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Authors
Maiti, A.
Falicov, L.M.

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LOCAL CHEMICAL POTENTIAL APPROACH TO SMALL-CLUSTER MANY-BODY SYSTEMS*

Amitesh Maiti and L. M. Falicov

Department of Physics
University of California, Berkeley, CA 94720

and

Materials and Chemical Sciences Division
Lawrence Berkeley Laboratory, Berkeley, CA 94720

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Amitesh Maiti and L. M. Falicov

Department of Physics
University of California
Berkeley, California, 94720

and

Materials and Chemical Sciences Division
Lawrence Berkeley Laboratory
Berkeley, California, 94720

ABSTRACT

Thermodynamic local-occupation averages and local-number-occupation fluctuations are studied in small-cluster many-body systems by introducing a single-site chemical potential at a particular site. This procedure allows the study of differential properties of thermodynamic functions by providing continuous variation of local occupations. The method, which starts from the quantum-mechanical grand canonical ensemble, gives a criterion to distinguish particular features of the small cluster that are likely to survive in the thermodynamic limit from those discontinuities that are characteristic of the finiteness of the cluster and the resulting discreteness of the energy spectrum. In particular the Mott-insulating state (a discontinuity in the chemical potential at a particular occupation) can

be clearly tested this way. Similar indications are obtained for spin-polarized states and for particle-pairing conditions. Two four-site Hubbard-model clusters -- a ring and a tetrahedron -- are used as examples.

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I. Introduction

Since its introduction[1] in 1963 the Hubbard model has been frequently used in the literature to investigate a whole range of many-body effects: ferromagnetism, antiferromagnetism, metal-insulator transition, charge-density waves and spin-density waves to name only a few[1-6]. The model has been applied to a variety of lattices of different dimensions[2,3,7] and general theorems have been proved in some cases[8]. Unfortunately, no three-dimensional macroscopic Hubbard system is susceptible to exact treatment. However, considerable insight into macroscopic systems can be obtained from the exact solution of small subsystems, which, though not expected to unfold the whole story, can sometimes provide important clues to the problem. This exact small-cluster approach has been used successfully in situations where local many-body effects are important: clusters of size two to eight[9-25], photoemission[13] behavior in Ni, intermediate-valence[14,15] behavior in Ce, magnetic behavior[16] in Fe, alloying in Cu-Au system[17], many-body effects in a heavy-fermion system[18], thermodynamic properties[19] , valence-bond formation[20] as well as in understanding of the two-dimensional (2D) electronic properties in the Cu-O planes of high-temperature superconductors[21].

In this contribution we focus on the study of properties of a small open subsystem of the cluster, one that exchanges particles with the rest of the system, in order to infer the behavior of the global properties of the system as a whole. In particular, an attempt is made to extract physical properties out of the analysis of the quantum

mechanical particle number fluctuation in the subsystem as a function of various parameters. Exact calculations were performed on two systems: a four-atom linear chain with periodic boundary conditions[26] and a four-atom tetrahedral cluster with periodic boundary conditions, the smallest non-trivial *fcc* cluster. The hamiltonian chosen is the Hubbard model with hopping matrix element $t > 0$ between nearest neighbors only and an on-site interaction U, which can be repulsive or attractive:

$$H_0 = - t \sum_{<ij>\sigma} (c_{i\sigma}^{\dagger} c_{j\sigma} + c_{j\sigma}^{\dagger} c_{i\sigma}) + U \sum_{i} \hat{n}_{i\uparrow} \hat{n}_{i\downarrow} \quad . \qquad (I.1a)$$

where i, j are the atomic site indices, <...> indicates nearest-neighbor pairs and σ is the spin index. For notational simplicity, henceforth, it would be convenient to choose $|t|$ as the unit of energy and express H_0, U and temperature T in dimensionless form : $H = H_0 / |t|$, $x = U/|t|$ and $\tau = k_B T/|t|$ respectively, where k_B is Boltzmann's constant. Thus the hamiltonian can be recast in the form:

$$H = - \sum_{<ij>\sigma} (c_{i\sigma}^{\dagger} c_{j\sigma} + c_{j\sigma}^{\dagger} c_{i\sigma}) + x \sum_{i} \hat{n}_{i\uparrow} \hat{n}_{i\downarrow} \quad . \qquad (I.1b)$$

Since the many-body correlations are short-ranged in the Hubbard model, it is interesting to study the local particle-number fluctuation Δ at a particular site, labelled α, as a function of n, x and τ. Here, n the average number of electrons at the α-site, is given by $\langle\langle \hat{n} \rangle\rangle$, the ensemble average of $\hat{n} = \hat{n}_{\alpha\uparrow} + \hat{n}_{\alpha\downarrow}$, the particle number

operator at the relevant site. The local particle fluctuation Δ is defined as :

$$\Delta = \Delta(n,x,\tau) = \langle\langle \hat{n}^2 \rangle\rangle - \langle\langle \hat{n} \rangle\rangle^2 \quad . \tag{I.2}$$

The generalized grand canonical ensemble average of any observable $\hat{A}$ is defined by :

$$\langle\langle \hat{A} \rangle\rangle = \frac{Tr[\, \hat{A} \exp\{-(H - M\hat{N} - \mu \hat{n})/\tau\}\,]}{Tr\,[\exp\{-(H - M\hat{N} - \mu \hat{n})/\tau\}\,]} \quad , \tag{I.3}$$

where M is the chemical potential associated with the total particle number operator $\hat{N} = \Sigma_i \hat{n}_i$ in the system, and μ is an 'extra' local chemical potential associated with the α-site, the usefulness of which is discussed below. In these expressions, the subscript i in the summation over $\hat{n}_i$ runs over N_0 sites, where N_0 is the total number of sites in the system. It should be noted that the ordinary grand canonical ensemble corresponds to the particular value $\mu = 0$. In the ensemble with $\mu = 0$, M is a monotonically increasing function of n, as is required by the chemical stability of the system. In view of the discussion to follow, it is to be noted that a discontinuity in the chemical potential M at a given value $n=n^*$, *i.e.*,

$$M_+ - M_- > 0 \quad , \tag{I.4}$$

where M_+ and M_- are the values of M as n^* is approached respectively from the positive and negative sides, characterizes, by definition, a Mott insulator at the occupation n^*.

II. Calculation and results

In order to calculate the local particle-number fluctuation Δ for general values of n and x, one has to take recourse to numerical calculations. To perform the ensemble averages *(I.2)* it is convenient to work in the basis of the eigenstates of the generalized hamiltonian $H'=(H-\mu\hat{N}-\mu\hat{h})$. Reduction in the size of the matrices to be diagonalized can be achieved by taking note of the following quantities that commute with the generalized hamiltonian H' :

(i) $\hat{N}$, the total number operator;

(ii) S_z , the z-component of the total spin-angular momentum;

(iii) $\mathbf{S}^2$, the total spin operator; and

(iv) the permutation operator of some site-indices.

For convenience, the calculations reported here have made use of the constants of motion (i), (ii) and (iv) only, which reduces the original problem of diagonalizing a 256 x 256 matrix to ones of size no greater than 18 x 18. Exact analytical results, however, are obtained for certain limiting values of n, x and τ. Thus, we have the following results :

$$\Delta(n,\ x=0,\ \tau) \ = \ n\,(2-n)\,/2 \quad ; \qquad (II.1)$$

$$\Delta(n,\ x\to\infty,\ \tau) = \begin{cases} n\,(1-n)\,, & 0 \le n \le 1\ , \\ (n-1)\,(2-n), & 1 \le n \le 2\ ; \end{cases} \qquad (II.2)$$

$$\Delta(n,\ x\to -\infty,\ \tau) \ = \ n\,(2-n) \quad ; \qquad (II.3)$$

$$\Delta(n,\ x,\ \tau\to\infty) = n\,(2-n)\,/\,2 \quad . \qquad (II.4)$$

It is also straightforward to show that, for bipartite[27] lattices Δ is symmetric about $n = 1$, *i.e.*,

$$\Delta(n, x, \tau) = \Delta(2 - n, x, \tau) \quad . \qquad (II.5)$$

Equation *(II.5)* holds for the four-atom ring, but not in general for the tetrahedral cluster, because *fcc* is not a bipartite lattice[27]. It should be noted here that Δ for a fully spin-polarized (loosely speaking ferromagnetic) state, for all interaction strengths, assume the value equal to that of the $x \to \infty$ limit as given by equation *(II.2)*.

We now focus our attention on the zero temperature ($\tau \to 0$) properties in order to deal with some of the difficulties involved in extrapolating small-cluster results to the thermodynamic limit at low temperatures. The difficulties arise from the discreteness of the energy spectrum of finite clusters. In particular, use is made of the additional local chemical potential μ to distinguish between the 'genuine' singularities in Δ (those that survive as the number of sites is increased up to the thermodynamic limit) and the 'spurious' singularities (those that are present only because of the finiteness of the cluster).

We begin with a zero-temperature identity that relates the local particle-number fluctuation to a derivative of the ground-state energy :

$$\Delta(n, x, \tau=0) = n(1 - n) + 2 \frac{\partial E_G(n,x)}{\partial x} \quad , \qquad (II.6)$$

where $E_G(n,x)$ is the ground state energy *per site* corresponding to the occupation n. This result is proven in **Appendix-I.** It is to be

noted that when $\mu=0$, *i.e.*, in the *exact* grand canonical ensemble average, all sites are equivalent, so that $n = \langle\langle\hat{N}\rangle\rangle/N_0$ is the *fractional occupation*, *i.e.*, the number of electrons per site. An important result to study the Mott insulator state is obtained by taking the derivative of *(II.6)* with respect to n and then the difference between values obtained by approaching the point of discontinuity from the positive and the negative sides; this procedure yields:

$$\left(\frac{\partial\Delta}{\partial n}\right)_+ - \left(\frac{\partial\Delta}{\partial n}\right)_- = 2\frac{\partial}{\partial x}(M_+ - M_-) \quad , \qquad (II.7)$$

where $M_\pm = (\partial E_G(n,x)/\partial n)_\pm$, corresponding to the partial derivatives on the right and left respectively. Equation *(II.7)* establishes a direct relationship between the discontinuity in the slope of Δ with that of the chemical potential M (both sides of *(II.7)* are zero in case of no discontinuity). Analyticity as a function of x has been assumed, as $(M_+ - M_-)$ is found to change smoothly with x, except at $x=0$ and at other *isolated* points.

We concentrate first on an analysis of the two small-cluster systems in the exact grand canonical ensemble $(\mu=0)$. Figures 1 and 2 display graphical tabulations of the values of the total particle number N that contribute to the relevant ground states at each point in the n-x plane, for the ring and the tetrahedral cluster respectively when the interaction is repulsive $(x > 0)$. Figure 3 gives the corresponding description in the attractive interaction $(x < 0)$ case for either system. The solid black lines correspond to the values where ground states belong to the subspace of a single N. The region in between are

'mixed' domains where relevant ground states belong to subspaces of more than one N. Several important results associated with the above structure follow :

(i) Results for $x \to 0$ and $x=0$ are different for finite-cluster systems and approach each other only in the thermodynamic limit. This discontinuity arises from the presence of several 'accidental degeneracies' for the particular value $x=0$. The singular $x=0$ line is, therefore, omitted in Figs. 1, 2 and 3.

(ii) The local particle fluctuation is a continuous function of n with a continuous partial derivative $\partial\Delta/\partial n$ and a *negative* second derivative $\partial^2\Delta/\partial n^2$ for all regions of phase-space except at the solid black (single N) lines.

(iii) On the solid black lines, where a single N value contributes, the local particle fluctuation $\Delta(x,n)$ exhibit discontinuities in $\partial\Delta/\partial n$ (*kinks*) as a function of n (for fixed x) with the vertex pointing either upwards or downwards. On these lines, the chemical potential takes a finite range of values $M_N(min) \leq M \leq M_N(max)$ and, when plotted as a function of M, *kinks* in $\Delta(x,M)$ occur at $M=M_N(min)$ and $M=M_N(max)$.

(iv) Ground states belonging to all N from 0 to $2N_0$ are not, in general, sampled as n increases from 0 to 2 for a fixed x. No odd N, for instance, contributes to the ground states for an attractive interaction $(x<0)$ for either system. Also for a repulsive interaction $(x>0)$, the $N=3$ and $N=5$ states do not contribute for $x<4.6$ in case of the four-atom ring whereas the $N=3$ state does not contribute for any $x>0$ in the tetrahedral cluster.

(v) In a white region, where more than a single N contribute, only the two N values corresponding to the two solid black lines bordering the relevant white region contribute in general. For specific models and/or specific values of the parameters, however, it is possible to have extra *accidental degeneracies*, where more than two values of N contribute to the ground state. [Such case can be seen, for example, in the tetrahedral cluster for $1.25 < n < 2$ for all $x > 0$.]

For finite clusters, only two behaviors (*i.e.* negative second derivative in a white region and *kinks* on the solid black lines) of $\Delta(x,n)$ are found, as discussed above.

As the number of sites N_0 increases, the *structures* of Figs. 1, 2 and 3 may change in a number of ways to lead to the following possible scenarios in the limit $N_0 \to \infty$:

(1) The number of solid black lines might increase with the attendant rearrangement of the mixed-N contribution and, in the thermodynamic limit, the n-x plane may consist of a continuous plane of single N contributions, *i.e.*, a "black" plane.

(2) The number of solid black lines might increase but remain a discrete set; in the thermodynamic limit the n-x plane would still look similar to Figs. 1, 2 and 3, but possibly with many more solid black lines separated by "white"(mixed N) areas.

(3) In general it is expected in the thermodynamic limit $N_0 \to \infty$, that, the n-x plane will exhibit regions of

(3a) continuous N values ("black" areas)

(3b) continuous admixture of two N values ("white" areas)

(3c) isolated lines of single N values (solid black lines)

(3d) perhaps regions of dense but discrete black lines (*e.g.* all rational values of n allowed, all irrational ones not present[22]).

In the thermodynamic limit ($N_0 \to \infty$), in a "white" region, where more than one N contribute, Δ is always a continuous function, with a continuous $\partial\Delta/\partial n$, and with a *negative second derivative* $\partial^2\Delta/\partial n^2$. This property is proven in **Appendix-II**. In a "black" area or line, where a single N contributes, there is a possibility of Δ behaving differently: either it may develop *positive second derivatives* with respect to n, discontinuities in $\partial\Delta/\partial n$, -- *i.e.*, *kinks* -- at discrete values of n or possibly other types of pathological behavior. Not all structures are physically possible, and each requires individual analysis. A *kink*, however, by necessity arises from the discontinuity in the slope, which along with (II.7) implies a Mott insulator. Other singular structures may be characteristic of other phases for the values (n^*, x^*) where they appear.

In the finite clusters under consideration here, the discontinuities in $\partial\Delta/\partial n$ occur only on the solid black *lines*. This behavior is shown in Figures 4 and 5. The discontinuities correspond to a single N at a particular value of n, labelled n^*. It is along these lines that the "local" chemical potential μ can be effectively used to test the stability of the single-N structures and to distinguish between *kinks* that are "genuine" and those that are "spurious" -- *i.e.*, induced by the finiteness of the cluster. The "local" chemical potential μ allows a local variation of n at the site in question, whereas the value of N in the cluster as a whole remains constant. This procedure "opens up" the α-site to be less dependent on its environment, which in this case is the small cluster. This partial decoupling emphasizes the local

aspects of the many-body problem and may shed light into the behavior of the system in the thermodynamic limit, when the environment becomes macroscopically large.

The resulting analysis is valid only in "single-N" regions, *i.e.*, along the isolated black lines, or in a black region, -- a finite interval of n around $n=n^*$ -- if that is the case in the thermodynamic limit. The analysis therefore, in the finite clusters, is carried out not only for the discrete values of n where a single N contributes, but also in their immediate neighborhoods.

The working assumption is that, by looking at the behavior of Δ as a function of n, as μ is varied from a small negative to a small positive value, one can decide whether the structure of $\partial\Delta/\partial n$ at that occupation n is genuine or just an effect of the finiteness of the cluster. The result of this analysis may produce the following situations in the thermodynamic limit :

(A) The curve $\Delta(n)$ takes at $n=n^*$ one of the limiting forms described in *(II.1)-(II.3)*; in particular the form *(II.2)* is taken for the ferromagnetic case. In such a situation, the exact grand canonical ensemble ($\mu=0$) itself yields the appropriate limiting form at the occupations in question.

(B) There is a *positive second derivative* of Δ with respect to n at $n=n^*$; this is a strong indication of instability, with the formation, in the thermodynamic limit, of an energy gap in the spectrum, *i.e.*, a real kink, as shown in *(II.7)*.

(C) If Δ exhibits a *negative second derivative* with respect to n several possibilities other than case (A) arise.

(C1) Even though the second derivative with respect to n is negative at $n=n^*$, it becomes positive for values of n reasonably close to n^* .

(C2) The second derivative with respect to n is negative everywhere in the immediate vicinity of $n=n^*$.

Case (A) should be interpreted as a possible magnetic phase at $n=n^*$; case (C1) as a tendency to the formation of a Mott insulator state -- in the thermodynamic limit -- at a value of n close or even equal to n^*; case (C2) as a "spurious" singularity, *i.e.*, a consequence of the finiteness of the cluster.

Figures 6 and 7 display the variation of Δ with n on and around each of the solid black lines for the four-atom ring and the tetrahedral cluster respectively, for various fixed values of x and at zero temperature. Both attractive ($x<0$) and repulsive ($x>0$) values of the interaction are considered. The case $x>0$ is more interesting and is considered first. For the four-atom ring the following features are worth noticing :

(i) The curve Δ versus n has *positive second derivative* at and around $n=1$ (i.e. half-filled band) for all values of $x>0$ (case (B)). This indicates a Mott insulator at that concentration, setting in at arbitrarily small repulsive interactions, in agreement with the results of Lieb and Wu[7]. Because of its isomorphism[26] to lattices in 2D and 3D, this result seems to indicate a Mott transition for all $x>0$ at $n=1$ for all bipartite lattices[27] in one, two or three dimensions.

It is interesting to note that if the second-nearest neighbor hopping is included, the positive second derivative does not appear at $n=1$, for small positive values of x, but only in a small neighborhood of

$n=1$, *i.e.*, case (C1). Whether that happens for $n>1$ or $n<1$ depends on the relative sign of the second-nearest neighbor to the first-nearest neighbor hopping parameters. As x increases, the interval of positive second derivative grows, and covers the $n=1$ point *i.e.*, case (B). In any case, the formation of a Mott insulator at the $n=1$ concentration for all $x>0$ is clearly indicated by the test.

(ii) The $N=3$ ($n=0.75$) and $N=5$ ($n=1.25$) cases exhibit a transition to a ferromagnetic state as a function of x for $x=x^*=18.5$. For $\mu=0$, *i.e.*, in the exact grand canonical ensemble, as x increases the local particle fluctuation Δ discontinuously drops from a value ~ 0.1946 for $x<x^*$ to the value 0.1875 given by equation *(II.2)* for $x>x^*$ and remains constant for any greater value of x.

(iii) The curve has *negative second derivative* at and around all other solid black lines. They all belong to the case (C2) discussed above except for $N=1$ and $N=7$.

(iv) For $N=1$ and $N=7$, Δ takes the limiting form given by *(II.2)* [case (A)]. The reason is a trivial transition to a spin-polarized behavior when a single carrier (electron or hole) exists in the finite lattice. For larger clusters this property appears at $n=1/N_0$ and $n=2-1/N_0$ which, in the thermodynamic limit, are the empty $n=0$ and fully occupied $n=2$ lattices.

From the analysis of the four-atom ring, it is possible to state that in the seven partial occupations where Mott-insulator singularities may occur for the infinite one-dimensional chain or the perfect square lattice, only n=1 should exhibit insulating behavior for all $x>0$. This behavior agrees with the Monte Carlo calculations for the infinite chain and the 2D square lattice[29,30].

The tetrahedral cluster has a more complicated and interesting structure. The main features are :

(i) The structure at $n=1$ falls in the category (C1) discussed above. For infinitesimal x (>0) a small portion of the curve has *positive second derivative* at $n\sim1.05$. As x increases, the interval of *positive second derivative* gradually grows, and includes the $n=1$ point for $x>1.2$. This result should be considered as a signature of a Mott insulator occurring at $n=1$ for arbitrarily small positive values of x. Interestingly, this behavior at $n=1$ is similar to the four-atom ring with positive second-nearest-neighbor hopping: when the second nearest-neighbor hopping parameter in the ring is equal to the nearest-neighbor hopping parameter, one obtains a system topologically identical to the tetrahedral cluster.

(ii) There is a transition to a ferromagnetic state for all $x>0$ as a function of n at $n=1.25$ $(N=5)$. The curve around the solid black line at this occupation assumes the limiting form of *(II.2)*. This behavior is not observed for the ring with second nearest neighbor hopping $(\neq t)$ and seems to be intrinsic to the tetrahedral cluster and possibly to the *fcc* lattice in the thermodynamic limit, of which the tetrahedral cluster is the basic building block.

(iii) The curve $\Delta(n)$ has the form *(II.2)* in the full interval $1.25 \leq n \leq 2$. This behavior is related to the accidental degeneracies shown in Fig 2.

(iv) There is the small-cluster induced spin-polarization behavior at $N=1$ $(n=0.25)$ and $N=7$ $(n=1.75)$, characteristic of all four-atom clusters.

In order to ascertain whether a spin-polarized (ferromagnetic) state exists at a given occupation in the thermodynamic limit, one could use an extension of the analysis with the local chemical potential μ. Thus, for instance, one could increase n from $n=1$ by increasing μ to the proper value corresponding to $n=1.25$ while staying within the $N=4$ subspace. One then looks for a 'flow' of the ground state from a spin-'unpolarized' state at $n=1$ to a fully spin-polarized (ferromagnetic) state at $n=1.25$, and as a result whether Δ at $n=1.25$ assumes a value given by *(II.2)*. The result holds for the tetrahedral cluster, indicating that the ferromagnetic transition in the tetrahedral cluster might survive in the thermodynamic limit possibly at an occupation close to $n=1.25$. On the other hand, similar analysis at $n=0.25$ $(N=1)$, by changing the occupation from $n=0.5$ down to $n=0.25$ by decreasing μ while remaining within the $N=2$ subspace[32] shows that the ground state does not 'flow' into a spin-polarized state at $n=0.25$ indicating that the transition to a magnetic state is 'spurious', *i.e.*, a consequence of the finite number of sites in the cluster. Similar analysis by decreasing n from $n=1$ to $n=0.75$ while remaining within the $N=4$ subspace for $x>18.5$ for the four-atom ring does not also result in a 'flow' into spin-polarized state. This implies that in the thermodynamic limit, this transition to a fully spin-polarized (ferromagnetic) state does not occur at $n=0.75$ (or 1.25) but at $N=N_0 \pm 1$ in accordance with the results of Nagaoka[33].

For an attractive interaction $x<0$, on the other hand, the Δ-n curve always has a *negative second derivative* everywhere in the vicinity of each solid black line (case (C2)), implying that there are no Mott insulators or magnetized states. The only interesting feature is

the absence of the *N=odd* values for either system at all values of $x<0$. This result indicates a tendency of the electrons to pair, which might imply superconductivity (Cooper pairing) or physically bound *bielectrons*, which might lead to Bose-condensation.

III. Discussion

By introducing a local chemical potential at a single site of a small cluster, the local occupation of that site can be allowed to vary with respect to the average site-occupation of the cluster as a whole. This partial decoupling of one site from the rest should be more sensitive to the local environment of the particular site than to the overall size and shape of the cluster.

This technique has been applied to clusters with varying occupation of particles, after the analysis of particular global states has been completed. Since the smallness of the cluster allows only a finite number of average occupations, the method proposed here introduces additional continuity into an essentially discrete system. It is thus possible to analyze differential properties of occupations, and analyze the local stability of particular solutions, distinguishing behaviors which are 'genuine' properties of the system as a whole (those that might survive in the thermodynamic limit) from those 'spurious' properties which are caused exclusively by the finiteness of the cluster.

Two examples were analyzed. Both are Hubbard models in four-atom clusters with different connectivities : a four-atom ring (representative of the infinite chain, 2D square lattice and the *bcc*

lattice) and a tetrahedral cluster (representative of the *fcc* structure). The following results were obtained :

(1) The $n=1$ half-filled band exhibits for all cases 'genuine' Mott-insulating states for all repulsive interactions.

(2) In bipartite lattices, the inclusion of an arbitrarily small second-nearest neighbor hopping seems to decrease the stability of the Mott-insulating state, although no supression has been observed.

(3) The intervals $0 \leq n \leq 0.25$ ($0 \leq n \leq 1/N_0$ for an arbitrary cluster of size N_0) and $1.75 \leq n \leq 2$ ($2 - 1/N_0 \leq n \leq 2$) yield trivial uninteresting result corresponding to a single electron or a single hole. The states are always fully spin-polarized and may or may not represent the behavior in the thermodynamic limit.

(4) The tetrahedral cluster exhibits a ferromagnetic state in the interval $1.25 \leq n \leq 2$, which remains stable under the test of the flow of states with changing local chemical potential μ .

(5) The four-atom ring exhibits a ferromagnetic state at $n=0.75$ and $n=1.25$ in the exact grand canonical ensemble ($\mu=0$) for $x>18.5$. Such state at the above fractional occupations is the well-known Nagaoka ferromagnetic state at $N=N_0 \pm 1$, and is not stable under the applied variable μ test; in the thermodynamic limit, in accordance with Nagaoka's theorem[33], this feeble ferromagnet could only occur at $n=1$, *i.e.*, only (exactly) at $N=N_0 \pm 1$.

(6) Attractive interactions lead to 'genuine' instabilities of odd N number states and 'genuine' stable conditions for even N. No magnetic solutions or Mott insulators appear in this case. Indication of electron pairing (*i.e.*, either Cooper pairs or *bielectrons*) is clearly evident.

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APPENDIX-I

Proof of equation *(II.6)* .

$$\hat{n}^2 = (\hat{n}_{\alpha\uparrow} + \hat{n}_{\alpha\downarrow})^2$$

$$= \hat{n} + 2\,\hat{n}_{\alpha\uparrow}\,\hat{n}_{\alpha\downarrow} ,$$

because $\hat{n}_{\alpha\uparrow}$ and $\hat{n}_{\alpha\downarrow}$ are projection operators, *e.g.* $(\hat{n}_{\alpha\uparrow})^2 = \hat{n}_{\alpha\uparrow}$.

Thus *(I.2)* yields :

$$\Delta = \langle\langle \hat{n}^2 \rangle\rangle - n^2 = n(1-n) + 2\langle\langle \hat{n}_{\alpha\uparrow}\,\hat{n}_{\alpha\downarrow} \rangle\rangle . \qquad (AI.1)$$

At $\tau=0$,

$$N_0 E_G = \langle H \rangle = \langle H_T \rangle + x \sum_i \langle \hat{n}_{i\uparrow}\,\hat{n}_{i\downarrow} \rangle ,$$

$$= \langle H_T \rangle + x\, N_0 \langle \hat{n}_{\alpha\uparrow}\,\hat{n}_{\alpha\downarrow} \rangle , \qquad (AI.2)$$

where use has been made of the assumption that all the N_0 sites have *identical* occupations and the ground state does not have any spontaneously broken symmetry, *i.e.*, there are no spin-density waves or spiral spin arrangements. In the equation above, <...> denotes the quantum mechanical expectation in the ground state, H_T is the (nearest neighbor) hopping part of the hamiltonian H and is independent of interaction parameter x. Use of the Feynman-Hellman

theorem on *(AI.2)* together with *(AI.1)* at zero temperature proves result *(II.6)*.

APPENDIX-II

This appendix proves that in a 'white' region (ignoring the special case of accidental degeneracies) Δ has a *negative second derivative* with respect to n. For a given value of x, let n_- and n_+ ($n_- < n_+$) be the occupations containing the solid black lines that border the 'white' region in question to the left and right respectively. An arbitrary occupation n, and the local particle fluctuation Δ at n inside the white region (*i.e.*, $n_- < n < n_+$) are given by the interpolation formulas :

$$n = \lambda\, n_- + (1 - \lambda)\, n_+ \quad ; \qquad \textit{(AII.1)}$$

$$\Delta = \lambda \langle\langle \hat{n}^2 \rangle\rangle_- + (1 - \lambda) \langle\langle \hat{n}^2 \rangle\rangle_+ - n^2 \ ,$$

$$= \lambda\, (\Delta_- + n_-^{\,2}) + (1 - \lambda)\, (\Delta_+ + n_+^{\,2}) - n^2 \ , \qquad \textit{(AII.2)}$$

where subscripts - and + refer to averages on the solid black lines at n_- and n_+ respectively. Inversion of *(AII.1)* and use of that result in *(AII.2)* yields,

$$\Delta = \frac{n - n_-}{n_+ - n_-} (\Delta_- + n_-^{\,2}) + \frac{n_+ - n}{n_+ - n_-} (\Delta_+ + n_+^{\,2}) - n^2 \ . \qquad \textit{(AII.3)}$$

The first two terms on the *RHS* of *(AII.3)* are linear in n and, therefore,

$$\frac{\partial^2 \Delta}{\partial n^2} = -2 < 0 \ ,$$

which is the result quoted.

references

[1] J. Hubbard, Proc. R. Soc. London, Ser. **A276**, 238 (1963); **227**, 237 (1964); **281**, 401 (1964); **285**, 542 (1965); **296**, 100 (1967).

[2] D. R. Penn, Phys. Rev. **142**, 350 (1966).

[3] D. Denley and L. M. Falicov, Phys. Rev. B**17**, 1289 (1978).

[4] D. Adler, in *Solid State Physics*, ed. by H. Ehrenreich, F. Seitz and D. Turnbull (Academic, New York, 1968), vol.21, p.1.

[5] *Proceedings of the International Conference on Metal-nonmetal Transitions*, San Francisco, 1968 [Rev. Mod. Phys. 40, 673 (1968)].

[6] N. F. Mott and Z. Zimmerman, Rep. Prog. Phys. **33**, 881 (1970).

[7] E. H. Lieb and F. Y. Wu, Phys. Rev. Lett. **20**, 1445 (1968).

[8] E. H. Lieb and D. Mattis, Phys. Rev. **125**, 164 (1962).

[9] H. Shiba and P. A. Pincus, Phys. Rev. B**5**, 1966 (1972).

[10] H. Shiba, Prog. Theor. Phys., **48**, 6B, 2171 (1972).

[11] L. M. Falicov and R. A. Harris, J. Chem. Phys. **51**, 3153 (1969).

[12] L. M. Falicov and R. H. Victora, Phys. Rev. B**30**, 1695 (1984).

[13] R. H. Victora and L. M. Falicov, Phys. Rev. Lett. **55**, 1140 (1985).

[14] A. Reich and L. M. Falicov, Phys. Rev. B**34**, 6752 (1986).

[15] J. C. Parlebas, R. H. Victora and L. M. Falicov, J. Phys. (Paris) **47**, 1029 (1986).

[16] E. C. Sowa and L. M. Falicov, Phys. Rev. B**35**, 3765 (1987).

[17] A. Reich and L. M. Falicov, Phys. Rev. B**36**, 3117 1987).

[18] A. Reich and L. M. Falicov, Phys. Rev. B**37**, 5560 (1988).

[19] J. Callaway, D. P. Chen and R. Tang, Z. Phys. D**3**, 91 (1986); Phys. Rev. B**35**, 3705 (1987).

[20] J. Callaway, Phys. Rev. B**35**, 8723 (1987).

[21] M. Ogata and H. Shiba, J. Phys. Soc. Jpn. **57**, 9, 3074 (1988).

[22] J. K. Freericks and L. M. Falicov, Phys. Rev. B**41**, 2163 (1990).

[23] D. J. Newman, K. S. Chan, and B. Ng, J. Phys. Chem. Solids, **45**, 6, 643 (1984).

[24] A. M. Oleś, B. Oleś, and K. A. Chao, J. Phys. C**13**, L979 (1980); J. Rossler and B. Fernández, Phys. Rev. B24, 5299 (1981).

[25] L. M. Falicov in *Recent Progress in Many-body Theories* Vol. 1, ed. by A. J. Kallio, E. Pajanne, and R. F. Bishop (Plenum Publishing Corp., New York (1988), p. 275 ; J. Callaway, Physica B**149**, 17 (1988).

[26] It could also be thought of as a four-atom 'square' in two dimensions with 'box' boundary conditions, or a square lattice with periodic boundary conditions if the substitution $t \rightarrow 2t$ is made. It could also be shown to be isomorphic to the four-atom *bcc* cluster[23] in three dimensions under the substitution $t \rightarrow 4t$.

[27] Bipartite lattices are the ones which break up into two sublattices A and B with non-zero hopping from A↔B but not from A↔A or B↔B, so that the energy spectrum is symmetric in $t \leftrightarrow -t$, *e.g.*, the linear chain, square lattice, simple cubic, *bcc* etc. It is important to note that *fcc* is not a bipartite lattice.

[28] Any four-atom cluster with a symmetric *1-2-1* one-electron energy structure should exhibit the same behavior; in addition to the linear chain, the isolated square and the simple square (2D) lattice, this property is found in the *bcc* structure with a sampling of four atoms. For further details see *ref. 23* .

[29] J. E. Hirsch, Phys. Rev. B**31**, 4403 (1985).

[30] J. E. Hirsch, Phys. Rev. B**35**, 1851 (1987).

[31] The result is first due to E. P. Wigner; for details see ref. 8.

[32] Because of the result regarding the $N=2$ being a very special case where the ground state is spin-unpolarized under very general conditions[31], the analysis was also done by studying 'flow' in the $N=3$ and $N=4$ subspaces to $n=0.25$. No spin-polarization was observed.

[33] Y. Nagaoka, Solid State Com. **3**, 409 (1965); D. J. Thouless, Proc. Phys. Soc. London **86**, 893 (1965); Y. Nagaoka, Phys. Rev. **147**, 392 (1966); H. Tasaki, Phys. Rev. B**40** , 9192 (1989).

FIGURE CAPTIONS

Figure 1. The "solid" (black) lines where a single N contributes to the ground state, for the four-atom ring and repulsive interactions $(x > 0)$. The white areas are regions where more than one value of N contribute. The dashed line indicates the value $x=4.6$ above which the solid lines at $N=3$ and $N=5$ appear. Note the y-axis (Δ) is in the LOG scale.

Figure 2. Same as Figure 1 for the tetrahedral cluster.

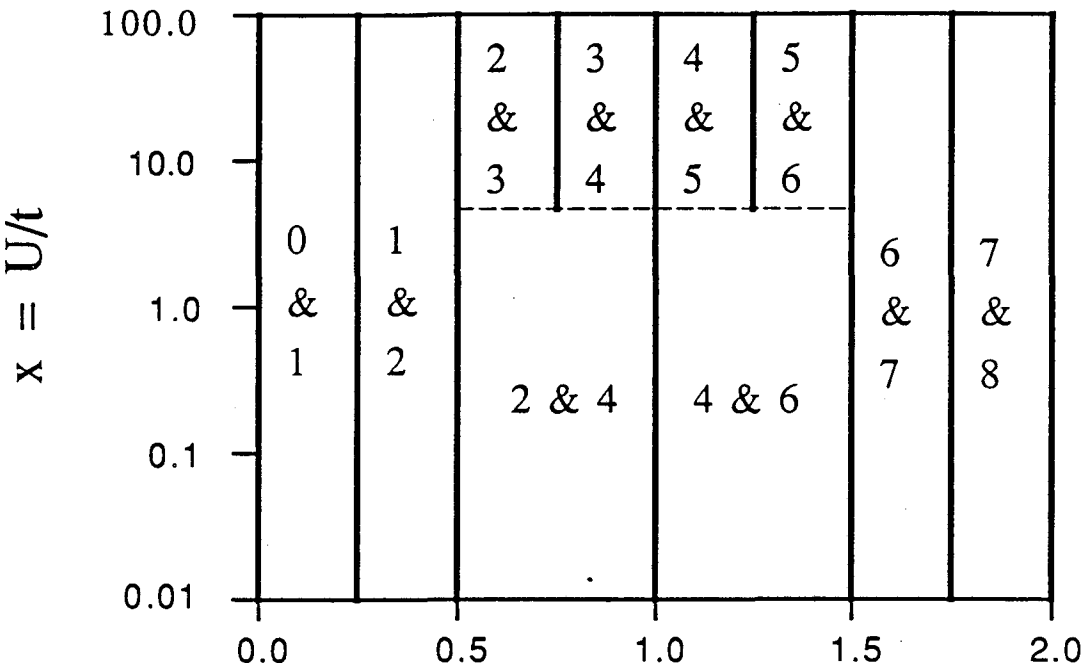
Figure 3. Same as Figure 1 for either cluster and attractive interactions $(x < 0)$.

Figure 4. Quantum mechanical particle fluctuation Δ in the four-atom ring at the α-site in the exact grand canonical ensemble $(\mu=0)$. "Solid" black lines where discontinuities in $\partial\Delta/\partial n$ occur are drawn. Both attractive and repulsive interactions are considered and values of x are indicated.

Figure 5. Same as Figure 4 for the tetrahedral cluster.

Figure 6. Quantum mechanical particle fluctuation Δ caused by the variation of the local chemical potential μ at the α-site in the four-atom ring on and around the "solid" black lines of Figure 4. Grey areas are regions away from the solid black lines where the analysis with non-zero μ is not appropriate.

Figure 7. Same as Figure 6 for the tetrahedral cluster (Figure 5).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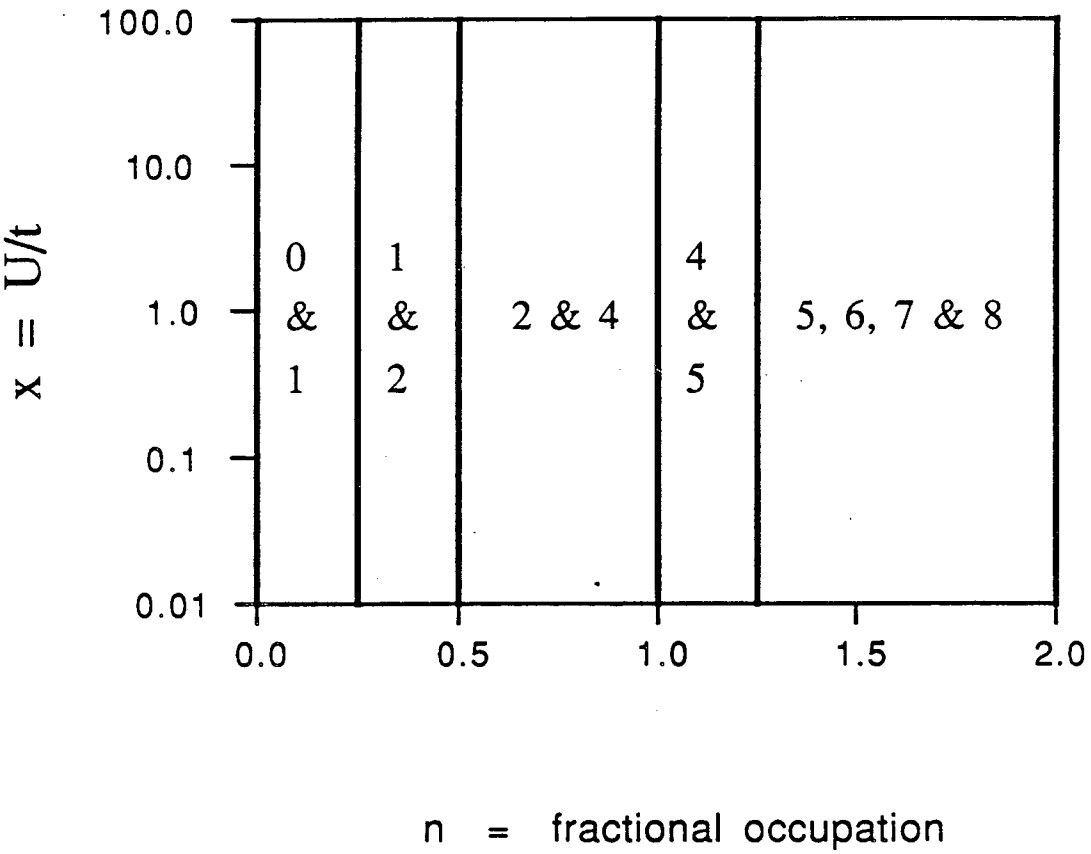
1.0
0.1
0.01
x = U/t
0.0
0.5
1.0
1.5
2.0
0 & 1
1 & 2
2 & 3
3 & 4
4 & 5
5 & 6
6 & 7
7 & 8
2 & 4
4 & 6
n = fractional occupation

Fig. 1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10.0
1.0
0.1
0.01
x = U/t
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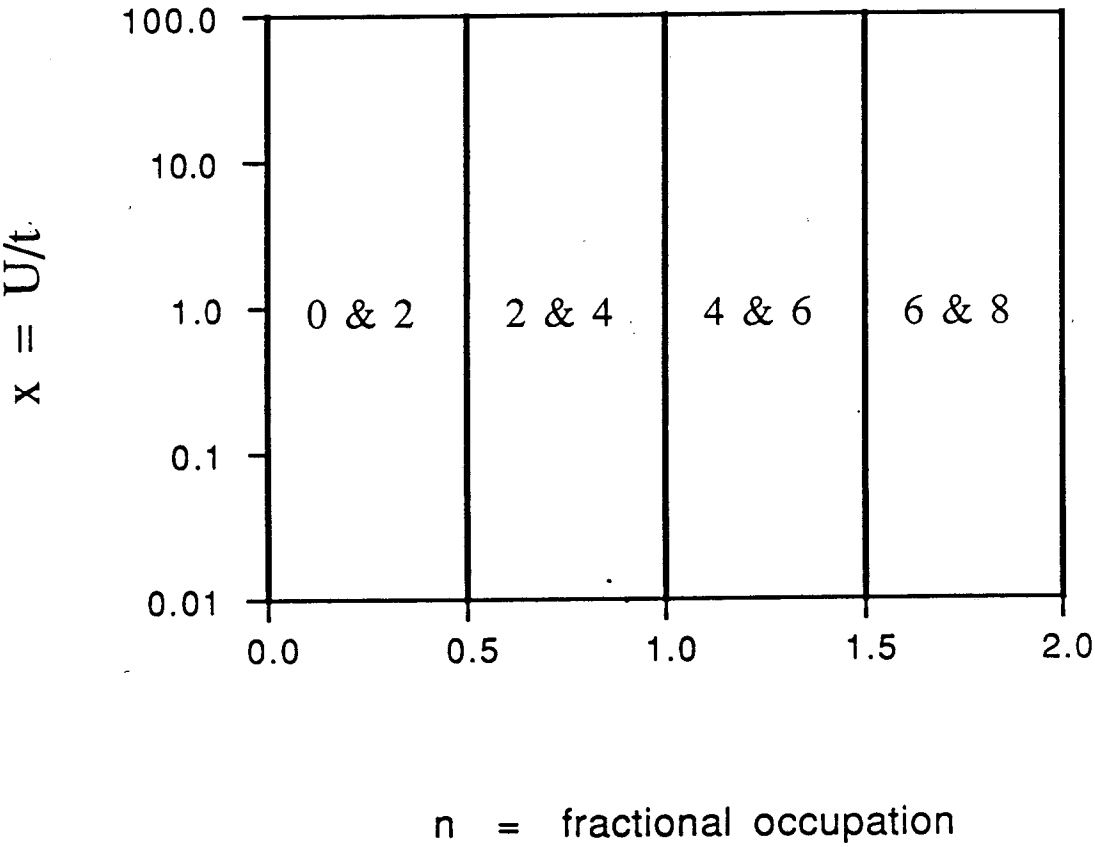
0.5
1.0
1.5
2.0
n = fractional occupation

Fig. 2


100.0
10.0
1.0
0.1
0.01
x = U/t
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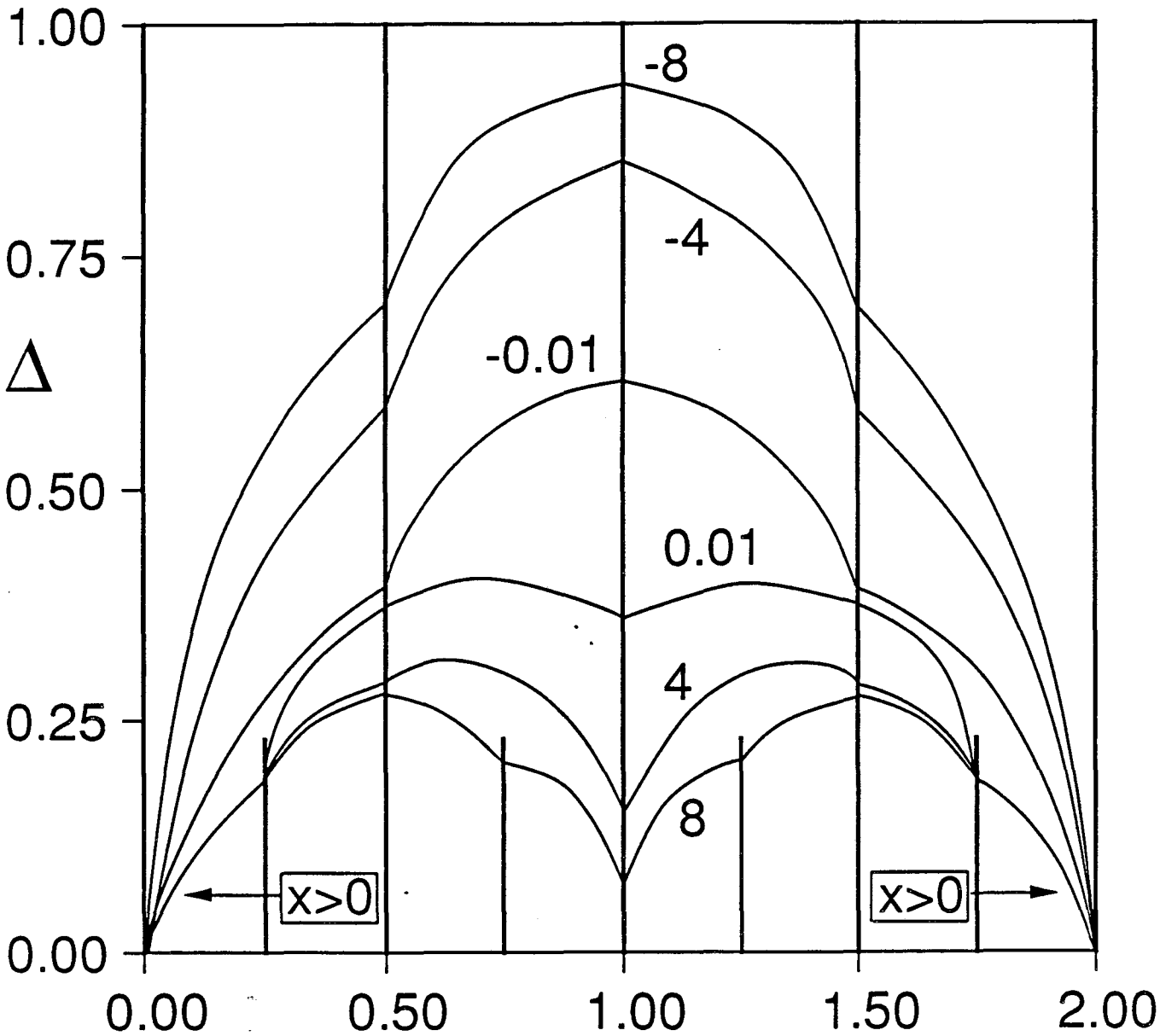
2 & 4
4 & 6
6 & 8
0.0
0.5
1.0
1.5
2.0
n = fractional occupation

Fig. 3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Δ
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-8
-4
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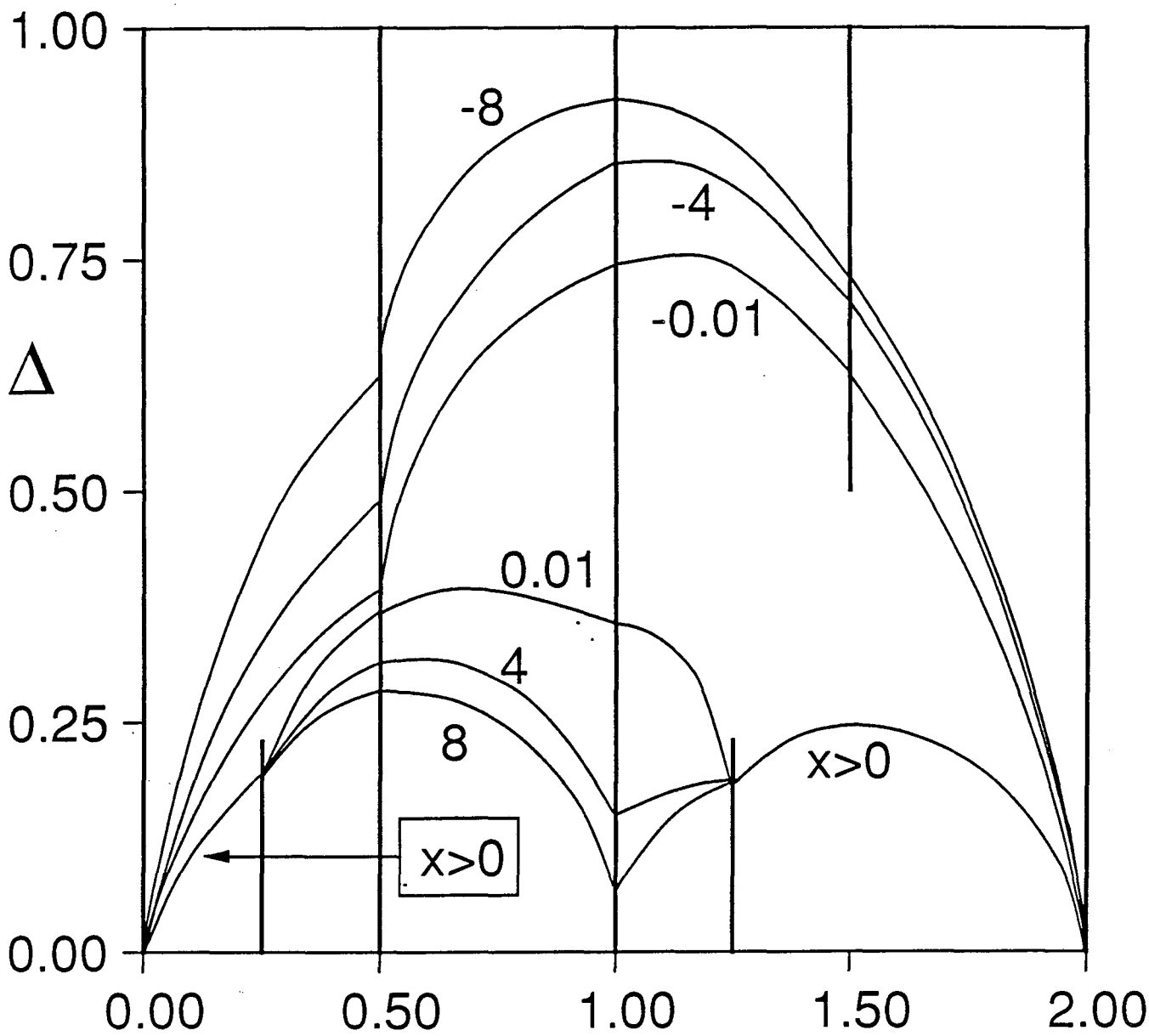
4
8
x>0
x>0
0.00
0.50
1.00
1.50
2.00
n = fractional occupation

Fig. 4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Δ
-8
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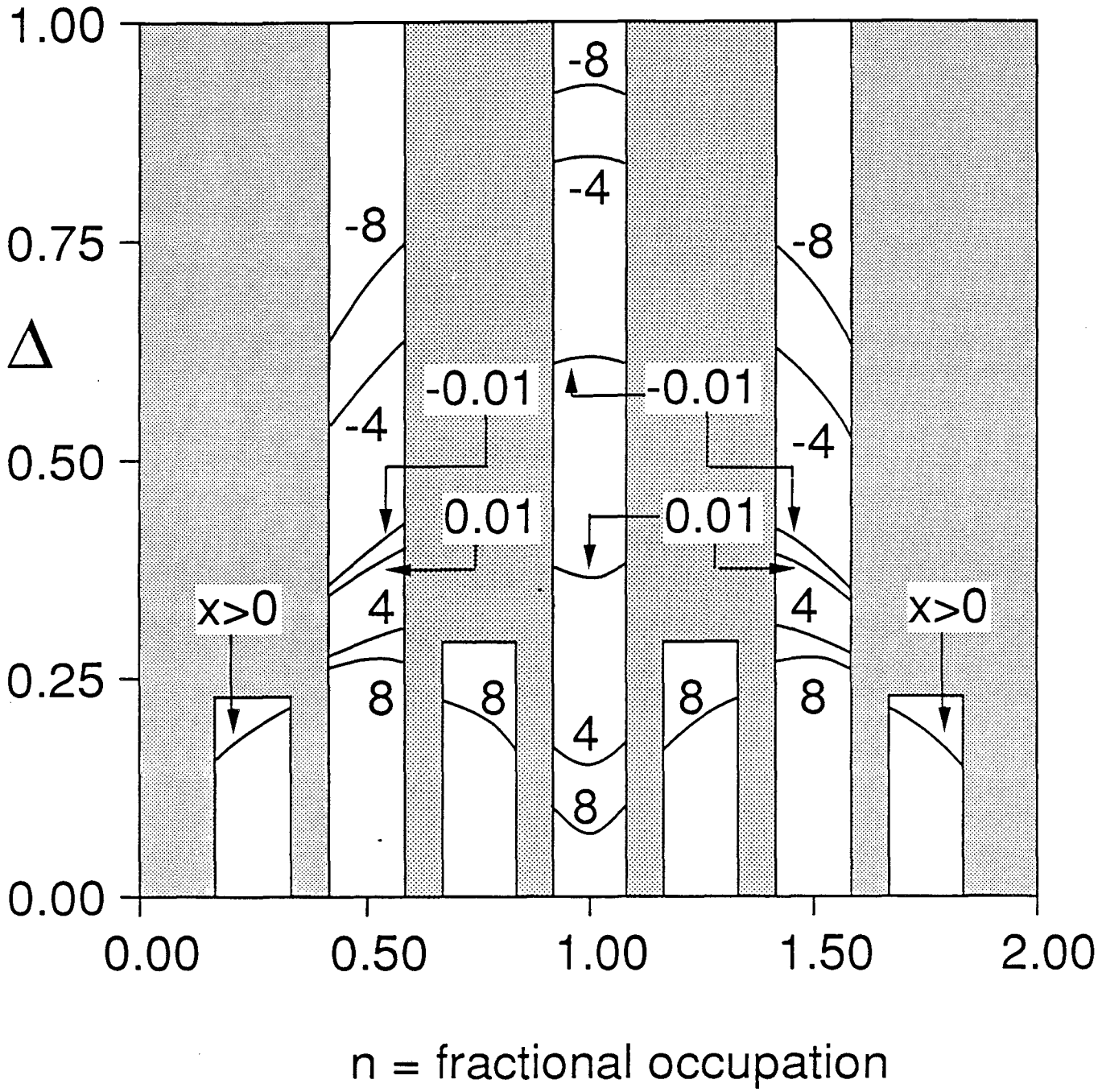
0.01
4
8
x>0
x>0
0.00
0.50
1.00
1.50
2.00
n = fractional occupation

Fig. 5


1.00
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0.50
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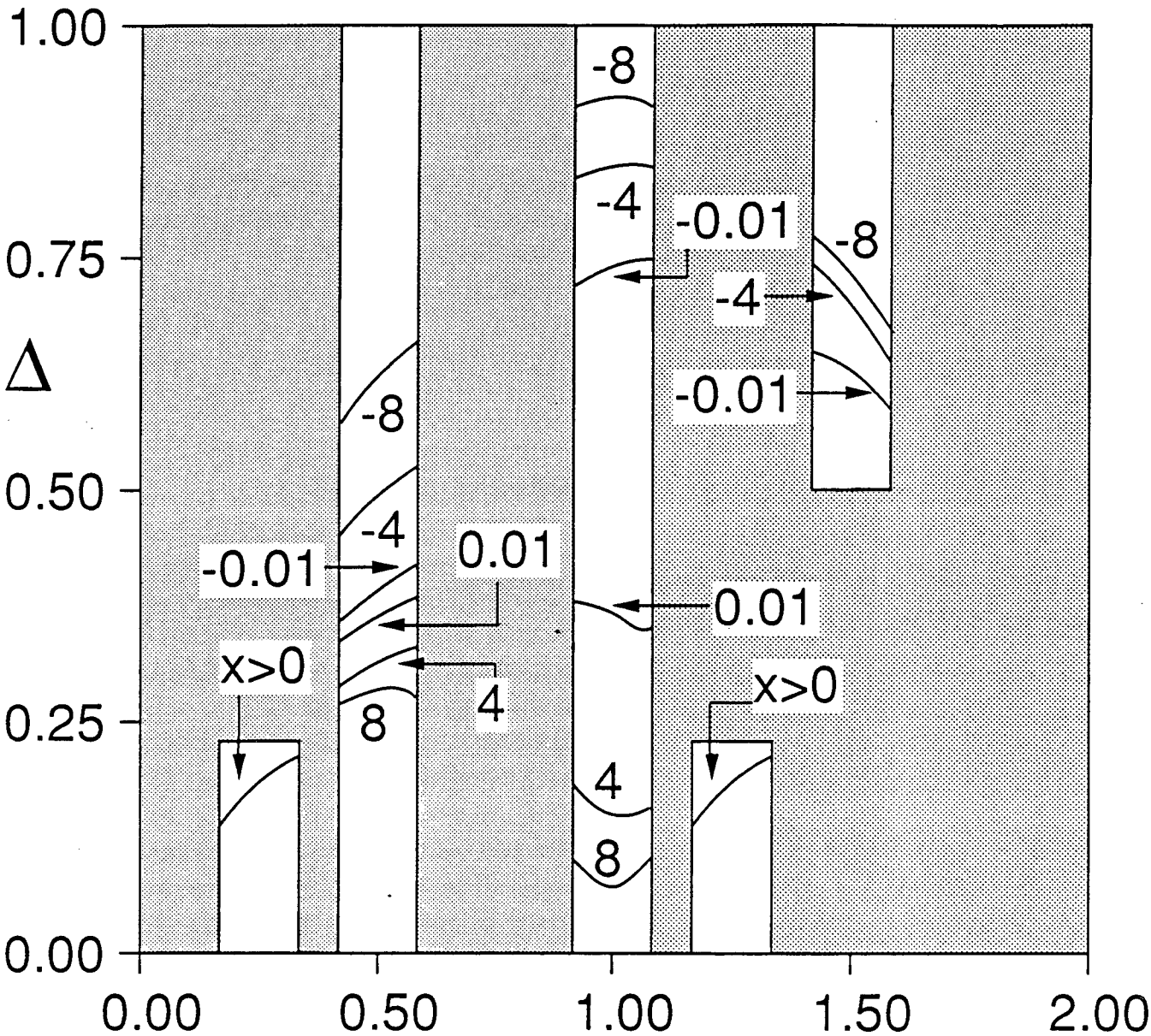
Δ
0.00
0.50
1.00
1.50
2.00
n = fractional occupation
-8
-4
-8
-8
-4
-4
-0.01
-0.01
0.01
0.01
x>0
x>0
4
4
8
8
8
8
4
8

Fig. 6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Δ
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1.00
1.50
2.00
-8
-4
-0.01
-8
-4
-0.01
-8
-4
-0.01
0.01
0.01
x>0
4
8
x>0
4
8
n = fractional occupation

Fig. 7

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UNIVERSITY OF CALIFORNIA
INFORMATION RESOURCES DEPARTMENT
BERKELEY, CALIFORNIA 94720