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A study of the effect of surface bandwidth and other many-body effects in atom-surface collisions using a non-equilibrium Green's function technique

by

Sarah J. Steuber

A Thesis Submitted in Partial Fulfillment of the Requirements for the Degree

Master of Arts

Approved, Thesis Committee:

[Signatures]

Peter Nordlander, Chairman
Associate Professor of Physics

Jim Hannon
Professor of Physics

Randy Hulet
Associate Professor of Physics

Houston, Texas
May, 1995
Abstract

A study of the effect of surface bandwidth and other many-body effects in atom-surface collisions using a non-equilibrium Green's function technique

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We are studying the charge transfer in atom-surface scattering using a recently developed many-body theory. The final population of the atom is studied as a function of the surface workfunction, which has a strong effect on the final population. The effects caused by degeneracy, surface bandwidth and velocity are investigated. The formation of the Kondo peak, strongly controls both the initial population and the rate of charge transfer, and consequently the final population. The results show a strong degeneracy and velocity dependence for both the positive and negative ion. For the negative ion we also find a significant bandwidth dependence.
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Chapter 1

Introduction

In recent years much research, both experimental and theoretical, involving systems with charge transfer has been done. Quantum dots and arrays of quantum dots have generated intense interest recently since the charge transfer into and out of the dot can be controlled and easily studied. [1, 2, 3, 4, 5, 6, 7] Quantum dots feature discrete energy levels which interact with continuum bands. By controlling the relative levels of the Fermi Energy in the continuum bands on either side of the dot, the charge into and out of the dot can be controlled. Because quantized charge transfer can be observed theorists are eager to model this system. In order to model the system well the theory must be able to describe both discrete and continuum levels well.

The charge transfer between atoms, or small molecules, and surfaces has also been of considerable interest recently[8, 9, 10, 11, 12]. There are many processes that can be studied including sticking, desorption, and scattering. These systems are of particular interest because of the many experimental parameters that can be changed. For instance, by changing the substrate surface properties such as the density of states and bandwidth can be changed. Adding an adsorbate to the surface can change the workfunction in a controllable manner. The atom can be chosen to be either negative or positive ions. The type of atom chosen also determines the degeneracy of the atomic level. Finally the velocity of the atom can be controlled experimentally. Because of the many parameters in the system the charge transfer between atoms and surfaces is of much interest to theorists. In order to describe this system well we must, once again, use a theory that is able to describe both discrete and continuum levels well.
Until recently most work has been based on the time-independent, single level Anderson model[13, 14]. This model proved to be insufficient to deal with the strong effects of degeneracy and intra-atomic correlation which are present in even the most simple cases, due to spin degeneracy. The fully time-dependent, multilevel and spin Hamiltonian, however, is very complicated and impossible to solve analytically even in equilibrium. Much work has been focused on finding approximate solutions to this problem[15, 16, 17].

Recently a general method was developed for the approximate solution to the time-dependent Anderson model using non-equilibrium Green's Functions and the slave-boson method.[18, 19] It was shown that many-electron effects can strongly influence the charge transfer in atom surface scattering in typical situations. In a recent paper, the effects of many-electron interactions on the velocity dependence of charge transfer was investigated. It was shown that the final charge transfer probability at low velocities could be strongly enhanced in situations when the atom induces a Kondo resonance in the substrate.

The main focus of this work is to study the influence of many-body interactions on the workfunction dependence of charge transfer. We investigate how this workfunction dependence is influenced by degeneracy, atomic velocity and substrate band width. The physical origin of the charge transfer is investigated by analyzing the instantaneous spectral functions of the atomic levels. The results show that for a proper understanding of the workfunction dependence of charge transfer in atom-surface scattering, it is important to include many-electron effects.
Chapter 2

Theory

In order to study the interaction between atoms and surfaces we must have a good model to describe the system. The system we will study involves an ion, which has an N-fold degenerate level, desorbing from a metal surface. We assume that the energy, $\varepsilon$, of the atomic impurity level varies with distance from the surface, and therefore with time. We are particularly interested in studying the many-body effects of the system by changing the degeneracy, $N$, of the system. The system we are studying is described well by the time dependent Anderson Hamiltonian,[20]

$$H(t) = \sum_a \varepsilon_a(t) n_a(t) + \frac{1}{2} \sum_{a \neq a'} U_{a,a'} n_a(t) n_{a'}(t) + \sum_k \varepsilon_k n_k(t) + \sum_{a,k} \left[ V_{a,k}(t) c_k^\dagger(t) c_a(t) + \text{H.c.} \right],$$

(2.1)

where $a$ denotes both spin and spatial quantum numbers for the atom and $k$ denotes both spin and spatial quantum numbers for the substrate. In this second quantization Hamiltonian the operators $c^\dagger$ and $c$ represent the fermion creation and annihilation operators for the states $a$ or $k$. The operator $n$ is simply $c^\dagger c$, the number operator. The first and third summations describe the bare atomic and continuous substrate levels. The second summation is the intra-atomic correlation term. In this term the Hubbard $U$ describes the energy required to multiply occupy a degenerate atomic level. The fourth term describes the tunneling between atomic states and the surface conduction band, where $V$ is the hopping matrix element. There are two limiting cases of interest for this Hamiltonian. The first is the large $U$ case. By large $U$ we mean $\varepsilon_a + U \gg \varepsilon_F + kT$ and $\varepsilon_a + U \gg \varepsilon_F + \Gamma$, where $\varepsilon_F$ is the Fermi energy of the surface and $\Gamma$ is the atomic level width. In this case the total population of the degenerate atomic levels is restricted to a maximum of one electron. The other limiting case is the $U = 0$ case, which represents the case of a singly degenerate level,
N=1. This case is described by the single-level Anderson model. In this case the Hamiltonian is reduced to

\[ H(t) = \epsilon_a(t)n_a(t) + \sum_k \epsilon_k n_k(t) + \sum_k [V_{ak}(t)c_k^\dagger(t)c_a(t) + \text{H.c.}] \]  \hspace{1cm} (2.2)

Both cases should be studied to fully understand the model.

2.1 \( U = 0 \) case

Without the intra-atomic correlation term, the Hamiltonian (2.2) can be solved exactly using an equations of motion technique, as was first done in 1976[13]. The single-level Anderson model can also be solved using a Green's function technique.

2.1.1 Non-equilibrium Green's function technique

Kadanoff and Baym[21] developed a non-equilibrium Green's function technique for the description of non-equilibrium processes. This method turns out to be very useful for modeling the system we are studying. Using this method, exact equations for the double-time Green's function can be developed. For the system we are studying the double-time Green's function is the thermal average

\[ iG_a(t, t') = \langle Tc_a(t)c_a^\dagger(t') \rangle \]  \hspace{1cm} (2.3)

It is more useful, however, to study the equations for the analytical pieces \( G_a^>(t, t') \) and \( G_a^<(t, t') \) which are given by

\[ iG_a(t, t') = G_a^>(t, t')\theta(t - t') - G_a^<(t, t')\theta(t' - t). \]  \hspace{1cm} (2.4)

The time-ordering operator \( T \) and the step functions \( \theta \) operate along a complex contour \( c \). There are many choices of contour depending on what specific problem is being solved.[22]
To get the equations needed to solve the Hamiltonian, we start with Dyson's equations for the double time Green's function $G$:

$$
\left[i\frac{\partial}{\partial t} - \varepsilon_a(t)\right] G_a(t, t') = \delta(t - t') + \int_c d\bar{t} \Sigma_a(t, \bar{t}) G_a(\bar{t}, t'),
$$

(2.5)

$$
\left[-i\frac{\partial}{\partial t'} - \varepsilon_a(t')\right] G_a(t, t') = \delta(t - t') + \int_c d\bar{t} G_a(t, \bar{t}) \Sigma_a(\bar{t}, t'),
$$

(2.6)

and an approximation for the self-energy of the atomic level, $\Sigma_a$, which describes the interaction between the atomic state and the continuum states. Like the Green's function $G$, the self-energy $\Sigma$ also has analytical pieces $\Sigma^<$ and $\Sigma^>$ which are defined in the same manner. The Eqs. (2.5) and 2.6 can be converted into equations for the analytical pieces of the Green's function $G^<_a(t, t')$ and $G^>_a(t, t')$ by using a set of identities[23, 24, 18]. The Green's functions $G^<_a(t, t')$ and $G^>_a(t, t')$ are the physical real-time correlation functions. Their equal-time values represent, respectively, the electron or hole population of the atomic impurity level as a function of time. The real-time Dyson's equations for $G^<$ are

$$
\left[i\frac{\partial}{\partial t} - \varepsilon_a(t)\right] G^<_a(t, t') = \int_{-\infty}^{\infty} d\bar{t} \left[\Sigma^R_a(t, \bar{t}) G^<_a(\bar{t}, t') + \Sigma^<_a(t, \bar{t}) G^>_a(\bar{t}, t')\right],
$$

(2.7)

$$
\left[-i\frac{\partial}{\partial t'} - \varepsilon_a(t')\right] G^<_a(t, t') = \int_{-\infty}^{\infty} d\bar{t} \left[G^R_a(t, \bar{t}) \Sigma^<_a(\bar{t}, t') + G^<_a(t, \bar{t}) \Sigma^>_a(\bar{t}, t')\right].
$$

(2.8)

In the previous equations $G^R_a$ and $G^A_a$ are the retarded and advanced Green's functions which are defined by

$$
iG^R_a(t, t') = [G^>_a(t, t') + G^<_a(t, t')]*\theta(t - t'),
$$

$$
-iG^A_a(t, t') = [G^>_a(t, t') + G^<_a(t, t')]*\theta(t' - t).
$$

(2.9)

The retarded and advanced self-energies, $\Sigma^R_a$ and $\Sigma^A_a$ are defined similarly. We see that the equations (2.7) and (2.8) are related in a simple manner. Either equation can be obtained from the other by simply switching the order of $G$ and $\Sigma$ and by
switching the advanced and retarded labels. In the future we will only write one of
the pair of equations.

One can obtain the advanced and retarded Green's functions by solving the con-
ventional real-time Dyson's equation

\[
\left[i \frac{\partial}{\partial t} - \varepsilon_a(t)\right] G_a^{A,R}(t, t') = \delta(t = t') + \int_{-\infty}^{\infty} d\bar{\tau} \Sigma_a^{A,R}(t, \bar{\tau}) G_a^{A,R}(\bar{\tau}, t'),
\]

(2.10)

and by using the boundary conditions that \( G_a^A(t, t') = 0 \) for \( t > t' \), and \( G_a^R(t, t') = 0 \)
for \( t < t' \). The population of the impurity level is simply the equal time component of
the "less than" Green's functions, \( G_a^<(t, t) = n_a(t) \) which can be shown from Eqs. (2.3)
and (2.4).

2.1.2 Exact solution

The \( U = 0, N = 1 \) problem can be solved using Dyson's equations and the self-
energies. An exact expression for the self-energies can be written as

\[
\Sigma_a(t, t') = \sum_{k, k'} V_{ak}(t) g^{(0)}_{kk'}(t, t') V_{ak}(t'),
\]

(2.11)

where \( g^{(0)} \) is the unperturbed Green's function for the substrate electrons. This
can be simplified by assuming that the hopping matrix element can be separated,
\( V_{ak}(t) = V(\varepsilon_k) u(t) \). Using this assumption we can write the level width

\[
\Gamma_a(\varepsilon, t) = 2\pi \sum_k |V_{ak}(t)|^2 \delta(\varepsilon - \varepsilon_k),
\]

(2.12)

as

\[
\Gamma_a(\varepsilon, t) = 2\pi \rho(\varepsilon) |V(\varepsilon) u(t)|^2.
\]

(2.13)

Using this the analytical pieces of the self-energy can be written as

\[
\Sigma_a^\Xi(t, t') = \sqrt{\Gamma_a(t)\Gamma_a(t')} f^{\Xi}(t - t'),
\]

(2.14)
where we have defined
\[ \bar{\Gamma}_a(t) = \frac{\int \Gamma_a(\varepsilon, t) d\varepsilon}{\int \xi(\varepsilon) d\varepsilon}, \] (2.15)
and the dimensionless shape function \( \xi(\varepsilon) \) is proportional to \( |V(\varepsilon)|^2 \rho(\varepsilon) \). We have also defined
\[ f^\xi(\tau) = \int_{-D}^D \frac{d\varepsilon}{2\pi} f^\xi(\varepsilon) e^{-i\varepsilon \tau}, \] (2.16)
where \( f^<(\varepsilon) \) is the Fermi function and \( f^>(\varepsilon) = 1 - f^<(\varepsilon) \). Using these expressions for the self-energy, Dyson's equation for the \( U = 0 \) case becomes
\[ i \frac{\partial}{\partial t} \bar{G}^<(t, t') = -i \frac{\bar{\Gamma}_a(t)}{2} \bar{G}^<(t, t') + \int_{-\infty}^{\infty} d\tau \sqrt{\bar{\Gamma}_a(t) \bar{\Gamma}_a(\tau)} \bar{f}^<(t, \tau) \bar{G}^A(t, t'), \] (2.17)
where we have introduced the functions
\[ \bar{G}_a(t, t') = G_a(t, t') \exp \left[ i \int_{t'}^{t} d\tau \varepsilon_a(\tau) \right], \] (2.18)
and
\[ \bar{f}_a(t, t') = f_a(t - t') \exp \left[ i \int_{t'}^{t} d\tau \varepsilon_a(\tau) \right]. \] (2.19)
In the \( U = 0 \) case the advanced Green's function can be solved exactly yielding
\[ \bar{G}^A_a(t, t') = i \theta(t' - t) \exp \int_{t'}^{t} d\tau \frac{\bar{\Gamma}_a(\tau)}{2}. \] (2.20)

Using this, Dyson's equation becomes
\[ i \frac{\partial}{\partial t} \bar{G}^<(t, t') = -i \frac{\bar{\Gamma}_a(t)}{2} \bar{G}^<(t, t') \] (2.21)
\[ + \int_{-\infty}^{\infty} d\tau \sqrt{\bar{\Gamma}_a(t) \bar{\Gamma}_a(\tau)} \bar{f}^<(t, \tau) \exp \left[ \int_{t'}^{t} d\tau \frac{\bar{\Gamma}_a(\tau)}{2} \right]. \]

The occupation of the atomic level \( |a\rangle \), \( n_a(t) = G^<(t, t) \), can be calculated from this equation. In the limit of small \( \bar{\Gamma}_a \) and low velocities a rate equation can be derived for \( n_a \). In the general case, the Full partial differential equation must be solved.
2.2 Large $U$ case

The large $U$ case describes a system where it is impossible to place more than one electron on the atom. For instance a positive ion can be neutralized but not become a negative ion, and a neutral atom can become a negative ion but cannot be doubly ionized. This describes a large number of real systems. To understand why this is the case we look at a system such as the hydrogen ion near a metal surface. The hydrogen ion has a doubly degenerate level, due to spin degeneracy, below the Fermi energy. The hydrogen ion can be neutralized by an electron from the Fermi energy resulting in a gain $\varepsilon_F - \varepsilon_H$ in energy. In order to make the negative hydrogen ion, however, would require $\varepsilon_F - (\varepsilon_H + U)$, which is often $> 0$, of energy. For many systems this amount of energy is large enough that both $\varepsilon_H + U \gg \varepsilon_F + kT$ and $\varepsilon_H + U \gg \varepsilon_F + \Gamma$ are satisfied. When this is the case we can take $U$ to be infinity, and restrict the atomic population to a single electron.

In order to simplify Eq. (2.1) in the $U = \infty$ limit we use the slave-boson method.[18, 25] In this method the hopping term $c_k^\dagger(t)c_a(t)$ is replaced by $c_k^\dagger(t)c_a(t)b^\dagger(t)$ where $b(t)$ is the boson annihilation operator which describes a massless boson. With this change we see that whenever an electron tunnels from the atom to the surface we create a boson, and whenever an electron tunnels from the surface to the atom we destroy a boson. By adding the restriction that $Q_B = 1$ where

$$Q_B \equiv \sum_a n_a + n_B,$$

and $n_B = b^\dagger b$, we can drop the intra-atomic correlation term. The resulting Hamiltonian is

$$H(t) = \sum_a \varepsilon_a(t)n_a(t) + \sum_k \varepsilon_k n_k(t) + \sum_{ak} [V_{ak}(t)c_k^\dagger(t)b^\dagger(t)c_a(t) + H.c.].$$

The $Q_B = 1$ restriction satisfies the $U = \infty$ limit by preventing more than one electron from occupying an atomic state at one time. With only one atomic state
occupied at a time the $U$ term is always 0 and can be dropped. Since only the $Q_B = 1$ subspace of the Hamiltonian is physically relevant, the projecting method described by Langreth-Nordlander [18] can be used to project Dyson's equation into this subspace.

2.2.1 Self-energies

The self-energies used for the calculations are the ones used previously by Langreth and Nordlander[18]. A diagrammatic representation of the self-energies is shown in Figure 2.1. These self-energies describe the reaction between the atom and the surface.

![Diagram](image)

**Figure 2.1** (a) Self-energy for the atomic state $|a\rangle$ and (b) self-energy for the slave-boson state. The solid line denotes the Green's function for an atomic state. The dashed line denotes the Green's function for the slave-boson state. The wavy line denotes the Green's function for the conduction electrons.

by showing that when an electron tunnels from the atom to the surface a boson is created, and a boson is destroyed when an electron tunnels from the surface to the
atom. These self-energies in principle allow for the Hamiltonian to be non-diagonal in $a$. The quality of this self-energy expression is discussed in a paper by Shao, Langreth, and Nordlander[19].

In the notation we use, $B$ represents the slave boson functions, $G_{aa'}$ represents the atomic state functions and $G_{kk'}$ represents the substrate electron functions. The $>_{i},<_j, A$, and $R$, superscripts indicate whether the function is "greater", "less", advanced, or retarded. The self-energy of the atomic states, shown in figure 2.1 (a) can be written as

$$\Sigma_{aa'}^{\xi}(t, t') = K_{aa'}^{\xi}(t, t') B^{\xi}(t, t').$$

(2.24)

The self-energy for the slave boson shown in figure 2.1 (b) can be written as

$$\Pi^{\xi}(t, t') = \sum_{aa'} K_{aa'}^{\xi}(t', t) G_{aa'}^{\xi}(t, t').$$

(2.25)

In these two expressions $K_{aa'}^{\xi}(t, t')$ is defined to be

$$K_{aa'}^{\xi}(t, t') = \sum_{k} \tilde{V}_{ak}(t) f^{\xi}(\varepsilon_{k}) \tilde{V}_{a'k}(t')$$

(2.26)

where $\tilde{V}_{ak}(t) = V_{ak}(t) \exp(i\varepsilon_{kt})$. The advanced and retarded self-energies are given by

$$\Sigma_{aa'}^{RA}(t, t') = K_{aa'}^{>}(t, t') B^{RA}(t, t'),$$

(2.27)

$$\Pi^{RA}(t, t') = \sum_{aa'} K_{aa'}^{<}(t', t) G_{aa'}^{RA}(t, t').$$

(2.28)

These self-energies have all been projected onto the $Q_{B} = 1$ subspace required by the slave boson technique. We notice that in Eq. (2.26) that the substrate functions $G_{kk'}^{\xi}(t, t')$ have been replaced by their unperturbed forms $\delta_{kk'} f^{\xi}(\varepsilon_{k}) \exp(-i\varepsilon_{k}(t - t'))$. This substitution is not an approximation but is required by the projection onto the $Q_{B} = 1$ subspace.

The kernel $K$ can be expressed in terms of the function $\tilde{\Gamma}$, Eq. (2.15), as in the $U = 0$ case

$$K_{aa'}^{\xi}(t, t') = \delta_{aa'} \sqrt{\tilde{\Gamma}_{a}(t)} \tilde{\Gamma}_{a}(t') f^{\xi}(t - t').$$

(2.29)
2.2.2 Dyson’s equations

Using the self-energies for the atomic and slave boson states we can generate Dyson’s equations (2.7) and (2.10, for the \( U = \infty \) system. The retarded Green’s function Dyson’s equation for the atomic states is

\[
\left[ i \frac{\partial}{\partial t} - \varepsilon_a(t) \right] G_{aa'}^{R}(t, t') = \delta_{aa'}\delta(t-t') + \sum_{a''} \int_{-\infty}^{\infty} d\tilde{t} K_{aa''}^{\geq}(t, \tilde{t}) B^{R}(t, \tilde{t}) G_{a'a''}^{R}(\tilde{t}, t').
\] (2.30)

Dyson’s equation for the retarded slave boson propagator is

\[
i \frac{\partial}{\partial t} B^{R}(t, t') = \delta(t-t') + \sum_{a''} \int_{-\infty}^{\infty} d\tilde{t} K_{a'a''}^{\leq}(\tilde{t}, t) G_{a''}^{R}(t, \tilde{t}) B^{R}(\tilde{t}, t')
\] (2.31)

The advanced Green’s function can be obtained directly from the retarded Green’s function by reversing the two time arguments and taking the complex conjugate. Dyson’s equation for the ”less than” Green’s function can also be written exactly using the expressions for the self-energies obtained in the previous section. For the atomic states the ”less than” Green’s function satisfies

\[
\left[ i \frac{\partial}{\partial t} - \varepsilon_a(t) \right] G_{aa'}^{\leq}(t, t') = \sum_{a''} \int_{-\infty}^{\infty} d\tilde{t} K_{aa''}^{\geq}(t, \tilde{t}) B^{R}(t, \tilde{t}) G_{a'a''}^{\leq}(\tilde{t}, t') + \sum_{a''} \int_{-\infty}^{\infty} d\tilde{t} K_{aa''}^{\leq}(t, \tilde{t}) B^{\leq}(t, \tilde{t}) G_{a''}^{A}(\tilde{t}, t'),
\] (2.32)

and for the slave boson state the ”less than” Green’s function satisfies

\[
i \frac{\partial}{\partial t} B^{\leq}(t, t') = \sum_{a''} \int_{-\infty}^{\infty} d\tilde{t} \left[ K_{a'a'}^{\leq}(\tilde{t}, t) G_{aa'}^{R}(t, \tilde{t}) B^{\leq}(\tilde{t}, t') + K_{a'a}^{\geq}(\tilde{t}, t) G_{a'a'}^{\leq}(t, \tilde{t}) B^{A}(\tilde{t}, t') \right]
\] (2.33)

Dyson’s equations can be simplified by introducing a function similar to ones introduced in the \( U = 0 \) case,

\[
\check{G}_{aa'}(t, t') \equiv G_{aa'}(t, t') \exp \left[ i \int_{t}^{t'} d\tau \varepsilon_a(\tau) \right].
\] (2.34)

In this expression \( t_0 \) can be any fixed time, and \( \check{G} \) can be either a Green’s function of \( K_{aa'}^{\geq} \). The retarded and advanced Green’s functions can be further simplified by
introducing \( g_{aa'}(t, t') \) and \( b(t, t') \) and by making the following definitions

\[
\begin{align*}
\tilde{G}_{aa'}^R(t, t') & \equiv -i\theta(t - t')g_{aa'}(t, t'), \\
\tilde{G}_{aa'}^A(t, t') & \equiv i\theta(t' - t)g_{aa'}(t, t'),
\end{align*}
\] (2.35)

and

\[
\begin{align*}
B^R(t, t') & \equiv -i\theta(t - t')b(t, t'), \\
B^A(t, t') & \equiv i\theta(t' - t)b(t, t').
\end{align*}
\] (2.36)

These new Green's functions satisfy the conditions that \( g_{aa'}(t, t) = \delta_{aa'} \) and \( b(t, t) = 1 \), which arise from the commutation relations at equal time[22]. We also notice the following relation:

\[
\begin{align*}
g_{aa'}(t', t) & = g_{aa'}^*(t, t'), \\
b(t', t) & = b^*(t, t').
\end{align*}
\] (2.37)

Using these equations the advanced Green's functions are trivially obtained from the retarded Green's function so it is only necessary to calculate the retarded Green's function. Dyson's equations for \( g_{aa'}(t, t') \) and \( b(t, t') \) for \( t \geq t' \) are

\[
\frac{\partial}{\partial t} g_{aa'}(t', t) = -\sum_{a''} \int_{t'}^{t} d\tilde{t} \tilde{K}_{aa''}(\tilde{t}, \tilde{t}) b(\tilde{t}, \tilde{t}) g_{a''a'}(\tilde{t}, t),
\] (2.38)

and

\[
\frac{\partial}{\partial t} b(t, t') = -\sum_{a} \int_{t}^{t'} d\tilde{t} \tilde{K}_{a}^{<}(\tilde{t}, \tilde{t}) g_{aa'}(\tilde{t}, \tilde{t}) b(\tilde{t}, t').
\] (2.39)

Using these equations and the previous relationship \( g_{aa'}(t, t') \) and \( b(t, t') \) can be determined for all \( t \) and \( t' \). Using this notation the "less than" Green's functions can be written as

\[
\frac{\partial}{\partial t} \tilde{G}_{aa'}^{<}(t, t') = \sum_{a''} \int_{-\infty}^{t'} d\tilde{t} \tilde{K}_{aa''}^{<}(\tilde{t}, \tilde{t}) B^{<}(\tilde{t}, \tilde{t}) g_{a''a'}^{*}(t', \tilde{t}) - \\
\sum_{a''} \int_{-\infty}^{t} d\tilde{t} \tilde{K}_{aa''}^{>}(\tilde{t}, \tilde{t}) b(\tilde{t}, \tilde{t}) \tilde{G}_{a''a'}^{<}(\tilde{t}, t'),
\] (2.40)
and

\[
\frac{\partial}{\partial t} B^<(t, t') = \sum_{aa'} \int_{-\infty}^{t'} d\bar{t} \bar{K}_{aa'}^>(\bar{t}, t) \bar{G}_{aa'}^<(t, \bar{t}) b^*(t', \bar{t}) - \sum_{aa'} \int_{-\infty}^{t} d\bar{t} \bar{K}_{aa'}^>(\bar{t}, t) g_{aa'}(t, \bar{t}) B^<(\bar{t}, t'),
\]

(2.41)

where the * means complex conjugate. The populations of the atomic and slave boson states can be obtained from the equal time components of their respective Green's functions. The population is found by first solving for the retarded Green’s functions and then solving for the “less than” Green’s functions.

2.2.3 Calculational method

In order to solve Dyson’s equations numerically they must be discretized[19]. In order to accomplish this each double-time Green’s function is represented by a two-dimensional matrix. There are several features of the equations which help to reduce the amount of memory required by the matrices. First we note that the advanced Green’s function does not need to be stored since it is obtained directly from the retarded Green’s function. The boundary conditions of \( t = t' \) are known. We can therefore store the retarded Green’s functions in triangular matrices. By making use of the fact that \( G_{aa'}(t, t') = [G_{a'a}(t', t)]^* \), the “less than” Green’s functions can also be stored in triangular matrices. We can therefore save storage space by storing both the retarded and "less than" Green’s functions in the same matrix.

In order to maintain accuracy we must use very small time steps in the integrations. In many calculations we can reduce the size of the matrix without reducing the number of time steps by noting that for slow velocities and narrow widths the Green’s functions tend to be localized around the equal time components. This means that the matrix in time tends to be band diagonal. By only storing the Green’s function in a matrix the size of the diagonal band we can save storage space. This smaller
matrix is then propagated along the diagonal of the larger time matrix. This method does not reduce the accuracy of the calculation provided the smaller matrix does not cut off any matrix elements larger than the error caused by the discrete integrals. A discussion of the accuracy of the method and the computational effort can be found in reference [19].

2.2.4 Spectral functions

The instantaneous spectral functions presented in this work are calculated from the two-particle correlation function

$$A^a(t, t') = G^a(t, t') b(t', t). \quad (2.42)$$

The Fourier transform of this correlation function, using the new variables $T = \frac{1}{2}(t+t')$ and $\tau = t - t'$, is the spectral density of occupied states:

$$\rho_{\text{occ}}^a(\omega, T) = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\tau A^a(\tau/2, T - \tau/2) \exp[i\omega\tau]. \quad (2.43)$$

The spectral function is is the probability that an electron tunneling from state $|a\rangle$ to the continuum at time $T$ will have an energy $\omega$ in the continuum. Looking at Eq. (2.42) we see that the equal time correlation function is:

$$A^a(t, t) = G^a(t, t)b(t, t) = G^a(t, t) = n_a(t). \quad (2.44)$$

This requires that the normalization of $\rho_{\text{occ}}^a$ is:

$$\int_{-\infty}^{\infty} d\omega \rho_{\text{occ}}^a(\omega, T) = n_a(t). \quad (2.45)$$

In the results presented later we are using the total population of the atom so we will use the total occupied spectral weight function for the atomic states. which is defined as

$$f_{\text{occ}}(\omega, T) = \sum_a \rho_{\text{occ}}^a(\omega, T). \quad (2.46)$$
2.3 Current work

The calculations, presented in this work, were performed using the following trajectory

\[ Z(t \leq 0) = 3 \text{a.u.} \]
\[ Z(t > 0) = Z(0) + vt, \tag{2.47} \]

where \( Z \) is the distance from the jellium edge. This trajectory models a desorption experiment where the ion is initially in equilibrium with the surface and then at some time, \( t \), moves away from the surface with constant velocity \( v \). The surface is modeled using the jellium model[26] with a parabolic density of states which is described by:

\[ \xi(\varepsilon) = \frac{3}{2} \left(1 - \varepsilon^2/D^2\right) \tag{2.48} \]

for \( |\varepsilon| \leq D \), where \( D \) is the energy difference between the Fermi energy and the band edge. In the present calculations we have used two different bandwidths. The small band has half width \( D = 5eV \), the large has \( D = 10eV \). As the atom moves away from this surface the shift of its energy level is described using the image potential interaction of an atom and a perfectly conducting metal surface. We will consider both the interaction of positive and negative ions with surfaces. The parameterization for the negative ion is,

\[ \varepsilon_N(Z) = \phi - \frac{27.2}{4(Z - 1)} eV, \tag{2.49} \]

and for the positive ion,

\[ \varepsilon_P(Z) = -\phi + \frac{27.2}{4(Z - 1)} eV. \tag{2.50} \]

An image plane at \( Z \approx 1 \) Bohr is assumed to be the center for the induced surface charges. The parameter \( \phi \) is the effective workfunction of the system, and is the absolute value of the difference between the Fermi energy of the surface and the affinity level of the atom. All energies shown will be with reference to the Fermi energy.
of the the surface. Fig. 2.2 shows $\epsilon_N(Z)$ and $\epsilon_P(Z)$ for a particular workfunction $\phi$. The dimensionless function $\xi(\epsilon)$ is plotted in the same figure to show the relationship between the continuum band and the atomic energy levels. The widths of atomic levels typically increase exponentially with decreasing atom surface separation[26]. As discussed in a paper by Shao, Langreth, and Nordlander[19], and in Eq. (2.15) the input which determines the tunneling rates involves a band average of the tunneling rates and substrate density of states. The parameterization for the averaged width
is:
\[ \bar{\Gamma}_a(t) = \bar{\Gamma}_a^0 \exp(-\alpha Z(t)). \] (2.51)

\( \bar{\Gamma}_a \) as an average over the band, which is described by \( \xi \). A detailed discussion of \( \bar{\Gamma}_a \) can be found in Shao, Langreth, and Nordlander.[19] As the degeneracy, \( N \), is changed the total width \( \bar{\Gamma} \)
\[ \bar{\Gamma} = \sum_a \bar{\Gamma}_a = N\bar{\Gamma}_a, \] (2.52)
is held constant. The calculations here were done using \( \alpha = 0.65 \text{Bohr}^{-1} \) and \( \bar{\Gamma}_0 = 27.2 eV \) for both ions. The temperature in all calculations is 300K.

2.4 Simple master's equation

Before applying the numerical Green's function method to calculate the charge transfer it is useful to investigate the workfunction, \( \phi \), and degeneracy, \( N \), dependence of the charge transfer using the simple master’s equation (SME). The SME provides a convenient method for a qualitative estimate of charge transfer probabilities in hyperthermal atom surface scattering. The SME can be obtained by Golden rule arguments or by making some simplifications to the Green’s function results. The SME for this system is[18]
\[ \frac{dn(t)}{dt} = -\frac{\Gamma(t)}{N} (1 - f(\varepsilon(t))) n(t) + \Gamma(t) f(\varepsilon(t)) (1 - n(t)), \] (2.53)

where \( f \) is the Fermi function. The first term controls the rate of charge transfer from the atom to the surface when the atomic energy level is above the Fermi energy. The second term controls the rate of charge transfer from the surface to the atom when the atomic energy level is below the Fermi energy. We can see that the first term is dependent on the degeneracy of the system whereas the second term is not. This is because an electron tunneling into the atom can go into any of the degenerate states so only the total level width is important. An electron tunneling out of the atom
can only come from one state so the width of the individual state controls the rate of charge transfer. We can see from Eq. (2.53) that if an atom is in equilibrium with the surface and has an energy level below the Fermi energy, as in the negative ion case, then that energy level will be completely occupied. Similarly if the energy level is above the Fermi energy the level will be completely empty. We therefore have the initial conditions \( n_N(Z \leq Z_c) = 1.0 \) and \( n_P(Z \leq Z_c) = 0.0 \) where \( Z_c = \left( \frac{27.2eV}{4\phi} + 1 \right) \) is the distance from the surface, in Bohr, where the atomic level crosses the Fermi energy. Using the SME we can calculate the population far from the surface. For rectangular band, where \( \xi(\varepsilon(t)) = 1 \), we obtain the simple result

\[
\begin{align*}
n_N(\infty) & = e^{-\frac{\xi(\varepsilon c)}{\alpha_N}} \\
n_P(\infty) & = 1 - e^{-\frac{\xi(\varepsilon c)}{\alpha_P}}.
\end{align*}
\] (2.54)

The results for the parabolic band are not analytical but can be obtained numerically.

We see that electron-hole pair symmetry is predicted by the SME for the case of \( N = 1 \). This is what we expect because the \( U=0 \) Hamiltonian 2.2 is symmetric for holes and electrons. Because of this symmetry it is useful to plot \( n_N(t) \) for the negative ion and \( 1 - n_P(t) \) for the positive ion. We therefore make the following definitions.

\[
\begin{align*}
\delta n_N(t) & = n_N(t) \\
\delta n_P(t) & = 1 - n_P(t)
\end{align*}
\] (2.55)

These quantities represent the deviations from the adiabatic limit in which both ions would be completely neutralized far from the surface, ie. \( n_N(\infty) = 0.0 \) and \( n_P(\infty) = 1.0 \). Figure 2.3 shows the results, for the parabolic band, for for positive and negative ions for different degeneracies \( N \). The solution shows several features of interest. First we notice the strong workfunction dependence. As \( \phi \) increases the crossing distance, \( Z_c \) moves closer to the surface. When \( Z_c \) is close to the surface there is more time for the ion to become neutralized. Close to the surface the level width is also broader which increases the chance of tunneling. We therefore expect
Figure 2.3 Simple master's equation results for final population. The N=1 curve is the same for both ions. $D = 5ev$.

to see the probability of ion survival to decrease with increasing workfunction. Next we notice that the negative ion has a strong $N$ dependence. The $N$ dependence comes from the rate at which the negative ion can de-populate. We see that a large degeneracy causes a slower tunneling rate and therefore a larger final population. For the positive ion, the SME predicts no $N$ dependence. Eqs. (2.54) also show a strong velocity dependence. As the velocity, $v$, approaches 0.0, $n_{N,P}(\infty)$ as a function of $\phi$ becomes steeper and eventually approaches a theta function centered a $\phi = 0.0$. 
Chapter 3

Results and Discussion

We will investigate the charge transfer as a function of the workfunction, \( \phi \). The workfunction of the system strongly influences the final population, as was seen in Figure 2.3, Figure 3.1 shows the final population as a function of \( \phi \) obtained using the

![Graph showing charge transfer as a function of workfunction for negative and positive ions with different bandwidths.]

**Figure 3.1** \( \delta n \) vs. \( \phi \) for negative and positive ions and each bandwidth. \( v = 0.01 \text{a.u.} \). The N=1 curve is the same in all figures.

Green's function technique. We can see that there are strong differences between the
four figures. Since the negative ion results and the positive ion results are so different they will be discussed separately. We will start with the negative ion case.

3.1 Negative ion results

In the workfunction dependence of figures 2.3 and 3.1 we see a degeneracy dependence and some bandwidth dependence. To understand how each parameter effects the final population we need to know what state the system is in at various points along the atoms trajectory. To do this we will study the spectral functions of the system.

3.1.1 Spectral functions

Figure 3.2 shows the instantaneous spectral functions, Eq. (2.43), for the negative ion for two different bandwidths at several distances from the surface for several values of \( N \). For \( N = 1 \), the spectral function is characterized by an impurity peak centered around the atomic energy level, \( \varepsilon_a \). This peak is caused by the discrete atomic state hybridizing with the continuum levels. The width of this peak is equal to \( \bar{\Gamma} \) when it is below the Fermi energy and \( \bar{\Gamma}/N \) when it is above the Fermi energy. For \( N > 1 \) an additional feature, the Kondo peak appears just below the Fermi energy. This peak is caused by electron-hole pair fluctuations at the Fermi energy which are induced by the degenerate level. This effect was first discovered by Kondo by using third order perturbation theory.

The width of the Kondo peak, which is present in the spectral function for degenerate atomic states, in the presence of electron correlation, can be written qualitatively as the Kondo temperature,[27, 28]

\[
T_K = \frac{D}{2N\pi} e^{\left(1.577 - \frac{\bar{\Gamma}}{2\pi D}\right)^{\frac{1}{N}}} e^{\left[2\pi \left(\frac{1}{2} - \frac{\bar{\Gamma}}{2\pi D}\right)\right]} \tag{3.1}
\]

From this expression it is clear that the Kondo peak will depend on the surface bandwidth, \( D \), the atomic degeneracy, \( N \), and in particular on the parameterization
Figure 3.2  Instantaneous spectral functions. $\nu = 0.005\text{a.u.}$, $\phi = 0.75\text{eV}$. 
of the level shift, $\varepsilon_a$, and broadening, $\Gamma$. The Kondo temperature is approximately linear in $D$ and $T_K$ for $N = 10$ is larger than $T_K$ for $N = 4$ which is larger than $T_K$ for $N = 2$.

We see that both the Kondo peak and the impurity peak are strongly influenced by the degeneracy. We see that increasing the bandwidth or degeneracy will increase the width of the Kondo peak. The appearance of the Kondo peak in the system fundamentally changes the charge transfer dynamics. Since the Kondo peak, in general, is very narrow, non-adiabatic effects can be very pronounced even at low velocities[29].

While the total population of the atomic level is relatively insensitive to $N$, the relative weight of the impurity peak and the Kondo peak changes with $N$. Since the $N = 1$ case shows no Kondo peak, the impurity peak is much larger for $N = 1$ than for the $N > 1$ cases. Another difference in the impurity peaks is that for larger $N$ the impurity peak is centered closer to the Fermi energy than for smaller $N$. This is particularly noticeable in the small band width case which shows larger shifts than the large band width case.

The energy shift of the impurity peak can be estimated using second order perturbation theory,

$$\Delta E = \sum_k \frac{|V_{ak}(t)|^2}{\varepsilon_a - \varepsilon_k} \propto \int_D d\varepsilon \frac{\xi(\varepsilon) \Gamma_a(t)}{\varepsilon_a - \varepsilon_k}.$$  (3.2)

Where $\xi(\varepsilon)$ is the shape function in Eq. (2.48). Using this equation, we see that the energy shift can approximately be written as

$$\Delta E = \frac{\Gamma(t)}{N} \left[ \left(1 - \frac{\varepsilon_a^2}{D^2}\right) \log \left|\frac{\varepsilon_a + D}{\varepsilon_a - D}\right| + 2\frac{\varepsilon_a}{D} \right].$$  (3.3)

This result shows that the energy shift is inversely proportional to $N$ and that the shift becomes larger when $\varepsilon_{i\omega}$ approaches the band edge. The impurity level is always shifted away from the Fermi energy. These results explain the results shown in figure 3.2.
We have shown that both the impurity and Kondo peaks are effected strongly by both degeneracy and bandwidth. For the case of $N = 1$ we notice that as the atom moves away from the surface the spectral functions for the two bandwidth cases become almost identical. This is because there is no Kondo peak and the shift of the impurity peak disappears at the Fermi energy. For the cases of $N > 1$ the bandwidth dependence in the Kondo peak effects the impurity peak even when the atomic energy level is close to the Fermi energy so the two bandwidth cases remain distinct.

Because the spectral functions reflect the population of the atom we expect to see both bandwidth and degeneracy dependence in the final populations.

3.1.2 Workfunction and degeneracy dependence

Figure 3.1 shows $\delta n$ as a function of $\phi$ for several different degeneracies. We see the same general workfunction dependence that the SME predicts, although there are also distinct differences. It can be seen from the figure that there is a strong degeneracy dependence which is different for the positive and negative ions. For the case of $N = 1$ there is hole-pair symmetry so the positive and negative ion results are identical and very similar to the results from the SME. From Figure 3.1 we see that the $\delta n_N(\infty)$ vs. $\phi$ curve becomes steeper with higher degeneracy. This behavior is the opposite of what is predicted by the SME. The SME limit includes many approximations resulting in the approximation that when the energy level is below the Fermi energy the atom is completely ionized. This is not the case, as we can see by looking at Table 3.1 which shows the results obtained using the Green’s function formalism. The initial population of the ion is influenced by the degeneracy. We see that $\delta n_N(0)$ increases with increasing $N$ for the small bandwidth case but decreases with increasing $N$ for the large bandwidth case. This is because the shift of impurity peak decreases as $N$ increases. The Kondo peak also becomes larger making the impurity peak smaller.
but the shift seems to be the dominant effect. For the small bandwidth case the shift of the impurity peak is quite pronounced. Since the large $N$ results in less of a shift the impurity peak is closer to the Fermi energy where the density of states is larger and therefore allows more charge transfer. For the large bandwidth case the shift is insignificant but the impurity peak is much smaller because of the larger Kondo peak. We therefore see a smaller population for larger $N$. This helps to explain the differences in initial population. We also see in table 3.1 that there is a smaller percent change in the differences between the two bandwidth cases as $N$ increases. This indicates that the $\Gamma/N$ charge transfer rate predicted by the SME is still qualitatively correct.

### Table 3.1 $\delta n_N$ at starting point and final point along trajectory for $\phi = 0.75 eV$

<table>
<thead>
<tr>
<th>$N$</th>
<th>$\delta n_N(0)$ 5eV</th>
<th>$\delta n_N(0)$ 10eV</th>
<th>Diff.</th>
<th>$\delta n_N(\infty)$ 5eV</th>
<th>$\delta n_N(\infty)$ 10eV</th>
<th>Diff.</th>
<th>$\delta n_N(0) - \delta n_N(\infty)$ 5eV</th>
<th>$\delta n_N(0) - \delta n_N(\infty)$ 10eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.818</td>
<td>0.794</td>
<td>0.024</td>
<td>0.684</td>
<td>0.685</td>
<td>-0.001</td>
<td>0.134</td>
<td>0.109</td>
</tr>
<tr>
<td>2</td>
<td>0.823</td>
<td>0.781</td>
<td>0.042</td>
<td>0.733</td>
<td>0.714</td>
<td>0.019</td>
<td>0.090</td>
<td>0.067</td>
</tr>
<tr>
<td>4</td>
<td>0.843</td>
<td>0.784</td>
<td>0.059</td>
<td>0.763</td>
<td>0.717</td>
<td>0.046</td>
<td>0.080</td>
<td>0.067</td>
</tr>
<tr>
<td>10</td>
<td>0.857</td>
<td>0.779</td>
<td>0.078</td>
<td>0.763</td>
<td>0.693</td>
<td>0.070</td>
<td>0.094</td>
<td>0.086</td>
</tr>
</tbody>
</table>

### 3.1.3 Bandwidth dependence

We have seen that the bandwidth of the substrate strongly affects the spectral function. Now we will examine how the bandwidth effects the final population. Figure 3.3 shows a comparison of the two bandwidths for several degeneracies. We see that for $N = 1$, the bandwidth has no significant effect on the final population. For $N > 1$, however, we see a distinct bandwidth dependence. This bandwidth dependence must be caused by the Kondo peak since we see that the effect increases with increasing $N$. Figure 3.4 shows the instantaneous population of the ion as it travels along its trajectory. The impurity level crosses the Fermi energy at about $Z = 10$ Bohr for a
Figure 3.3  Negative ion $\delta n$ vs. $\phi$. $v = 0.01$ a.u.

workfunction of $0.75\text{eV}$. We can see that for $N = 1$, the two populations merge at about the distance where the impurity level crosses the Fermi energy. We also see that most of the differences in instantaneous populations occur before the impurity level crosses the Fermi energy. After the impurity level crosses the Fermi energy both the small and the large band width cases seem to lose the same amount of population, for each $N$. The large differences in the final population is caused by the differences in the initial population for the two bandwidths. At larger degeneracies the charge transfer rate is lower, as can be clearly seen in figure 3.4, and the initial population differences survive. Figure 3.5 shows the initial and final populations for several band-
Figure 3.4 Instantaneous population for Negative ion. $v = 0.01 \text{a.u.}$, $\phi = 0.75 \text{eV}$.

widths at two different workfunctions. We can clearly see that both the initial and final populations have similar bandwidth dependence although the curve is shifted down in the final population. This clearly shows that the bandwidth dependence we observe in the final population, is caused by the preservation of initial population differences. This preservation is only possible with a strong Kondo peak. We see that none of the initial bandwidth dependence of the $N = 1$ case is present in the final population.
Figure 3.5  Bandwidth population for negative ion. $v = 0.01\,a.u.$.

3.2 Positive ion results

3.2.1 Spectral functions

All the spectral functions shown are for the negative ion case. The spectral functions for the positive ion case are very different. Because the atomic energy level is above the Fermi energy when the atom is close to the surface there is no Kondo peak in the occupied spectral function. The only spectral weight is due to the tail of the impurity peak extending below the Fermi energy. In this limit, the width of the impurity peak is $\Gamma/N$. Since both the width and the shift of the impurity peak are $N$ dependent
the population will be $N$ dependent. Since there is no Kondo peak, the bandwidth
dependence is weak. At large atom surface separations the atomic level shifts below
the Fermi energy and a Kondo resonance appears below the Fermi energy. Since $\bar{\Gamma}$ is
very small, the Kondo peak is minor.

3.2.2 Workfunction and degeneracy dependence

Figure 3.1 also shows $\delta n$ as a function of $\phi$ for several different degeneracies for
the positive ion. We see the same general workfunction dependence that the SME
predicts, although there are also distinct differences. It can be seen from the Figure 3.1
that there is a strong degeneracy dependence which does not exist in Figure 2.3. The
slope of $\delta n_P(\infty)$ vs. $\phi$ decreases with increasing $N$ while the SME solution predicts
no $N$ dependence. The SME limit assumes that the atom is completely ionized when
the energy level is above the Fermi energy. This is not the case, as we can see by
looking at Table 3.2 which shows the results obtained using the Green's function
formalism. The initial population of the ion is strongly influenced by degeneracy.
This is due to the strong $N$ dependence of the spectral function when the atom is
close to the surface. We see from table 3.2 that $\delta n_P(0)$ increases with increasing $N$
for both bandwidths. We also see that there is no significant degeneracy dependence

<table>
<thead>
<tr>
<th>$n_P$ at starting point and final</th>
</tr>
</thead>
<tbody>
<tr>
<td>point along trajectory for $\phi = 1.00 \text{ eV}$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$N$</th>
<th>$\delta n_P(0)$</th>
<th>$\delta n_P(0) - \delta n_P(\infty)$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$5eV$ $10eV$ Diff.</td>
<td>$5eV$ $10eV$ Diff.</td>
</tr>
<tr>
<td>1</td>
<td>0.800 0.775 0.025</td>
<td>0.241 0.242 -0.001</td>
</tr>
<tr>
<td>2</td>
<td>0.827 0.807 0.020</td>
<td>0.315 0.332 -0.017</td>
</tr>
<tr>
<td>4</td>
<td>0.850 0.832 0.018</td>
<td>0.359 0.378 -0.019</td>
</tr>
<tr>
<td>10</td>
<td>0.862 0.845 0.017</td>
<td>0.381 0.402 -0.021</td>
</tr>
</tbody>
</table>
in $\delta n_p(0) - \delta n_p(\infty)$. This shows that the rate of charge transfer in the positive ion is relatively independent of $N$ as was predicted by the SME.

### 3.2.3 Bandwidth dependence

Figure 3.6 shows $\delta n_p$ vs workfunction for the various $N$. Only very small bandwidth differences can be seen. The major reason for this is that, near the surface the level lies above the Fermi energy. In this limit the bandwidth dependence of the population is very weak. (Table 3.2) At larger distances when the atomic level shifts below the Fermi energy the Kondo peak will be very small. For a large workfunction, $1 - 1.5 eV$, 

![Graph showing $\delta n_p$ vs workfunction for various N values.](image-url)
the impurity level crosses the Fermi energy closer to the surface allowing a larger Kondo peak to form which results in the slight increase in bandwidth dependence observed. Figure 3.7 shows the $\delta n_P(t)$ along the trajectory for the positive ion for various $N$. Since we are plotting $(1-n_p(t))$ we can see that the small bandwidth case has a lower initial population than the large band case. This can be explained by the fact that the impurity peak for the small band is shifted to a higher energy than the impurity peak for the large band. As the atom moves from the surface the population in the small bandwidth case changes more rapidly than the population
in the large bandwidth case. In table 3.2 we can clearly see both the degeneracy and bandwidth dependence in the system. We see that for increasing $N$ we have increasing $\delta n_P(0)$. This is true for both bandwidths, although the differences between the two cases decreases with increasing $N$. More importantly we see that the difference between initial and final populations decreases with increasing $N$, despite the SME predicting no $N$ dependence in the rate of charge transfer. There is also a slight bandwidth dependence in the difference between initial and final populations which is not predicted by the SME. Figure 3.8 shows the initial and final populations for

![Graph showing dependence of $\delta n_P$ on bandwidth and $N$.](image)

**Figure 3.8** Bandwidth population for positive ion. $\nu = 0.01$ a.u.,
several bandwidths at two different workfunctions. Unlike the negative ion case there is very little bandwidth dependence. We do see very strong $N$ dependence though.

3.3 Velocity Dependence

In this section we will investigate the effects of velocity on $\delta n_{N,P}(\phi)$. Figure 3.9 compares the $\delta n$ results for various cases. We see that in each case the slower velocity results have a steeper slope. This is expected since the slower an atom moves, the more time there is for the population to tunnel in or out of the surface. The steeper slope is also predicted by the SME. Another interesting feature is that for the negative
ion the curves cross. This shows a fundamental difference between the positive ion and negative ion cases. For the positive ion a lower velocity always results in a lower final $\delta n_p$ for all workfunctions studied. For the negative ion we see that the velocity dependence of the system is sensitive to which workfunction is chosen. For small $\phi$, the final population of the negative ions can increase with decreasing velocity. This is in direct contrast to the results of the SME which predicts a monotonic decrease in final population with decreasing velocity. To see how the spectral functions are affected by velocity we compare the $v=0.005$ a.u. instantaneous spectral functions with the equilibrium spectral functions for the same distance and parameters. Figure 3.10 shows the small bandwidth results for $N = 1$ and $N = 4$. For the case of $N = 4$ we see that the $V = 0.005$ and $V = 0.0$ spectral functions are very similar when the atom is close to the surface at $Z = 4.0$ a.u.. This is because the atom starts in equilibrium near the surface. We see that as the atom moves away from the surface the two spectral functions become different. We see that at 5.0 a.u. the $N = 4$ instantaneous spectral function has a smaller Kondo peak than the equilibrium spectral function. This is because the Kondo peak requires a finite amount of time to form because it is so narrow. In this case the atom is moving too fast to allow the Kondo peak to properly form. We see that for $N = 1$ both spectral functions are nearly identical. The broad impurity peak forms very quickly and responds to the changing position of the atom almost immediately. This is one of the fundamental differences between the $N = 1$ and $N > 1$ cases. The Kondo peak is very sensitive to velocity and the delay in the formation or decay of the Kondo peak strongly influences the rate of charge transfer. This is the reason that the SME does not properly describe the velocity dependence of the workfunction curve for the negative ion. This is clearly evident in figure 3.9 since the negative ion curves cross which would not happen in the SME limit.
Figure 3.10  Velocity dependence of spectral functions. $\phi = 0.75eV$, $D = 5eV$. 
Chapter 4
Conclusion

We have shown that the calculated $\delta n$ vs workfunction is very sensitive to a variety of many-body effects. In particular the negative ion species displays many-electron effects. The reason for this is that for the negative ion a Kondo state is formed when the atom is near the surface. For the negative ion results we have seen that parameters that affect the Kondo peak strongly affect the final population. Enhancing the Kondo peak by increasing $N$, or increasing the bandwidth $D$ has resulted, in each case, with a steeper slope on the graph of $\delta n$ vs workfunction. The positive ion case is quite different however. Increasing $N$ decreases the slope of the graph. Increasing the bandwidth also decreases the slope, but only by a small amount. Since the Kondo peak is not formed until the atom is some distance from the surface in the positive ion case it is reasonable the it produces a smaller effect than in the negative ion case where the Kondo peak is present at the beginning of the trajectory close to the surface. In all cases the lower velocity results in a steeper $\delta n$ vs workfunction slope. We see that degenerate systems have strong many-body effects which are not explained by simple $N=1$ theory. It is our hope that some experimental groups that we collaborate with will perform scattering or desorption experiments on a variety of metal surfaces using a variety of atoms to study the effects that we predict.
Bibliography


