to+\infty$ (where $|\text{HL}\rangle$ is good), and $x\to-\infty$ (where $|C\rangle$ is good); see Fig. 4. This procedure applied to the NON's $n_\pm$ and to the pair occupancy n_{ij}, yield

$$\tilde{n}_+=2\Theta(1-|x|)+\Theta(|x|-1), \qquad (2.16)$$

$$\tilde{n}_-=\Theta(|x|-1)$$

and

$$\tilde{n}_{ii}=\Theta(-x-1)+\frac{1}{2}\Theta(1-|x|), \qquad (2.17)$$

$$\tilde{n}_{i\bar{i}}=\frac{1}{2}\Theta(1-|x|)+\Theta(x-1).$$

These deviations of $\tilde{E}$, $\tilde{n}_\pm$, and $\tilde{n}_{ij}$ from their corresponding true GS values E, $n_\pm$, and n_{ij}, respectively, are largest for $x\approx 1$ and vanish for $x\to 0$ and $\pm\infty$. Note that $\partial T/\partial U$ and the (reduced) interaction energy $V-2U\Theta(-x)$ have qualitatively the same behavior (with maxima at $|x|\approx 1$).

How are these differences (of $|\text{HF}\rangle$ as well as $|\tilde{\Psi}\rangle$ compared with $|0\rangle$) displayed by correlation entropies built up from the site NON's $n_\pm$? While the entropy

$$S_1=-(n_+-1)\ln(n_+-1)-n_-\ln n_- \qquad (2.18)$$

vanishes for $x\to 0$ and $\pm\infty$ and has a maximum near $|x|=1$ (like ΔE), the entropy

$$S_2=-\frac{n_+}{2}\ln\frac{n_+}{2}-\frac{n_-}{2}\ln\frac{n_-}{2} \qquad (2.19)$$

vanishes for $x\to 0$ and increases monotonically (like $|E_{\text{corr}}|$) and approaches ln2 for $x\to\pm\infty$ [in contrast to $|E_{\text{corr}}|$, which diverges, but in qualitative agreement with $T(x)-T(0)$ and $E(x)-E(0)-2U\Theta(-x)$, which both saturate at t]; see Fig. 5. It shows that the true GS $|0\rangle$ for $x\to\pm\infty$ strongly deviates from $|\text{HF}\rangle$, whereas it weakly deviates from $|\tilde{\Psi}\rangle$. Figure 6 presents energy differences vs correlation entropies (in the spirit of Collins' conjecture[6]).

Note that $x\to+\infty$ can be viewed as $t\to 0$ (for fixed $U>0$) or as $U\to+\infty$ (for fixed t). The first case can be understood as suppressing the hopping between the sites, so the sites decouple and the electrons are (similarly to the stretched H_2 molecule) well described by the HL wave function; the deviations of this reference state from the true GS $|0\rangle$ seem to be reasonably described by S_1. The second case can be understood as suppressing double occupancy at one site due to the increasing Hubbard repulsion [similarly to H_2 if the coupling constant λ of the Coulomb repulsion $\lambda(\epsilon^2/r_{12})$ is turned on]; this seems to be described by S_2. The peculiarity of the simple Hubbard model (2.1) is that its system energy parameters t and U scale mutually according to their dimensionless ratio x, whereas in $H_2(R,\lambda)$ the dimensionless quantities R/a_B and λ are independent of each other, so that, as mentioned in the Introduction, the phenom-

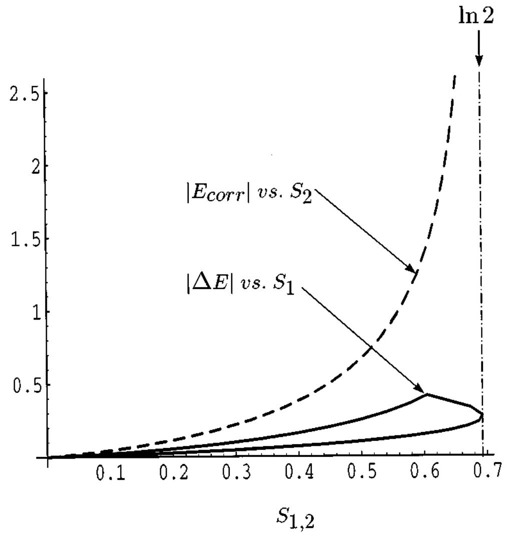

FIG. 6. Hubbard model (2.1): energy differences vs correlation entropies. The full line is $|\Delta E|$ vs S_1 and the dashed line $|E_{\mathrm{corr}}|$ vs S_2. Energy is in units of t.

enon correlation can be discussed in terms of different correlation entropies separately for $R\rightarrow\infty$ (and fixed λ) or $\lambda\rightarrow\infty$ (and fixed R).

III. CORRELATION ENTROPY OF THE BCS GROUND STATE

Here we ask to what extent the electron correlation in the superconducting state can be measured on a 1P level. The appropriate quantity is again the 1PDM

$$\gamma(x,x')=\langle|\psi^{+}(x')\psi(x)|\rangle, \tag{3.1}$$

where the angular brackets in Eq. (3.1) denote the BCS ground state, which is the vacuum state of quasiparticles (ν,σ),

$$\alpha_{\nu\sigma}|\rangle=0. \tag{3.2}$$

The annihilation and creation operators $\alpha_{\nu\sigma},\alpha^{\dagger}_{\nu\sigma}$ for a quasiparticle (ν,σ) are given by the Bogoliubov relation (see e.g., Ref. 23)

$$\psi(\mathbf{r},\uparrow)=\sum_{\nu}\,[u_{\nu}(\mathbf{r})\alpha_{\nu\uparrow}-v^{*}_{\nu}(\mathbf{r})\alpha^{\dagger}_{\nu\downarrow}], \tag{3.3}$$

$$\psi(\mathbf{r},\downarrow)=\sum_{\nu}\,[u_{\nu}(\mathbf{r})\alpha_{\nu\downarrow}+v^{*}_{\nu}(\mathbf{r})\alpha^{\dagger}_{\nu\uparrow}];$$

$$\psi^{+}(\mathbf{r},\uparrow)=\sum_{\nu}\,[u^{*}_{\nu}(\mathbf{r})\alpha^{\dagger}_{\nu\uparrow}-v_{\nu}(\mathbf{r})\alpha_{\nu\downarrow}],$$

$$\psi^{+}(\mathbf{r},\downarrow)=\sum_{\nu}\,[u^{*}_{\nu}(\mathbf{r})\alpha^{\dagger}_{\nu\downarrow}+v_{\nu}(\mathbf{r})\alpha_{\nu\uparrow}].$$

The amplitudes $u_{\nu}(\mathbf{r}),v_{\nu}(\mathbf{r})$ are the eigenfunctions of the Bogoliubov–de Gennes Hamiltonian

$$\mathcal{H}=\begin{pmatrix} H_0 & \Delta(\mathbf{r}) \\ \Delta^{*}(\mathbf{r}) & -H^{*}_0 \end{pmatrix} \tag{3.4}$$

with positive energies $\xi_{\nu}>0$, following from

$$\mathcal{H}\begin{pmatrix} u_{\nu} \\ v_{\nu} \end{pmatrix}=\xi_{\nu}\begin{pmatrix} u_{\nu} \\ v_{\nu} \end{pmatrix}, \tag{3.5}$$

and the normalization

$$(u_{\nu},u_{\nu})+(v_{\nu},v_{\nu})=1, \tag{3.6}$$

where $(f,g)=\int d^3r f^{*}(\mathbf{r})g(\mathbf{r})$. Using Eqs. (3.2) and (3.3) for the 1PDM (3.1) results in

$$\gamma(x,x')=\delta_{\sigma\sigma'}\sum_{\nu}\,v^{*}_{\nu}(\mathbf{r})v_{\nu}(\mathbf{r}'). \tag{3.7}$$

In general, the amplitudes $v_{\nu}(\mathbf{r})$ are not mutually orthogonal and the nonzero NON's n_{κ} must be calculated from the zeros of the determinant

$$\det\{n_{\kappa}\delta_{\nu\mu}-(v_{\nu},v_{\mu})\}=0. \tag{3.8}$$

In the following we consider only the case of a homogeneous superconductor without a magnetic field. Then the amplitudes u_{ν},v_{ν} are plane waves (Ω is the volume of normalization)

$$u_{\nu}\equiv U_k\frac{e^{i\mathbf{kr}}}{\sqrt{\Omega}},\quad v_{\nu}\equiv V_k\frac{e^{i\mathbf{kr}}}{\sqrt{\Omega}}, \tag{3.9}$$

with real coefficients U_k,V_k and the normalization $U^2_k+V^2_k=1$. For the 1PDM in the $(\mathbf{k},\sigma)$ representation we obtain

$$\gamma_{\mathbf{k}\sigma,\mathbf{k}'\sigma'}=\delta_{\sigma\sigma'}\delta_{\mathbf{kk}'}V^2_k. \tag{3.10}$$

Therefore, the NON's are V^2_k with $2\Sigma_k V^2_k=N$ and the correlation entropy per particle is

$$s=-\frac{2}{N}\sum_{k}\,V^2_k\ln V^2_k. \tag{3.11}$$

The coefficients V_k may be expressed by the gap function Δ_k,

$$V^2_k=\frac{1}{2}\left(1-\frac{\epsilon_k}{\sqrt{\epsilon^2_k+\Delta^2_k}}\right), \tag{3.12}$$

with

$$\Delta_k=\begin{cases}\Delta & \text{for } |\epsilon_k|<\delta \\ 0 & \text{otherwise.}\end{cases} \tag{3.13}$$

The single-particle energies ϵ_k are measured from the Fermi energy and δ is of the order of magnitude of the Debye frequency.

If there is no interaction ($\Delta_k=0$), then the NON's V^2_k are idempotent because $V^2_k=\Theta(-\epsilon_k)$. The interaction $\Delta_k\neq 0$ makes the NON's nonidempotent in a small region $|\epsilon_k|<\delta$ at the Fermi energy. Assuming that the density of states per electron $\rho(\epsilon)$ is constant in the small interval 2δ, the entropy s is given by the relation

$$s=-\rho(0)\int_{-\delta}^{+\delta}d\epsilon\frac{1}{2}\left(1-\frac{\epsilon}{\sqrt{\epsilon^2+\Delta^2}}\right)$$

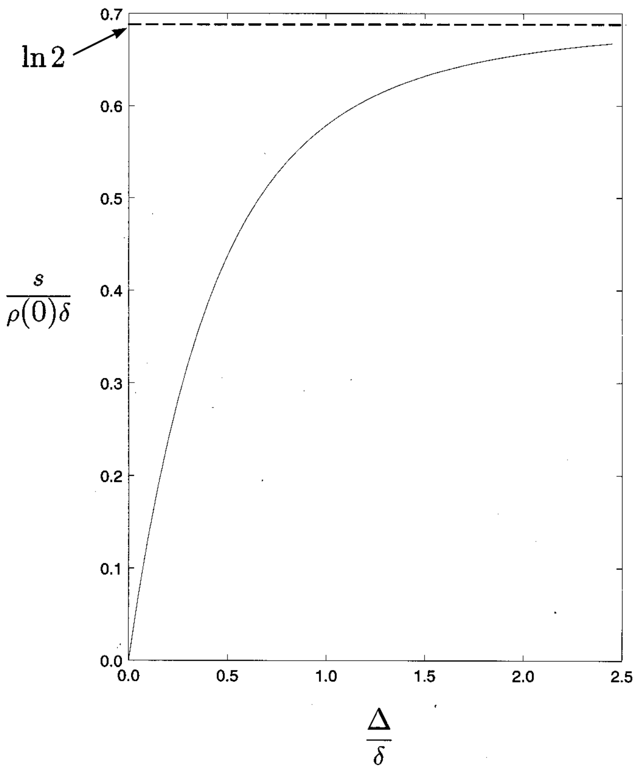

FIG. 7. BCS model (3.4): correlation entropy s of the GS vs gap parameter Δ according to Eq. (3.15).

$$\ln\left\{\frac{1}{2}\left(1-\frac{\epsilon}{\sqrt{\epsilon^2+\Delta^2}}\right)\right\}. \tag{3.14}$$

The integration in Eq. (3.14) can be performed analytically $[x=\sqrt{1+(\Delta/\delta)^2}]$

$$s=\rho(0)\delta\left(\frac{\Delta}{\delta}\arctan\frac{\delta}{\Delta}-\frac{1}{2}\left\{(1-x)\ln\left[\frac{1}{2}\left(1-\frac{1}{x}\right)\right]\right.\right.$$
$$\left.\left.+(1+x)\ln\left[\frac{1}{2}\left(1+\frac{1}{x}\right)\right]\right\}\right). \tag{3.15}$$

Figure 7 shows s vs Δ. In the weak-coupling limit $\Delta\ll\delta$ we obtain from Eq. (3.15), for the correlation entropy,

$$s=\frac{\pi}{2}\rho(0)\Delta\left\{1+\frac{\Delta}{2\pi\delta}\left[2\ln\left(\frac{\Delta}{2\delta}\right)-3\right]+\cdots\right\}. \tag{3.16}$$

s vanishes with Δ and higher-order terms are proportional to $\Delta^2\ln\Delta$ and Δ^2. In the opposite limit $\Delta\gg\delta$, i.e., $V_k^2\approx 1/2$ within the shell 2δ at the Fermi energy and the entropy per particle approaches the limit $\rho(0)\delta\ln 2$.

This result may be compared with the interaction energy of the BCS ground state. As it is well known, the shift of e, the ground-state energy per particle, against $e^{(0)}$, the energy per particle of the ideal Fermi gas, is given by

$$e-e^{(0)}=-\frac{1}{2}\rho(0)\delta^2(x-1). \tag{3.17}$$

In the weak-coupling limit we obtain

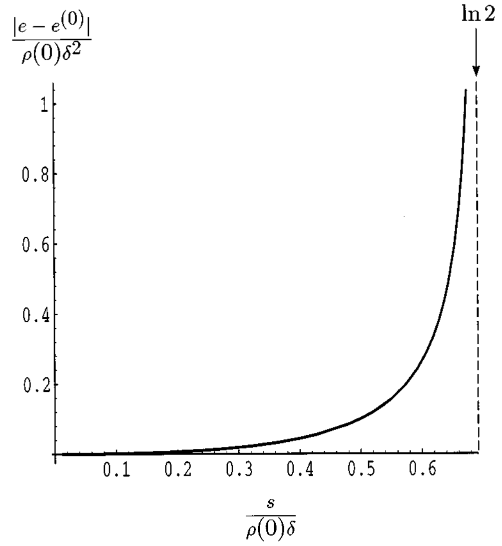

FIG. 8. BCS model (3.4): GS energy shift $e-e^{(0)}$ vs correlation entropy s according to Eqs. (3.15) and (3.17).

$$e-e^{(0)}=-\frac{1}{4}\rho(0)\Delta^2. \tag{3.18}$$

The interaction energy for the BCS ground state is proportional to Δ^2 and changes slowly with Δ in comparison to the correlation entropy, which is a sensitive measure of the change of the free-particle ground state due to the BCS interaction. The energy shift vs the correlation entropy (Fig. 8) shows a qualitatively similar behavior to $|E_{\mathrm{corr}}|$ vs S_2 in the two-site Hubbard model (Fig. 6), see also Figs. 5 and 7.

IV. SUMMARY AND OUTLOOK

On the 1P level a correlation is displayed by the 1PDM: the correlation makes the 1PDM nonidempotent. (For recent papers studying the relations between the 1PDM and the correlation see Refs. 24 and 25.) From the nonidempotency of the 1PDM a nonvanishing correlation entropy can be derived, which thus provides a purely quantum-kinematic correlation measure on the 1P level. These general conclusions are confirmed by the above studies of the two-electron two-site Hubbard model (as an example of a finite system) and the BCS model (as an example of an extended system). The Hubbard model shows for $U\rightarrow\infty$ that different reference states (HF or HL) can be used for the discussion of the phenomenon of ''correlation'' and that to each reference state a special correlation entropy corresponds. If one uses the HL description (two Slater determinants), then the asymptotically vanishing coupling corresponds to the asymptotically vanishing entropy S_1 of Eqs. (1.2) or (2.18) and Fig. 5. If one uses the HF description (a single Slater determinant), then the strongly correlated hopping (to avoid double occupancy at one site) corresponds to the asymptotically saturating entropy S_2 of Eqs. (1.3) or (2.19) and Fig. 5. Note the relation of such a discussion to the distinction between a ''static correlation'' (with a multireference state to account properly for the symmetry of the problem, e.g., dissociation limits or eigenstates of angular momenta, or for cases where near degeneracies exist) and a ''dynamic correlation'' (manifested in the correlation tail of the CI expansion).[18] The situation for the BCS model is much more simple because the ideal Fermi gas is the unique relevant reference state in this case and the entropy saturates at large energy shifts. As in Ref. 26, further work is called for before the importance of the correlation entropy and other correlation measures (see Refs. 1–5) in the many-electron theory of atoms, molecules, and solids can be assessed more deeply and comprehensively.

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