Intraatomic Coulomb Interaction Effects in the Time-Dependent Newns-Anderson Model

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Abstract

The intraatomic Coulomb interaction effects on the charge state of a moving atom near a metal surface in the time-dependent Newns-Anderson model are investigated in the Hartree-Fock approximation, the electron-hole pair expansion method and the brute force numerical method for a small system. In the Hartree-Fock approximation, several cases of the time dependence for parameters in the Hamiltonian are examined. The exponential growth of spin polarization on the atom is found. The polarization is described by a rate equation. The oscillatory convergence in time to the equilibrium value appears in the Hartree-Fock approximation. The approximate asymptotic solution is obtained for the long time behavior of the spin polarization and also the detailed analytic property of the solution is discussed. When initial condition of the system is symmetic in spin space, a symmetry breaking term is necessary to reach the spin polarized solution in time-evolution. In the electron-hole pair expansion method, the manybody effects are investigated in a special case. In paticular, the memory effects in the interacting case are conjectured to be same as the noninteracting case. In the numerical method for a small system, the manybody effects are examined in comparison with the Hartree-Fock results. From the results, it is believed that the Hartree-Fock approximation is rather good approximation, but manybody treatment is necessary to examine the fraction of negative ion.

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§1 Introduction

§1-1 Surface Physics

Any piece of solid or liquid matter is necessarily bounded by a surface of contact with a vacuum or with an atmosphere, or by an interface of contact with another piece of solid or liquid matter. The mere existence of this surface or interface can modify the properties of a material, and it is through this surface or interface that the material interacts with the outside world (Friedel 1978).

Because the surface is the end of the solid, the structure of the surface region is modified or sometimes quite different from that of bulk, and there frequently arise the surface localized states or surface localized elementary excitations, for instance, surface phonons, surface excitons, surface polaritons, etc. It is more difficult to study such systems theoretically than to study the bulk system, mainly because the Bloch theorem does not hold in the direction normal to the surface. In other point of view, solids face the external space, vacuum, so that other atoms or molecules interact with solids through the surface. For example, atoms or molecules are adsorbed on the surface, or desorbed from the surface. Furthermore, atoms or molecules moving in the vacuum are scattered by the surface. In such solid and particle systems, there are various interesting theoretical as well as experimental problems. In particular,

investigation of the systems consisting of a metal solid and a moving atom or molecule are very interesting and important, because in such a system, localized and discrete electron states are coupled with continuous metallic electron states, and the Fermi statistics may be involved in the dynamical processes.

§1-2 Dynamical Process

Now we consider a system consisting of a semi-infinite metal and a moving atom near the surface. In such a system, the moving atom is regarded as a perturbation to the electron states in the metal. The strength of the perturbation depends on the distance z between the surface and the atom, so the Hamiltonian for electrons has a parameter z. If the motion of the atom is infinitely slow, the total electronic state stays in the ground state of the Hamiltonian H(z) at every distance, that is the adiabatic process. In such cases the charge state of the atom observed after scattering does not depend on the perturbation or the trajectory of the atom. That is simply the ground state of the system where the atom is infinitely separated from the metal surface. When the atom moves with a finite velocity, the electronic state cannot respond immediately to the variation of the pertubation. Therefore the electronic state can be neither in the ground state nor in the eigenstate of H(z). The state is described with the linear combination of the eigenstates of H(z). Thus physical quantities observed after scattering are found to be distributed, and the distribution depends on the history of

the system reflecting the motion of the atom, that is, nonadiabatic or dynamical effects appear (Hagstrum 1954, 1961, Blandin, Nourtier and Hone 1976, Bloss and Hone 1978, Brako and Newns 1981). Since the metal has continuous one electron states, theoretical studies on dynamical process of such a system are not so simple and are difficult particularly for the interacting electron system. In recent years more and more atom scattering experiments have been done and the effects of the interaction between electrons seem to be recognized. The necessity of the theoretical studies for the interacting electron system seems urgent (Makoshi, Kawai and Yoshimori 1984, Yoshimori, Kawai and Makoshi 1984, Yoshimori, Makoshi and Kawai 1985, Kawai, Makoshi and Yoshimori 1986).

§1-3 Charge Transfer

THe low energy atom or ion scattering is an important technique to analyze the properties of a surface (Hagstrum 1954, 1961, Smith 1971, 1976, Erickson and Smith 1975, Sau and Merrill 1973, Wunnik, Brako, Makoshi and Newns 1983). This technique was used earlier by Hagstrum. While an atom is near the surface, electrons, which carry charge, transfer between the atom and the surface. The electronic structure of the surface as well as the motion of the atom affects the distribution of the charge states on the scattered atom. The mechanism of the charge transfer processes are classified into two groups. One of them is the Auger process, and the other is the direct resonance process.

When there is a deep lying unoccupied level in a moving atom, the Auger neutralization process is most dominant; He^+ scattering experiments are a typcal case of this. Early theoretical investigations of this Auger neutralization process were done by Hagstrum (1954). When a valence level of the moving atom lies in the metal conduction band, the direct resonance process between the valence state and the conduction band is dominant for charge transfer. If a core state level of the metal is near the ionization level of the moving atom, the direct process is also effective (Erickson and Smith 1975). The first theoretical detailed analysis on the direct charge transfer process in surface problem was done by Blandin, Nourtier and Hone (1976). In this thesis, situations are considered that the valence level of the atom lies in the conduction band, and the Auger process will not be considered.

§1-4 Newns-Anderson Model

The time-dependent Newns-Anderson model has been used intensively to analyze the direct charge transfer process on the system consisting of a metal surface and an atom moving near the surface. The Anderson model was invented to analyze the magnetism of the dilute magnetic alloys by Anderson (1961). Though the Anderson model is very simple, the model has the wealth of physics. The model describes well the magnetic properties of the system. The Kondo effect (Kondo 1969, Wilson 1975) has been one of the central topics on the model, the

valence fluctuation effect (Haldane 1978) has been also. Now the rigorous solution of the model is obtained, which was discovered about 20 years after the Kondo effect (Andrei 1980, Wiegman 1980, Okiji and Kawakami 1984).

The Anderson model had been considered to serve as a good model for chemisorption problem on metal surfaces, (Bennet and Falicov 1966, Edwards and Newns 1967, Grimley 1967, Newns 1969). In the surface problem, the chemisorbed atom on the surface corresponds to the magnetic impurity in the metal, the surface states and the conduction states in the semi-infinite metal to the conduction states in the metal. In particular Newns has used the model to the equilibrium problem extensively, and has achieved great success in understanding the chemisorption on the metal surface(Newns 1969, Muscat and Newns 1978). Thus, when the Anderson model is employed to the surface problem, the model is often called the Newns-Anderson model or Anderson-Newns model.

When we make an approximation that in surface scattering problem the atom moves along a classical trajectory, the position of the atom is determined with time. In this approximation, the strength of the perturbation by the atom to the electronic state of the metal surface depends on the time explicitly. This is called the trajectory approximation. The time-dependent Newns-Anderson model with time-dependent parameters was used earlier by Toulouse to discuss the charge transfer problem between an atom and a metal surface (Toulouse 1974); this is probably the first use of the time-dependent Newns-Anderson model. Many authors have used this model to discuss the charge

transfer problem. There also many studies of the energy dissipation probability when an atom is scattered by a metal surface (Brivio and Grimley 1979, Nørskov and Lundqvist 1979, Schönhammer and Gunnarsson 1980, Brako and Newns 1980). In this thesis the charge transfer problem is investigated, and the energy dissipation probability problem is outside of the scope. In the Anderson model for the dilute magnetic alloys, it is well recognized that the intraatomic Coulomb interaction in the impurity atom plays a central role. The effect of the interaction in the time-dependent version, however, has not been investigated so far except for two cases, that is, the rigorous exponent of the X-ray absorption singularity (Yamada and Yosida 1978) and the Hartree-Fock treatment also for the X-ray absorption spectra (Schönhammer and Gunnarsson 1978). In the surface charge transfer problem, it is also important to study the effect of the interaction on the moving atom in the time-dependent Newns-Anderson model.

§1-5 Purpose of Investigation in this Thesis

In this thesis, the effects of the intraatomic Coulomb interaction is investigated in the time-dependent Newns-Anderson model on the charge transfer between a moving atom and a metal surface. In the section (2) the non-interacting case of this model will be surveyed. In the section (3) the effects will be treated in the Hartree-Fock approximation, and then they will be treated in the manybody calculation methods (the sections (4) and (5)).

§2 Time-Dependent Newns-Anderson Model

In this section, the known results on the time-dependent Newns-Anderson model are briefly reviewed.

§2-1 Trajectory Approximation

We consider the system consisting of a semi-infinite metal and an atom moving near the surface with kinetic energy less than a few hundred eV, the valence level of which lies in the conduction band. In such a system, the core electrons of the metal and the atom do not participate in the charge transfer between the metal and the atom. The total Hamiltonian of the problem is

$$H = - \frac{\hbar^2}{2M} \nabla_R^2 + V(R) + H_e(R), \qquad (2\text{-}1)$$

where M and R are the mass of the moving atom and the coordinate of the atom, respectively, V(R) is an adiabatic potential for the atom and $H_e(R)$ the Hamiltonian for the electronic system. Since the first term in Eq.(2-1) does not commute with the third, it is generally difficult to solve the problem. The trajectory approximation has been employed for this difficulty to be avoided. In the approximation, it is assumed that the atom moves along a given classical trajectory; the position of the atom is determined with time. When the kinetic energy of the atom is not so small, the position uncertainty of the atom due to the

uncertainty principle is not so large, and the energy dissipation during the scattering is much less than the kinetic energy, so that distribution of R for $H_e(R)$ is not so wide. Thus the trajectory approximation is justified in the situation of larger kinetic energy of the atom; uncertainty of 0.1A corresponds to kinetic energy of 8eV for the hydrogen atom. There are also studies to improve the trajectory approximation (Newns 1985). The Hamiltonian $H_e(R)$ depends on time explicitly through the motion of the atom in the approximation, so that the Hamiltonian for the electronic system can be rewritten as $H_e(t)$. In the trajectory approximation, the problem left is to solve the electronic motion. The time-dependent Newns-Anderson model is employed for $H_e(R)$. Thus $H_e(R)$, now simply denoted as H, is written as

$$H = \sum_{k\sigma} \varepsilon_{k\sigma} C^{\dagger}_{k\sigma} C_{k\sigma} + \sum_{\sigma} \varepsilon_a(t) C^{\dagger}_{a\sigma} C_{a\sigma} + \sum_{k\sigma} (V_k(t) C^{\dagger}_{a\sigma} C_{k\sigma} + \text{h.c.})$$

$$+ U(t) C^{\dagger}_{a\uparrow} C_{a\uparrow} C^{\dagger}_{a\downarrow} C_{a\downarrow} \ , \qquad (2\text{-}2)$$

where $C_{a\sigma}$ and $C_{k\sigma}$ are annihilation operators of electrons in the orbital on the moving atom with spin σ, and in the metallic electron states, including the conduction band and surface states, with quantum number "k", respectively. Since in the surface region the Bloch theorem does not hold in the direction normal to the surface, as mentioned already, the wave vectors parallel to the surface are good quantum number, but not normal to the surface. For this reason, the quantum number "k" in

Eq.(2-2) runs over in the wave vector parallel to the surface and the quantum number for the motion normal to the surface. Furthermore ε_k is one-electron nergy of the metallic electron states, $\varepsilon_a(t)$ time-dependent energy level of the electronic state in the atom, $V_k(t)$ the time-dependent admixture matrix element between the metal states and the atom state, and U(t) the time-depedent intraatomic Coulomb interaction. In the following the Fermi energy is chosen as the origin of one electron energy levels, and the unit of $\hbar=1$ is used.

The time dependence of the parameters is determined through the position dependence of the parameters and R(t). The simple assumption often made on the trajectories is of the constant velocity and the parameters are assumed to depend simply on Z(t), the z-component of R(t). When the parallel velocity is very large, however, the Doppler effect must be considered (Wunnik, Brako, Makoshi and Newns 1983). The time-and k-dependence of the admixture $V_k(t)$ is quite often separated as $V_k(t)=V_k u(t)$ for simplicity, where u(t) expresses the time dependence, and V_k is a value of $V_k(t)$ when the atom is nearest to the surface. The time dependence of u(t) so far used is given by, for example,

$$u(t) = \exp[-Z(t)/\alpha] = \exp[-\gamma|t|],$$

$$u(t) = \exp[-(Z(t)/\alpha)^2] = \exp[-(\gamma t)^2],$$

$$u(t) = 1/[1+(Z(t)/\alpha)^2] = 1/[1+(\gamma t)^2], \qquad (2\text{-}3\text{-}a)$$

$$\gamma = v/\alpha, \qquad (2\text{-}3\text{-}b)$$

where α and v are the decay length of the admixture, the velocity of the atom normal to the surface, respectively, γ is proportional to v. The time dependence shown in Eq.(2-3), especially the third, is somewhat artificial, which is assumed in order to simplify the calculation. If we discuss the sputtering or sticking case, u(t) should be constant 1 at $t<0$ or $t>0$ respectively. Furthermore, the simplest assumption is sometimes done (Makoshi, Kawai and Yoshimori 1984, Yoshimori, Kawai and Makoshi 1984, Yoshimori, Makoshi and Kawai 1985, Kawai, Makoshi and Yoshimori 1986); it is assumed that the atom arrives at the surface region at time t_0, and interacts during the period τ, and scattered out to the vacuum. During the interacting interval τ, the admixture is approximated to be some average over a surface region, and at time $t<t_0$ and $t>t_0+\tau$, the admixture is assumed to vanish. When the admixture does not exist, the electron can not transfer between the atom and the metal, so that charge state on the atom remains unchanged at $t>t_0+\tau$. Thus, for this simplest assumption, the time dependence of u(t) is to be taken as

$$u(t) = \begin{cases} 0 & t<0 \\ 1 & t>0 \end{cases} . \qquad (2\text{-}4)$$

In a simplified model, ε_a and U are taken constant during the time when the admixture exists. The image charge correction are considered in another model, that is,

$$\varepsilon_a(t) = \varepsilon_{a\infty} + \frac{e^2}{4Z(t)} \quad ,$$

$$U(t) = U_\infty - \frac{e^2}{2Z(t)} \quad , \qquad (2\text{-}5)$$

where Z(t) is the distance from the surface to the atom. Other forms are found in literature, for example (Tukada and Shima 1985, Lang 1985),

$$\varepsilon_a(t) = A + B\, Z(t). \qquad (2\text{-}7)$$

In this example, the level crossing with the Fermi level is important.

§2-2 Time-Dependent Expectation Value of Electron Occupation Number

In this subsection, the results on the charge exchange for the case of U=0 in the time-dependent Newns Anderson model are briefly summarized, that is a one-particle problem as will be seen. In the one-particle problem, spin is decoupled in the Hamiltonian, so that, the spin index σ will be suppressed in the following. The expectation value of the electron occupation number on the atom, $n(t)=\langle t|C_a^\dagger C_a|t\rangle$, is the quantity to be calculated for discussing the charge transfer problem, where $|t\rangle$ is the electronic state at time t in the Schrödinger representation. The expression of n(t) was obtained firstly by

Blandin, Nourtier and Hone (1976) who used the Keldysh Green function. In their paper, it is shown that there is no anomalous behavior in n(t) due to the infrared catastrophe (Anderson 1967) at least in the one-particle problem, which is not limited to the time-dependent Newns-Anderson model. Bloss and Hone (Bloss and Hone 1978) showed that the expression of n(t) is the same as that by Blandin, et al. with a much simpler method. The method of Bloss and Hone is shown in the following. The Heisenberg equations of motion are obtained as

$$\begin{aligned}\frac{\partial C_a(t)}{\partial t} &= i[\, H(t),\, C_a(t)\,] \\ &= -i\varepsilon_a(t)C_a(t) - i\sum_k V_k(t)C_k(t), \\ \frac{\partial C_k(t)}{\partial t} &= i[\, H(t),\, C_k(t)\,] \\ &= -i\varepsilon_k C_k(t) - iV_k^*(t)C_a(t), \end{aligned} \tag{2-7}$$

where $C_a(t)$, $C_k(t)$ and $H(t)$ are the Heisenberg operators corresponding to the Schrödinger operators C_a, C_k and H, respectively. The coupled Eq.(2-7) is reduced to the integro-differential equation for $C_a(t)$, that is,

$$\begin{aligned}\frac{\partial C_a(t)}{\partial t} = &-i\varepsilon_a(t)C_a(t) - \sum_k V_k(t)\int_{t_0}^{t} d\tau\, \exp[-i\varepsilon_k(t-\tau)]V_k^*(\tau)C_a(\tau) \\ &- i\sum_k V_k(t)\exp[-i\varepsilon_k(t-t_0)]\, C_k(t_0)\ . \end{aligned} \tag{2-8}$$

In the solution of Eq.(2-8), $C_a(t)$ is to be expressed in terms of $C_a(t_0)$ and $C_k(t_0)$, so that $n(t)=\langle C_a^\dagger(t)C_a(t)\rangle$ is expressed in

terms of $\langle C_a^\dagger(-\infty)C_a(-\infty)\rangle$ and $\langle C_k^\dagger(-\infty)C_k(-\infty)\rangle$ with the initial condition $t_0=-\infty$ and $V_k(-\infty)=0$. Thus, it is shown that the Fermi statistics is only in the initial condition, and there is no anomalous behavior due to the Anderson infrared catastrophe in $n(t)$.

With the assumption $V_k(t)=V_k u(t)$, the factor in the second term in Eq.(2-8) is rewritten as

$$\sum_k |V_k|^2 \exp[-i\varepsilon_k(t-\tau)] = \frac{1}{\pi}\int d\varepsilon\ \Delta(\varepsilon)\exp[-i\varepsilon(t-\tau)], \qquad (2\text{-}9)$$

with

$$\Delta(\varepsilon) = \pi \sum_k |V_k|^2 \delta(\varepsilon-\varepsilon_k)\ . \qquad (2\text{-}10)$$

The integral (2-9) is rewritten as $2\Delta\delta(t-\tau)$ with assumption that $\Delta(\varepsilon)$ takes a constant value Δ, and the band width is infinite, that is the wide-band limit. In this limit, the expression of $n(t)$ is obtained as

$$n(t)=-\frac{\Delta}{\beta}\int_{-\infty}^{t}dt_1\int_{-\infty}^{t}dt_2 u(t_1)u(t_2)\frac{\sin\left[\int_{t_2}^{t_1}\varepsilon_a(\tau)\,d\tau\right]}{\sinh\left[\frac{\pi}{\beta}(t_1-t_2)\right]}$$

$$\times\exp\left[\Delta\int_{t}^{t_1}u^2(\tau)\,d\tau+\Delta\int_{t}^{t_2}u^2(\tau)\,d\tau\right]$$

$$+\left[n(-\infty)-\frac{1}{2}\right]\exp\left[-2\Delta\int_{-\infty}^{t}u^2(\tau)\,d\tau\right]+\frac{1}{2}\,, \qquad (2\text{-}11)$$

where $\beta=1/k_BT$ (T is temperature of the metal). The expression is derived by Blandin, et al. (1976) for T=0 and discussed by Brako and Newns for T≠0 (Brako and Newns 1981).

§2-3 Memory Factor

There is the term including $n(-\infty)$ in Eq.(2-11). This term represents the memory of the initial condition of n(t). Thus, it is usually called the memory term (Brako and Newns 1981). The exponent of the memory term is

$$2\Delta\int_{-\infty}^{t}u^2(\tau)\,d\tau. \qquad (2\text{-}12)$$

When the energy level $\varepsilon_a(t)$ in the atom state is far from the Fermi level of the metal ε_F (=0), this is easily obtained at T=0 in the limit of $|\varepsilon_a(t)|\to\infty$

$$n(t) - \theta(-\varepsilon_a) = [\, n(-\infty) - \theta(-\varepsilon_a)\,] \exp[\, -2\Delta \int_{-\infty}^{t} u^2(\tau)\, d\tau\,]. \quad (2\text{-}13)$$

This means that the memory effect dominates, when $|\varepsilon_a| \to \infty$. The solution (2-13) satisfies the rate equation

$$\frac{dn(t)}{dt} = -\, 2\Delta u^2(t)[\, n(t) - \theta(-\varepsilon_a)\,], \quad (2\text{-}14)$$

which can be derived simply from the usual "golden rule" too. When the level $\varepsilon_a(t)$ lies near ε_F, the first term in Eq.(2-11) is important, where the Fermi statistics in the initial condition plays an important role.

If the velocity of the atom is slow enough, the exponent (2-12) is to be very large. In this situation, the memory term becomes negligible, that is, the memory of the initial state is erased. In the first term in Eq.(2-11), there is the factor with the form

$$\exp[\, -\Delta \int_{t'}^{t} u^2(\tau)\, d\tau\,], \quad (2\text{-}15)$$

where t' is the integration variable. In the case of very slow velocity, the time interval $t-t' \gg 1/\Delta$ does not contribute to the integration in Eq.(2-11), when the exponent of Eq.(2-15) is large negative. Therefore, the incoming trajectory to the suface does not affect the obserbed charge state of the atom with $t \to \infty$, and only the outgoing trajectory affects it. When $u(t)=\exp(-\gamma|t|)$ with sufficiently small γ, and ε_a=constant, $n(\infty)$ turns out to be

$$n(\infty) = \frac{1}{2\gamma}\int d\varepsilon\ f(\varepsilon,T)/\cosh[\ \pi(\varepsilon-\varepsilon_a)/2\gamma\ ], \qquad (2\text{-}16\text{-}a)$$

which holds for $\Delta>>\gamma$. In the above $f(\varepsilon,T)$ is the Fermi distribution function. For T=0, the integration with respect to ε can be carried out, that is, $n(\infty)=0.5-\tan^{-1}[\sinh(\pi\varepsilon_a/2\gamma)]/\pi$. Under the additional condition $|\varepsilon_a|>>\gamma$,

$$n(\infty)=\theta(-\varepsilon_a)+2\mathrm{sign}(\varepsilon_a)\exp[-\pi|\varepsilon_a|/2\gamma]/\pi, \qquad (2\text{-}16\text{-}b)$$

is obtained at T=0K. A more general but approximate form of $n(\infty)$ is obtained by Brako and Newns (Brako and Newns 1981), using a saddle point method, again under the condition $\Delta>>\gamma$ at T=0, that is,

$$n(\infty)= -\frac{1}{\mathrm{Im}\ t_0}\left|\frac{\Delta(t_0)}{\Delta'(t_0)+i\varepsilon_a'(t_0)}\right|\exp\left[i\int_{t_0^*}^{t_0}\varepsilon(\tau)d\tau - 2\mathrm{Re}\int_C\Delta(\tau)\ d\tau\right]$$

$$+\ \theta(-\varepsilon_a), \qquad (2\text{-}17)$$

where t_0 is the solution of $\Delta(t)+i\varepsilon_a(t)=0$ in the complex plane and the integration path C runs from t_0 to the real axis at ∞. In Eq.(2-16), it is assumed that $\varepsilon_a(t)$ does not change sign along the outgoing part of the trajectory. From Eq.(2-17) $n(\infty)$ can be written in the form $n(\infty)=\theta(-\varepsilon_a)-A\exp(-B/v)$ (v is velocity of the atom normal to the surface as before.) In the high temperature limit $k_BT>>\gamma$, the integration (2-16-a) gives, $n(\infty)=f(\varepsilon_a(t'),T)$, where t' is defined by $2\gamma t'=\log(\Delta/\gamma)$ (Brako and Newns 1981). There is sometimes the case that $\varepsilon_a(t')$ is very different from

$\varepsilon_a(\infty)$ which is the value at infinite distance from the surface, for instance, Na/W(110) problem (Overbosch, Rasser, Tenner and Los 1980). In order that the memory is erased, it is necessary that the velocity is much less than $\Delta\alpha$ ($u(t)=\exp(-vt/\alpha)$ is assumed). If the admixture decay length α is taken 1A and Δ 1ev, the normal velocity v is necassary to be much less than $v=1.5\times10^5$m/s, which correspond to the kinetic energy 120eV for H and 2.8KeV for Na.

§2-4 Finite Width Band

In the subsections (2-2) and (2-3), the cases of the wide-band limit are discussed mainly. Another limit to the wide-band limit is the surface molecule limit. In the surface molecule limit, it is assumed that the admixture matrix element is much larger than the width of the conduction band. In such limit, the Hamiltonian (2-2) can be rewritten approximately as

$$H = \varepsilon_0(t)C_0^\dagger C_0 + [\ W(t)C_0^\dagger C_a + h.c.] + \varepsilon_a(t)C_a^\dagger C_a, \qquad (2\text{-}18)$$

where

$$\varepsilon_0(t) = \textstyle\sum_k \varepsilon_k |V_k(t)|^2/W^2(t),$$

$$C_0^\dagger = \textstyle\sum_k [\ V_k(t)/W(t)\ ]\ C_k^\dagger,$$

$$W(t) = [\ \textstyle\sum_k |V_k(t)|^2\ ]^{1/2}. \qquad (2\text{-}19)$$

The Hamiltonian (2-18) corresponds to the two atom collision process. The charge transfer in this process is discussed first on the surface case by Tully (1977). In the simplest case $\varepsilon_a(t)=\varepsilon_0(t)$=constant, n(t) is obtained as

$$n(t) = n(-\infty)\cos^2[\int_{-\infty}^{t} d\tau\ W(\tau)] + n_0(-\infty)\sin^2[\int_{-\infty}^{t} d\tau\ W(\tau)]. \quad (2\text{-}20)$$

The integral in Eq.(2-20) is in proportion to 1/v (v is the velocity of the atom normal to the surface) with the constant velocity trajectory, so that observed charge state n(∞) show an oscillatory behavior with 1/v (Erickson and Smith 1975, Tolk, Tully, Kraus, White and Neff 1976).

There are not so many studies of charge transfer in the finite band case which are neither the wide-band limit nor the surface molecule limit. There are a few numerical calculations in a linear chain model of metal (Muda and Hanawa 1980, Sebastian, Jyothi Bhasu and Grimley 1981).

§3 Hartree-Fock Approximation

§3-1 Electron Occupation Number

As mentioned in the section (1), the effect of the intraatomic Coulomb interaction in the time-dependent Newns-Anderson model has not been investigated in the surface charge transfer problem, though its importance is recognized. We have started to analyze the effects of the interaction, using the time-dependent Hartree-Fock approximation (Makoshi, Kawai and Yoshimori 1984, Yoshimori, Kawai and Makoshi 1984, Yoshimori, Makoshi and Kawai 1985, Kawai, Makoshi and Yoshimori 1986). The time-dependent expectation value of electron occupation number $n_\sigma(t)$ ($=\langle C^\dagger_{a\sigma}(t)C_{a\sigma}(t)\rangle$) appears in the Hamiltonian in the Hartree-Fock approximation, and must be determined in the self-consistent way. Even if a physical quantity of interest is other than the charge transfer, for instance, the energy dissipation spectrum (Yoshimori, Makoshi and Kawai 1985), $n_\sigma(t)$ must be known to determine the time-dependent Hartree-Fock Hamiltonian, that is, $n_\sigma(t)$ are the key quantities in the time-dependent Hartree-Fock approximation. In the Hartree-Fock approximation, the Hamiltonian (2-2) is approximated by

$$H = \sum_{k\sigma} \varepsilon_k C^\dagger_{k\sigma} C_{k\sigma} + \sum_\sigma \varepsilon_\sigma(t) C^\dagger_{a\sigma} C_{a\sigma} + [\sum_{k\sigma} V_k(t) C^\dagger_{a\sigma} C_{k\sigma} + \text{h.c.}], \quad (3\text{-}1)$$

where

$$\varepsilon_\sigma(t) = \varepsilon_a(t) - \sigma\varepsilon_m + U(t)n_{-\sigma}(t). \qquad (3\text{-}2)$$

The energy level of the orbital in the moving atom is assumed spin-dependent, that is $\sigma\varepsilon_m$ where σ means + for spin ↑, and - for spin ↓. When U is large enough, n_σ have a magnetic solution $n_{eq,\sigma} \neq n_{eq,-\sigma}$ in the equilibrium, which is obtained as $n_{eq,\sigma}=1/2-\tan^{-1}[(\varepsilon_a+Un_{eq,-\sigma})/\Delta]/\pi$ (Anderson 1961). When the initial condition is symmetric in spin space ($n_\sigma(-\infty)=n_{-\sigma}(-\infty)$),and $\varepsilon_m=0$, everything is symmetric in spin space. In this situation, the time-dependent solution $n_\sigma(t)$ never goes to the magnetic solution even for large U. Thus, the parameter ε_m is introduced here to break the symmetry in spin space. The parameter ε_m may correspond to the magnetic field on the atom and the physical meaning will be discussed later. The expression of $n_\sigma(t)$ in the Hartree-Fock approximation is obtained in the wide-band limit as

$$n_\sigma(t) = -\frac{1}{\beta}\int_{-\infty}^{t} dt_1 \int_{-\infty}^{t} dt_2 u(t_1)u(t_2) \frac{\sin\left[\int_{t_2}^{t_1} \varepsilon_\sigma(\tau)\, d\tau\right]}{\sinh\left[\frac{\pi}{\beta}(t_1 - t_2)\right]}$$

$$\times \exp\left[\int_{t}^{t_1} u^2(\tau)\, d\tau + \int_{t}^{t_2} u^2(\tau)\, d\tau\right]$$

$$+ \left[n(-\infty) - \frac{1}{2}\right]\exp\left[-2\int_{-\infty}^{t} u^2(\tau)\, d\tau\right] + \frac{1}{2}, \qquad (3\text{-}3)$$

where time is scaled in $1/\Delta$ (h=1) and energy in Δ. These units

are used throughout in the remaining part of the section (3). Equation (3-3) is the same as Eq.(2-11) except that $\varepsilon_a(\tau)$ in Eq.(2-11) is replaced by $\varepsilon_\sigma(\tau)$ in Eq.(3-3). In this thesis, only the cases at the absolute zero temperature are investigated. Equation (3-3) is coupled nonlinear integral equations for $n_\sigma(t)$ and $n_{-\sigma}(t)$, and it is impossible to solve it analytically. In the following subsections, Eq.(3-3) will be solved numerically on the assumed time dependence of the parameters. From solutions of Eq.(3-3), fractions of charge state are determined within the Hartree-Fock approximation as

$$
\begin{aligned}
I^0(t) &= \textstyle\sum_\sigma n_\sigma(t)[1-n_{-\sigma}(t)] \\
&= N(t) - 2I^-(t), \\
I^+(t) &= \textstyle\prod_\sigma [1-n_\sigma(t)] \\
&= 1 - N(t) + I^-(t), \\
I^-(t) &= n_\uparrow(t) n_\downarrow(t), \\
N(t) &= n_\uparrow(t) + n_\uparrow(t), \\
M(t) &= n_\uparrow(t) - n_\downarrow(t),
\end{aligned}
\qquad (3\text{-}4)
$$

where $I^0(t)$, $I^+(t)$ and $I^-(t)$ are the fraction of the neutral atom, positive ion and negative ion, respectively, $N(t)$

corresponds to the total charge on the atom and M(t) the spin polarization on the atom.

§3-2 Sudden Switch-on Case

The simplest case of the time dependence of parameters is assumed in this subsection; the admixture exists only in the inside region of finite distance L from the surface, where U(t), $\varepsilon_a(t)$ and $V_k(t)$ are assumed to have average constant values. In this case, the admixture starts suddenly when the atom arrives at the region and remains constant during the time interval 2L/v (v is assumed to be constant). After the atom is scattered out from the region to vacuum, the admixture stops and electrons can not transfer between the surface and the atom. The charge states of the atom at the distance L remain after. Thus, for this simplest assumption, the time dependence of u(t) is to be taken as Eq.(2-4), and U(t) and $\varepsilon_a(t)$ are assumed to be constant U and ε_a (Makoshi, Kawai and Yoshimori 1984, Yoshimori, Makoshi and Kawai 1984, Yoshimori, Kawai and Makoshi 1985, Kawai, Makoshi and Yoshimori 1986).

The results of numerical calculations in the symmetric case of U=16 and ε_a=-8 are shown in Fig.(3-1) for ε_m=0.1, 0.01 and 0.001 with the initial condition $n_\uparrow(0)=n_\downarrow(0)=0$ corresponding to positive ion incoming. Since $U>\pi$ is the condition for the magnetic solution in equilibrium in the symmetric case $\varepsilon_a=-U/2$, the case of U=16 and ε_a=-8 is under a strong magnetic condition. The solid lines represent $n_\sigma(t)$ and the dashed line N(t).

Results of asymmetric case are shown in Fig.(3-2). In Fig.(3-1) the total electron number N(t) saturates to its equilibrium value (=1) much sooner than the spin polarization M(t). In Fig.(3-1) and Fig.(3-2) there is overshooting of N(t). Initially the state on the atom is empty and $\varepsilon_\sigma(t)$ is negative, that is, below ε_F (=0), then the both spin electrons transfer from metal to the atom with the rate Δ. This determines the initial slope of $n_\sigma(t)$, which is 1 (time is in unit of $1/\Delta$). As electrons transfer to the state, $\varepsilon_\sigma(t)$ is pushed up because of the Hartree-Fock field, and soon $\varepsilon_\sigma(t)$ becomes positive (above ε_F). For positive $\varepsilon_\sigma(t)$, N(t) decreases with time. This overshooting of N(t) is seen also in Fig.(3-3) for U=0 and $\varepsilon_a>0$, and in Fig.(3-4) for $U\neq 0$ and $\varepsilon_a<0$ which has a non-magnetic solution in equilibrium. In Fig.(3-5), the numerical results in the symmetric case under the initial condition $n_\uparrow(0)=1$ and $n_\downarrow(0)=0$, where ε_m is not needed. Under this condition the electron-hole symmetry holds, so that N(t) takes the value 1 at any time. There is the oscillatory convergence of $n_\sigma(t)$ to the equilibrium value in Fig.(3-1) and Fig.(3-2), and there is also in Fig.(3-5), though it is small in amplitude. This oscillation will be investigated in detail in the subsections (3-3) and (3-4) (Kawai, Makoshi and Yoshimori 1986). We can see the exponential-like growth of M(t) dependent on ε_m in early time region in Fig.(3-1). This growth is discussed in the next subsection (3-3) (Makoshi, Kawai and Yoshimori 1984).

§3-3 Exponential Growth of Spin Polarization

As it is mentioned in the subsection (3-2), M(t) in Fig.(3-1) shows exponential-like growth and its starting time depends on ε_m. After M(t) growth, curve shapes for various values of ε_m fit to each other almost completely, where it is necessary to shift the origin of time t. In this subsetion, this exponential-like growth is investigated under the symmetric condition $\varepsilon_a=-U/2$. Under the condition where the results of Fig.(3-1) are obtained, Eq.(2-3) is rewritten as

$$\sigma(t)=\frac{1}{\pi}\int_0^t dt_1\int_0^t dt_2 \frac{\exp[-2t+t_1+t_2]}{t_1-t_2}\sin\left[\int_{t_2}^{t_1} d\tau\{\frac{U}{2}(1-N(\tau))+\sigma(\frac{U}{2}M(\tau)+\varepsilon_m)\}\right]$$

$$+\frac{1}{2}(1-\exp[-2t]). \qquad (3\text{-}5)$$

Since ε_m and M(t) are small when t is not so large, we neglect the second order of M(t) and ε_m. Furthermore the second order of the integration for $1-N(\tau)$ is neglected also in Eq.(3-5), because, for large t, N(t) goes soon to the equilibrium value (=1) and for small t the integration interval is small. Thus the equation for M(t) is obtained from Eq.(3-3) as

$$M(t) = \frac{U}{\pi}\int_0^t dt_1\int_0^t dt_2 \exp[\,-2t+t_1+t_2\,]\, M(\frac{t_1+t_2}{2})$$

$$+\varepsilon_m\frac{2}{\pi}(1-\exp[-t])^2, \qquad (3\text{-}6)$$

where the integration for $M(\tau)$ in Eq.(3-5) is approximated by

$(t_1-t_2)M((t_1+t_2)/2)$. From Eq.(3-6) the linear differential equation for M(t) is obtained as

$$\frac{d^2M(t)}{d\,t^2} + 4\frac{dM(t)}{d\,t} - 4(\frac{U}{\pi}-1)M(t) = \varepsilon_m\frac{4}{m\pi}(2-\exp[-t]) - 2\frac{U}{\pi}\exp[-t]M(\frac{t}{2}). \tag{3-7}$$

Neglecting the term of M(t/2), which can be shown to be small from the obtained solution, we get the solution of Eq.(3-7) easily. The exponential growth term of the solution is

$$M(t) \propto \varepsilon_m \exp[\ 2(\sqrt{U/\pi}\ -1)t\ ]. \tag{3-8}$$

The growth occurs only for $U>\pi$ that is the Hartree-Fock criterion for magnetic solution in equilibrium. It is interesting that $\sqrt{U/\pi}$ appears in the exponent, because it is not regular as a function of U at U=0. The solution of Eq.(3-7) fits well to the numerical results of M(t) (Makoshi, Kawai and Yoshimori 1984). The Eq.(3-8) shows that the curve shapes of M(t) after growth of M(t) occurs does not depend on ε_m, which is seen in Fig.(3-1). Thus Eq.(3-8) is valid generally for the growth of M(t). It may be considered that the artificial parameter ε_m is caused by the spin fluctuation effects, and further consideration is necessary to determine the value of ε_m.

§3-4 Oscillatory Convergence

In this subsection the oscillatory convergence of $n_\sigma(t)$ seen in Fig.(3-1) is investigated in detail (Kawai, Makoshi and

Yoshimori 1986). Defining $X_\sigma(t)$ as difference $n_\sigma(t)-n_\sigma(\infty)$ between $n_\sigma(t)$ and its equilibrium value, we have the following approximate equation linear in $X_\sigma(t)$, which is valid for sufficiently long time

$$\frac{dX_\sigma(t)}{dt} = \frac{2}{\pi}\int_t^\infty dt' \frac{\exp(-t')}{t'} \sin(\varepsilon_\sigma(\infty)t')$$

$$- \int_0^t dt' K_\sigma(t,t-t')X_{-\sigma}(t') - 2X_\sigma(t) \ , \qquad (3\text{-}9)$$

with

$$K_\sigma(t,t-t') = \frac{2U}{\pi}\int_{t-t'}^t d\tau \frac{\exp(-\tau)}{\tau} \cos(\varepsilon_\sigma(\infty)\tau) \ . \qquad (3\text{-}10)$$

Since N(t) takes a constant value 1 where the oscillation is appreciable as seen in Fig.(3-1), we consider the case of $X_\sigma=-X_{-\sigma}(t)$ under the symmetric condition $\varepsilon_a=-U/2$. Neglecting the first term in the right hand side of Eq.(3-9), extending the lower integration limit from 0 to $-\infty$, and approximating $K_\sigma(t,t-t')$ by $K_\sigma(\infty,t-t')$, we get the homogeneous linear integro-differential equation for M(t) from Eq.(3-9) in which $X_\sigma(t)$ and $-X_{-\sigma}(t)$ are replaced by m(t)

$$\frac{dm(t)}{dt} = -2m(t) + \int_{-\infty}^t dt' K_\sigma(\infty,t-t')m(t'), \qquad (3\text{-}11)$$

where $m(t)=M(t)-M(\infty)$. For the integro-differential equation, we

assume the solution takes a form of $m(t)=A\exp(\lambda t)$, where λ is an undetermined complex quantity. From the equation for $m(t)$, the equation for λ is given by

$$\lambda = -2 + \frac{U}{\lambda\pi}\log(1+\lambda(2+\lambda)\cos^2\delta) \ , \qquad (3\text{-}12)$$

with

$$\delta = \tan^{-1}(\varepsilon_\infty) \ ,$$

$$\varepsilon_\infty \equiv |\varepsilon_\sigma(\infty)| \ ,$$

where $\tan^{-1}(x)$ takes values between $-\pi/2$ and $\pi/2$. Equation (3-12) is valid for $\mathrm{Re}\lambda \geqq -1$. We pick up the solution of $m(t)$ which decays most slowly because Eq.(3-11) is valid for very long time.

The trajectory of the solution of Eq.(3-12) on the complex λ plane with varying U is shown in Fig.(3-6). There are singular points in the asymptotic solution as a funtion of U in addition to π which is the boundary between the magnetic and nonmagnetic solutions in the symmetric case. One of the additional singular points, U_c, is determined by $\sin\delta_c=\exp(-\pi/2U_c)$; the value of U_c is 3.843$\cdots$ which is larger than π. For every U value larger than U_c the real part λ_1, of λ takes a constant value -1 and the imaginary part, λ_2, is finite, while for U less than U_c, λ becomes real and larger than -1, leading to the absence of oscillation of $m(t)$. The results obtained by the asymptotic solution are compared with those of the numerical selfconsistent

calculation in Fig.(3-7) and Fig.(3-8) in three cases of the U values. As U increases ($U>>U_c$), λ_2 approaches ε_∞. The asymptotic form of λ_2 for large U is given by

$$\lambda_2 = \varepsilon_\infty - \frac{U}{4} \exp(2 - \frac{\pi U}{4}) \ . \qquad (3\text{-}13)$$

Another singular point is U=0. For small U ($U\sim 0$), λ approaches -1 with the asymptotic form

$$\lambda = -1 + \exp(-\frac{\pi}{2U}) \ . \qquad (3\text{-}14)$$

This indicates that λ has the essential singularity at U=0. For U=0, however, Eq.(3-11) is solved as $m(t)=m(0)\exp(-2t)$. Thus we have an apparent discrepancy between the exponent λ for the asymptotic $U\to 0$ solution and that of the U=0 solution. What occurs for $U\to 0$ actually is that there are two regions for m(t), $m(t)\sim\exp(-2t)$ and $m(t)\sim\exp(-t)$, and the transient boundary moves toward ∞ as $U\to 0$. This may be seen by the following examination of the difference, between the right hand sides of Eq.(3-9) and Eq.(3-11). It is expressed as P(t)+Q(t), where

$$P(t) = -\frac{4}{\pi} \int_t^\infty dt' \, \frac{\exp(-t')}{t'} \sin(\varepsilon_\infty t') \ , \qquad (3\text{-}15\text{-}a)$$

$$Q(t) = -\frac{2U}{\pi} \int_t^\infty d\tau \, \frac{\exp(-\tau)}{\tau} \cos[\varepsilon_\infty \tau] \int_{t-\tau}^{t} d\tau' m(\tau') \ . \qquad (3\text{-}15\text{-}b)$$

The long time asymptote of P(t) is

$$P(t) \sim -4\cos^2\delta(\sin\varepsilon_\infty t+\varepsilon_\infty\cos\varepsilon_\infty t)\exp(-t)/\pi t$$

so that we can neglect P(t). Q(t) can be estimated by using the solution $m(t)=A\exp(\lambda t)$ of Eq.(3-11). The result of the integration is

$$Q(t)= -\frac{U}{\pi\lambda}\, m(t)\{2E_1^R((1+i\varepsilon_\infty)t)-E_1((1+\lambda+i\varepsilon_\infty)t)-E_1((1+\lambda-i\varepsilon_\infty)t)\}, \qquad (3\text{-}15\text{-}c)$$

where

$$E_1(z) \equiv E_1^R(z)+iE_1^I(z) = \int_z^\infty d\tau\, \frac{\exp(-\tau)}{\tau} .$$

The asymptotic form of Q(t) at $t\to\infty$ is found to be

$$Q(t) \sim \frac{2Um(t)}{\pi\lambda(1+\lambda)t}\exp(-(1+\lambda)t) , \qquad \text{for } U<\pi \qquad (3\text{-}16\text{-}a)$$

$$Q(t) \sim \frac{2Um(t)}{\pi\lambda(\lambda_2^2-\varepsilon_\infty^2)t}(\varepsilon_\infty\cos\lambda_2 t\sin\varepsilon_\infty t-\lambda_2\sin\lambda_2 t\cos\varepsilon_\infty t$$

$$-i\varepsilon_\infty\sin\lambda_2 t\sin\varepsilon_\infty t-i\lambda_2\cos\lambda_2 t\cos\varepsilon_\infty t), \text{ for } U>U_c \qquad (3\text{-}16\text{-}b)$$

We see that Q(t) is usually negligible except for $1+\lambda=0$ when the denominator in Eq.(3-16-a) vanishes. It is the case when U=0. This tells us that the region of time where our approximation is valid moves toward ∞ as U approaches 0.

The asymptotic solution is useful, because it gives a reasonably good numerical approximation, and it is simple. However, those additional singularities of the asymptotic

solution should not exist in the full solution, because only singularities in the Hartree-Fock approximation are at $U=\pi$ and $U=\infty$. We discuss the full solution of Eq.(3-9) in the next subsection, which is not so simple for the numerical calculation, and the relation between the present results and that obtained in the linear response theory.

§3-5 Analyticity of the Asymptotic Solution

Here, we analyze the full solution of Eq.(3-9) by the Laplace transform method assuming $X_{\uparrow}(0)=-X_{\downarrow}(0)$ in the symmetric case. The solution for m(t) is given by,

$$m(t) = \frac{1}{2\pi i}\int_{-i\infty}^{i\infty} dp\ \exp(tp)\ \frac{\frac{2i}{\pi}\log\frac{(1+p-i\varepsilon_\infty)(1+i\varepsilon_\infty)}{(1+p+i\varepsilon_\infty)(1-i\varepsilon_\infty)} + pm(0)}{p(p+2)-\frac{U}{\pi}\log\{1+p(p+2)\cos^2\delta\}}, \quad (3\text{-}17)$$

where the imaginary part of log(x) takes values between $-\pi$ and π. We see that the solutions of Eq.(3-12) correspond to poles of the integrand in Eq.(3-17). In the complex p plane the path for the integral can be changed as to give pole and cut contributions. The pole contribution corresponds to the asymptotic solution discussed above. We can show, however, that the pole contribution cancels out with a part of the cut contribution. The integral in Eq.(3-17) can be rewritten as

$$m(t)=\frac{1}{\pi}\exp(-t)\,\mathrm{Im}\int_c dz\,\frac{\left\{i\left(\frac{4\delta}{\pi}+m(0)\right)-\left(m(0)z+\frac{2}{\pi}\log\frac{z-\varepsilon_\infty}{z+\varepsilon_\infty}\right)\right\}\exp(-itz)}{(1+z^2)\left\{1+\frac{U}{\pi}\,\frac{\log\{(1+z^2)\cos^2\delta-1\}-i\pi}{1+z^2}\right\}},\qquad(3\text{-}18)$$

with path of the integration shown in Fig.(3-9), where the imaginary part of log(x) in numerator and denominator takes values between $-\pi$ and π, 0 and 2π respectively. With a sufficient large radius R shown in Fig.(3-9), the coefficient of U in the denominator of the integrand is smaller than 1/U, so that the integrand can be expanded in powers of U as a uniformly convergent series. A uniformly convergent series of analytic functions may be integrated term by term in the region of uniform convergence, and the obtained series converges uniformly in the same region (Titchmarsh 1939). We see that m(t) is regular as the function of U except for $U=\infty$ and $U=\pi$; for $U=\pi$, the phase shift δ is singular as a function of U. It is clear that the singularity in the asymptotic form at $U=U_c$ and U=0 is caused by our approximation to obtain Eq.(3-11). Since the pole contribution is shown in the subsection (3-4) to give a good numerical fit, the integral in Eq.(3-18) should be approximated well by the pole contribution except at its false singular points. Period of the oscillation for $U_c>U>\pi$ is so long that it can not be seen.

The spin polarization m(t) can be discussed also in terms of the response function within the linear response theory, when m(t) is sufficiently small. We show how the spin polarization at

the adatom site decays after the switching-off of the applied magnetic field giving the initial value m(0) in the RPA corresponding to the time-dependent Hartree-Fock approximation for the electron-electron interaction. The linear response function $\phi(t)$ for this system is given by the Fourier transform of the ω-dependent RPA susceptibility:

$$\phi(t) = -\frac{1}{\pi^2}\int_{-\infty}^{\infty} d\omega\ e^{-i\omega t}\frac{\log(1-\omega(\omega+2i)\cos^2\delta)}{\omega(\omega+2i)+\frac{U}{\pi}\log(1-\omega(\omega+2i)\cos^2\delta)} \quad ,(3\text{-}19)$$

where the imaginary part of log(x) takes values between $-\pi$ and π. Inserting $i\lambda$ into ω, we find again Eq.(3-12) as giving the poles of the integrand. The integral (3-19) can be rewritten as

$$\phi(t) = \frac{2\exp(-t)}{\pi U}\ \mathrm{Re}\int_c dz\ \frac{\exp(-itz)}{1+U\{\log((1+z^2)\cos^2\delta-1)-i\pi\}/\pi(1+z^2)} \quad , \qquad (3\text{-}20)$$

with path of the integration shown in Fig.(3-9), where the imaginary part of log(x) is taken beween 0 and 2π. From Eq.(3-20), it is easily shown that the response function has no singularity as a function of U even at U=0 and $U=U_c$, except for $U=\infty$ and $U=\pi$.

When U=0, Eq.(3-11) has a solution of Aexp(-2t). We note here this decay form is given by the non-linear response to the magnetic field. For U=0, we can derive exactly m(t) after the switching-off of the magnetic field of arbitrary strength applied to the adatom orbital of arbitrary strength, as

$$m(t) \underset{t\geqq 0}{=} -\frac{4}{\pi}\left[\mathrm{Im}\frac{\exp(iht)}{2+ih}E_1((1+ih)t)+\frac{h}{4+h^2}\exp(-2t)\{E_1^R(-t-i0^+)\right.$$

$$\left.-\frac{1}{2}\log(1+h^2)\}\right]+\frac{h^2}{4+h^2}\,m(0)\exp(-2t)\ , \qquad (3\text{-}21)$$

where the initial value m(0), is given by $m(0)=(2/\pi)\tan^{-1}h$. When we approximate Eq.(3-21) linear in h, we find no exp(-2t) term at long time.

§3-6 Various Cases of the Time Dependence

In this subsection smooth switch-on cases of the admixture are discussed (Yoshimori, Kawai and Makoshi 1984). The time dependence of the admixture is assumed to have the form

$$u(t) = \exp[\ -(t/T_u)^2\ ], \qquad (3\text{-}22)$$

where T_u is a time constant related to the motion of the atom. A large value of T_u corresponds to a slow motion of the atom. In Fig.(3-10) the numerical results under the condition of constant U and ε_a and $n_\uparrow(-\infty)=n_\downarrow(-\infty)=0$ are shown. The parameter values are $\varepsilon_a=-8$, U=16, $\varepsilon_m=0.01$ and $T_u=3$. The behavior of the results shown in Fig.(3-10) is qualitatively the same as in Fig.(3-1) after $t\simeq -2$, though $T_u=3$ (>1) is not so small. The numerical results of $n_\sigma(\infty)$ versus T_u in the same parameters as in Fig.(3-10) except T_u are shown in Fig.(3-11). The time constant T_u in Fig.(3-11) corresponds t (=2L/v) in the sudden switch-on case shown in Fig.(3-1). The whole shape in Fig.(3-11) is similar to those in

Fig.(3-1), but the oscillation is suppressed out. In Fig.(3-12) the numerical results with parameters ε_a=-1, U=10 and T_u=10 under the codition $n_\uparrow(-\infty)$=1 and $n_\downarrow(-\infty)$=0 are shown. Growth of the spin polarization is seen after t≃10 in Fig.(3-12), though the parameters ε_a=-1 and U=10 do not meet the magnetic condition at equilibrium. In the smooth switch-on cases like Eq.(3-22), the parameters $U(t)/\Delta u^2(t)$ and $\varepsilon_a(t)/\Delta u^2(t)$ meet the magnetic condition at the position of the atom beyond the certain distance from the surface even if the parameters do not meet the condition at the distance nearest to the surface, because as the position of the atom is far from the surface, the strength of the admixture become small and the Coulomb interaction effectively large. Thus the growth of spin polarization seen in Fig.(3-12) can occur. In Fig.(3-13), the numerical results are shown in the case where $\varepsilon_a(t)$ and U(t) are time-dependent. The time dependence is assumed as,

$$\varepsilon_a(t) = - U(t)/2,$$

$$U(t) = U_\infty - (U_\infty - U_0)\exp[\ -(t/T_U)^2\ ], \qquad (3\text{-}23)$$

where U takes a value U_0 at distance nearest from the surface and U_∞ at infinite distance from the surface. T_U is a time constant expressing the reduction of the Coulomb interaction near the surface due to the screening or the image potential, where the reduction is arbitrarily simplified. The parameter values are U_0=1, U_∞=16, T_u=T_U=3 and ε_m=0.01, and the initial condition

is $n_{\uparrow}(-\infty)=n_{\downarrow}(-\infty)=0$ in Fig.(3-13). The parameters U=1 and $\varepsilon_a=-0.5$ at the distance nearest to the surface do not meet the magnetic condition at equilibrium. The results shown in Fig.(3-13) indicate that in spite of the reduction of U and ε_a, the magnetic solution can occur. In Fig.(3-14) the numerical results for the sputtering case are shown. The time dependence of parameters is assumed as,

$$u(t) = \begin{cases} 1 & t<0 \\ \exp[\,-(t/T_u)^2\,] & t>0, \end{cases}$$

$$U(t) = \begin{cases} U_0 & t<0 \\ U_\infty - \dfrac{U_\infty - U_0}{1 + (v/z_0)t} & t>0, \end{cases}$$

$$\varepsilon_a(t) = -U(t)/2, \qquad (3\text{-}24)$$

where the image potential correction is considered; U(t) takes a value U_0 at surface and U_∞ at infinite distance from the surface. In the results shown in Fig.(3-14) the parameters are $U_0=1$, $U_\infty=16$, $v/z_0=0.5$, $T_u=3$ and $\varepsilon_m=0.001$. These results indicate that inspite of the rather strong screening, the magnetic solution can occur also.

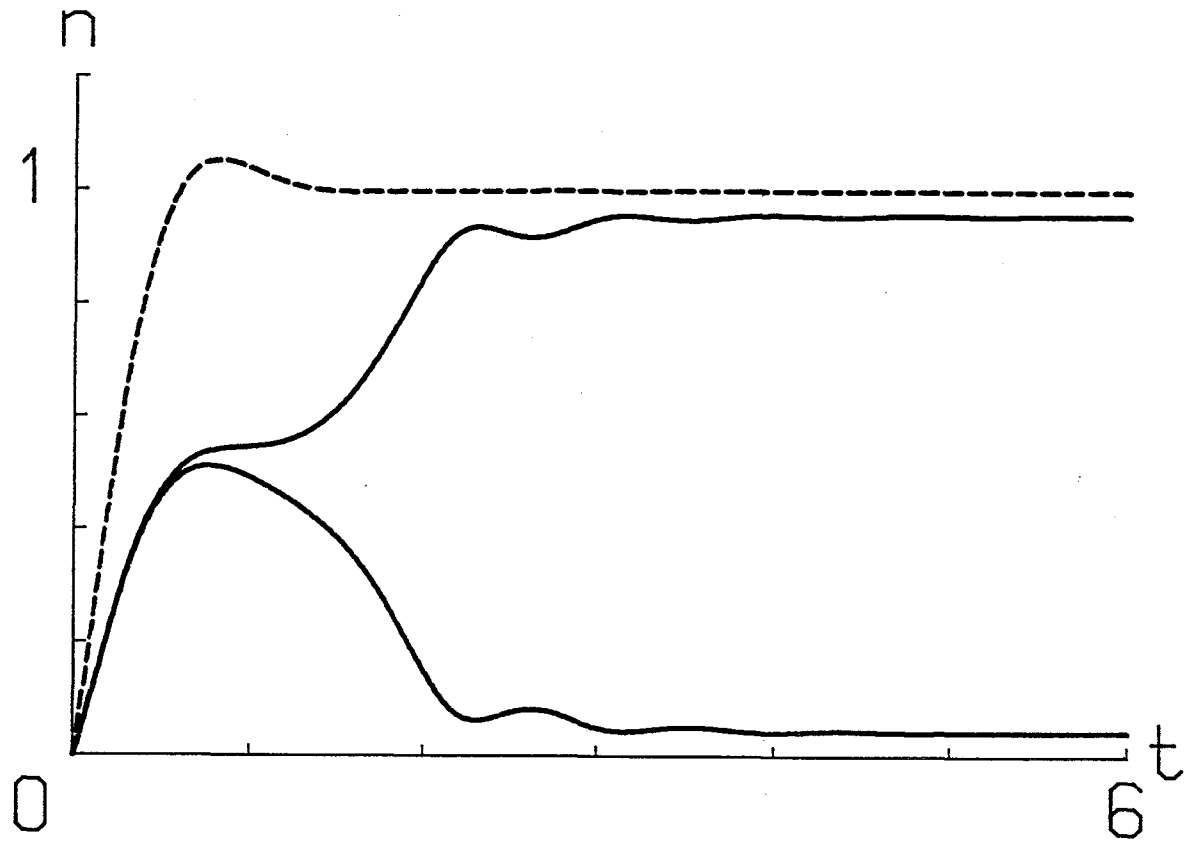

Fig.(3-1-a)

Fig.(3-1) Numerical results for various values of ε_m with $\varepsilon_a=-U/2=-8$. The time dependence of u(t) is shown in Eq.(2-4). Solid lines represent the electron number for each spin, and dashed lines the total electron number. a) $\varepsilon_m=0.1$, b) $\varepsilon_m=0.01$, c) $\varepsilon_m=0.001$.

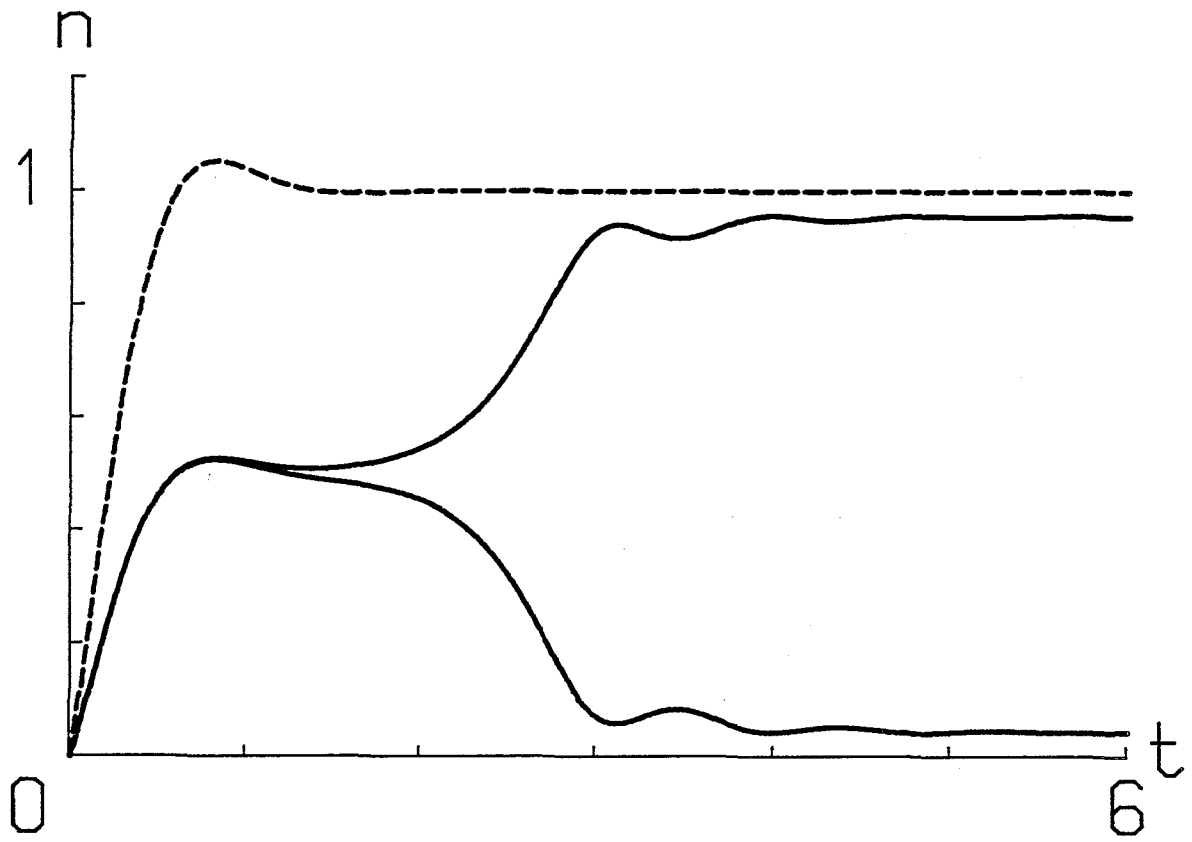

Fig.(3-1-b)

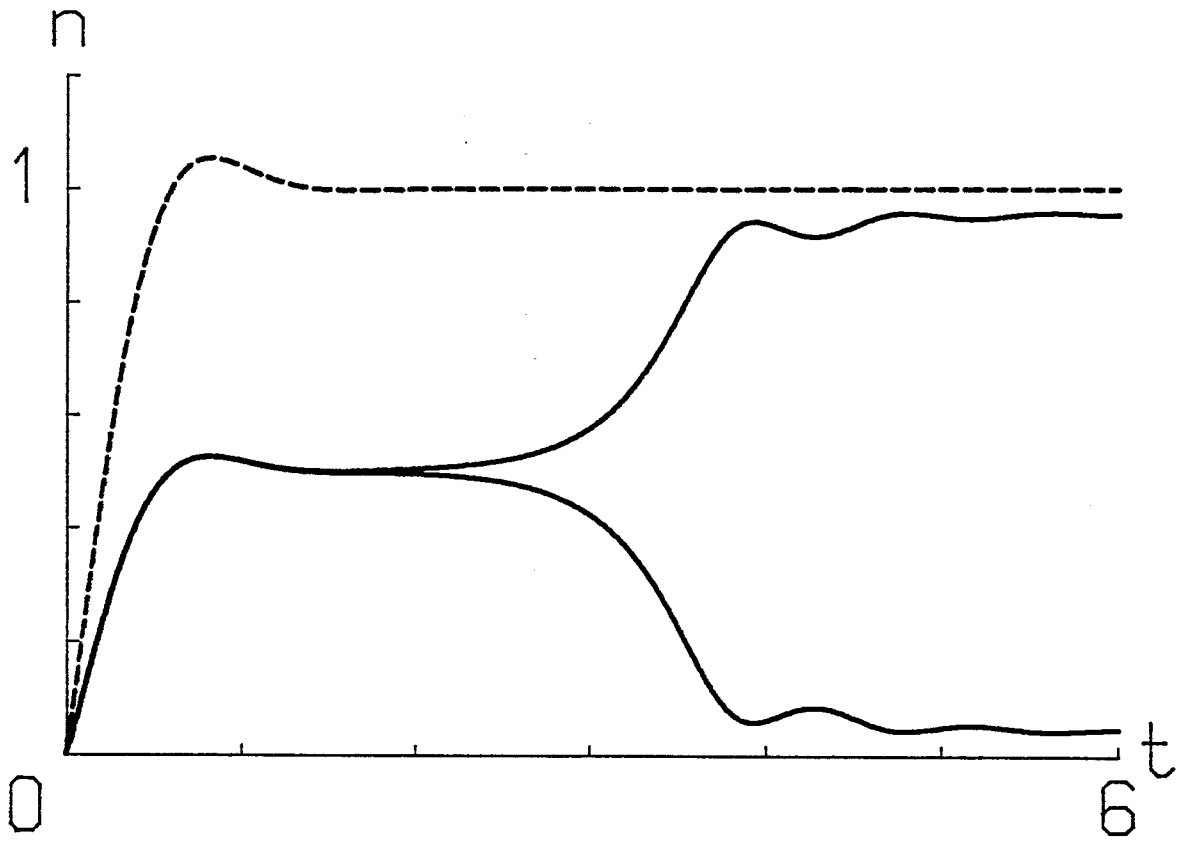

Fig.(3-1-c)

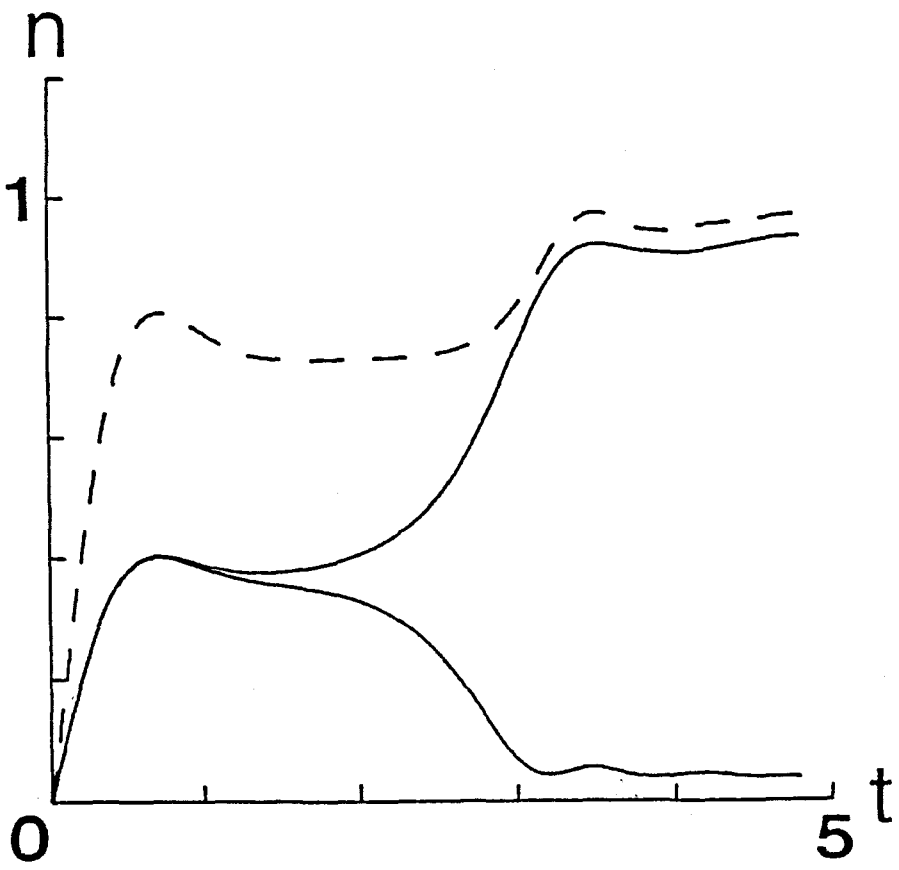

Fig.(3-2) Same as Fig.(3-1), ε_a=-5, U=15 and ε_m=0.01.

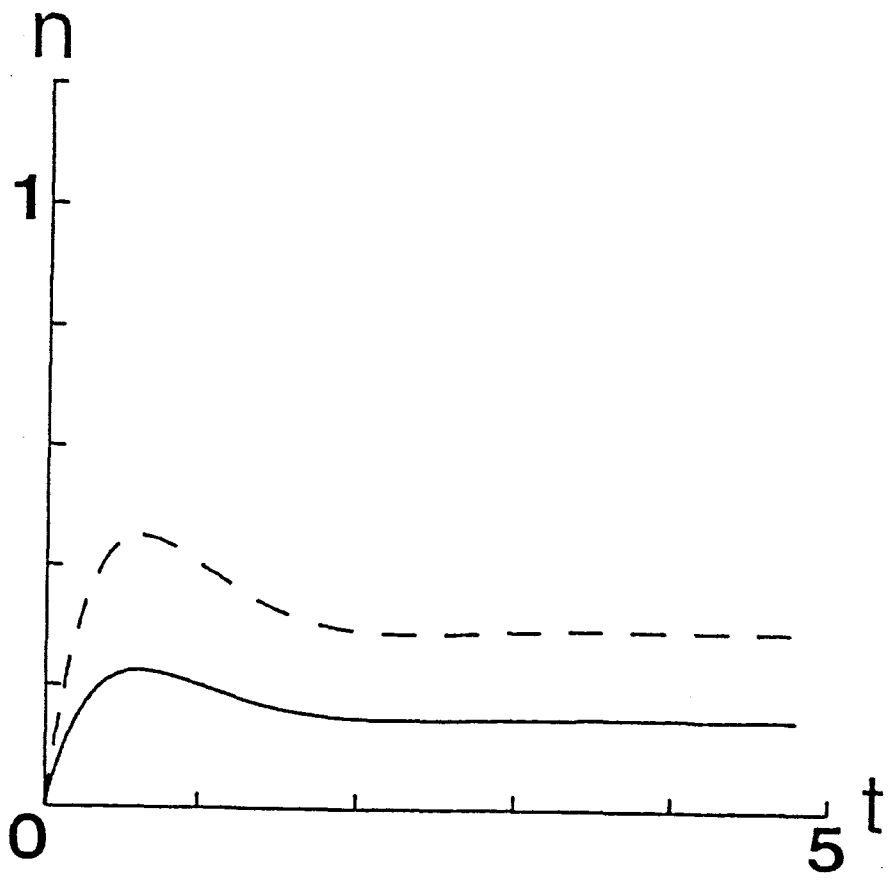

Fig.(3-3) Same as Fig.(3-1), ε_a=2 and U=0.

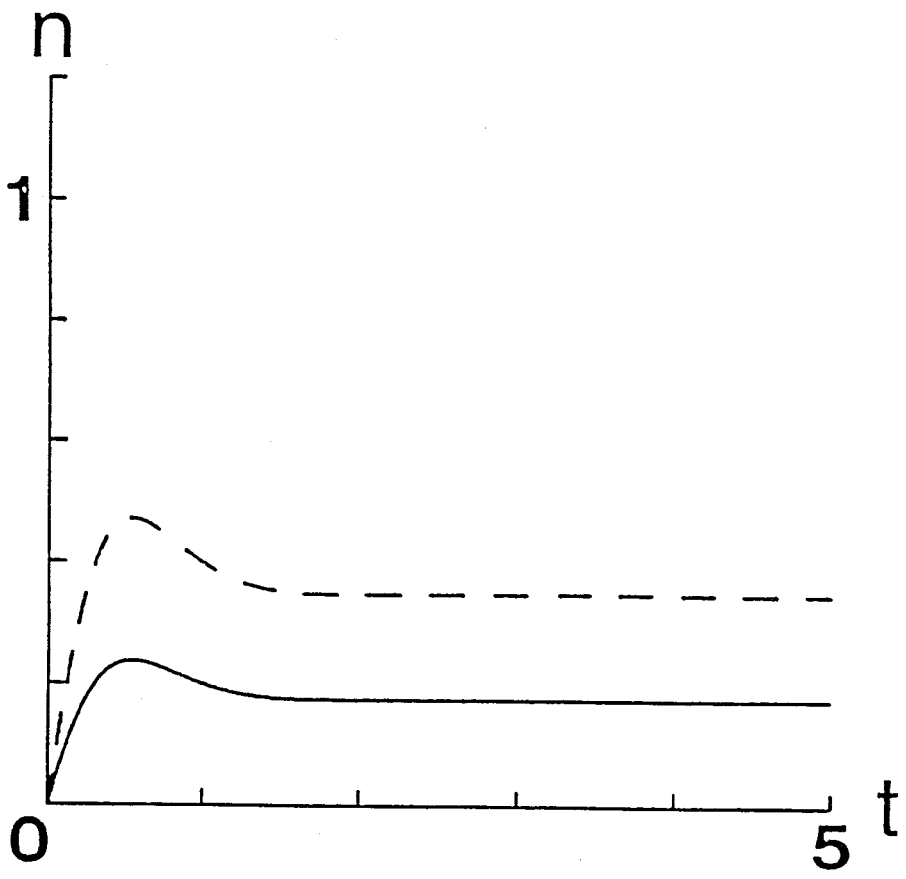

Fig.(3-4) Same as Fig.(3-1), ε_a=-0.1 and U=10.

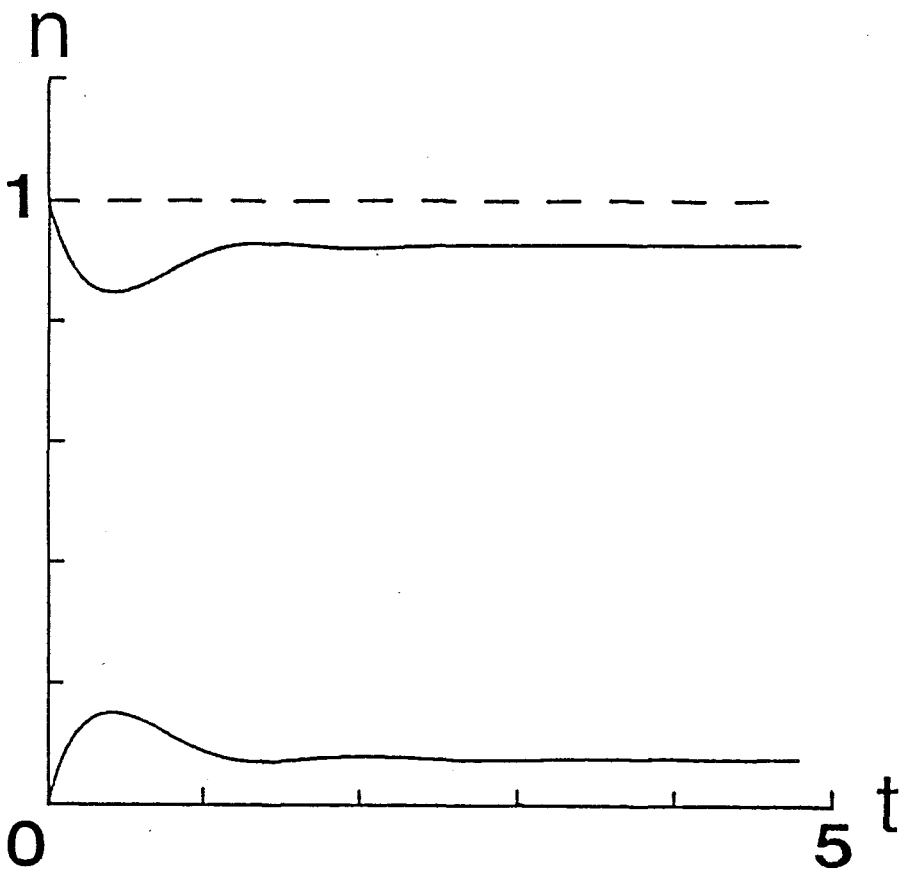

Fig.(3-5) Same as Fig.(3-1), ε_a=-5 and U=10.

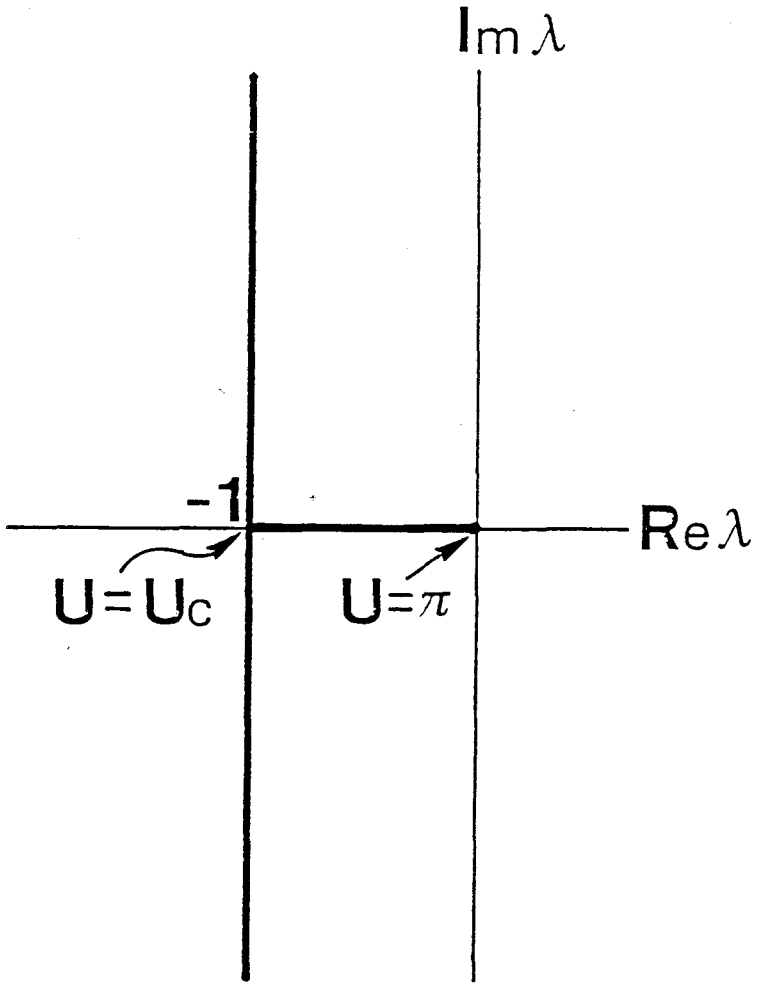

Fig.(3-6) Trajectory of the solution of Eq.(3-12) on the complex λ plane with varying U. For $U>U_c$, the real part of λ, λ_1 takes a constant value -1 and the imaginary part λ_2 is finite. For $U<U_c$, λ_2 vanishes, leading to the absence of the oscillation of m(t). The value of U_c is 3.843··· defined by $\sin\delta_c=\exp(-\pi/2U_c)$.

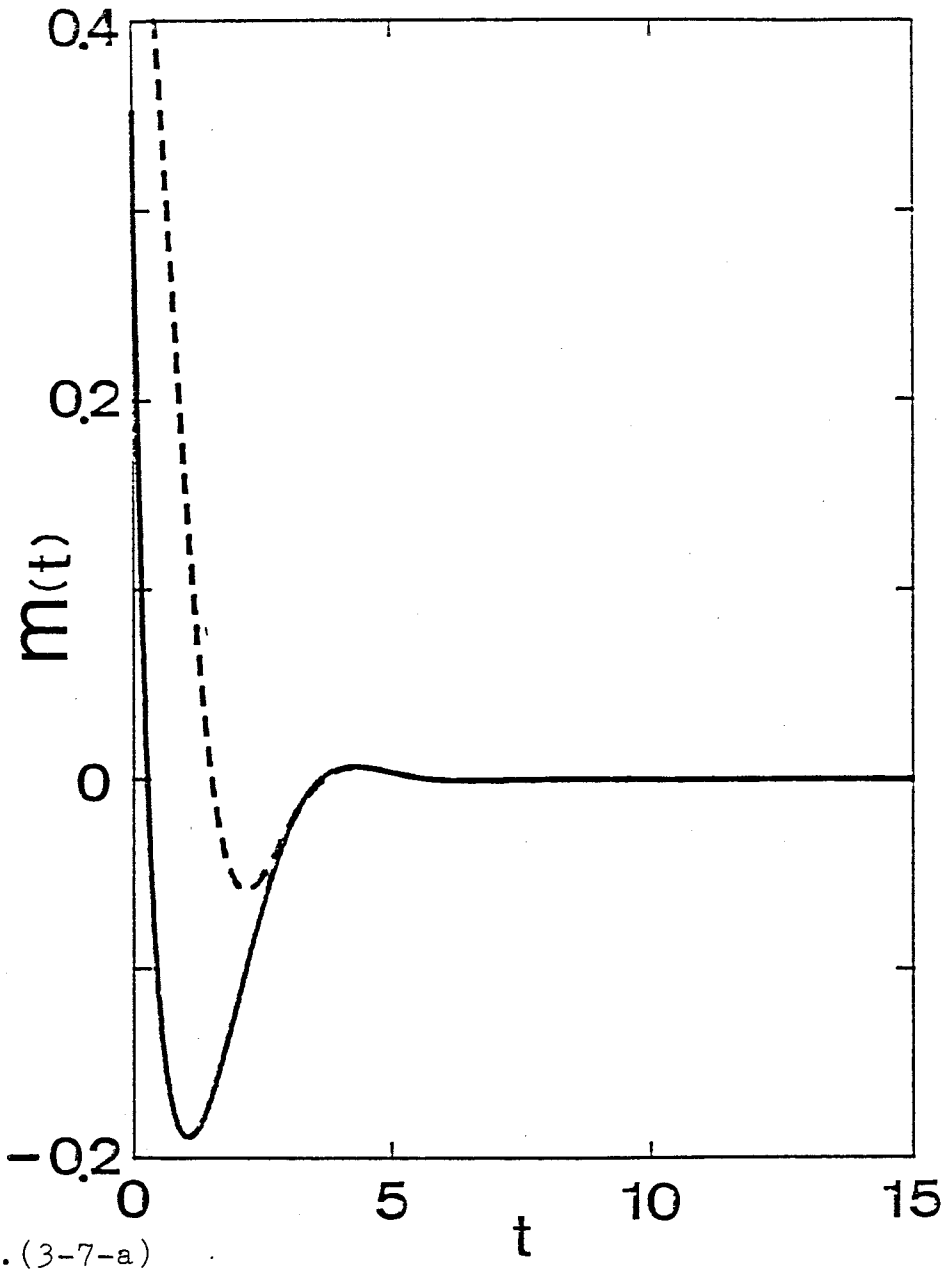

Fig.(3-7-a)

Fig.(3-7) Comparison of the numerical results of m(t) from Eq.(3-3) with those of the asymptotic solution. Solid lines represent the numerical results for U=5 ($U>U_c$) with the initial condition $n_\uparrow(0)=1$, $n_\downarrow(0)=0$, and dashed lines the asymptotic ones, which take a form $A\exp(-t)\sin(\lambda_2 t+\phi)$. The frequency λ_2 (=1.4525) is the imaginaly part of the solution of Eq.(3-12). The amplitude A and the phase ϕ are determined at t=12.996 where m(t) takes a local maximum. a) m(t) versus t, b) m(t)exp(t) versus t.

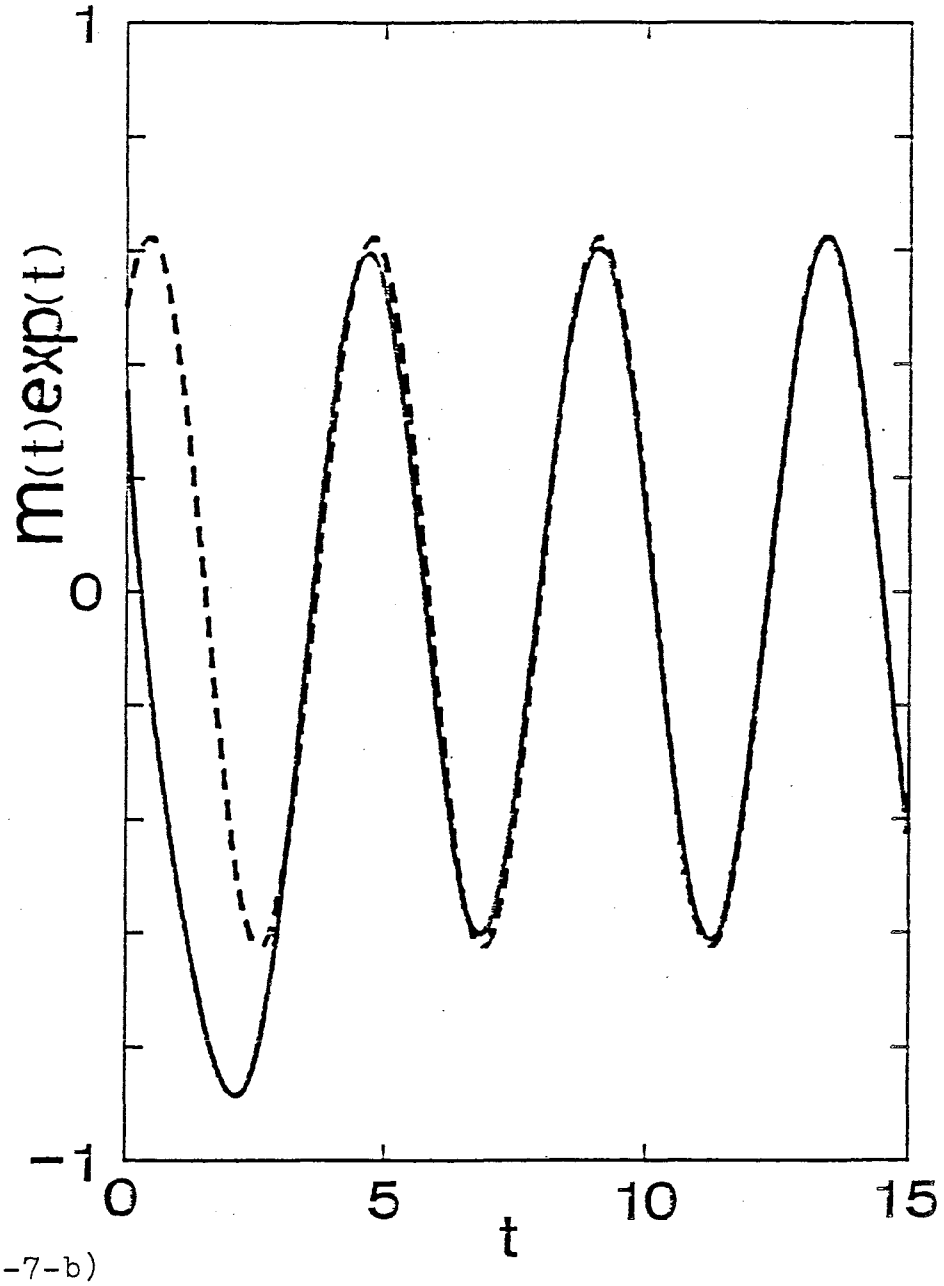

Fig.(3-7-b)

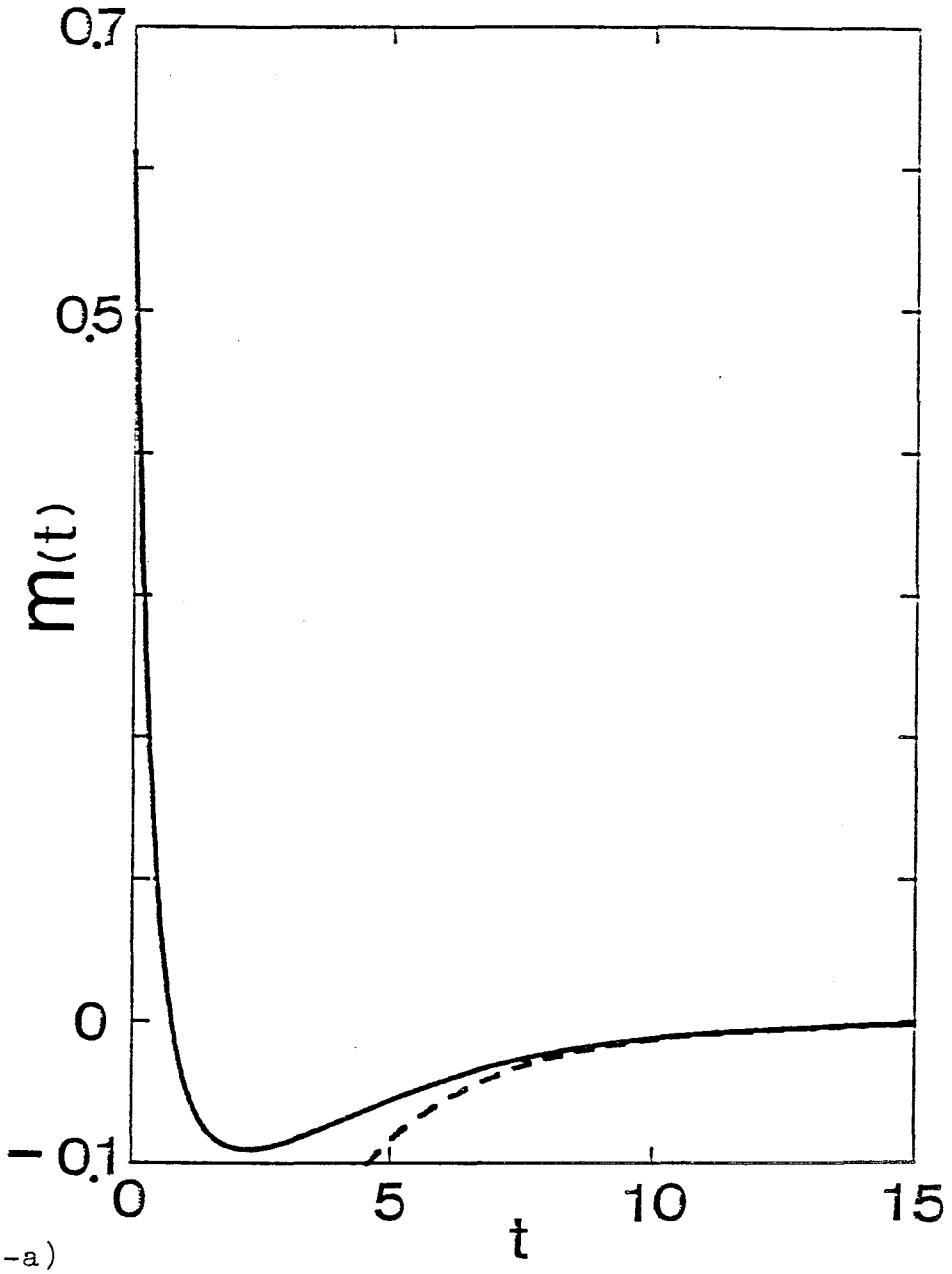

Fig.(3-8-a)

Fig.(3-8) Same as Fig.(3-7) for $U<U_c$. The asymptotic solusion is now given by $A\exp(\lambda t)$, λ being the solution of Eq.(3-12). The amplitude A is determined at t=13.725. a) for U=3.6 ($U_c>U>\pi$ and $\lambda=-0.3908\cdots$) b) for U=2 ($U<\pi$ and $\lambda=-0.3883\cdots$.)

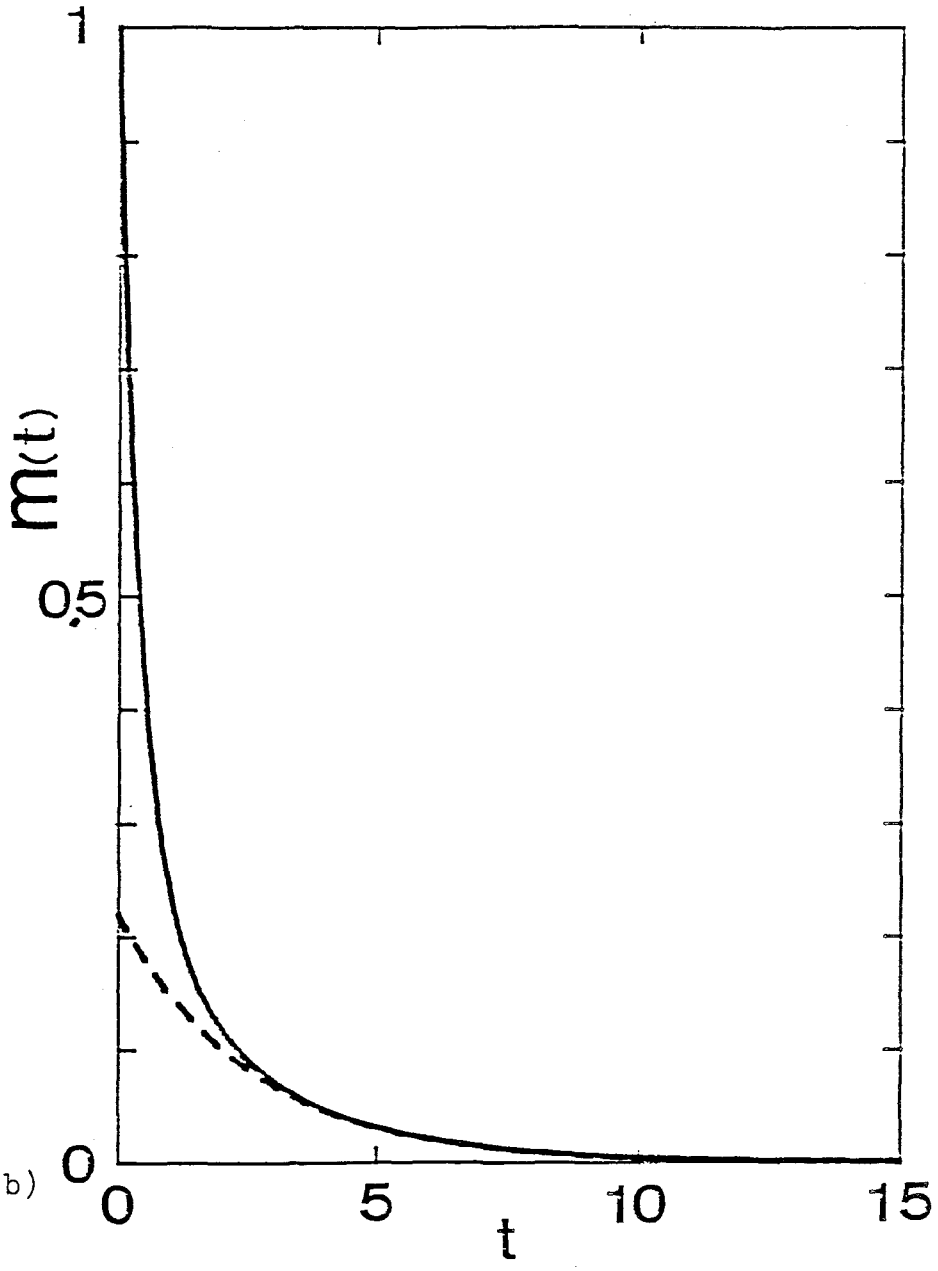

Fig.(3-8-b)

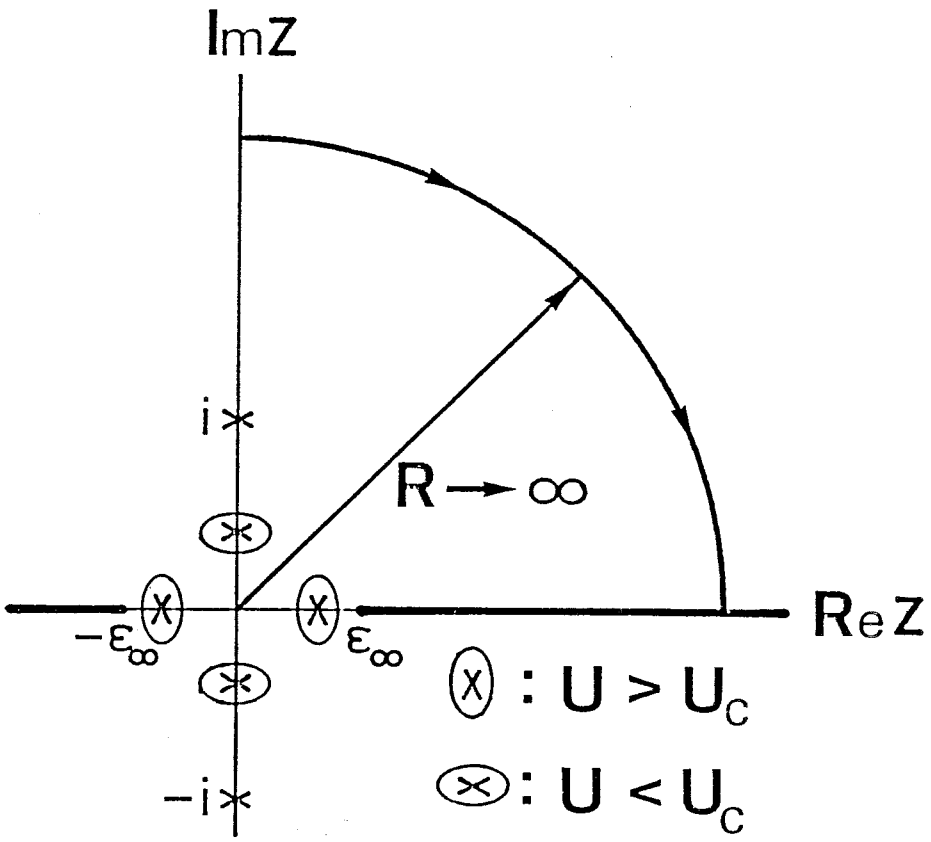

Fig.(3-9) Path for the integrations (3-18) and (3-20). The integrations are to be made along the quarter circle with the infinite radius. Heavy lines are the branch cuts of the integrand in Eq.(3-20) or the cuts of denominator in Eq.(3-18). The branch cut of the numerator in Eq.(3-18) is not shown. Crosses are poles of the integrands. There are poles at $z=\pm i$ for all values of U. The other poles are on the real axis for $U>U_c$, and on the imaginary axis for $U<U_c$.

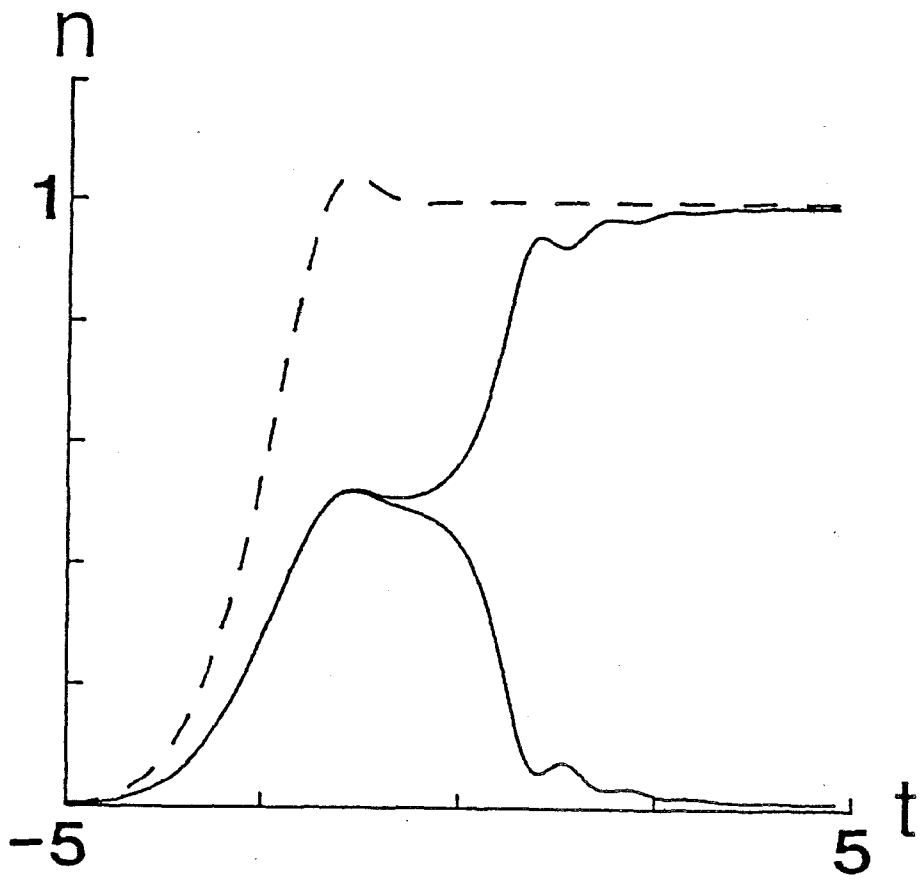

Fig.(3-10) Numerical results for $n_\sigma(t)$. ε_a=-8, U=16, ε_m=0.01 and T_u=3. The time dependence of u(t) is shown in Eq.(3-22). Solid lines represent the electron number for each spin, and dashed lines the total electron number.

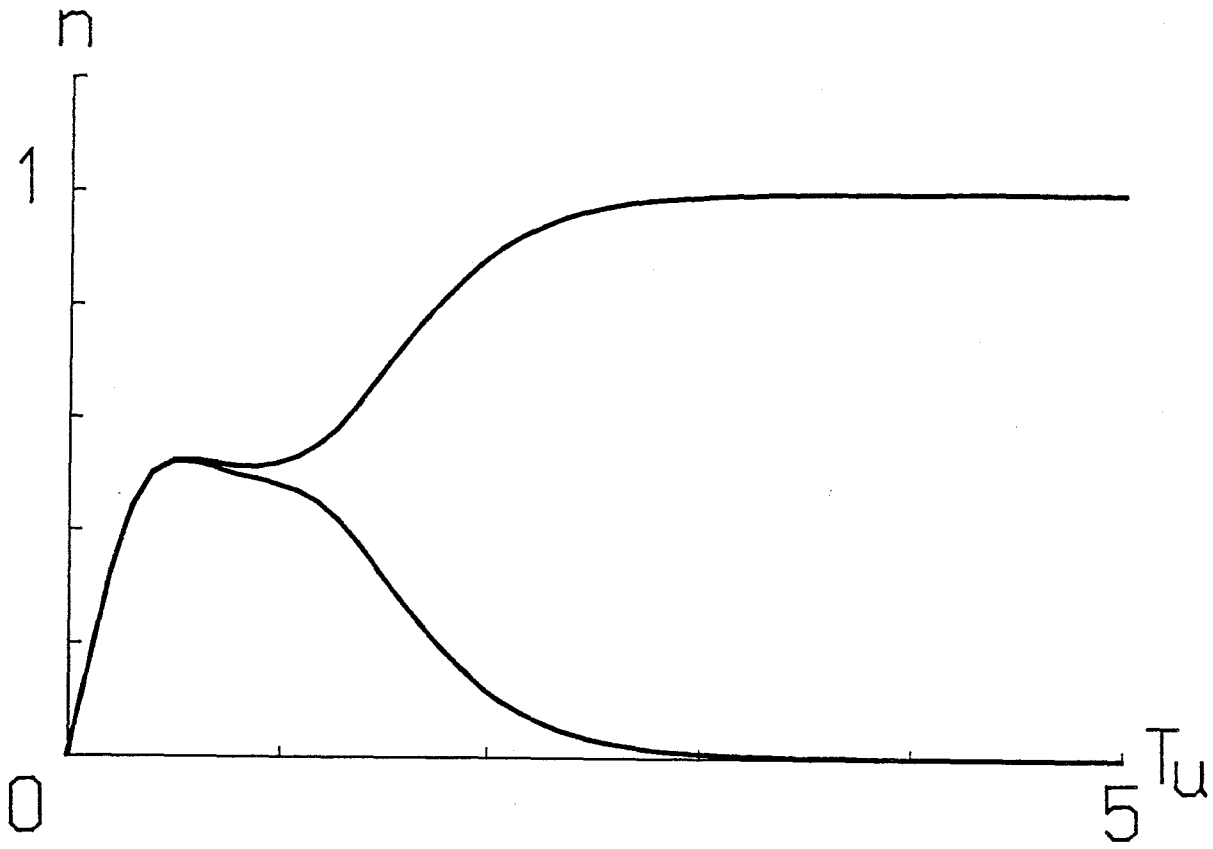

Fig.(3-11) Numerical results for $n_\sigma(\infty)$ versus T_u. ε_a=-8, U=16, ε_m=0.01. The time dependence of u(t) is shown in Eq.(3-22).

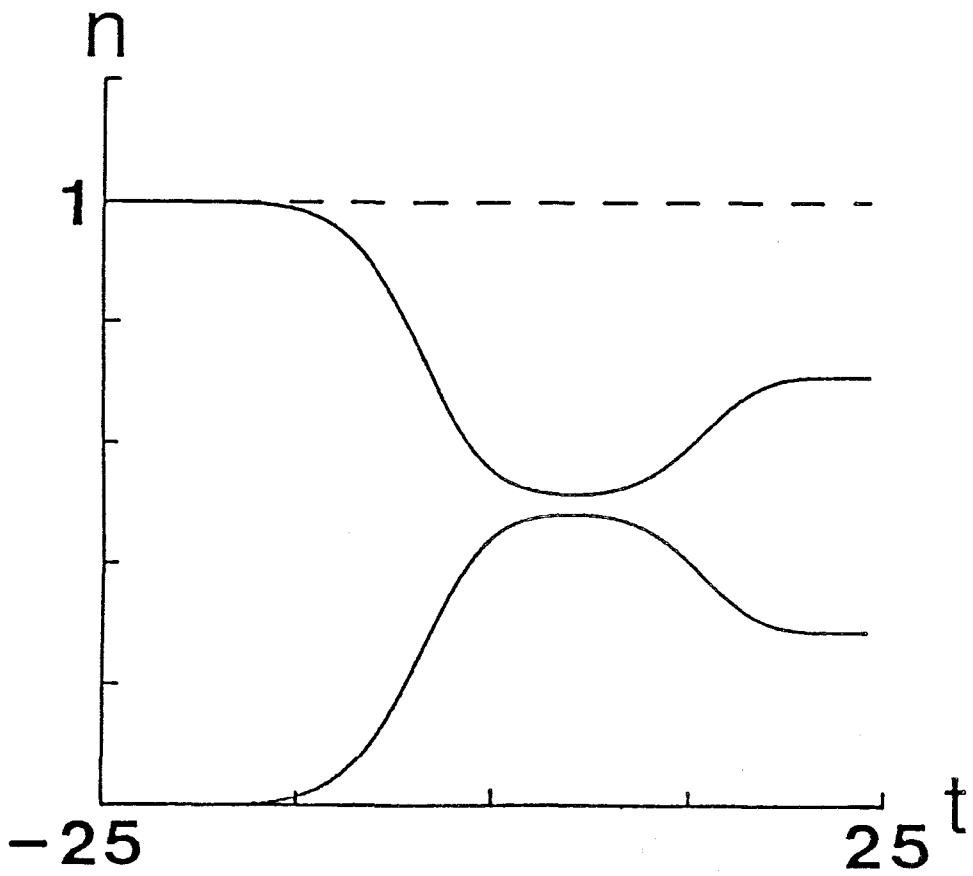

Fig.(3-12) Same as Fig.(3-10), ε_a=-1, U=10 and T_u=10.

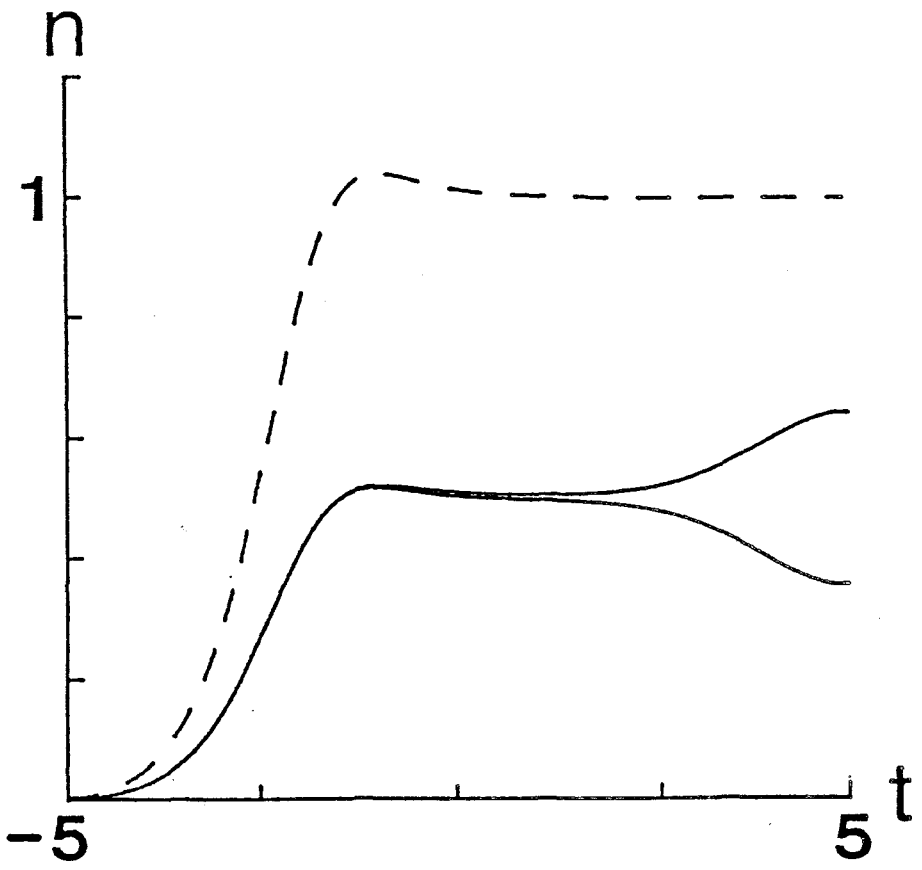

Fig.(3-13) Same as Fig.(3-10), U_0=1, U_∞=16, ε_m=0.01 and T_u=T_U=3. The time dependence of the parameters is shown in Eq.(3-22) and Eq.(3-23).

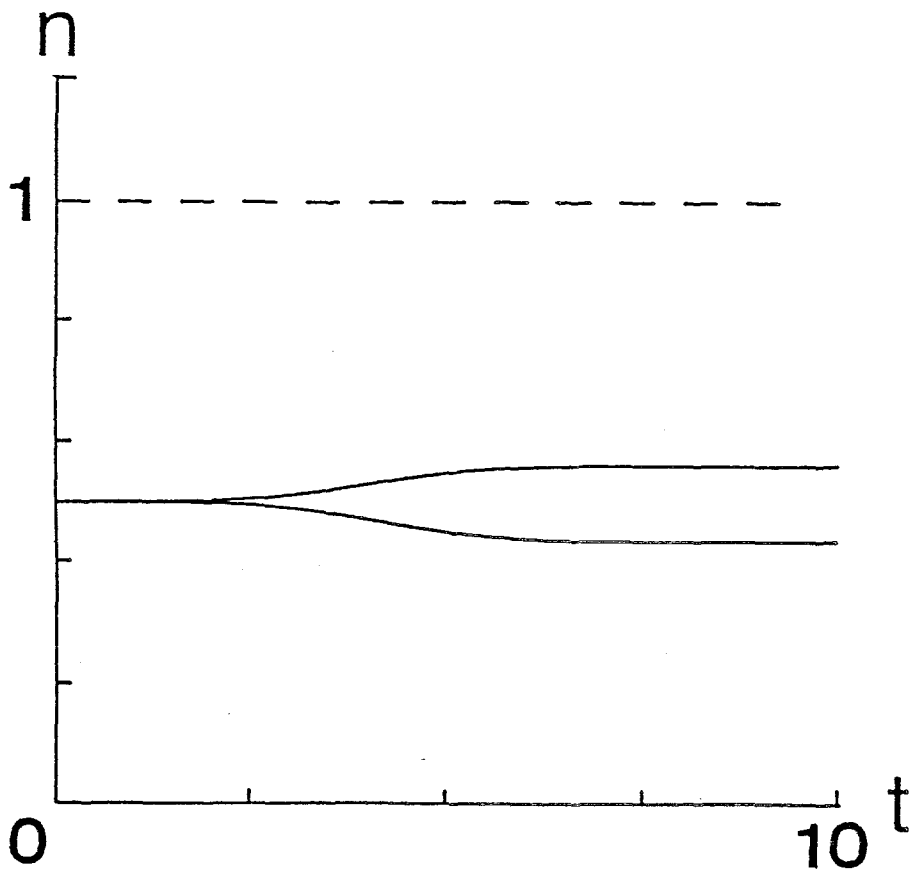

Fig.(3-14) Same as Fig.(3-10), U_0=1, U_∞=16, v/Z_0=0.5, ε_m=0.001 and T_u=3. The time dependence of the parameters is shown in Eq.(3-24).

§4 Electron-Hole Pair Expansion

§4-1 Expansion with Respect to the Admixture

Effects of the intraatomic Coulomb interaction in the time-dependent Newns-Anderson model are investigated in the Hartree-Fock approximation in the section (3). Though the approximation is very simple, various interesting effects of the interaction are found within the approximation. The approximation, however, may be oversimplified; in equilibrium problem it is well recognized that the Hartree-Fock approximation in Anderson model has some defects. There are few studies to improve the approximation in the time-dependent Newns-Anderson model for the charge exchange problem (Okiji and Kawakami 1985). Recently the 1/N expansion method has been applied to the charge transfer problem in the N-fold orbital-degenerate time-dependent Newns-Anderson model by Brako and Newns (1985). They employed the electron-hole pair expansion. In the equilibrium problem the electron-hole pair expansion method has achieved success (Yosida and Yoshimori 1973, Gunnarson and Schönhammer 1983). In the charge exchange problem, however, the 1/N expansion gives rather strange results, which is mentioned in the subsection (4-3). Here, we investigate the effects on the charge transfer problem following Brako and Newns, but we do not employ the 1/N expansion; we employ the expansion with respect to the admixture constant between the electron states between the atom and

metallic states, and examine each term for the total electron occupation number on the atom up to the eighth order of the admixture (Kawai and Yoshimori 1987).

The Hamiltonian of the N-fold degenerate time-dependent Newns-Anderson model is given by

$$H = \sum_{km} \varepsilon_k C^{\dagger}_{km} C_{km} + \sum_{m} \varepsilon_a(t) C^{\dagger}_{am} C_{am}$$

$$+ \sum_{km} [\, V_k(t) C^{\dagger}_{am} C_{km} + \text{h.c.} \,] + \sum_{m_1 \neq m_2} U(t) C^{\dagger}_{am_1} C_{am_1} C^{\dagger}_{am_2} C_{am_2}, \quad (4\text{-}1)$$

where C_{am} is the annihilation operator in the m-th (m=1,2, $\cdots$ N) electron state of N-fold degenerate orbitals (including spin) on the atom, C_{km} the annihilation operator in the corresponding m-th partial wave state of metallic electron of quantum number k in the metal, the other notations are the same as in previous sections. The expansion bases of the total wavefunction necessary to examine the total electron occupation number up to the eighth order are

$$|0\rangle,$$

$$|ak\rangle = \frac{1}{\sqrt{N}} \sum_{m} C^{\dagger}_{am} C_{km} |0\rangle, \qquad \varepsilon_k < 0 \ (\varepsilon_F = 0)$$

$$|k_1\ k_2\rangle = \frac{1}{\sqrt{N}} \sum_{m} C^{\dagger}_{k_1 m} C_{k_2 m} |0\rangle, \qquad \begin{cases} \varepsilon_{k_1} > 0 \\ \varepsilon_{k_2} < 0 \end{cases}$$

$$|1{:}a\ k_1\ k_2\ k_3\rangle = \frac{1}{\sqrt{N}} \sum_m C^\dagger_{am} C^\dagger_{k_1 m} C_{k_2 m} C_{k_3 m} |0\rangle, \qquad \begin{cases} \varepsilon_{k_1} > 0 \\ \varepsilon_{k_3} < \varepsilon_{k_2} < 0 \end{cases}$$

$$|2{:}a\ k_1\ k_2\ k_3\rangle = \frac{1}{\sqrt{N(N-1)}} \sum_{m_1 \neq m_2} C^\dagger_{am_1} C^\dagger_{am_2} C_{am_2} C_{am_1} |0\rangle, \begin{cases} \varepsilon_{k_1} > 0 \\ \varepsilon_{k_2} < 0 \\ \varepsilon_{k_3} < 0 \end{cases}$$

$$|1{:}k_1\ k_2\ k_3\ k_4\rangle = \frac{1}{\sqrt{N}} \sum_m C^\dagger_{k_1 m} C^\dagger_{k_2 m} C_{k_3 m} C_{k_4 m} |0\rangle, \qquad \begin{cases} \varepsilon_{k_1} > \varepsilon_{k_2} > 0 \\ \varepsilon_{k_4} < \varepsilon_{k_3} < 0 \end{cases}$$

$$|2{:}k_1\ k_2\ k_3\ k_4\rangle = \frac{1}{\sqrt{N(N-1)}} \sum_{m_1 \neq m_2} C^\dagger_{k_1 m_1} C^\dagger_{k_2 m_2} C_{k_3 m_2} C_{k_4 m_1} |0\rangle,$$

$$\begin{cases} \varepsilon_{k_1} > \varepsilon_{k_2} > 0 \\ \varepsilon_{k_3} < 0 \\ \varepsilon_{k_4} < 0 \\ \quad \text{or} \\ \varepsilon_{k_1} > 0 \\ \varepsilon_{k_2} > 0 \\ \varepsilon_{k_4} < \varepsilon_{k_3} < 0 \end{cases} \qquad (4\text{-}2)$$

where $|0\rangle$ denotes the ground state of the metal and empty atom orbital. Throughout this section, the $U \to \infty$ case is assumed, so that the wavefunction for whole system does not contain the bases of more than one electron on the atom. Furthermore $\varepsilon_a > 0$ is assumed, so that $|0\rangle$ is the ground state of the whole system at $V_k = 0$.

The wavefunction of the whole system $|\psi(t)\rangle$ is expressed in

the linear combination of the bases in the form

$$|\psi(t)\rangle = B(t)|0\rangle + \sum B(\,a\ k_1{:}t)|a\ k_1\rangle + \sum B(k_1\ k_2{:}t)|k_1\ k_2\rangle$$

$$+ \sum B_1(a\ k_1\ k_2\ k_3{:}t)|1{:}a\ k_1\ k_2\ k_3\rangle$$

$$+ \sum B_2(a\ k_1\ k_2\ k_3{:}t)|2{:}a\ k_1\ k_2\ k_3\rangle$$

$$+ \sum B_1(k_1\ k_2\ k_3\ k_4{:}t)|1{:}k_1\ k_2\ k_3\ k_4\rangle$$

$$+ \sum B_2(k_1\ k_2\ k_3\ k_4{:}t)|2{:}k_1\ k_2\ k_3\ k_4\rangle + \cdots. \qquad (4\text{-}3)$$

Summations in Eq.(4-3) should be carried out over k. The amplitudes b(t), etc. are determined from the time-dependent Schrödinger equation. The coupled differential equation is obtained as

$$i\frac{d}{dt}B(t) = \sqrt{N}V(t)\sum_{\varepsilon_1<0} B(a\ 1{:}t),$$

$$i\frac{d}{dt}B(a\ k{:}t) = \sqrt{N}V(t)B(t) + (\varepsilon_a - \varepsilon_k)B(a\ k{:}t) + V(t)\sum_{\varepsilon_1>0} B(1\ k{:}t),$$

$$i\frac{d}{dt}B(k_1\ k_2{:}t) = V(t)B(a\ k_2{:}t) + (\varepsilon_{k_1} - \varepsilon_{k_2})B(k_1\ k_2{:}t)$$

$$+ V(t)\sum_{\varepsilon_{k_2}>\varepsilon_1} B_1(a\ k_1\ k_2\ 1{:}t) - V(t)\sum_{\varepsilon_{k_2}<\varepsilon_1<0} B_1(a\ k_1\ 1\ k_2{:}t)$$

$$+ \sqrt{N-1}V(t)\sum_{\varepsilon_1<0} B_2(a\ k_1\ k_2\ l:t),$$

$$i\frac{d}{dt}B_1(a\ k_1\ k_2\ k_3:t) = V(t)B(k_1\ k_2:t) - V(t)B(k_1\ k_3:t)$$

$$+ (\varepsilon_a + \varepsilon_{k_1} - \varepsilon_{k_2} - \varepsilon_{k_3})B_1(a\ k_1\ k_2\ k_3:t)$$

$$- V(t)\sum_{\varepsilon_{k_1}>\varepsilon_l>0} B_1(k_1\ l\ k_2\ k_3:t)$$

$$+ V(t)\sum_{\varepsilon_l>\varepsilon_{k_1}} B_1(l\ k_1\ k_2\ k_3:t),$$

$$i\frac{d}{dt}B_2(a\ k_1\ k_2\ k_3:t) = \sqrt{N-1}V(t)B(k_1\ k_2:t)$$
$$(\varepsilon_{k_2}>\varepsilon_{k_3})$$

$$+ (\varepsilon_a + \varepsilon_{k_1} - \varepsilon_{k_2} - \varepsilon_{k_3})B_2(a\ k_1\ k_2\ k_3:t)$$

$$+ V(t)\sum_{\varepsilon_{k_1}>\varepsilon_l>0} B_2(k_1\ l\ k_3\ k_2:t)$$

$$+ V(t)\sum_{\varepsilon_l>0} B_2(l\ k_1\ k_2\ k_3:t),$$

$$i\frac{d}{dt}B_2(a\ k_1\ k_2\ k_3:t) = \sqrt{N-1}\ V(t)B(k_1\ k_2:t)$$
$$(\varepsilon_{k_2}<\varepsilon_{k_3})$$

$$+(\varepsilon_a + \varepsilon_{k_1} - \varepsilon_{k_2} - \varepsilon_{k_3})B_2(a\ k_1\ k_2\ k_3:t)$$

$$+ V(t)\sum_{\varepsilon_l>0} B_2(k_1\ l\ k_3\ k_2:t)$$

$$+ V(t)\sum_{\varepsilon_1>\varepsilon_{k_1}} B_2(1\ k_1\ k_2\ k_3:t),$$

$$i\frac{d}{dt}B_1(k_1\ k_2\ k_3\ k_4:t) = - V(t)B_1(a\ k_1\ k_3\ k_4:t)$$
$$+ V(t)B_1(a\ k_2\ k_3\ k_4:t)$$
$$+ (\varepsilon_{k_1} + \varepsilon_{k_2} - \varepsilon_{k_3} - \varepsilon_{k_4})B_1(k_1\ k_2\ k_3\ k_4:t)$$
$$+ \cdots ,$$

$$i\frac{d}{dt}B_2(k_1\ k_2\ k_3\ k_4:t) = V(t)B_2(a\ k_1\ k_4\ k_3:t)$$
$$+ V(t)B_2(a\ k_2\ k_3\ k_4:t)$$
$$+ (\varepsilon_{k_1} + \varepsilon_{k_2} - \varepsilon_{k_3} - \varepsilon_{k_4})B_2(k_1\ k_2\ k_3\ k_4:t)$$
$$+ \cdots , \qquad (4\text{-}4)$$

where the admixture constant $V_k(t)$ is written as $V(t)$ which is assumed to be real and independent of k, the energy of the whole system is measured from the eigenenergy of $|0\rangle$. We solve these coupled equations by iteration, starting from b(t). The solution is obtained in the expanded form with respect to V. In order to obtain the solution up to V^8, those bases written out in Eq.(4-2) and Eq.(4-3) are enough.

The total charge on the atom at $t\to\infty$ is given from the solution of Eq.(4-4), that is,

$$N(\infty)=\langle\psi(\infty)|\sum_m C_{am}^{\dagger}C_{am}|\psi(\infty)\rangle$$

$$=\sum|B(a\ k:\infty)|^2+\sum|B_1(a\ k_1\ k_2\ k_3:\infty)|^2+\sum|B_2(a\ k_1\ k_2\ k_3:\infty)|^2. \tag{4-5}$$

where the summation are again over k.

§4-2 Laplace Transformation

In this subsection, $\varepsilon_a(t)$ is assumed to be constant in time for simplicity. Furthermore the time dependence of V(t) is taken to be

$$V(t) = Vu(t)$$

$$u(t) = \begin{cases} 1 & t < 0 \\ \exp[-\gamma t] & t > 0 \end{cases} \tag{4-6}$$

where γ expresses the motion of the atom; small γ corresponds to the slow velocity of the atom ($\gamma=v/\alpha$, see the subsection (2-1)). The time dependence in Eq.(4-6) corresponds to the sputtering case. In order to get the solution of Eq.(4-4), the Eq.(4-4) is transformed by the Laplace transformation. The coupled equations are obtained as

$$b(p) = \frac{1}{ip}[iB(0)+\sqrt{N}\ V\sum_{\varepsilon_1<0} b(a\ 1:p+\gamma),$$

$$b(a\ k:p) = \frac{1}{ip-\varepsilon_a+\varepsilon_k}[iB(a\ k:0)+\sqrt{N}Vb(p+\gamma)+V\sum_{\varepsilon_1>0} b(1\ k:p+\gamma)],$$

$$b(k_1\ k_2:p) = \frac{1}{ip-\varepsilon_{k_1}+\varepsilon_{k_2}}[iB(k_1\ k_2:0)+Vb(a\ k_2:p+\gamma)$$

$$+V\sum_{\varepsilon_{k_2}>\varepsilon_1} b_1(a\ k_1\ k_2\ 1:p+\gamma)-V\sum_{\varepsilon_{k_2}<\varepsilon_1<0} b_1(a\ k_1\ 1\ k_2:p+\gamma)$$

$$+\sqrt{N-1}V\sum_{\varepsilon_1<0} b_2(a\ k_1\ k_2\ 1:p+\gamma)],$$

$$b_1(a\ k_1\ k_2\ k_3:p) = \frac{1}{ip-\varepsilon_a-\varepsilon_{k_1}+\varepsilon_{k_2}+\varepsilon_{k_3}}[iB_1(a\ k_1\ k_2\ k_3:0)$$

$$+Vb(k_1\ k_2:p+\gamma)-Vb(k_1\ k_2:p+\gamma)$$

$$-V\sum_{\varepsilon_{k_1}>\varepsilon_1>0} b_1(k_1\ 1\ k_2\ k_3:p+\gamma)+V\sum_{\varepsilon_1>\varepsilon_{k_1}} b_1(1\ k_1\ k_2\ k_3:p+\gamma)],$$

$$b_2(a\ k_1\ k_2\ k_3:p) \quad (\varepsilon_{k_2}>\varepsilon_{k_3}) = \frac{1}{ip-\varepsilon_a-\varepsilon_{k_1}+\varepsilon_{k_2}+\varepsilon_{k_3}}[iB_2(a\ k_1\ k_2\ k_3:0)$$

$$+\sqrt{N-1}Vb(k_1\ k_2:p+\gamma)+V\sum_{\varepsilon_{k_1}>\varepsilon_1>0} b_2(k_1\ 1\ k_3\ k_2:p+\gamma)$$

$$+V\sum_{\varepsilon_1>0} b_2(1\ k_1\ k_2\ k_3:p+\gamma)],$$

$$b_2(a\ k_1\ k_2\ k_3:p) \quad (\varepsilon_{k_2}<\varepsilon_{k_3}) = \frac{1}{ip-\varepsilon_a-\varepsilon_{k_1}+\varepsilon_{k_2}+\varepsilon_{k_3}}[iB_2(a\ k_1\ k_2\ k_3:0)$$

$$+\sqrt{N-1}Vb(k_1\ k_2:p+\gamma)+V\sum_{\varepsilon_1>0} b_2(k_1\ 1\ k_3\ k_2:p+\gamma)$$

$$+V\sum_{\varepsilon_1>\varepsilon_{k_1}} b_2(1\ k_1\ k_2\ k_3:p+\gamma)],$$

$$b_1(k_1\ k_2\ k_3\ k_4:p) = \frac{1}{ip-\varepsilon_{k_1}-\varepsilon_{k_2}+\varepsilon_{k_3}+\varepsilon_{k_4}}[iB_1(k_1\ k_2\ k_3\ k_4:0)$$

$$-Vb_1(a\ k_1\ k_3\ k_4:p+\gamma)+Vb_1(a\ k_2\ k_3\ k_4:p+\gamma)]$$

$$b_2(k_1\ k_2\ k_3\ k_4:p) = \frac{1}{ip-\varepsilon_{k_1}-\varepsilon_{k_2}+\varepsilon_{k_3}+\varepsilon_{k_4}}[iB_1(k_1\ k_2\ k_3\ k_4:0)$$

$$-Vb_2(a\ k_1\ k_3\ k_4:p+\gamma)+Vb_2(a\ k_2\ k_3\ k_4:p+\gamma)], \qquad (4\text{-}7)$$

where b(p), etc. are the Laplace coefficients of B(t), etc. which are defined as

$$b(p) = \int_0^\infty \exp(-pt)B(t)\ dt. \qquad (4\text{-}8)$$

Since the system is in equilibrium at t=0 from the time dependence of Eq.(4-6), B(0), B(a k:0), etc. are the amplitudes of the equilibrium state. The amplitudes can be found by putting idB/dt=EB into the Eq.(4-4), where E is the energy eigenvalue of the whole system in equilibrium measured from the ground state energy of the Fermi state $|0\rangle$. From the solution of the Eq.(4-7), B(t), etc. are obtained by the inverse Laplace transformation,

$$B(t) = \frac{1}{2\pi i} \int_{-i\infty+0^+}^{i\infty+0^+} \exp(pt)b(p)\, dp. \qquad (4\text{-}9)$$

In order to obtain $N(\infty)$, contributions of residue by the poles only on the imaginary axis are needed in the integration (4-9) (Brako and Newns 1985). We obtain $B(\infty)$, etc. by iteration of Eq.(4-7) up to the eighth order of V using partially the symbolic manipulation system, REDUCE (Hearn 1985). In the following subsection, We rearrange these terms in $N(\infty)$ again in the expanded form with respect to V and carry out the k-summation in the limit of $\varepsilon_a/\gamma \to \infty$ in the wide-band limit.

§4-3 Manybody Effects

In order to rearrange the terms in $N(\infty)$ appropriately and to compare the results, we derive the expression of $N(\infty)$ for the N=1 case, that is, the noninteracting case. The expression for N=1 is obtained in the wide-band limit from Eq.(2-8),

$$N(\infty)_{(N=1)} = \sum_{k_1 k_2} V^2 \int_0^\infty dt_1 \int_0^\infty dt_2 \exp[\, \{i(\varepsilon_{k_1}-\varepsilon_a)-\gamma\}t_1 + \{-i(\varepsilon_{k_1}-\varepsilon_a)-\gamma\}t_2 \,]$$

$$\times \exp[\, -\frac{\Delta}{2\gamma}\{ \exp(-2\gamma t_1) + \exp(-2\gamma t_2) \} \,] \langle c^\dagger_{k_1} c_{k_2} \rangle$$

$$+ 2\mathrm{Im} \exp[\, -\frac{\Delta}{2\gamma} \,] \sum_k V \int_0^\infty dt_1 \exp[\, -\{i(\varepsilon_k-\varepsilon_a)+\gamma\}t_1 \,]$$

$$\times\exp\left[-\frac{\Delta}{2\gamma}\exp(-2\gamma t_1) \right]\langle C_a^\dagger C_k\rangle$$

$$+ \exp\left[-\frac{\Delta}{\gamma} \right]\langle C_a^\dagger C_a\rangle, \qquad (4\text{-}10)$$

where $\langle\cdots\rangle$ expresses the expectation value in equilibrium at $t\leqq 0$. The expanded form of $N(\infty)$ for N=1 with respect to V is obtained from Eq.(4-10) as

$$\underset{(N=1)}{N(\infty)} = A_1\langle C_a^\dagger C_a\rangle + \sum_k A_2(k)\langle C_a^\dagger C_k\rangle + \sum_{k_1}\sum_{k_2} A_3(k_1,k_2)\langle C_{k_1}^\dagger C_{k_2}\rangle, \qquad (4\text{-}11)$$

where

$$A_1 = \left[1 - \frac{\Delta}{\gamma} + \frac{\Delta^2}{2\gamma^2} + \cdots \right],$$

$$A_2 = 2\mathrm{Im}\left(V\frac{1}{i(\varepsilon_k-\varepsilon_a)+\gamma} - \frac{\Delta V}{2\gamma}\left[\frac{1}{i(\varepsilon_k-\varepsilon_a)+\gamma} + \frac{1}{i(\varepsilon_k-\varepsilon_a)-3\gamma} \right] \right.$$

$$\left. + \frac{\Delta^2 V}{8\gamma^2}\left[\frac{1}{i(\varepsilon_k-\varepsilon_a)+\gamma} + \frac{2}{i(\varepsilon_k-\varepsilon_a)+3\gamma} + \frac{1}{i(\varepsilon_k-\varepsilon_a)+5\gamma} \right] + \cdots \right),$$

$$A_3(k_1,k_2) = \left(V^2 \frac{1}{\{i(\varepsilon_{k_1}-\varepsilon_a)-\gamma\}\{-i(\varepsilon_{k_2}-\varepsilon_a)-\gamma\}} \right.$$

$$- \frac{\Delta V^2}{2\gamma}\left[\frac{1}{\{i(\varepsilon_{k_1}-\varepsilon_a)-\gamma\}\{-i(\varepsilon_{k_2}-\varepsilon_a)-3\gamma\}} \right.$$

$$\left. + \frac{1}{\{i(\varepsilon_{k_1}-\varepsilon_a)-3\gamma\}\{-i(\varepsilon_{k_2}-\varepsilon_a)-\gamma\}} \right]$$

$$+ \frac{\Delta^2 V^2}{8\gamma^2}\left[\frac{1}{\{i(\varepsilon_{k_1}-\varepsilon_a)-5\gamma\}\{-i(\varepsilon_{k_2}-\varepsilon_a)-\gamma\}} \right.$$

$$+\frac{2}{\{i(\varepsilon_{k_1}-\varepsilon_a)-3\gamma\}\{-i(\varepsilon_{k_2}-\varepsilon_a)-3\gamma\}}$$

$$+\frac{1}{\{i(\varepsilon_{k_1}-\varepsilon_a)-\gamma\}\{-i(\varepsilon_{k_2}-\varepsilon_a)-5\gamma\}}\Big] + \cdots \Big\}. \qquad (4\text{-}12)$$

On the other hand, for arbitrary N, $\sum_m \langle C^\dagger_{am} C_{am}\rangle$, etc. are obtained from Eq.(4-2) as

$$\sum_m \langle C^\dagger_{am} C_{am}\rangle = \sum |B(a\ 1{:}0)|^2 + \sum |B_1(a\ l_1\ l_2\ l_3{:}0)|^2$$

$$+ \sum |B_2(a\ l_1\ l_2\ l_3{:}0)|^2 + \cdots,$$

$$\sum_{m\ (\varepsilon_k<0)} \langle C^\dagger_{am} C_{km}\rangle = \sqrt{N}B(a\ k{:}0)B(0) - \sum B_1(a\ l_1\ k\ l_2{:}0)B(l_1\ l_2{:}0)$$

$$+ \sum B_1(a\ l_1\ l_2\ k{:}0)B(l_1\ l_2{:}0)$$

$$+ \sqrt{N-1}B_2(a\ l_1\ l_2\ k{:}0)B(l_1\ l_2{:}0) + \cdots,$$

$$\sum_{m\ (\varepsilon_k>0)} \langle C^\dagger_{am} C_{km}\rangle = \sum B(a\ l_1{:}0)B(k\ l_1{:}0)$$

$$+ \sum B_1(a\ l_2\ l_3\ l_4{:}0)B_1(k\ l_2\ l_3\ l_4{:}0)$$

$$- \sum B_1(a\ l_1\ l_3\ l_4{:}0)B_1(l_1\ k\ l_3\ l_4{:}0)$$

$$+ \sum B_2(a\ l_2\ l_3\ l_4{:}0)B_2(k\ l_2\ l_3\ l_4{:}0)$$

$$+ \sum B_2(a\ l_2\ l_3\ l_4{:}0)B_2(k\ l_2\ l_3\ l_4{:}0)$$

$$+ \sum B_2(a\ l_1\ l_4\ l_3{:}0)B_2(l_1\ k\ l_3\ l_4{:}0)$$

$$+ \sum B_2(a\ l_1\ l_4\ l_3{:}0)B_2(l_1\ k\ l_3\ l_4{:}0) + \cdots,$$

$$\sum_{\substack{m \\ (\varepsilon_{k_1}>0,\ \varepsilon_{k_2}>0)}} \langle C^{\dagger}_{k_1 m} C_{k_2 m} \rangle = \sum B(k_1\ l_1{:}0)B(k_2\ l_1{:}0)$$

$$+ \sum B_1(a\ k_1\ l_1\ l_2{:}0)B_1(a\ k_2\ l_1\ l_2{:}0)$$

$$+ \sum B_2(a\ k_1\ l_1\ l_2{:}0)B_2(a\ k_2\ l_1\ l_2{:}0) + \cdots,$$

$$\sum_{\substack{m \\ (\varepsilon_{k_1}>0,\ \varepsilon_{k_2}<0)}} \langle C^{\dagger}_{k_1 m} C_{k_2 m} \rangle = \sqrt{N} B(k_1\ k_2{:}0)B(0) + \sum B_1(a\ k_1\ k_2\ l_1{:}0)B(a\ l_1{:}0)$$

$$- \sum B_1(a\ k_1\ l_1\ k_2{:}0)B(a\ l_1{:}0)$$

$$+ \sqrt{N-1} \sum B_2(a\ k_1\ k_2\ l{:}0)B(a\ l{:}0)$$

$$+ \sum B_1(k_1\ l_1\ l_2\ k_2{:}0)B(l_1\ l_2{:}0)$$

$$- \sum B_1(k_1\ l_1\ k_2\ l_2{:}0)B(l_1\ l_2{:}0)$$

$$- \sum B_1(l_1\ k_1\ l_2\ k_2{:}0)B(l_1\ l_2{:}0)$$

$$+ \sum B_1(l_1\ k_1\ k_2\ l_2{:}0)B(l_1\ l_2{:}0)$$

$$+ \sqrt{N-1} \sum B_2(k_1\ l_1\ l_2\ k_2{:}0)B(l_1\ l_2{:}0)$$

$$+ \sqrt{N-1}\sum B_2(l_1\ k_1\ k_2\ l_2{:}0)B(l_1\ l_2{:}0) + \cdots,$$

$$\sum_{\substack{m \\ (\varepsilon_{k_1}>0,\ \varepsilon_{k_2}<0)}} \langle C^{\dagger}_{k_1 m} C_{k_2 m}\rangle = \Big[\sum_{m} \langle C^{\dagger}_{k_2 m} C_{k_1 m}\rangle \Big]^{\dagger},$$

$$\sum_{\substack{m \\ (\varepsilon_{k_1}<0,\ \varepsilon_{k_2}<0)}} \langle C^{\dagger}_{k_1 m} C_{k_2 m}\rangle = \delta_{k_1 k_2} N |B(0)|^2$$

$$+ \delta_{k_1 k_2} N\sum |B(a\ l_1{:}0)|^2 - B(a\ k_2{:}0)B(a\ k_1{:}0)$$

$$+ \delta_{k_1 k_2} N\sum |B(l_1\ l_2{:}0)|^2 - \sum B(l_1\ k_2{:}0)B(l_1\ k_1{:}0)$$

$$+ \delta_{k_1 k_2} N\sum |B_1(a\ l_1\ l_2\ l_3{:}0)|^2$$

$$- \sum B_1(a\ l_1\ k_2\ l_2{:}0)B_1(a\ l_1\ k_1\ l_2{:}0)$$

$$- \sum B_1(a\ l_1\ l_2\ k_2{:}0)B_1(a\ l_1\ l_2\ k_1{:}0)$$

$$+ \sum B_1(a\ l_1\ k_2\ l_2{:}0)B_1(a\ l_1\ l_2\ k_1{:}0)$$

$$+ \sum B_1(a\ l_1\ k_1\ l_2{:}0)B_1(a\ l_1\ l_2\ k_2{:}0)$$

$$+ \delta_{k_1 k_2} N\sum |B_2(a\ l_1\ l_2\ l_3{:}0)|^2$$

$$- \sum B_2(a\ l_1\ k_2\ l_2{:}0)B_2(a\ l_1\ k_1\ l_2{:}0)$$

$$- \sum B_2(a\ l_1\ l_2\ k_2{:}0)B_2(a\ l_1\ l_2\ k_1{:}0) + \cdots, \quad (4\text{-}13)$$

where summations for l_1, l_2, etc. are performed over the same region as for the bases in Eq.(4-2). In the following, we derive $N(\infty)$ for arbitrary N in the form like Eq.(4-11), using Eq.(4-13) in the limiting case of $\varepsilon_a/\gamma \to \infty$.

It is very difficult to carry out the k-summations for $N(\infty)$ for arbitrary N and ε_a. In the following the wide-band limit and the limit of $\varepsilon_a/\gamma \to \infty$ are assumed in order to perform the k-summations. In the expression of $N(\infty)$, there are many denominators of a form like $(\varepsilon_k - \varepsilon_a + i m\gamma)$. In the above limits the factors can be rewritten as

$$\sum_k V^2 \frac{1}{\varepsilon_k - \varepsilon_a + i m\gamma} F(\varepsilon_k) = \frac{\Delta}{\pi} \int d\varepsilon \left[P\left(\frac{1}{\varepsilon - \varepsilon_a}\right) - i\pi\delta(\varepsilon - \varepsilon_a)\,\mathrm{sign}(m) \right] F(\varepsilon)$$

$$\frac{1}{(\varepsilon - \varepsilon_a + in\gamma)(\varepsilon - \varepsilon_a + im\gamma)} = \frac{\pi}{i(n-m)\gamma} [\mathrm{sign}(n) - \mathrm{sign}(m)]\,\delta(\varepsilon - \varepsilon_a). \quad (m \neq n) \qquad (4\text{-}14)$$

Thus, using the Eq.(4-13), we can show the expression of $N(\infty)$ for arbitrary N in those limits, that is

$$N(\infty) = \sum_m \langle \psi(\infty) | C_{am}^\dagger C_{am} | \psi(\infty) \rangle$$

$$= A_1 \sum_m \langle C_{am}^\dagger C_{am} \rangle + \sum_k A_2(k) \sum_m \langle C_{km}^\dagger C_{am} \rangle$$

$$+ \sum_{k_1 k_2} A_3(k_1, k_2) \sum_m \langle C_{k_1 m}^\dagger C_{k_2 m} \rangle. \qquad (4\text{-}15)$$

We note that, in order to show that Eq.(4-15) holds, we have to

use the expanded terms with respect to V for $\sum_m \langle C_{am}^\dagger C_{am} \rangle$ etc. as well as A_1, A_2 and A_3 and perform the k-summation partially for the second and third terms in Eq.(4-15). The expression (4-15) is verified in the expanded form up to V^8, and we believe that it is valid up to infinite order of V in the limit of $\varepsilon_a/\gamma \to \infty$ and the wide-band limit. Equation (4-15) has the same form as that for N=1 except the initial conditions. The manybody effects in $N \geqq 2$ are only in the initial condition B(0), etc. In the noninteracting case of N=1, the limit of $|\varepsilon_a|/\gamma \to \infty$ corresponds to the case where the memory effects dominates. Equation (4-15) expresses that the memory effect dominates also for arbitrary N in those limits. On the basis of the present result, we conjecture that the statement "In the limit of $\varepsilon_a/\gamma \to \infty$, the memory effect dominates" holds for arbitrary value of U, as far as the total charge, $N(\infty)=\sum_m \langle \psi(\infty) | C_{am}^\dagger C_{am} | \psi(\infty) \rangle$ of the atom is concerned.

A comment is made here on the 1/N expansion for the charge transfer problem (Brako and Newns 1985) that the $N \to \infty$ limit may lead to a rather strange situation. Because in the 1/N expression $N\Delta$ is kept equal to the constant Γ; Δ goes to 0 in the limit of $N \to \infty$. On the other hand, the memory factor for arbitrary N is $A_1=\exp(-\Delta/\gamma)$ not $\exp(-\Gamma/\gamma)$, so that the memory term stays at the initial value in the condition of constant $\Gamma=N\Delta$ and $N \to \infty$.

§5 Exact Calculation in Small System

§5-1 Manybody Bases for Small System

In the section (4), the total electron number on the atom is examined by the electron-hole pair expansion method, where the k-summations are made in the limit of $\varepsilon_a/\gamma \to \infty$. In this limit the Kondo effect and the valence fluctuation effect are ineffective. It is very interesting how these effects appear in the non-adiabatic charge exchange problem, though the Kondo effect would not play a significant role in the charge exchange problem (see the Hartree-Fock results for charge and spin variations). These effects come into the problem on $\varepsilon_a < 0$ and $\varepsilon_a \to 0$ for very large U. The case of $\varepsilon_a \to 0$ may correspond to the most difficult case to be analyzed with the electron-hole pair expansion. As another way to approach, we attempt to carry out the exact calculation of the time-dependent Newns-Anderson model in a small system with finite U, ε_a and γ, whose Hamiltonian is given by Eq.(2-2). Since the metallic states have the infinite degrees of freedom, infinite number of manybody bases are necessary for the manybody calculation. Because of this difficulty, we begin to study the exact manybody problem in small system, having an idea to apply the numerical renormalization group method (Wilson 1975) to this problem in the future step of this investigation.

The case is considered that there are M one-electron eigenestates at V=0, and its energy eigenevalues ε_k are

distributed at constant intervals in the range of "the bandwith" D. These one-electron eigenstates in the small system correspond to the metallic states, and there is the admixture V(t) between the M states and a single one-electron state on the atom with the energy level ε_a, where the k dependence of the admixture is neglected. The wavefunction of the whole system is described by the linear combination of such manybody states, that is,

$$\phi[\{l_i,\sigma_i\}] = \prod_i C^{\dagger}_{l_i\sigma_i}|0>, \qquad (5\text{-}1)$$

where $C^{\dagger}_{l_i\sigma_i}$ is the creation operator for the l_i-th one-electron state for spin σ_i (including the sate on the atom), $|0>$ is the vacuum state. The total spin S of electrons in the whole system is assumed to be S=0, and the total electron number is assumed to be one half of the total number of the one-electron states, that is, to be equal to M+1. This may be called the total system neutral. Under this condition, numerous manybody bases are necessary to calculate the wavefunction, that is,

M+1	the number of necessary bases
2	3
4	20
6	175
8	1764
10	19404
12	226512

(5-2)

Because of the memory space limit of our computer system at hand,

it is impossible to carry out the numerical calculation for the system with M+1 more than 8. Thus numerical calculations for M+1=8 are carried out.

§5-2 Numerical Results and Comparison with the Hartree-Fock Results

The structure of one-electron energy level is shown in Fig.(5-1) assumed D=12, ε_a=-2 and M+1=8. The time dependence of V(t) is assumed as Eq.(4-6) which corresponds to the sputtering case. Excitations of the electronic state in the metal may occur in energy of the order of γ ($\hbar$=1), which is a measure, in energy, of the disturbance by the moving atom, during the motion of the atom leaving from the metal surface. In the small system, however, the exitations with energy much less than the energy interval (=2 in Fig.(5-1)) do not occur. For this reason, the small system calculation discussed here is not valid for γ much less than 2, as an approximation to the large system. In a similar argument, for large γ (γ>>D), the finite band effects come into the results. In Fig.(5-2) - Fig.(5-5) the numerical results for U=6, ε_a=-2 with varing γ are compared with the results calculated in the Hartree-Fock approximation with the wide-band limit and there are also the Hartree-Fock results calculated in the small system. In the small system with the finite degrees of freedom, Δ in large system corresponds to

$$\Delta = \pi \frac{M}{D} V^2. \qquad (5\text{-}3)$$

The results for the total charge, the fraction of positive ion, neutral atom and negative ion are shown in Fig.(5-2)-Fig.(5-5), respectively. In order to discuss the dynamical effects, the results shown in Fig.(5-2)-Fig.(5-5) are shifted to coincide with each other at $\gamma=2$. The shifted results are shown in Fig.(5-6)-Fig.(5-9). Since the excitations occur in the energy range of order of γ as mentioned above, the finite-band effects are to be appreciable, when γ is much larger than D. Those are seen in $1/\gamma<1/3$ in Fig.(5-6)-Fig.(5-8), where the results of the wide-band limit deviate from those of the small system. In $1/\gamma>1/3$, however, the results except for the fraction of the negative ion show rather good fit, where the finite-band effects and the manybody effects are supposed to be small. On the other hand, the results for the fraction of the negative ion in Fig.(5-9) show that the dynamical effects in manybody calculation are remarkable compared with those in the two Hartree-Fock calculation, although the absolute values of the fraction is very small. From these results, we believe that the Hartree-Fock approximation is rather good approximation except for the fraction of the negative ion.

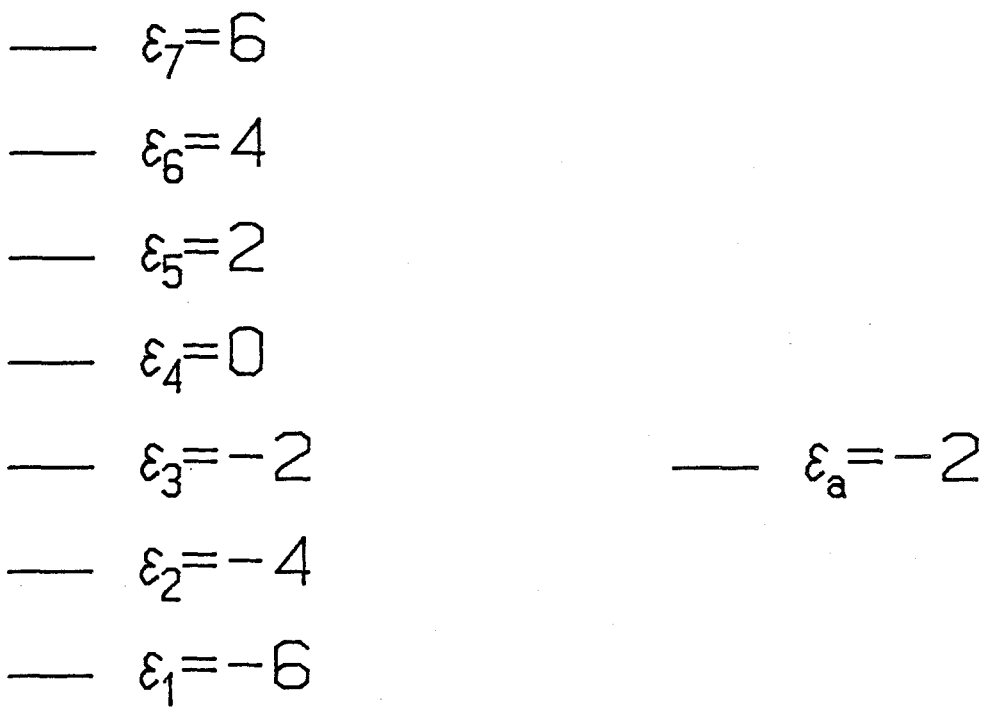

Fig.(5-1) The one-electron energy structure, D=12, ε_a=-2 and M+1=8.

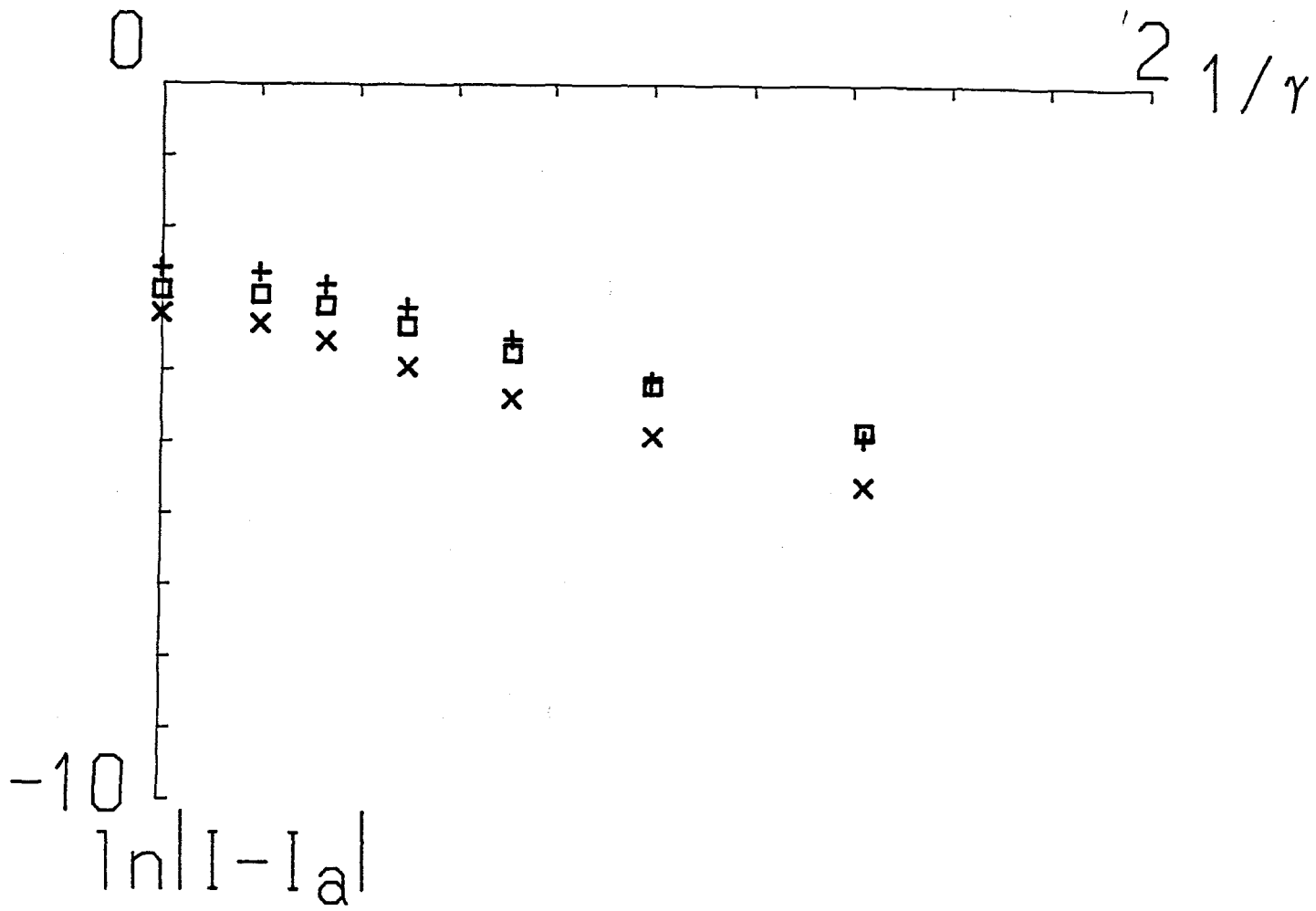

Fig.(5-2) The total electron number at $t=\infty$ versus $1/\gamma$. I_a represents the value at $\gamma \to 0$, that is, the adiabatic limit. (+): exact results in the small system for the parameters D=12, M+1=8, ε_a= -2 and V=0.5. (□): the Hartree-Fock approximation results in the small system. (×): the Hartree-Fock approximation results in the wide-band limit for ε_a=-2, U=6 and $\Delta=\pi(M/D)V^2=0.458\cdots$.

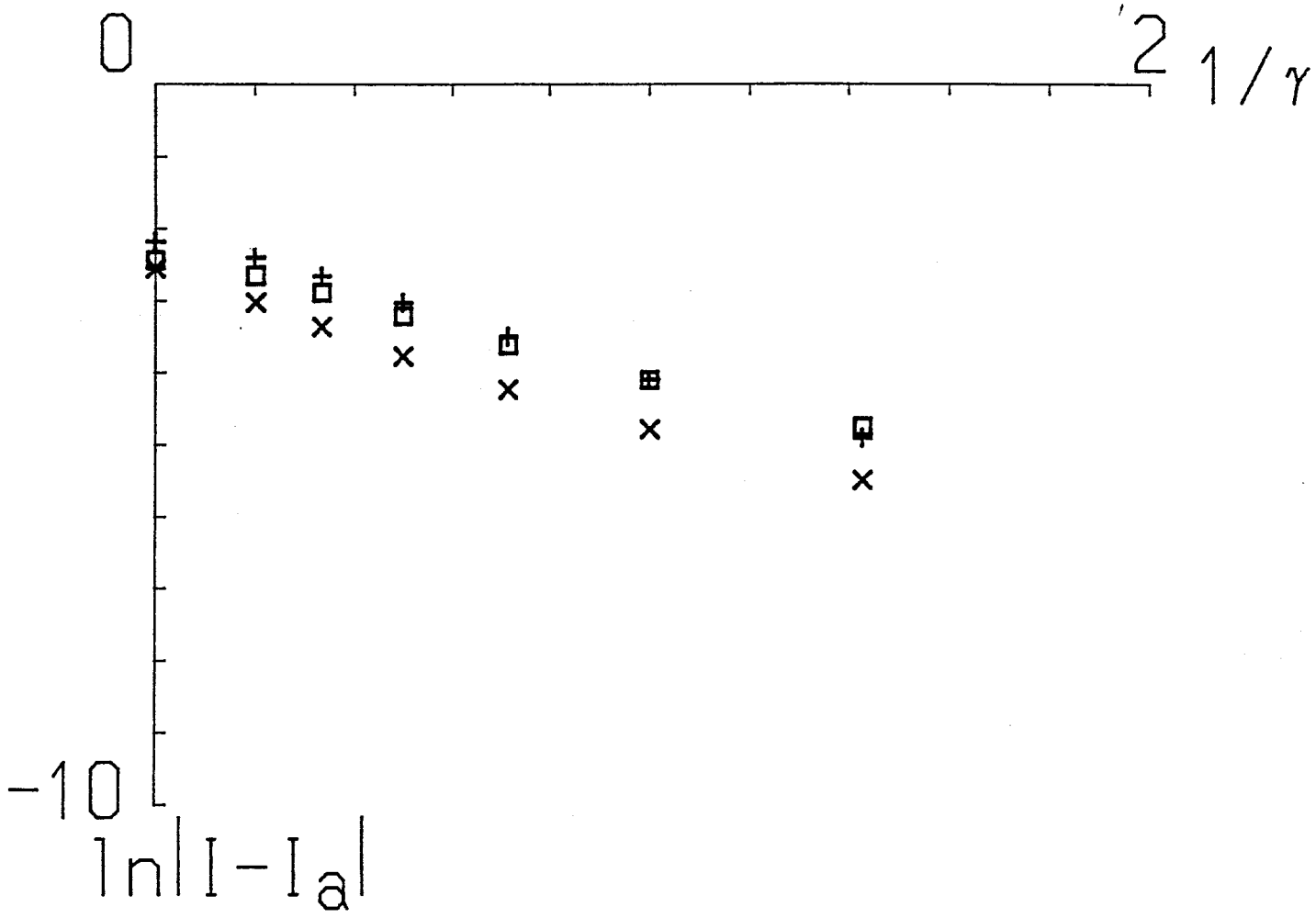

Fig.(5-3) The fraction of the positive ion, same as Fig.(5-2).

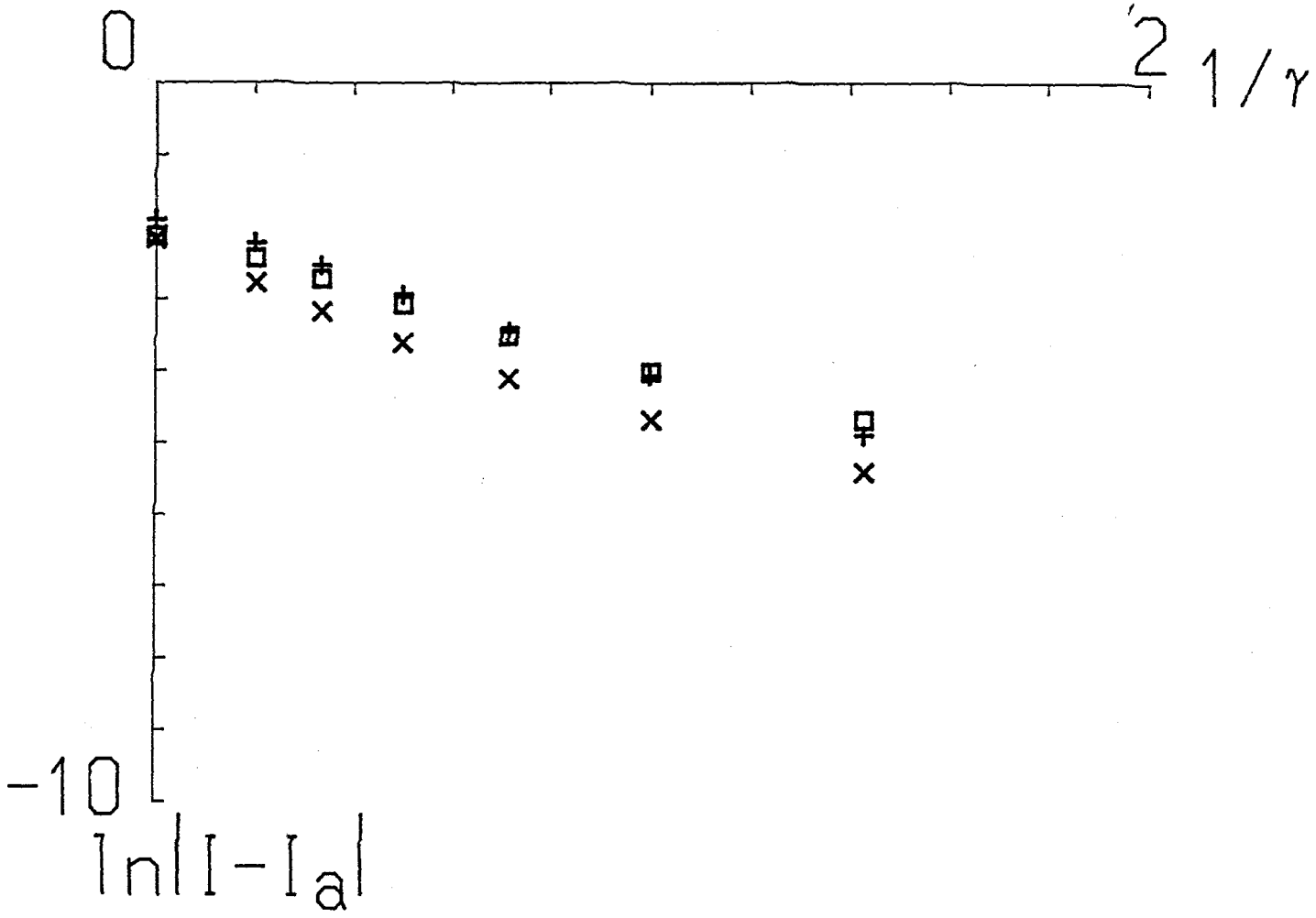

Fig.(5-4) The fraction of the neutral atom, same as Fig.(5-2).

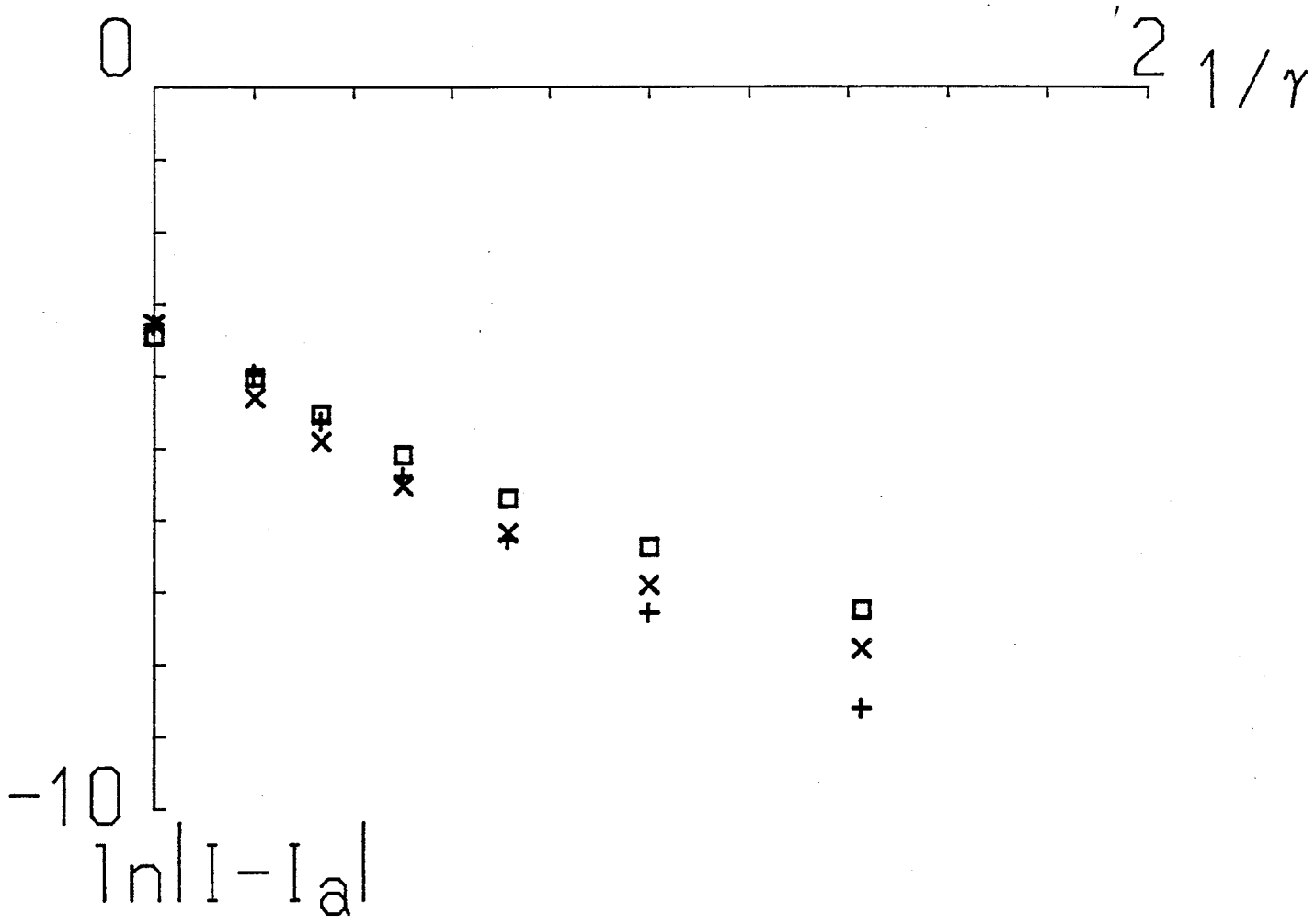

Fig.(5-5) The fraction of the negative ion, same as Fig.(5-2).

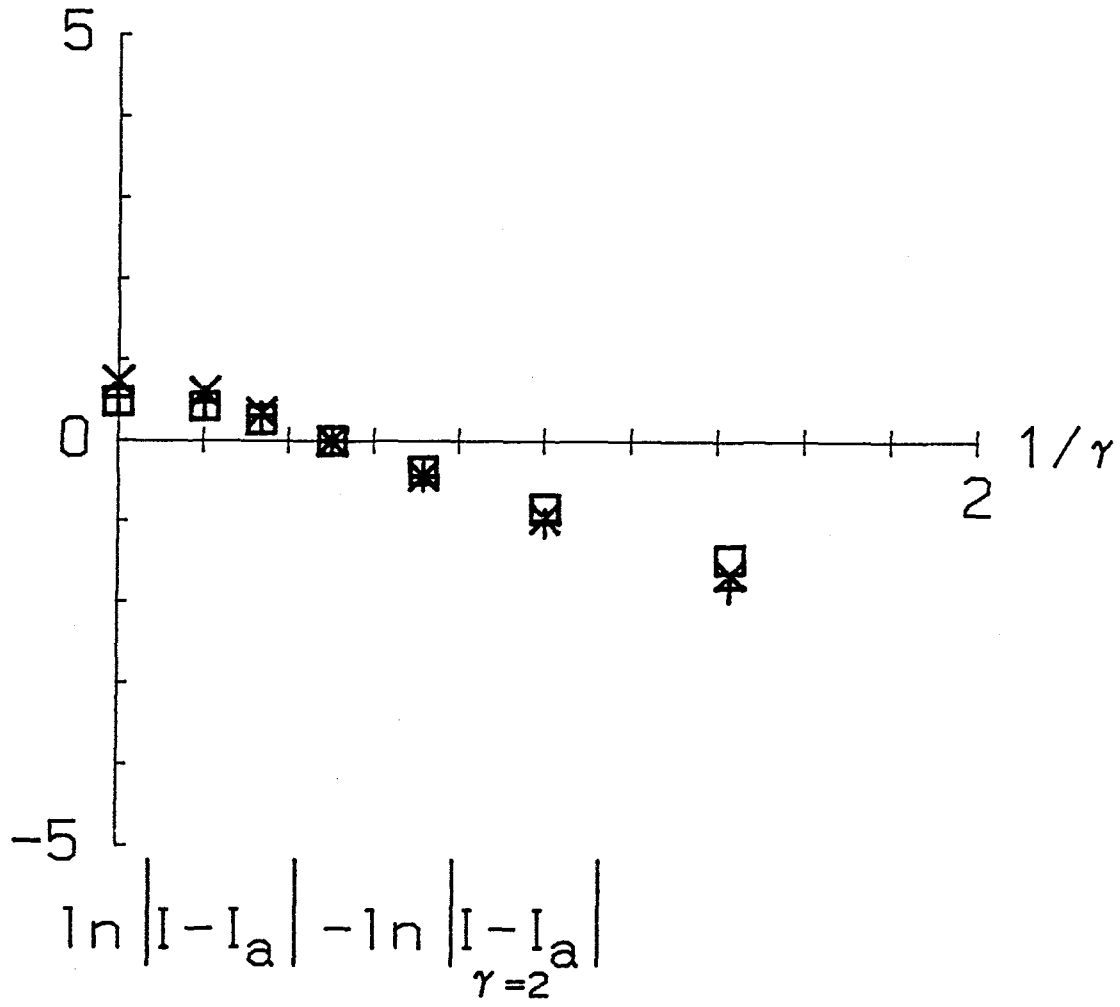

Fig.(5-6) The results for the total charge shifted to coincide with each other at $\gamma=2$, from Fig.(5-2).

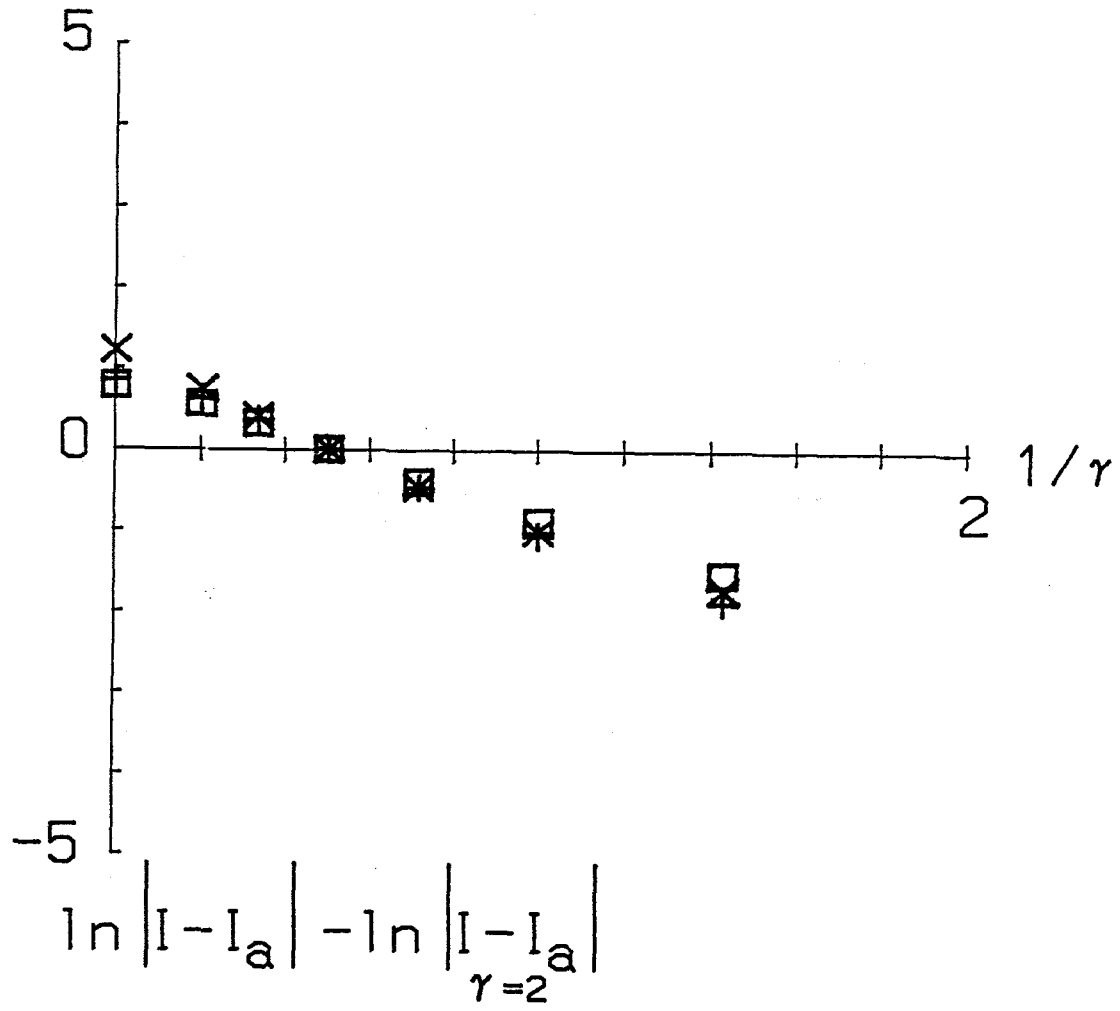

Fig.(5-7) The results for the fraction of the positive ion shifted to coincide with each other at $\gamma=2$, from Fig.(5-3).

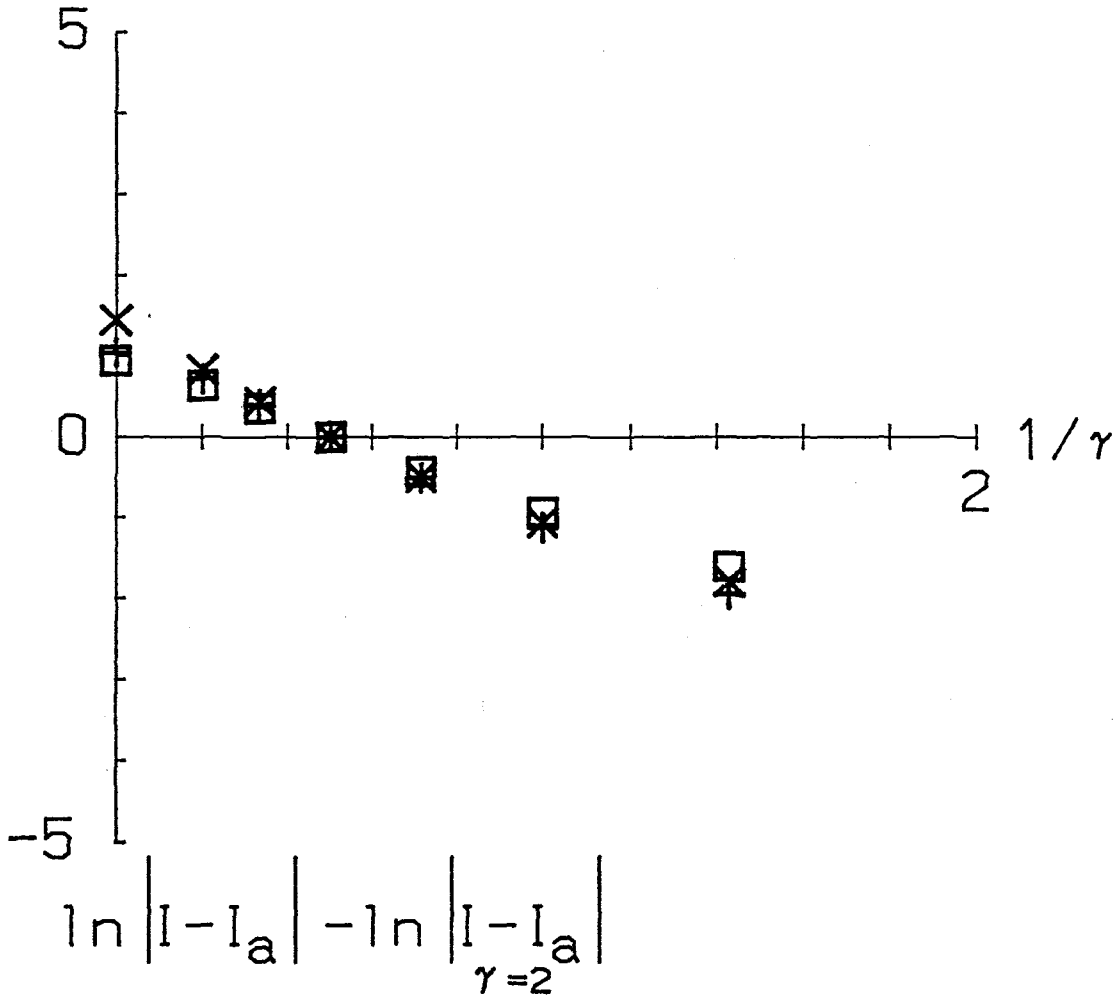

Fig.(5-8) The results for the fraction of the neutral atom shifted to coincide to each other at $\gamma=2$, from Fig.(5-4).

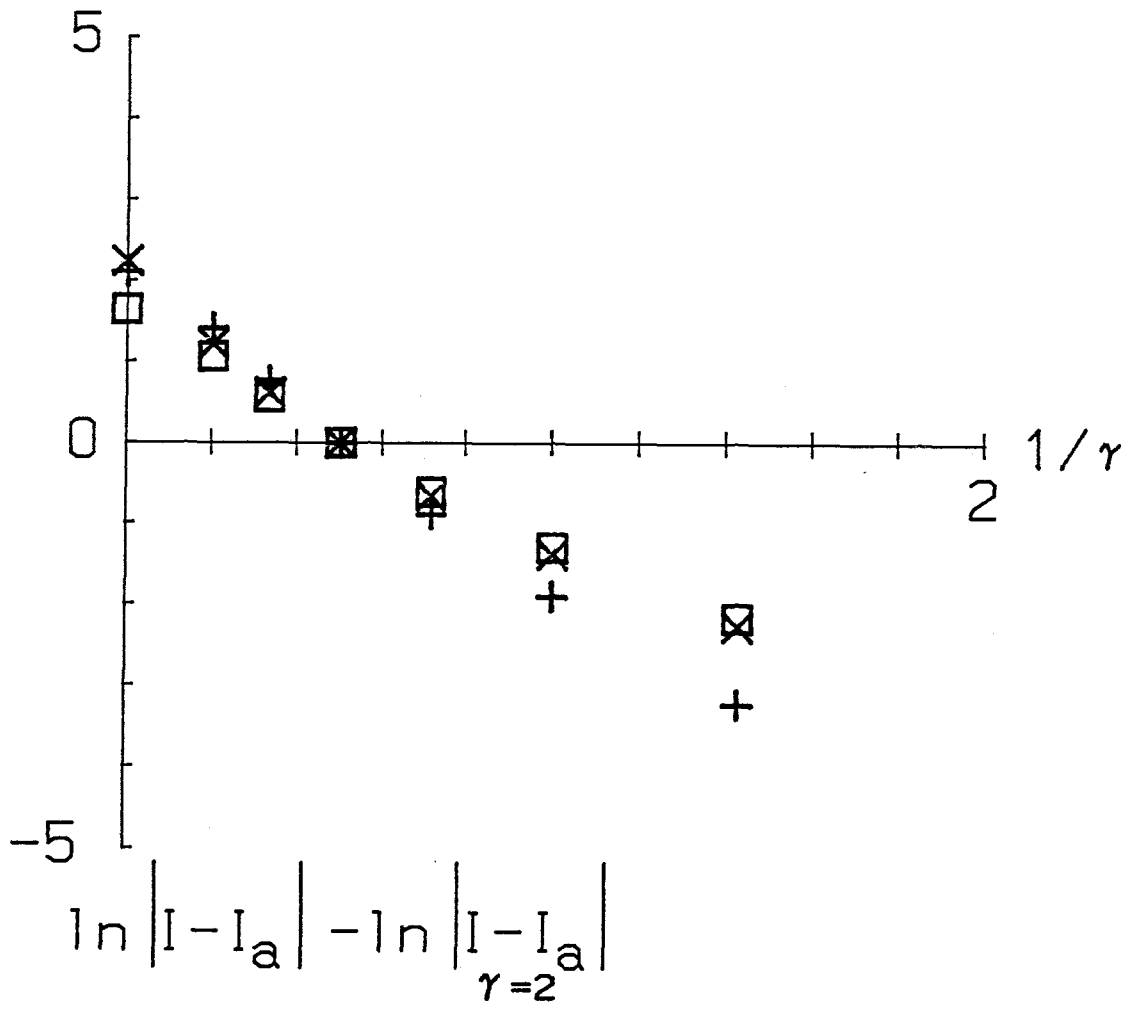

Fig.(5-9) The results for the fraction of the negative ion shifted to coincide to each other at $\gamma=2$, from Fig.(5-5).

§6 Discussion

In the section (3), the intraatomic Coulomb interaction has been treated in the Hartree-Fock approximation. In spite of the simplified assumptions, the various interesting effects of the interaction are found. However, when the initial conditions are same for both spin, the artificial parameter ε_m is necessary to be introduced, even if there is no external magnetic field. This parameter ε_m may be regarded as representing an effect due to the spin fluctuation on the atom. A problem remains to determine the value of ε_m, though, as it is seen in the subsection (3-2), the behavior after the growth of spin polarization started does not depend on the magnitude of ε_m. A manybody calculation, which keeps rotational invariance in spin space, does not need ε_m of course. We have tried in such a sence the two attempts the electron-hole pair expansion method and the calculations for the small system. The manybody effects, for instance the Kondo effect, or the valence fluctuation effect, come into the charge exchange problem in the case of $\varepsilon_m<0$ and $|\varepsilon_a|\to 0$, respectively, for large U, though, as it is pointed out in the section (2) and section (3), the Kondo effect may not be appreciable in the charge exchange. The analysis in the section (3) shows that the charge exchange is normal, but spin exchange indicates some anormaly related to the Kondo effect (see $\mathrm{Im}\lambda$ for large U). The condition of $\varepsilon_a\to 0$ corresponds to the most difficult case to be analyzed by the electron-hole pair expansion (the section (4)).

The calculation in the small system (the section (5)) is not so valid under the condition where $|\varepsilon_a|$ is less than the energy interval, because, in this case, there are no one-electron states of metal between ε_a and the Fermi level. In the case of γ less than the interval, the discrete energy system does not represent the true metal state. For these reasons, the numerical manybody calculation in the system with narrower energy interval is necessary to examine the many-body effects. On the other hand, the higher energy states of the metallic electron would not contribute significantly to the nonadiabatic charge exchange in the atom motion of smaller γ. From this observation, the numerical renormalization group method of Wilson (1975) is believed to be applied to this problem.

§7 Summary

The intraatomic Coulomb interaction effects for the charge transfer problem in the time-dependent Newns-Anderson model have been investigated by the Hartree-Fock approximation, the electron-hole pair expansion method and the brute force numerical method for small system.

In the Hartree-Fock approximation, it is found that 1) the spin polarization M(t) on the atom is described by the rate equation, when M(t) is small. 2) there is oscillatory convergence of $n_\sigma(t)$ to the equilibrium value when U is large. Furthermore the behavior of the oscillation is investigated in detail. 3) When the initial condition of $n_\sigma(t)$ are the same for both spin, the artificial parameter ε_m is necessary in order to break the symmetry in spin space.

In the limit of $\varepsilon_a/\gamma \to \infty$, it is obtained that the total charge $N(\infty)$ on the atom has the same expression for arbitrary orbital degeneracy N on the atom as that of the noninteracting case. In particular the memory effects dominate even for the arbitrary value of N.

By the numerical calculation for the small system, we believe that the Hartree-Fock approximation is rather good approximation except for the fraction of the negative ion, and the manybody effect is remarkable in the fraction of the negative ion.

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