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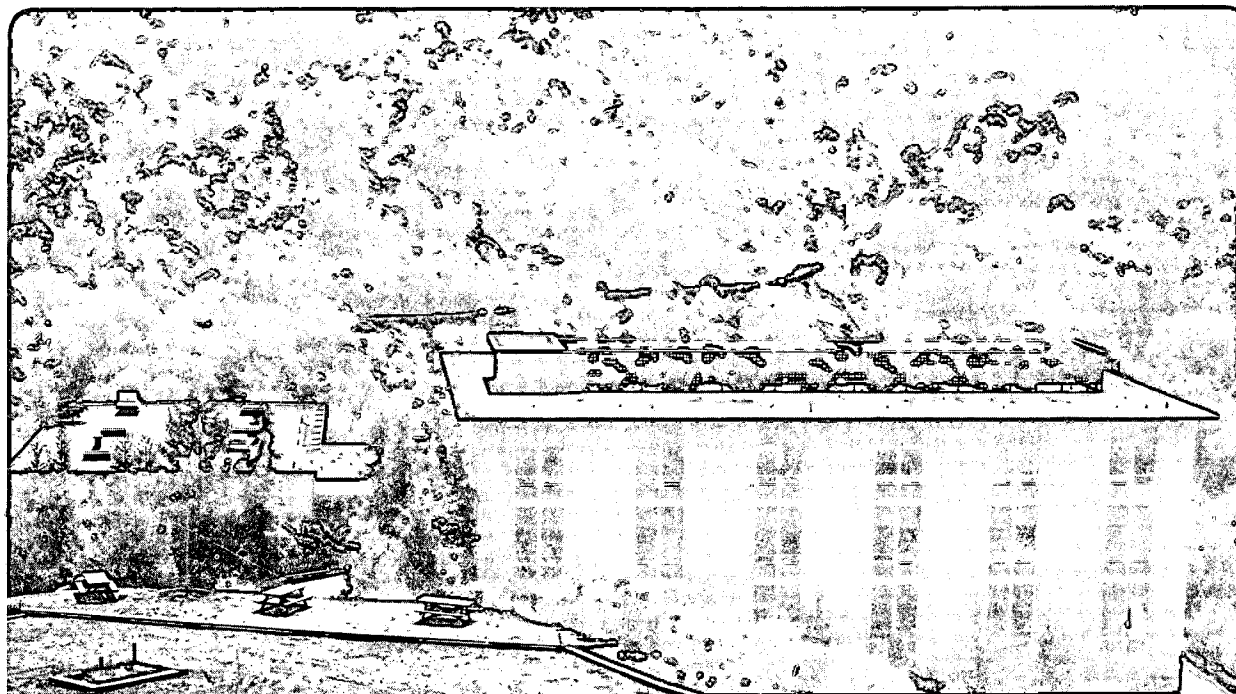
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### Open Fermionic Quantum Systems

E. Artacho and L.M. Falicov

May 1992



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OPEN FERMIONIC QUANTUM SYSTEMS\*

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## *ABSTRACT*

A method to treat a quantum system in interaction with a fermionic reservoir is presented. Its most important feature is that the dynamics of the exchange of particles between the system and the reservoir is explicitly included via an effective interaction term in the Hamiltonian. This feature gives rise to fluctuations in the total number of particles in the system. The system is to be considered in its full structure, whereas the reservoir is described only in an effective way, as a source of particles characterized by a small set of parameters. Possible applications include surfaces, molecular clusters, and defects in solids, in particular in highly correlated electronic materials. Four examples are presented: a tight-

binding model for an adsorbate on the surface of a one-dimensional lattice, the Anderson model of a magnetic impurity in a metal, a two-orbital impurity with inter-orbital hybridization (intermediate-valence center), and a two-orbital impurity with inter-orbital repulsive interactions.

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# Open fermionic quantum systems

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## 1. INTRODUCTION

Surfaces, local or extended defects, impurities, and clusters are subjects of great relevance in condensed-matter physics. They can all be described as relatively "small" systems embedded or in contact with a larger body, the bulk of the material that contains them. To study such systems, even when strictly focusing on their local properties, interaction with the environment cannot be meaningfully neglected. One-particle-like approximations -- mean-field theories, the Kohn-Sham treatment of density functional theory, or quasi-particles theories treated in perturbation expansions -- are usually flexible enough to make possible an explicit, albeit laborious study of the defect and the bulk material surrounding it. However, when many-body correlations become important these treatments are of little use.

The most widely and successfully used techniques to study highly correlated elec-



tronic materials are based on three approaches: (1) perturbative methods, of restricted and/or dubious convergence; (2) *ad hoc* (variational) methods, tailored to a particular problem; and (3) small-cluster approximations. In the last approach, a small system with appropriate boundary conditions is considered to be representative of the larger system. The problem is then solved by an exact diagonalization of the Hamiltonian in the Hilbert space spanned by all the possible many-body basis vectors, or by Monte-Carlo simulation techniques. Because of the exponential growth of Hilbert space with cluster size, the method can in practice handle only clusters with very few electron orbitals in the cell, less than say 50. It is therefore difficult to conduct realistic studies of a defect, embedded cluster or surface, including in the calculation or simulation a sizable portion of the bulk.

The method proposed here to study surfaces or defects in highly correlated electronic materials considers the defect (surface, cluster) -- and possibly its immediate surroundings -- as the "system", and the bulk of the material only as a particle reservoir characterized in an effective way by a small set of parameters. These parameters reflect the information available about the bulk, such as electron density, magnetization, density of states at the Fermi level, etc. and are part of the input in the problem, *i.e.*, the bulk properties are assumed to be known and well characterized. The system, however, is treated differently. Its properties are determined including all its internal degrees of freedom, plus the effective interaction with the particle reservoir. The most important feature of this treatment is thus the exchange of particles between system and reservoir. The total number of particles in the system is therefore subject to fluctuations, which can be considerable in a small system.

The approach is very well suited for many problems. In particular surfaces can be examined by including only very few layers, periodic in two dimensions, with vacuum on one side and attached on the other to a bulk crystal, the reservoir. Similarly an interface is a two-dimensional periodic system attached to two different reservoirs, one

on each side. A point defect, an impurity, or a cluster is an even more natural candidate to be treated by this approach. It is even possible to study in this way local properties of three-dimensional homogeneous materials.

The crucial issue of this method is the proper description of the reservoir, and the exchange of particles between system and reservoir. The goal is to focus only on the system, where particles enter and exit in a way consistent with Fermi-Dirac statistics. The idea of a "classical" reservoir and a small quantum system is standard for bosons,<sup>1,2</sup> where it forms the basis for the Bogoliubov transformation which describes superfluidity and Bose-Einstein condensation. In the case of the Bose condensate, the  $k = 0$  state constitutes the reservoir and all other  $k \neq 0$  states are the "small" quantum system. Whenever a particle gets scattered from a  $k \neq 0$  state to the macroscopically occupied  $k = 0$  state, it effectively disappears from the system of excitations. The creation and annihilation operators for the  $k = 0$  state (reservoir) are replaced by a classical  $N^{\frac{1}{2}}$  number, a scalar characterized only by the density of particles in the container. Similar treatments exist for superconductivity, where the "particles" in the reservoir are Bose-like Cooper pairs,<sup>1,3</sup> and in theories of quantum dissipation,<sup>4</sup> where the reservoir consists of phonons.

The procedure, which is adequate for bosons, is not suitable for fermions. The anticommutation relations of the creation or annihilation fermion operators create difficulties which do not exist in the case of bosons. The present contribution overcomes these drawbacks and presents a consistent formulation and some applications.<sup>5,6</sup>

The formulation of the general method is presented in Section 2. Section 3 contains some applications: (a) a tight-binding model for an adsorbate on the surface of a one-dimensional lattice, (b) Anderson's model of a magnetic impurity in a metal, (c) a two-orbital impurity with inter-orbital hybridization (intermediate-valence center), and (d) a two-orbital impurity with inter-orbital repulsive interactions. Section 4 consists of the conclusions.

## 2. METHOD

The exact Hamiltonian for a fermion *complex* consisting of the (small) *system* connected to a *reservoir* has the general form:

$$H = H_s + H_r + H_{int} \quad , \quad (1)$$

where  $H_s$  includes operators that refer to the system but not to the reservoir,  $H_r$  refers to that part of the Hamiltonian related to the reservoir but not to the system, and  $H_{int}$  contains interactions and transfer of particles between system and reservoir. The Hamiltonian (1) completely defines the dynamics of the problem. All necessary information for the complex is included in the density operator, which, to be determined, requires complete knowledge of the dynamics of the system and the reservoir. Because only information about the system is required, the usual procedure in quantum statistical mechanics is to define a density matrix

$$\rho = e^{-(H_s + \mu - N_s)/kT} / Z \quad , \quad (2a)$$

where

$$Z = \text{Trace} [ e^{-(H_s + \mu N_s)/kT} ] \quad , \quad (2b)$$

the trace in (2b) is taken over the Hilbert space of the states of  $H_s$ , and all other symbols have the standard meaning.

The reservoir defines the chemical potential  $\mu$ , which in turns determines the average number of particles in the system, given by the expectation value  $\langle N_s \rangle$ . Because  $H_s$  commutes with the fermion-number operator of the system,  $N_s$ , its eigenstates are characterized by a given number of fermions, with no fluctuations in them. Therefore, even though (2) sums over states with any number of fermions in it (statistical fluctuations), the *quantum mechanical* states involved there have no particle fluctuation whatever. For this approach to be valid one condition must apply: the fluctuations caused by  $H_{int}$  in the number of particles in the system must either be zero (no particle transfer between reservoir and system) or those fluctuations must be small compared with the mean number of particles in the system. Thus  $N_s$  is a good (or an

approximately good) quantum number and the only effect of the reservoir is to control the number of particles in the system via the chemical potential  $\mu$ .

It is the aim of this contribution to restrict the formalism to the system only, even in those cases in which the *quantum mechanical* particle fluctuations in the system are of the same order of magnitude of the particle number  $N_s$  itself.

The approach presented here is intended mainly for small systems, where the effects of  $H_{int}$  are not negligible, and must be explicitly kept. The most important effect of  $H_{int}$  which gives rise to the particle fluctuations in the system is contained in those terms where transfer -- hopping, tunneling -- of particles between system and reservoir is explicit. In second quantization such terms are of the form

$$H_{int}(transfer) = \sum_{i,j,\sigma} (t_{ij} c_{s_i\sigma}^\dagger c_{r_j\sigma} + t_{ij}^* c_{r_j\sigma}^\dagger c_{s_i\sigma}) \quad , \quad (3)$$

where the operators  $c_{s_i\sigma}$  refer to orbitals within the system and the operators  $c_{r_j\sigma}$  to orbitals in the reservoir. As usual  $\sigma$  stands for the spin degree of freedom of the particle. This term cannot be used directly in (2) or equivalent formulations because it explicitly contains operators which are connected with the reservoir. It has to be replaced by an  $H_{eff}$  that has the same effect on the system but averages out in some way the details of the reservoir. In principle this is similar to the treatment of bosons,<sup>1-3</sup> where the creation and annihilation operators on the reservoir are replaced by  $N^{\frac{1}{2}}$ . In this sense  $H_{int}$  would take the form

$$H_{eff} = \sum_{i,\sigma} (\tau_{i\sigma}^* c_{s_i\sigma}^\dagger + \tau_{i\sigma} c_{s_i\sigma}) \quad . \quad (4)$$

Here the parameters  $\tau_{i\sigma}$  describe the effect of the hopping between the orbital  $i$  of the system and the reservoir. They include, in principle, a sum over all the orbitals  $j$  of the reservoir of the hopping factors  $t_{ij}$  multiplied by a "classical" average of the fermionic creation and annihilation operators associated with the orbital  $(j,\sigma)$ . What the Hamiltonian (4) describes is the process of creation and annihilation of particles in various orbitals of the system, with strength  $\tau_{i\sigma}$ . This term accounts effectively for the

hopping from/to the reservoir. Such a substitution permits the concentrating exclusively on the system. The reservoir degrees of freedom have been eliminated.

The introduction of  $H_{eff}$  in equation (4), however, presents, several difficulties. Fermionic creation and annihilation operators anticommute among themselves and with the other fermionic operators -- such as those in the system and in the reservoir. They have been replaced by scalars that commute with the other scalars and with fermionic operators. This replacement gives rise to inconsistencies and undesirable effects. For example, if the connection with the reservoir is through a single orbital of the system,  $H_{eff}$  would read

$$H_{eff} = \tau_{\uparrow}^* c_{\uparrow}^{\dagger} + \tau_{\downarrow}^* c_{\downarrow}^{\dagger} + \tau_{\uparrow} c_{\uparrow} + \tau_{\downarrow} c_{\downarrow} \quad (5)$$

for spin 1/2 particles. Regardless of the values of  $\tau_{\uparrow}$  and  $\tau_{\downarrow}$ , (5) can be rewritten as

$$H_{eff} = \theta_{\sigma}^* c_{\sigma}^{\dagger} + \theta_{\sigma} c_{\sigma} \quad (6)$$

where the subindex  $\sigma$  indicates a well defined direction of the spin -- a different quantization axis for the spin degree of freedom. This transformation means that, whatever the parameters, particles are created or annihilated in the system with a single, well defined spin direction, which depends on the *phases* of  $\tau_{\uparrow}$  and  $\tau_{\downarrow}$ . The system does conserve the number of particles for the other component of the spin. In other words, the system is in contact with a single-spin -- a purely ferromagnetic -- reservoir of arbitrary but well defined orientation. This is indeed a pathological and unacceptable property, which is related to the loss of fermionic character of the particles while being transferred between the system and the reservoir.

A necessary condition is then to keep *fermionic consistency*, *i.e.*, the states of the reservoir, in any of its forms, must retain fermionic character: they must satisfy antisymmetry properties with the fermionic states of the system and among themselves. It is important to stress that the main object here is to replace the reservoir with a simple "set of outside parameters", and that guaranteeing fermionic consistency -- a requirement -- in no way changes the aim. The formal development that follows

insures fermionic consistency; the main objective has been already achieved in the introduction -- albeit not in its final form -- of  $H_{eff}$  in (4).

Fermionic consistency is obtained if a *fermionic* reservoir is explicitly considered. The only way a reservoir may contain many fermions is by having many internal one-particle states, *i.e.*, a rich Hilbert space, with its consequent danger of complications and the possibility of an intractable problem. The solution proposed here is to allow for change in the occupation of the states in the reservoir *in a single, unique and orderly fashion*, compatible with Fermi statistics. With this aim in mind the reservoir is assumed to contain (in principle an infinity of) *hierarchical* one-particle fermionic states. A hierarchy is established, *i.e.*, each orbital -- occupied or empty -- is labelled with a natural number within its symmetry set. States are occupied and emptied in a set of well defined sequences -- one sequence for each symmetry of the complex. Within each sequence -- say spin up states -- there is a unique order in which the reservoir states get occupied and emptied; in other words, there is never an exchange of occupation of particles of the same symmetry within the reservoir; states far away from the Fermi level never change their occupation number. Therefore only a few one-particle states (as many as needed, essentially, but always very few and always in the neighborhood of the Fermi level) are relevant.

For each global state of the system (the eigenstates of  $H_s$ ) there is a *single* corresponding state of the reservoir. (The converse is not necessarily true.) This assignment yields a one-to-one correspondence (mapping) of the eigenstates of  $H_s$  and the relevant states of  $H$  of the complex. In other words the retained Hilbert space for the complex can now be mapped onto the Hilbert space of  $H_s$ .

With this mapping the interaction Hamiltonian  $H_{eff}$  becomes again a clean fermion hopping between orbitals. Fermionic consistency is guaranteed, since the only operation done on the full fermionic reservoir is a projection to a restricted, well defined set of states. The approximation essentially means that the transfer to and from

conduction electrons (the Kondo effect).<sup>12</sup>

The physics of this model can be correctly described by the scheme presented here. The localized orbital is considered to be the open system. The metallic band is the reservoir, and the hybridization term becomes the coupling term. Three parameters characterize this problem:  $U$  internal to the system,  $\mu$  defined for the system by the reservoir, and  $\tau$  the effective system-reservoir interaction (modified hybridization).

$$H_s = \epsilon_0 (n_{0\uparrow} + n_{0\downarrow}) + U n_{0\uparrow} n_{0\downarrow} \quad , \quad (18a)$$

$$H_{eff} = \sum_{\sigma} (\tau^* c_{0\sigma}^{\dagger} R_{\sigma} + \tau R_{\sigma}^{\dagger} c_{0\sigma}) \quad . \quad (18b)$$

This open problem can be solved exactly by a diagonalization of the  $4 \times 4$  matrix for  $G = H_s + H_{eff} - \mu N_s$ , given by

$$G = \begin{pmatrix} 0 & \tau & \tau & 0 \\ \tau & (\epsilon_0 - \mu) & 0 & \tau \\ \tau & 0 & (\epsilon_0 - \mu) & \tau \\ 0 & \tau & \tau & U + 2(\epsilon_0 - \mu) \end{pmatrix} \quad . \quad (19)$$

For the particular case  $\langle n_0 \rangle = 1$  the chemical potential  $\mu$  is equal to  $(\epsilon_0 + \frac{1}{2}U)$ . For this occupation there is a particle-hole symmetry that allows the reduction of the matrix to be diagonalized (for the ground state) to a  $2 \times 2$ . It easily yields the following results: for the energy

$$E = -\frac{1}{4} \left[ U + (U^2 + 64\tau^2)^{\frac{1}{2}} \right] \quad ; \quad (20)$$

for the particle fluctuation,

$$\Delta n_0 \equiv \langle n_0^2 \rangle - \langle n_0 \rangle^2 = \langle n_0 \rangle (1 - \langle n_0 \rangle) + 2 \langle n_{0\uparrow} n_{0\downarrow} \rangle \quad , \quad (21)$$

$$\Delta n_0 = 32\tau^2 \left[ U^2 + 64\tau^2 + U(U^2 + 64\tau^2)^{\frac{1}{2}} \right]^{-1} \quad , \quad (22)$$

for  $\langle n_0 \rangle = 1$ ; and the magnetic moment

$$\mathbf{m}_0 \equiv \sum_{\sigma, \sigma'} \langle c_{0\sigma}^{\dagger} \mathbf{S}_{\sigma, \sigma'} c_{0\sigma'} \rangle \quad , \quad (23)$$

where  $\mathbf{S}_{\sigma, \sigma'}$  are the standard Pauli matrices, is zero for all three components. (In other

particular the density of states at the Fermi level can be obtained in the open system from  $(d\langle N_s \rangle / d\mu)$  evaluated at the value  $\mu$  that gives the correct average number of particles  $\langle N_s \rangle$  in the system.

### 3. APPLICATIONS

#### 3a. Adsorbate on a one-dimensional lattice

A first application of the method is to a problem that can be solved exactly for the complex, so that the exact results can be compared with the ones obtained with the scheme proposed here. The specific problem is that of an adsorbate on the surface of a one-dimensional lattice. It consists of a semi-infinite sequence of atoms, equally spaced, each containing a single orbital. The on-site energy is the same for all orbitals, except for the surface adsorbate (outer site). There is, in addition, a hopping matrix element  $(-t)$  between nearest neighbors, a constant throughout the lattice. The hopping matrix element between the adsorbate and its neighbor is also assumed to be  $(-t)$ , identical to that between two sites in the lattice. The Hamiltonian -- which does not include interactions -- is given by<sup>8</sup>

$$H = -t \sum_{\langle i,j \rangle \sigma} (c_{i\sigma}^\dagger c_{j\sigma} + c_{j\sigma}^\dagger c_{i\sigma}) + \epsilon_0 \sum_{\sigma} n_{0\sigma} \quad , \quad (12)$$

where label 0 indicates the adsorbate orbital, and  $\langle i,j \rangle$  means nearest-neighbor pairs, including the adsorbate. Since spin does not play any role in this model it is solved for spinless fermions (a simple doubling of the occupation gives the solution for the two-spin case).

At zero temperature the model is completely characterized by the dimensionless parameter  $(\epsilon_0/t)$  and by the number of electrons per bulk atom  $n_b$ . The quantity of interest is the excess charge at the adsorbate

$$\delta n = n_0 - n_b \quad . \quad (13)$$

It is straightforward to determine the chemical potential  $\mu$  that corresponds to a specific  $n_b$ . Since Bloch's theorem applies in the bulk and the band structure is



analytic in this case,

$$\mu = 2t \sin\pi(n_b - \frac{1}{2}) \quad (14)$$

The use of recursion techniques<sup>9</sup> for the resolvent of the Hamiltonian, yields for  $D_0(\epsilon)$ , the density of one-particle states of the system projected on the adsorbate site:

$$D_0(\epsilon) = \frac{1}{2\pi} \frac{(4t^2 - \epsilon^2)^{\frac{1}{2}}}{\epsilon_0 (\epsilon_0 - \epsilon) + t^2} \quad (15)$$

Integration of  $D_0(\epsilon)$  from  $-\infty$  to  $\mu$  yields  $n_0$  and  $\delta n$ . This quantity is plotted as a function of  $(\epsilon_0/t)$  in Figure 1 for  $n_b = 0.50$ ,  $n_b = 0.35$ , and  $n_b = 0.20$  (continuous lines).

A first attempt to approximate this problem in the scheme described above is to consider only the adsorbate site as the (open) system. It interacts with a reservoir provided by the lattice. The only energy parameters entering the Hamiltonian of this system are  $\epsilon_0$ ,  $\tau$ , and  $\mu$ . The first one,  $\epsilon_0$ , is part of  $H_s$ , the input to the problem. The chemical potential  $\mu$  is provided by the reservoir, and is related to  $n_b$  by (14). That equation also provides a measure of the band width  $4t$ , *i.e.*, the bulk hopping parameter  $t$ . The effective interaction  $\tau$  between system and reservoir is a strong function of bulk parameters (band width, band occupation) as well as of the coupling (strength of the hopping parameter  $t_{01}$ ) between the adsorbate and the lattice. It can be obtained from one additional piece of information. For example, by fitting  $\delta n$  to the exact result for one value of  $\epsilon_0$ , *e.g.*,  $\epsilon_0 = 0$ . The Hilbert space associated to this system is spanned by only two states, one for the empty and the other for the occupied adsorbate orbital. The solution of the problem reduces to the diagonalization of a 2x2 matrix of  $G$ , equation (11):

$$G = \begin{pmatrix} 0 & \tau \\ \tau & \epsilon_0 - \mu \end{pmatrix} \quad (16)$$

The solution is trivial. The charge transfer  $\delta n$  can be computed again as a function of  $\epsilon_0$  and compared with the exact result. The results, which are satisfactory, are shown in Figure 1 (dotted lines). Inclusion of particle fluctuations in a very small system (one

only orbital!) is sufficient to approximate well the  $\delta n$  versus  $\epsilon_0$  curve, with one fitted parameter  $\tau$ . The solution for a small cluster not coupled to the reservoir -- equation (2) -- gives for this graph a step function with the discontinuity at  $\epsilon_0 = \mu$ .

The approximation can be improved systematically by including one or more lattice sites (substrate) in the definition of the system. Results are presented also in Figure 1 for the open system consisting of the adsorbate atom and its nearest neighbor (dashed lines). It is solved by repeating the same procedure as before and diagonalizing the  $G$  matrix for the two sites, a Hilbert space consisting of four states. Results for larger clusters rapidly converge to the exact result, especially in the cases of  $n_b = 0.50$  and  $n_b = 0.35$ , where the continuous and the dashed lines are practically indistinguishable.

### 3b. Anderson's impurity model

Anderson's model for a magnetic impurity embedded in a metal is the next application, an example of a many-body Hamiltonian. The model describes the impurity atom with a localized orbital (labelled 0) with an on-site Coulomb repulsion  $U$  and hybridized to extended, uncorrelated states of a reservoir (the metal host). The Hamiltonian has the form<sup>10</sup>

$$H = \epsilon_0 (n_{0\uparrow} + n_{0\downarrow}) + U n_{0\uparrow} n_{0\downarrow} + \sum_{k\sigma} \epsilon(k) a_{k\sigma}^\dagger a_{k\sigma} + \sum_{k\sigma} (V_{0k} c_{0\sigma}^\dagger a_{k\sigma} + V_{0k}^* a_{k\sigma}^\dagger c_{0\sigma}) \quad , \quad (17)$$

where  $V_{0k}$  is the hybridization strength, the operators  $c_{0\sigma}$  ( $c_{0\sigma}^\dagger$ ) refer to the localized impurity state, the operators  $a_{k\sigma}$  ( $a_{k\sigma}^\dagger$ ) correspond to the extended, band states of the metallic host,  $U$  is the localized-state Coulomb interaction, and  $\epsilon(k)$  describes the metal band structure. This model was solved initially by Anderson in the mean-field approximation<sup>10</sup> and subsequently in other ways<sup>11</sup>. In all cases there is a critical value of the interaction  $U$  above which a localized magnetic moment develops. The magnetic moment, when present, is now known to be screened at low temperatures by the

conduction electrons (the Kondo effect).<sup>12</sup>

The physics of this model can be correctly described by the scheme presented here. The localized orbital is considered to be the open system. The metallic band is the reservoir, and the hybridization term becomes the coupling term. Three parameters characterize this problem:  $U$  internal to the system,  $\mu$  defined for the system by the reservoir, and  $\tau$  the effective system-reservoir interaction (modified hybridization).

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For the particular case  $\langle n_0 \rangle = 1$  the chemical potential  $\mu$  is equal to  $(\epsilon_0 + \frac{1}{2}U)$ . For this occupation there is a particle-hole symmetry that allows the reduction of the matrix to be diagonalized (for the ground state) to a  $2 \times 2$ . It easily yields the following results: for the energy

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for the particle fluctuation,

$$\Delta n_0 \equiv \langle n_0^2 \rangle - \langle n_0 \rangle^2 = \langle n_0 \rangle (1 - \langle n_0 \rangle) + 2 \langle n_{0\uparrow} n_{0\downarrow} \rangle \quad , \quad (21)$$

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where  $\mathbf{S}_{\sigma, \sigma'}$  are the standard Pauli matrices, is zero for all three components. (In other

words, there is no magnetic moment in the ground state.)

Values of  $E$ ,  $|m_0|$  and  $\Delta n_0$ , given by equations (20), (23) and (21) respectively, are shown in full lines in Figure 2. As a didactical exercise, also shown in Figure 2 are the solutions of the Hamiltonian (18) in the restricted (symmetry conserving, dotted lines) and unrestricted (broken spin symmetry, dashed lines) Hartree-Fock approximations. The latter is qualitatively identical to Anderson's Hartree-Fock solution<sup>10</sup> of the problem.

Comparison of the three sets of curves gives a clear appreciation of the advantages of the present method. Particle fluctuations are built into the model from the start. Large *local* fluctuations are necessary to minimize the band-energy term; small (zero) *local* fluctuations are necessary to minimize interaction energy. In the original problem, treated in the Hartree-Fock approximation, the best compromise is achieved by breaking spin-symmetry and thus creating a local magnetic moment. In the present approach, on the other hand, the *system*, as opposed to the complex, is allowed to exhibit particle fluctuations, governed by the medium through equation (18b). It has therefore more flexibility to compromise between the opposing effects -- band energy (18b), center of gravity effects [(18a) first term], and interaction energy [(18a), second term]. These can be accomplished without artificially producing a magnetic moment, and within the very restricted, small Hilbert space of the *system*.

It should be emphasized that the appearance of a spin singlet, *i.e.*, a state with zero magnetic moment, is a consequence of the participation of the reservoir through its fermionic character, as described in this particular example by  $H_{eff}$  of equation (18b). The Fermi-level fermions of the reservoir -- identified by the annihilation (creation) operators  $R_\sigma$  ( $R_\sigma^\dagger$ ) -- are coupled to the particle in the system and produce a singlet state. That is, in simplified terms, the physics that governs the ground state of the Kondo Hamiltonian.

### 3c. Hybridized two-orbital (intermediate-valence) impurity.

An intermediate-valence impurity<sup>13</sup> is characterized by two types of electron orbitals: one of the extended type, where band effects are dominant, and a second one, localized and dominated by the strong Coulomb repulsion. A hybridization between them results in "an intermediate valence". For the present purposes the system is taken to consist of one orbital of each type, their hybridization and the (infinite strength) Coulomb interaction between electrons in the localized state, *i.e.* a localized state that does not permit double occupation. The reservoir is the conduction band of the host metal, and the transfer of particles to and from the system can only occur through the (system) extended state.

The Hamiltonian is given by

$$H_s = (-\Delta)(n_{0\uparrow} + n_{0\downarrow}) + U n_{0\uparrow} n_{0\downarrow} + \sum_{\sigma} (V^* c_{1\sigma}^{\dagger} c_{0\sigma} + V c_{0\sigma}^{\dagger} c_{1\sigma}), \quad (24a)$$

$$H_{eff} = \sum_{\sigma} (\tau^* c_{1\sigma}^{\dagger} R_{\sigma} + \tau R_{\sigma}^{\dagger} c_{1\sigma}) \quad (24b)$$

Here  $U \rightarrow \infty$  is the intra-orbital Coulomb repulsion,  $\Delta$  is the energy difference between the center of gravity of the band of the impurity extended state (indicated by the subscript 1) and the localized-orbital energy (subscript 0),  $V$  is the localized-extended state hybridization energy, and  $\tau$  has the usual meaning.

The hamiltonian matrix  $G$  is now  $12 \times 12$ , corresponding to four possible occupations of the extended orbital 1 ( $0, \uparrow, \downarrow, \text{ and } \uparrow\downarrow$ ), and three possible occupations of the localized orbital 0 ( $0, \uparrow, \text{ and } \downarrow$ ). It should be diagonalized as a function of the parameters and the total number of particles  $N_s = \langle n_0 \rangle + \langle n_1 \rangle$  in the center.

Results are shown in Figure 3 for the case of  $N_s = 2$ . Shown in the graph are the lines of constant  $\langle n_0 \rangle$  in parameter space. The intermediate-valence region, located in the neighborhood of  $\Delta = 0$  is evident. This is in qualitative agreement with the expected behavior, and in quantitative agreement with other, more involved calculations.<sup>13</sup>

### 3d. Two-orbital impurity with repulsive interaction.

This case corresponds to the single impurity of what is commonly known -- in the periodic case -- as the Falicov-Kimball model,<sup>14</sup> which has been applied to a variety of problems, including the metal-insulator transition<sup>15</sup> and the valence transition in rare-earth and actinide compounds.<sup>13</sup>

The Hamiltonian in this case is given by

$$H_s = (-\Delta)(n_{0\uparrow} + n_{0\downarrow}) + U n_{0\uparrow}n_{0\downarrow} + W \sum_{\sigma,\sigma'} n_{0\sigma} n_{1\sigma'} \quad , \quad (25a)$$

$$H_{eff} = \sum_{\sigma} (\tau^* c_{1\sigma}^\dagger R_{\sigma} + \tau R_{\sigma}^\dagger c_{1\sigma}) \quad . \quad (25b)$$

All symbols have the same meaning as in (24); the differences are the absence of a hybridization term, and the presence of a repulsive interaction  $W$  between electrons in the localized and extended states. As in (24), the intra-orbital interaction  $U$  is taken in the limit  $U \rightarrow \infty$ , *i.e.*, no double occupation of the 0 orbital.

Many questions can be answered by solving the 12×12 secular equation for  $G$  as a function of the parameters  $\Delta$ ,  $W$ , and  $\tau$  and the number of electrons  $N_s$  in the impurity. As an example Figure 4 shows the variation of  $\langle n_0 \rangle$  as a function of the one-electron energy difference  $\Delta$  for  $N_s = 1.5$  and for various values of  $W$ . The unit of energy is taken to be  $\tau$ . It should be noted that application of pressure to a material changes, in general, all parameters; however while the energy difference  $\Delta$  tend to be normally very sensitive to pressure, the parameters  $\tau$  and  $W$  are not, and the total charge of the impurity  $N_s$  remains essentially unchanged.<sup>16,17</sup> Therefore Figure 4 is, in a sense, the plot of the change in the valence of the impurity as a function of (increasing or decreasing) pressure.

It can be seen that there are two values of  $\Delta$ ,

$$\Delta_{c1}(W, \tau) = W - \Delta_{c2}(W, \tau) \quad , \quad (26)$$

$$\Delta_{c2}(W, \tau) = -\left(2\tau/3^{1/2}\right) + \left[W^2 - (4W\tau/3^{1/2}) + (16\tau^2/3)\right]^{1/2} \quad , \quad (27)$$

such that the occupation  $\langle n_0 \rangle$  is 0 for  $\Delta \leq \Delta_{c1}$  and is 1 for  $\Delta \geq \Delta_{c2}$ . It varies continuously between 0 and 1 for  $\Delta_{c1} \leq \Delta \leq \Delta_{c2}$ . A singular point occurs only at  $N_s = N_{crit} \equiv 1.5$ ,  $W = W_{crit} \equiv (4\tau/3^{1/2}) = 2.3094 \tau$  where a discontinuous jump from 0 to 1 at  $\Delta_{c1} = \Delta_{c2} = \Delta_{crit} \equiv (2\tau/3^{1/2})$  appears.

It should be noted that in the regime where  $\langle n_0 \rangle$  is neither 0 nor 1, there is an abrupt change in the number of particles in the system with chemical potential, *i.e.*, the quantity  $(\partial N_s / \partial \mu)$  at constant  $\Delta$ ,  $W$  and  $\tau$  has an infinite value. In other words, there is an *effective* infinite density of one-electron states, which, in common one-electron language, would correspond to an accumulation of states at the Fermi level.

#### 4. CONCLUSIONS

A method has been proposed for treating a quantum system that exchanges fermions with a reservoir. The system is treated with its full quantum-mechanical structure, whereas the reservoir -- a source and sink of fermions -- is characterized by only a few parameters, as few as possible, but compatible with Fermi-Dirac statistics and with the nature of the problem under study. There is a one-particle transfer term in the Hamiltonian,  $H_{eff}$ , with strength  $\tau$ , which allows hopping between orbitals of the system and states of the reservoir.

The scheme has been applied successfully to a variety of problems. The results are very satisfying, since they reproduce, with a minimum of numerical effort, results for local properties found much more laboriously by other techniques. The quantitative agreement, is also satisfactory, since convergence with system size seems to be very rapid.

Possible applications of the method to real problems and model Hamiltonians are obviously many: surfaces, defects, layers, heterostructures, etc. In particular highly correlated and disordered solids and liquids seem to be ideal candidates. It should be remarked, however, that the appeal of the approach is mainly for *very small* systems,

since the complexity of the problem increases -- as in the case of all many-body problems -- exponentially with the number of orbitals involved in the system. Additional symmetry imposed on the problem, *e.g.*, point symmetry, periodicity in one, two, or three dimensions, may reduce the order of the relevant secular equation. But, in any case, the method should prove useful for very small systems embedded in an arbitrarily large reservoir.

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7. It should be remembered that the reservoir also determines the chemical potential  $\mu$ , which governs the mean number of particles in the system.
8. For this particular example the zero on one-particle energies is chosen at the center of the band.
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14. For general references on the metal-insulator and valence transition see L. M. Falicov, in *New Developments in Semiconductors*, edited by P. R. Wallace, R. Harris and M. J. Zuckermann (Noordhoff, Leyden, 1973) p. 191ff and references therein. See also reference 13.
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16. The problem presents a critical value of the parameters, for which there is a truly singular behavior. These values are:  $N_{crit} = 1.5$ ;  $W_{crit} = (4\tau/3^{\frac{1}{2}})$ ;  $\Delta_{crit} = (2\tau/3^{\frac{1}{2}})$ . Figure 4(c) contains the singularity -- the only point with a discontinuity in  $\langle n_0 \rangle$  as a function of  $\Delta$  for constant  $W = W_{crit}$  and constant  $N_s = N_{crit}$ .
17. The charge transfer between impurity (system) and host (reservoir) is essentially suppressed because of long-range Coulomb interaction effects, not included here. Charge transfer in transition-metal and rare-earth materials, once the chemical composition is established, is always considerably less than 0.1 electron per site. The *sign* of the small charge transfer, however, can be determined by the variations of the chemical potential  $\mu$  necessary to keep  $N_s$  constant. An increase in  $\mu$  indicates a tendency for electron transfer from the impurity to the system; a decrease in  $\mu$  has the opposite effect. In the case of Figure 4  $\mu$ , the chemical potential, (a) is constant if  $\langle n_0 \rangle$  is constant; (b) increases with increasing  $\Delta$  as  $\langle n_0 \rangle$  increases, for  $W > W_{crit}$ ; (c) decreases with increasing  $\Delta$  as  $\langle n_0 \rangle$  increases, for  $W < W_{crit}$ .

## FIGURE CAPTIONS

### Figure 1

Comparison between the exact calculation and the open systems for an adsorbate on a non-interacting one-dimensional surface. The plots are of the excess number of particles at the adsorbate  $\delta n$  as a function of the adsorbate on-site energy  $\epsilon_0$  in units of the bulk hopping parameter  $t$  for (a) a half-filled band  $n_b = 0.50$ ; (b)  $n_b = 0.35$ ; and (c)  $n_b = 0.20$ . The parameter  $\tau$  fits the  $\delta n$  of the exact calculation at  $\epsilon_0 = 0$ . Full lines are for the exact results; dotted lines are for an open system consisting only of the adsorbate site; dashed lines are for an open system which includes the adsorbate atom and the site immediately next to it. For  $n_b = 0.50$  and  $n_b = 0.35$  the two-site system and the exact results are barely distinguishable.

### Figure 2

The results of the calculation for the Anderson impurity model. Plotted as a function of the impurity (system) on-site interaction  $U$ , in units of the system-reservoir (impurity-host) hopping parameter  $\tau$  are (a) the total energy of the system  $E$  (measured from its value at infinite  $U$ ,  $E_\infty$ ); (b) the magnitude of the magnetic moment at the impurity  $|m_0|$ ; and (c) the fluctuations in the number of particles at the impurity site  $\Delta n_0 \equiv \langle n_0^2 \rangle - \langle n_0 \rangle^2$ . Full lines are the exact results of the open-system calculation; dotted lines are for the symmetry-conserving Hartree-Fock solution; dashed lines are for the unrestricted (broken spin symmetry) Hartree-Fock solution of the same problem -- the  $4 \times 4$  problem discussed in the text. Note that the full lines give the best energy and no magnetic moment.

### Figure 3

The contours of constant localized-orbital occupation  $\langle n_0 \rangle$  for an intermediate-valence impurity with a total number of electrons  $N_s = 2$ . The parameters  $\Delta$ ,  $V$ , and  $\tau$

are defined in the text. The valence of the impurity can be defined by the mean number of electrons in the extended orbital  $\langle n_1 \rangle = N_s - \langle n_0 \rangle = 2 - \langle n_0 \rangle$

**Figure 4**

The variation in the mean occupation of the localized orbital  $\langle n_0 \rangle$  for a two-orbital impurity with repulsive interaction as a function of  $\Delta$  for zero temperature,  $N_s = 1.5$  and for various values of the interaction parameter  $W$ . There is a valence transition as a function of  $\Delta$  (pressure). The occupation  $\langle n_0 \rangle$  is 0 for  $\Delta \leq \Delta_{c1}$  and is 1 for  $\Delta \geq \Delta_{c2}$ ; it varies continuously between 0 and 1 for  $\Delta_{c1} \leq \Delta \leq \Delta_{c2}$ . A singular point occurs only at  $N_s = 1.5$ ,  $W = (4\tau/3^{\frac{1}{2}}) = 2.3094 \tau$  with a discontinuous jump from 0 to 1 at  $\Delta_{c1} = \Delta_{c2} = (2\tau/3^{\frac{1}{2}})$ . The graphs correspond to (a)  $W = 0$  ; (b)  $W = 1.1547 \tau = (2\tau/3^{\frac{1}{2}})$  ; (c)  $W = 2.3094 \tau = (4\tau/3^{\frac{1}{2}})$  ; (d)  $W = 4.6188 \tau = (8\tau/3^{\frac{1}{2}})$  ; (e)  $W = 11.5470 \tau = (20\tau/3^{\frac{1}{2}})$  .

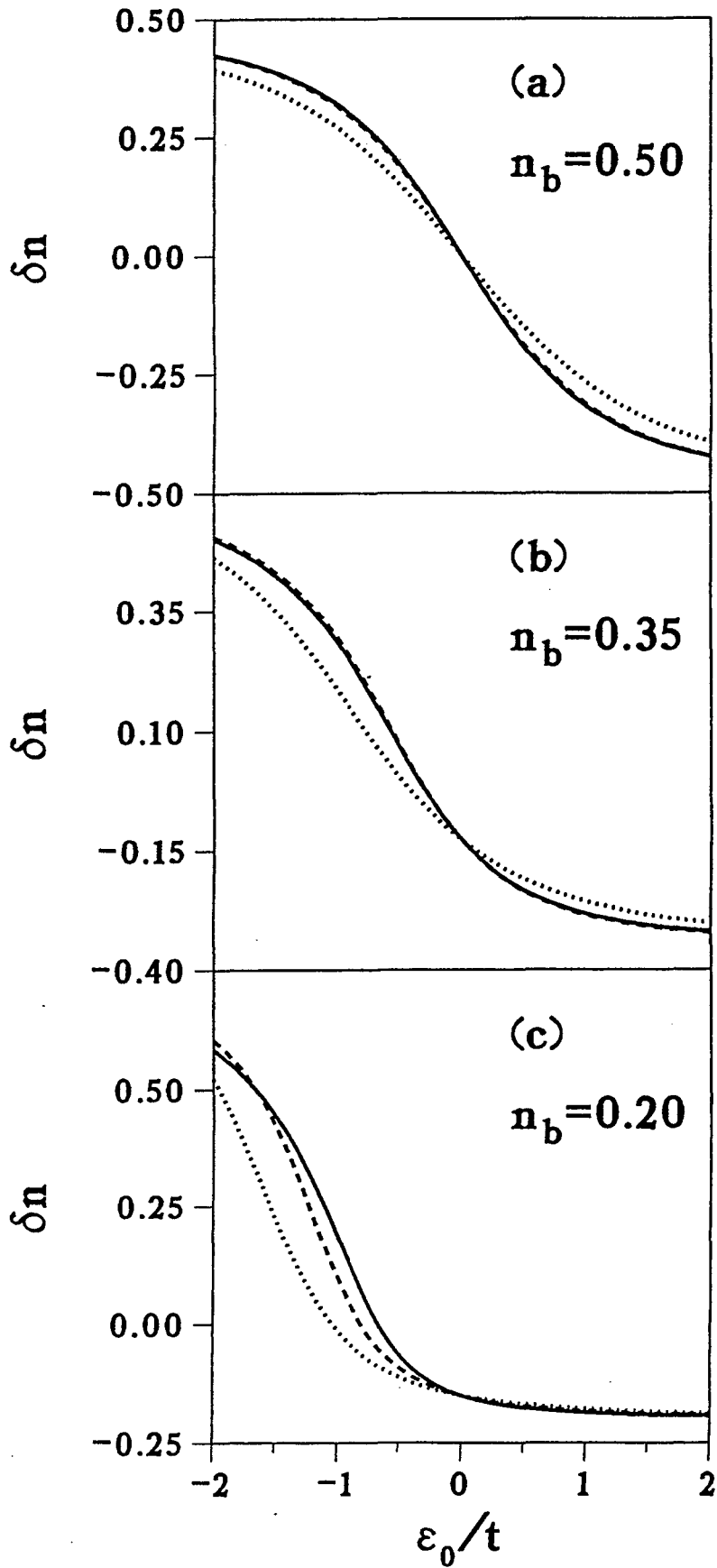


Figure 1

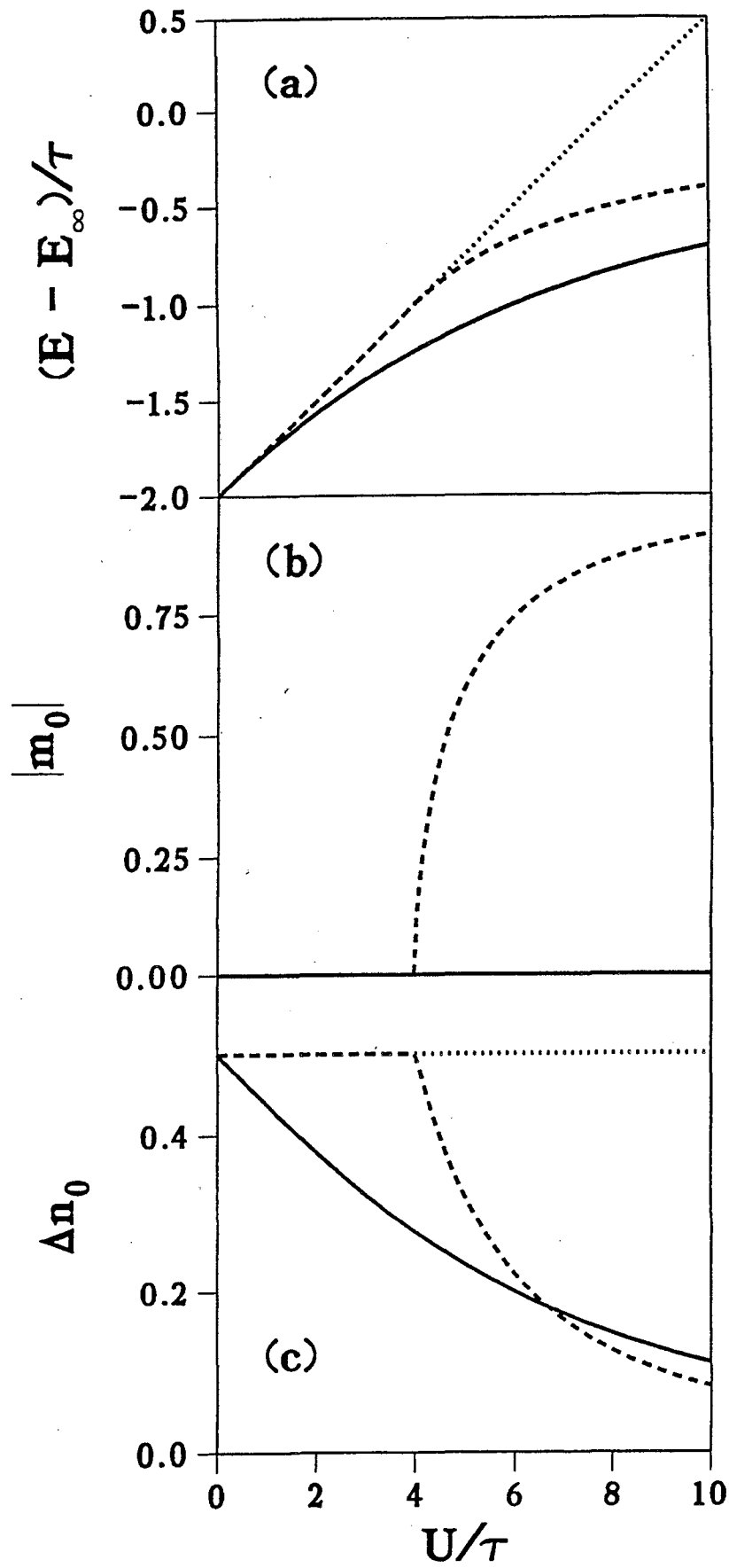


Figure 2

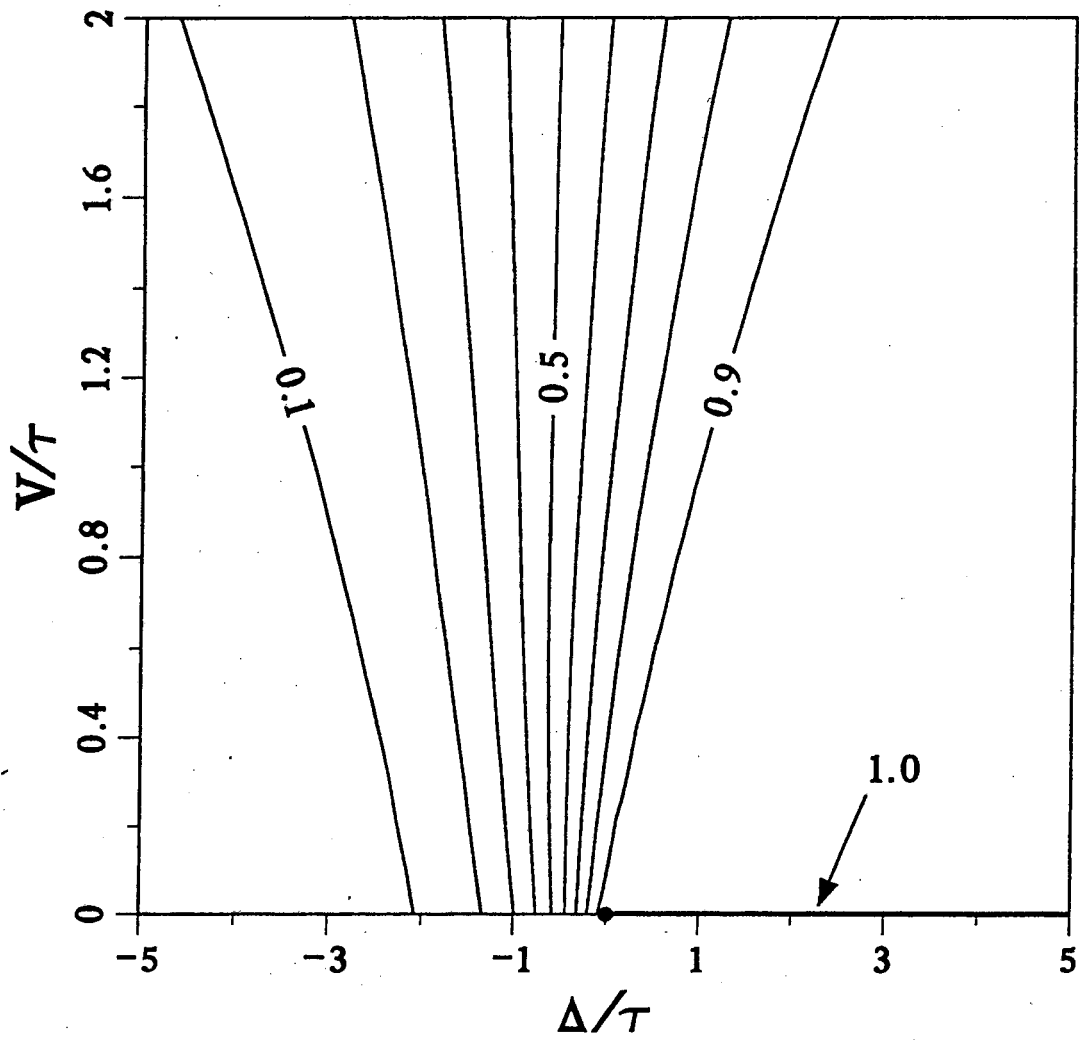


Figure 3

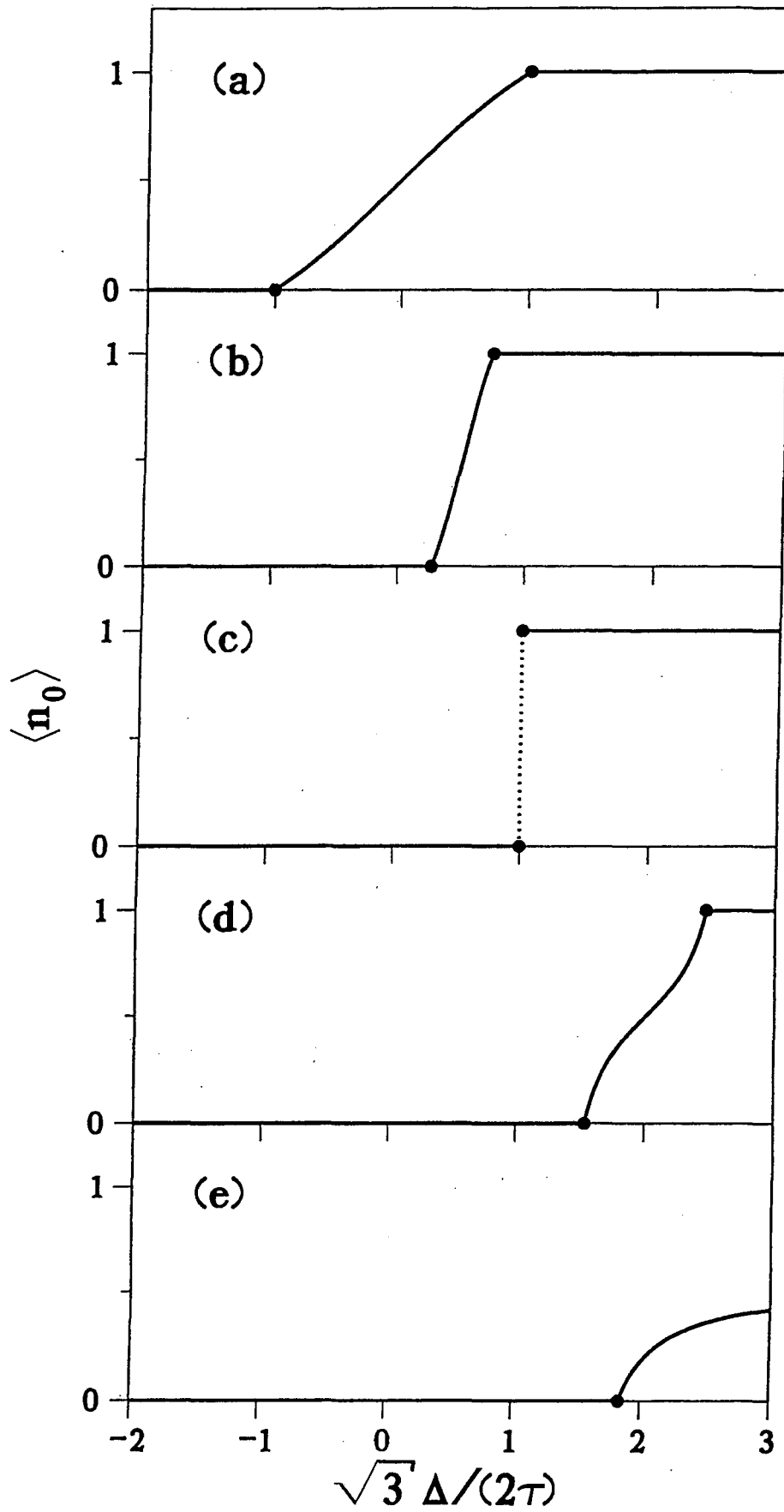


Figure 4



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