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NONADIABATIC MECHANISM FOR THE PRODUCTION OF
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Interactions of Atoms with Solid Surfaces: Nonadiabatic Mechanism for the Production of Excited State Hydrogen and Helium Atoms at a Metal Surface

by

Lawrence Walter Carlson

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF

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Chapter I  Introduction

The nature of the electronic interaction of simple atoms and ions with metal surfaces has been the object of a large amount of experimental and theoretical study over a long period of time. Oliphant and Moon\textsuperscript{1} and others\textsuperscript{2} have described the neutralization of an ion in the vicinity of a metal surface in an early application of quantum mechanics. Various mechanisms of the de-excitation and ionization of metastable atoms and the neutralization of ions have subsequently been proposed.\textsuperscript{3–12} Yet, the theory relates only loosely to the experimental observations.\textsuperscript{13–16}

The present study is a theoretical investigation of some electronic processes which may occur in the collision of a simple atom with a metal surface. Particular attention is paid to the configuration interaction of the atomic states in the vicinity of the surface. The time evolution of the system is then studied in an effort to determine the final state of the atom as it leaves the surface.

To establish a conceptual picture, consider an atom in an excited metastable state approaching a smooth metal surface. The metal is represented by a broad potential well filled to the Fermi level by a sea of free electrons and the atom by a single filled state at energy $\varepsilon_a$ (figure 1.1). Those states in the metal above the Fermi level are unfilled, and the atomic electron has at all times a finite probability of tunneling through the interstitial
Figure 1.1 Energy level diagram for an atom near a metal surface. Arrows '1' and '2' refer to the resonant neutralization and ionization processes, respectively. Ref. 6.
potential barrier. The transition probability becomes large as atom-surface distance $S$ decreases. This resonant ionization process is denoted by arrow "2" of the figure. Similarly, if the atomic state is initially empty and energy $\epsilon_a'$ is below the Fermi level, an electron may leave the metal and fill the atomic state. Arrow "1" symbolizes the resonant neutralization process.

A bare ion may, alternatively, be neutralized through the Auger neutralization process. The "direct" Auger process described by Shekhter$^3$ (figure 1.2) involves two metallic electrons. In the final state, one electron from the metal occupies the ground state of the atom and a second metallic electron has been ejected with the resultant energy surplus.

De-excitation of a metastable atom near a metal surface may proceed through a similar mechanism (figure 1.3). Here, an energy transfer from a metallic electron to the excited atomic electron ensures energy conservation. The broken lines in the figure indicate the exchange process, which is possible if the Pauli principle is not therein violated.

The object of the present investigation has been to study the electronic development of an atom as it is reflected at a metal surface. Description of the metal is included only so far as it affects the final state spectrum of the atom as it leaves the surface. Provision has not been made for the calculation of bulk or surface excitation
Figure 1.2 Energy level diagram for an atom near a metal surface. The arrows denote electron transitions in the 'direct' Auger neutralization process.
Figure 1.3 Energy level diagram for an atom near a metal surface. The arrows denote electron transitions in the Auger de-excitation process.
probabilities, although they may be large, because this aspect of the total picture is probably only weakly coupled to the evolution of the atomic states. The nonadiabatic excitation of surface plasmons\textsuperscript{17,18} and bulk excitons\textsuperscript{19,20} by fast ions has been described elsewhere.

The neutralization process for ions at metal surfaces is useful in the study of solid surfaces\textsuperscript{21}: in determining both the electronic structure of the surface itself and that of an adsorbed or chemisorbed layer.\textsuperscript{22,23} In ion neutralization spectroscopy, for instance, the energy of electrons ejected through Auger neutralization (or resonant neutralization followed by Auger de-excitation) is analyzed. The technique has not been widely used because of the difficulty in interpretation of the observed convoluted energy distribution. It is also possible to study the charge state,\textsuperscript{23-27} or excitation spectrum\textsuperscript{13-16} of the reflected atoms.

This thesis is structured in the following way. In Chapter 2 the elements of a model which serves to describe the atom/ion-metal surface system are discussed. The choice of basis functions and the interaction potential is made. Relevant processes in the metal which may accompany the passage of an ion through a metal surface are discussed.

Chapter 3 consists largely of a discussion of the time dependent evolution of the system. Elements of the actual calculation are restricted to the description of the atom as it leaves the metal surface so that a soluble
system of equations for the time development of the atomic state can be found. The derivation is discussed in detail in order to emphasize the relation of those elements of the complete interaction which are explicitly followed in the calculation to those which are not.

In Chapter 4 the limitations of the model and calculational process are discussed. Results of a series of numerical computations are presented for the evolution of hydrogen and helium from some characteristic surfaces are presented and some implications of this study for subsequent work are discussed.

Some qualifications on the terminology must be made. The terms "ion" and "atom" are used almost interchangeably in referring to the external projectile in the vicinity of the surface. The word "atom" is sometimes used to emphasize the significance of the unfilled electronic states of the ion. Also, we often refer to "metallic" and "atomic" electrons. Of course, these electrons are intrinsically indistinguishable. The "atomic" electron is that electron which is, even briefly, in an atomic state. At some point as the atom leaves the surface, the then "atomic" electron becomes genuinely distinguishable, by virtue of its position or energy. The assumption in pursuing a single-electron model here is that this localization occurs close enough to the surface that the observable characteristic atomic behavior occurs subsequently.
The theory which is developed in Chapters II and III is not, in general, restricted to any single projectile or surface. The detailed calculations which are described in Chapter IV are limited to electronic processes which occur along the outgoing (surface exit) trajectory outside the surface for light ions (hydrogen and helium).
References - Chapter I

11. J.C. Tully and N.H. Tolk, to be published.
Chapter II. Elements of the Model

2.1 Introduction

The general problem that we wish to treat is the determination of the final electronic state of an atom or ion which collides with a metal surface and the mechanism through which that state has evolved. The precise determination of that state involves a full quantum mechanical many body collision problem which we cannot hope to solve exactly. We must, therefore, make certain assumptions about those aspects of the collision that are likely to have the greatest effect on the electronic evolution of the atom.

We assume that the interaction between the atom and the metal resembles that between an atom and a gas of electrons immersed in a continuous positive charge background (jellium) rather than that between an atom and an array of positive cores and localized electrons. This assumption is more likely to be valid for processes involving loosely bound excited atomic projectile states than for the tightly bound ground atomic state simply because of the size of the atom and the extent of its environment which it "samples" in an interaction. Accordingly, the diffuse model should be more accurate for charge transfer mechanisms effective at long range (e.g., resonant neutralization). Some recent work\(^1\) on neutralization to the ground state has been done using a localized atomic basis
for both the projectile and the metal. The advantages of such a procedure are not clear when excited states are involved, however, and the calculational effort is many times as great.

2.2 Atomic Trajectory

Central to our model of the atom-surface interaction is the following argument. An atom or ion approaches and collides with a metal surface at appreciable velocity. To achieve a large instantaneous momentum transfer it must strike a metal core. This collision may occur at the surface layer, or deep within the metal; the depth of penetration increases with projectile energy.\(^2,3\) Now, the determination of the electronic state of foreign ions in metals is largely an unsolved problem in the static case and we cannot hope to follow the time development of such a highly statistical collision explicitly. But, if the interaction of the ion with the metal is strong enough, the details of its electronic evolution along the incoming trajectory and, perhaps, for the entire time the ion is within the metal, may not be relevant to its subsequent development along the outward trajectory. This is certainly true if the ion has no bound states in the metal (the charge state of a moving ion in a metal is unknown\(^4-6\)).

This argument implies that at some time as the ion moved along the outward trajectory it must reach a point at which the history of the system has no effect on its future
and only specification of the velocity and state of the ion and some properties of the metal (e.g., core and electronic structure, magnetic properties) determine the final excited state spectrum. That point might be taken to be the surface plane of the metal, perhaps the point at which the energy of the ground state of the atom passes through the Fermi level of the metal. We shall explore the consequences of various choices of the "initial state" with the realization in mind that it is really a mixed state of the many body system and has more resonance than bound state character.  

At large distances from the surface, however, the atom is in a true bound state. The transition from a diffuse to local state is the Mott transition for this system. The order in which the diffuse-local transition occurs and the various neutralization and excitation mechanisms become likely to occur is extremely important in determining the final state of the atom. It is really this ambiguity concerning the degree of localization of atomic states, in the presence of competing processes involving these states, that makes both the standard many body treatment (using an unperturbed atomic basis) and the strictly one-electron approach inadequate. The one-electron (Hartree Fock) theory is known to predict relatively accurate energies, but poor wave functions. One hopes that in this case energetic variations, more than the exact
spatial structure of the wave function determine the final electronic state of the atom. Such behavior may be caused by strong nonadiabatic coupling of the basis states, which occurs in the vicinity of rapid variation of the energy curves, or by displacement of the energy levels above or below the Fermi level of the metal, which allows transfer of an electron to or from the metal, respectively (cf. Fig. 1-1).

2.3 Hamiltonian Function and Basis States

The total Hamiltonian for the system is

\[ \mathcal{H} = T_\mathbf{R} + H_{\text{el}} \]  \hspace{1cm} 2.3.1

\( T_\mathbf{R} \) is the nuclear kinetic energy operator for the projectile and \( H_{\text{el}} \) is the electronic Hamiltonian for the external atom and for the metal.

We assume that nuclear motion is so slow compared to electronic motion that nuclear coordinate \( \mathbf{R} \) can be treated as a slowly varying parameter and not as a dynamical variable in the determination of the electronic wave function. In this case the wave function for the system can be written as

\[ \Psi(\mathbf{r}, \mathbf{R}) = \sum_k \chi_k(\mathbf{R}) \psi_k(\mathbf{r}, \mathbf{R}) \]  \hspace{1cm} 2.3.2

where \( \chi_k(\mathbf{R}) \) is the nuclear wave function and \( \{\psi_k(\mathbf{r}, \mathbf{R})\} \) is a complete set of electronic wave functions which depends
parametrically on \( \vec{r} \).\(^8\) Substituting this expression in the time independent wave function we find the following set of \( N \) coupled second order differential equations for the nuclear motion,

\[
\left[ T_{\vec{r}} + \Lambda_{jj} + H_{jj} - \xi \right] \chi_j = \sum_{k \neq j} \left[ H_{jk} + \Lambda_{jk} \right] \chi_k ; \quad j = 1,N
\]

where \( \xi \) is the total energy and

\[
H_{kj} = \langle \psi_k | H_{el} | \psi_j \rangle \quad 2.3.4
\]

\[
\Lambda_{kj} = \langle \psi_k | T_{\vec{r}} | \psi_j \rangle - \langle \psi_k | V_{\vec{R}} | \psi_j \rangle \cdot \nabla_{\vec{R}}
\]

are the operators for the configuration interaction of the atomic states and the kinematic coupling of nuclear and electronic motion, respectively.

There is some flexibility in the choice of the basis set \( \{ \psi_k \} \); we are free to choose it in such a way that the equations 2.3.3 are simplified. This is usually done in one of two ways. A set of functions \( \{ \psi_k \} \) are constructed such that either \( H_{kj} \quad (k \neq j) = 0 \) or \( \Lambda_{kj} \quad (k \neq j) = 0 \); such functions are called the adiabatic or diabatic basis functions, respectively.

With \( \psi \) represented in the adiabatic basis \( \{ \psi_k^{(a)} \} \) equation 2.3.3 reduces to
\[
\left[ \hat{T} - \varepsilon_j^a + \hat{H}_{jj} - \varepsilon \right] \chi_j^a - \sum_{k \neq j} \lambda_{jk}^a \chi_k^a \quad ; \quad j = 1, N \quad 2.3.6
\]

where \( \varepsilon_j^a \) is the energy eigenvalue of the \( \psi_j^{(a)} \) state. In the Born-Oppenheimer approximation we neglect the coupling term in equation 2.1.6. The resulting set of uncoupled equations describes the nuclear motion, which is constrained to the potential energy surface defined by the electronic configuration. The \( \lambda_{kj} \) term generally becomes important in the region of avoided crossings of the electronic energy curves.

The diabatic basis set consists of those functions \{\( \psi_k^{(d)} \)\} which render the kinematic coupling term \( \lambda_{kj} \) negligible. The matrix element \( \hat{H}_{kj} \) of the diabatic functions is not, in general, diagonal. Equation 2.3.3 assumes the form

\[
\left[ \hat{T} + \hat{H}_{jj} - \varepsilon \right] \chi_j^d = -\sum_{k \neq j} \hat{H}_{jk} \chi_k^d \quad ; \quad j = 1, N \quad 2.3.7
\]

The diabatic functions have some desirable properties if perturbation theory is used.\(^{12}\)

These equations, 2.3.6 and 2.3.7, may still contain more information, and are more complex, than necessary if the details of the nuclear motion are unlikely to have a strong influence on the electronic evolution of the system. This condition is probably well satisfied for atom-metal
surface collisions in which penetration of the surface has occurred, because of the translational invariance along the surface. The interaction geometry is characterized completely by ion velocity and azimuthal angle. In this case, a semiclassical approximation is appropriate. We assume that the nucleus is sufficiently massive that its trajectory can be found classically, as a function solely of time, i.e., $R = R(t)$. The time dependent Schrödinger equation is solved for the evolution of the electronic part of the system as the nucleus moves along its trajectory,

$$H \left( \vec{r}, R \right) \Psi(\vec{r}, t) = i \frac{\partial \Psi(\vec{r}, t)}{\partial t} \quad 2.3.8$$

Substitution of this time dependent wave function

$$\Psi(\vec{r}, t) = \sum_k a_k(t) \psi_k(\vec{r}, R) \exp \left( -i \int_0^t Hkatd't' \right) \quad 2.3.9$$

in equation 2.3.8 produces the set of coupled first order equations for the complex coefficients $a_k(t)$,

$$i \dot{a}_j(t) = \sum_{k \neq j} a_k(t) \Lambda_{jk}^{(s)} \exp \left( -i \int_0^t (H_{kk} - H_{jk}) dt' \right) \quad 2.3.10$$

The semiclassical kinematic coupling operator

$$\Lambda_{jk}^{(s)} = \langle \psi_j | H_{el} - i \frac{\partial}{\partial t} | \psi_k \rangle$$

becomes, in the adiabatic representation,

$$\Lambda_{jk}^{(s)} = -i \nu(R) \langle \psi_j | \nabla_\mathbf{R} | \psi_k \rangle \quad 2.3.11$$
where $v(R)$ is the core velocity. This is the nonadiabatic (kinematic) coupling term employed in the following analysis, which is carried out in the adiabatic basis described in Section 2.4.

Some indication of the importance of kinematic coupling of adiabatic states is provided by the Massey adiabatic criterion,\textsuperscript{13} according to which two states $\psi_k$ and $\psi_j$ are weakly coupled at an avoided crossing about some point $R'$ if

$$\left| \varepsilon (R') - \varepsilon (R) \right| \frac{\delta R'}{v(R')} \gg 1 \quad 2.3.12$$

where $\varepsilon_k(R')$ is the electronic energy eigenvalue at $R'$, $v(R')$ is the core velocity and $\delta R'$ is the extent of the region over which the avoided crossing occurs. States for which this criterion is fulfilled are effectively uncoupled in the solution of the simultaneous equations 2.3.10. Since adiabatic states of the same symmetry do not cross we may have "diagonal blocks" of states which interact among themselves.

Furthermore, the kinematic coupling operator for an adiabatic basis can be divided into radial and rotational parts

$$\Lambda_{kj} = i v(R) \langle \psi_j | \frac{\partial}{\partial R} | \psi \rangle + \omega \langle \psi | \underline{L} | \psi \rangle \quad 2.3.13$$
where R is collinear with the internuclear axis, \( L_\perp \) is the component of angular momentum perpendicular to the plane of the trajectory, and \( \omega \) is the angular frequency. In atom-surface interactions in the structureless surface approximation the "internuclear axis" is that surface normal which passes through the atomic core. For oblique surface scattering angle this axis moves along the surface with the projectile, always perpendicular to the surface; therefore, the angular frequency \( \omega \) is zero. The selection rules for the radial and rotational coupling of states by the kinematic coupling operator (eq. 2.3.11) are:

- **radial coupling**: \( \Delta L_z = 0 \), parity conserved
- **rotational coupling**: \( \Delta L_z = \pm 1 \), parity conserved,

where \( L_z \) is the component of angular momentum along the surface normal axis. Thus, since the rotational coupling term vanishes with \( \omega \), a smooth surface, with no adsorbed atoms, can mix only states of the same \( L_z \) through a non-adiabatic (kinematic) mechanism. Of course, if there is an actual transfer of electrons between the atom and surface the final state can be of any \( L_z \).

### 2.4 Adiabatic States

The discrete adiabatic basis states used to describe the evolution of the atom are those which diagonalize the electronic Hamiltonian but do not include coupling to the quasicontinuum of states in the metal. These states can be
represented as
\[ \psi_i^a(S) = \sum_{j=1}^{N} c_{ij} \phi_j^{(u)} \] 2.4.1

where \( \{\phi_j^{(u)}\} \) is the complete set of free space atomic wave functions. The functions \( \psi_i^{(a)} \) are solutions of the equation
\[ \left( H_{el} - \epsilon_i^a(S) \right) \psi_i^a(S) = 0 \] 2.4.2

where \( \epsilon_i^{(a)}(s) \) are the adiabatic eigenenergies, which are dependent on the atom-surface distances.

In principle, the exact solution of the scattering problem involves an infinite number of basis states, including both bound atomic and continuum states, and, hence, an infinite number of adiabatic states. Since this exact expansion is obviously computationally impossible the usual approach is to truncate the basis set at some manageable size. Those states which have the appropriate symmetry to allow the atom to distort in response to the interaction potential and which are within a narrow energy range of the initial state or final states of interest are retained. In this work we use a hydrogenic basis and include only the \( m_{\mathbf{z}} = 0 \) states \( \phi_j^{(u)} = \{1s, 2s, 2p_{z}, 3s, 3p_{z}, 3d_{z}\} \), the choice of which is discussed below.
If we multiply the set of equations 2.4.2 by 
\((\psi_k^{(a)} (s))^*\) and integrate over all space we find that the 
eigenvalues and coefficients are given by the matrix 
equation,

\[
\begin{pmatrix}
H_{11} - \epsilon_1 & H_{12} - \epsilon_1 \Delta_{12} & \cdots & H_{1N} - \epsilon_1 \Delta_{1N} \\
H_{21} - \epsilon_2 \Delta_{21} & \ddots & & \vdots \\
\vdots & & \ddots & \vdots \\
H_{N1} - \epsilon_N \Delta_{N1} & \cdots & H_{NN} - \epsilon_N \Delta_{NN}
\end{pmatrix}
\begin{pmatrix}
c_{i1} (s) \\
c_{i2} (s) \\
\vdots \\
c_{iN} (s)
\end{pmatrix}
= 0,
\]

where,

\[
H_{ij} = \langle \phi_i^u | H_{el} (s) | \phi_j^u \rangle = \epsilon_i \delta_{ij} + V_{ij},
\]

\[
\Delta_{ij} = \langle \phi_i^u | \phi_j^u \rangle
\]

Equation 2.4.3 can be solved by the usual matrix diagonalization procedures (e.g., Gaussian elimination) to yield 
the set of coefficients \(c_{ij} (s)\) and eigenenergies \(\epsilon_i (s)\) for 
as many values of the atom-surface distance as are desired. 
From the viewpoint of computational costs the calculation 
of the set of matrix elements \(H_{ij}\) for a single value of 
separation \(s\) is far more expensive than solution of the 
matrix equation 2.4.3. Since the numerical values of the 
matrix elements \(H_{ij} (s)\) are relatively smooth in \(s\), and 
generally monotonic, we fit an approximation function to 
the matrix elements and solve the matrix equation 2.4.3 
using the full set of actually calculated \(H_{ij} (s)\) values.
and an approximated set of intermediate values (cf. Appendix 3-4 for details).

Furthermore, we must choose a representation for the basis set of unperturbed hydrogenic wave functions $\phi^{(u)}_i$. The hydrogenic wave functions can be expressed exactly, of course, in the form of Slater type orbitals (STO's), however, the matrix elements $H_{ij}$ are somewhat easier to evaluate in the general case, and much easier to evaluate in the asymptotic case (large $z$), if we employ Gaussian type orbitals (GTO's). In the Gaussian orbital the radial dependence of the wave function is expanded as an (in principle) infinite sum of weighted exponentials of the square of the electron coordinate. The angular dependence can be expressed either as a sum over Legendre polynomials or by centering clusters of Gaussian exponentials on the various charge centers of the represented state. The latter case is usually referred to as that of floating Gaussian orbitals. In the representation of floating Gaussian orbitals the unperturbed wave function has the form

$$\Phi(x) = \sum_{j=1}^{N} \sum_{k=1}^{M} A^{(i,j)}_k \exp \left[ - \alpha^{(i,j)}_k (x - R_j)^2 \right]$$

where the sum on $j$ is over the Gaussian centers displaced from the atomic core by $R_j$ and index $k$ is over the parameters $A$ and $\alpha$ relevant to center $j$. 

2.4.6
The expansion 2.4.6 is, in principle, complete. If, however, we truncate the sum on $k$ at some computationally reasonable limit the function $\phi(\vec{r})$ must deviate from its exact value. Since the exact $\phi_j$ are composed of simple exponentials the truncated Gaussian $\phi_j$ which fall off much more rapidly with $\vec{r}$ cannot reproduce them accurately in the asymptotic region. Now, in the final formulation of this problem we must evaluate two different types of matrix element involving the atomic wave functions, those in which both of the functions are centered on the atomic core (e.g., $\langle \psi | V | \psi \rangle$), and those in which one function is centered on the atomic core and the other at the metal surface (e.g., $\langle \psi | V | \kappa \rangle$, where $\kappa$ is the metallic wave function). When both functions are centered on the same point, the largest contribution to the matrix elements comes from the region in which the maxima of the two functions overlap, a region in which the Gaussian orbitals represent the exact wave functions most closely. We therefore use Gaussian orbitals to represent the atomic wave functions in the calculation of the discrete-discrete matrix elements. When the two wave functions have different centers, one at the atom and the other at the metal surface, the region of greatest overlap, and consequently greatest contribution to the matrix elements, is approximately midway between the atom and metal. This region may well be in the asymptotic range of the atomic wave function and, hence, be poorly represented by an expansion in Gaussian
orbitals. In the evaluation of matrix elements involving both discrete and continuum states we use Slater type orbitals, which are asymptotically correct.

2.5 Atom-Surface Interaction Potential

2.5.A Image Potential

Consider a simple atom consisting of a positively charged core and single valance electron in the vicinity of a smooth, structureless metal surface (fig. 2.1). Let the perpendicular distance from the atomic core to the surface of the metal (image plane of fig. 2.2) be s, and that from the electron to the surface be d. A discrete positive charge, such as the core, near a metal surface induces the accumulation of negative charge in a narrow layer near the surface. This surface charge is distributed in such a way that the positive core is subject to the same force as it would be in the presence of a symmetrically placed charge of equal magnitude but opposite sign, the familiar image charge.\(^16\)

The simple image potential model remains a valid approximation to the actual potential for a real metal composed of discrete screening charges as long as it is not used very close to the surface (less than 4 or 5 \(a_o\)), and if the image plane is shifted outward somewhat from the half density plane (approximately 2 \(a_o\) for a metal of unit sphere radius \(r_s = 2 a_o\)).\(^17,18\)
Figure 2.1 Geometry of the atom-(image charge) system.
Figure 2.2 Displacement of the image plane from the half-density plane.
The potential energy of the electron in figure 2.5.1 in the field of its self image is

\[ V'(d) = \int_0^\alpha F(z) \, dz = \int_0^\alpha \frac{-1}{4z^2} \, d\zeta = 1/4d \] 2.5.1

whereas the potential energy of the electron in the field of the core image is just

\[ V(R) = \frac{1}{R} \approx -\frac{1}{2d} \] 2.5.2

These approximate energies differ by a factor of two. The physical origin of the difference is the symmetric motion of the electron image in response to changes in the position of the electron itself. There is no such motion of the core. Inclusion of the interaction energy of the core with its own image and that of the electron causes the Coulomb component of the total energy to vanish, as it must for a neutral atom and metal.

2.5.B Dynamical Effects

Use of an image potential is not justified if the external charge is moving very rapidly. Two effects are particularly important. The first pertains to the case in which there is an atomic state with a short lifetime near the surface so that there are frequent electronic transitions between the atom and metal. A time delay in the response of metallic screening charge to the change in occupation number of the atomic state can cause a large
shift in the energy. Second if the electron (or atom itself) is moving rapidly enough the screening charge will not follow the electron motion adiabatically.

In discussing the first of these two issues we follow the analysis of Hewson and Newns.\textsuperscript{19} The valence level of an electron in an atom with ionization energy, I, in the presence of the core image alone (without self-image energy) is just

\[ \varepsilon = -I + \frac{1}{R} \approx -I + \frac{1}{2d} \quad (2.5.3) \]

Suppose that metallic electrons sequentially hop into and out of the atomic orbital, which has a short lifetime against decay into the metallic continuum. For very short lifetimes the interaction resembles resonant scattering. If the response time of the metal to changes in the external screened charge were comparable to the lifetime of the atomic state, the average image energy would be \((1 - \langle n_a \rangle)/2d\), where \(\langle n_a \rangle\) is the expectation value of the occupation number of the atomic state. Thus, the total energy of the level would be

\[ \varepsilon_{\text{eff}}^S = -I + \frac{1}{2d} \left[ 1 - \langle n_a \rangle \right] \quad \text{(Static approximation)} \quad (2.5.4) \]

If, however, the response of the metal screening charge were instantaneous the energy of the atomic level would be

\[ \varepsilon_{\text{eff}}^i = -I + \frac{1}{4d} \quad \text{(Adiabatic approximation)} \quad (2.5.5) \]
Each of these expressions shows the characteristic upward shift of energy levels first described by Hagstrum and Stemberg.

Hewson and Newns have calculated the actual energy level shifts by representing the image potential with the electron-surface plasmon interaction in the Green function formalism. They found that if \( \omega_p \ll \Delta \), \( \varepsilon_{\text{eff}} = \varepsilon_{\text{eff}}^s \), while if \( \omega_p \gg \Delta \), \( \varepsilon_{\text{eff}} = \varepsilon_{\text{eff}}^i \); where \( \omega_p \) is the surface plasmon frequency and \( \Delta \) is the width of the lifetime broadened atomic level. That is, the adiabatic approximation is justified if the lifetime of the atomic state is much longer than the surface plasmon period. Now, since the surface plasmon energy for most metals is typically 10–25 eV, and the atomic level width even at small atom-surface separation is considerably smaller than this (1 eV is the often quoted estimate in chemisorption theory), the adiabatic approximation to the image potential is relevant to the present calculation. At large atom-surface distances the width, \( \Delta \), is much smaller; the adiabatic approximation is asymptotically exact.

This simple model of the image potential, in which,

\[
V = - \frac{1}{R} + \frac{1}{4d^2}
\]

(2.5.6)

can be modified to include the effects of electron spin. If the atomic states are energy degenerate with respect to spin, and atomic orbital \( \psi_i \) is filled at level \( I' = I - 1/4d \), then the effective electron affinity, \( A' \), of the atom is
\[ \mathbf{A}' = \mathbf{I} - \mathbf{U} + \frac{1}{4} \mathbf{d} \]  \hspace{1cm} (2.5.7)\\

where \( \mathbf{U} \) is the additional repulsive Coulomb energy between the two electrons. The effective value of \( \mathbf{U} \) is just

\[ \mathbf{U}_{\text{eff}} = \mathbf{I} - \mathbf{A}' = \mathbf{U} + \mathbf{1}/4 \mathbf{d} \]  \hspace{1cm} (2.5.8)\\

If the core is screened by metallic conduction electrons, however, \( \mathbf{U}_{\text{eff}} \) may be greatly reduced.

The significance of the \( \mathbf{U}_{\text{eff}} \) term in the atom-surface interaction is apparent from the structure of the Anderson Hamiltonian for this system,\(^{24-26}\) which is (in the notation of second quantization),

\[ H_A = \sum_{\sigma} \epsilon_n a_{\sigma}^+ a_{\sigma} + \sum_{\mathbf{k} \sigma} \epsilon_{\mathbf{k}} c_{\mathbf{k} \sigma}^+ c_{\mathbf{k} \sigma} + \sum_{\mathbf{k} \sigma} \left( V_{\mathbf{ak}} c_{\mathbf{k} \sigma}^+ c_{\mathbf{a} \sigma} + V_{\mathbf{ak}^*} c_{\mathbf{a} \sigma}^+ c_{\mathbf{k} \sigma} + \mathbf{U}_{\text{eff}} n_{\mathbf{a} \sigma} n_{\mathbf{a} \sigma} \right) \]  \hspace{1cm} (2.5.9)\\

where \( \sigma, \mathbf{a}, \) and \( \mathbf{k} \) refer to spin, atomic, and continuum states, respectively; \( n_{\mathbf{a} \sigma} \) is the number operator; \( c_{\mathbf{a} \sigma}^+ \) is the creation (and \( c_{\mathbf{a} \sigma} \) the destruction) operator for the atomic state; and \( V_{\mathbf{ak}} \) is the transition matrix element. The last term represents the Coulomb interaction between electrons of opposite spin on the single atomic orbital. In Hartree Fock Theory this term is taken to be \( \mathbf{U}_{\text{eff}} n_{\mathbf{a} \sigma} \langle n_{\mathbf{a} \sigma} \rangle \), where \( \langle n_{\mathbf{a} \sigma} \rangle \) is the expectation value of the number operator. Thus, for sparsely populated atomic states this term may be ignored.
Lucas and Sunjic\textsuperscript{27,28} have studied the dynamical response of a metal surface to a moving external charge in an effort to find the velocity dependence of the potential function and excitation probability for surface plasmons. The interaction Hamiltonian for a charged particle near a metal surface is taken to be

\[ H_I = \mathcal{A} \int d\vec{k} \mathcal{C}(k) \left[ a_{\vec{k}} \exp(-i\vec{k} \cdot \vec{r}) + a_{\vec{k}}^\dagger \exp(i\vec{k} \cdot \vec{r}) \right] \cdot \exp(-kz) F(z) \]  

(2.5.10)

where \( \vec{r} = (\vec{r}, z) \), \( a_{\vec{k}}^\dagger \) and \( a_{\vec{k}} \) are creation and destruction operators for surface plasmons. The form of \( F(z) \) depends on the nature of the scattering event. For a particle of charge \( z \)

\[ \mathcal{C}(k) = \left( \frac{z^2 \omega_p^2}{8\pi A k} \right)^{1/2} \]  

(2.5.11)

where \( \omega_p \) is the plasma frequency of the metal.

The surface plasmon excitation probability depends primarily on the magnitude of the ratio

\[ \frac{|\cdot|}{\omega_p k} \]  

(2.5.12)

and the time derivative of the coupling strength \( F(z) \). The form of the velocity dependence suggests that fast electrons are much more likely to excite surface plasmons than are ions.

If \( F(z) \) changes rapidly in less than \( \tau_p = 1/\omega_p \), the screening charge at the surface cannot respond
adiabatically. For an ion leaving a metal surface $F(z)$ may change rapidly at the instant of neutralization. Since in the region in which a distinct transition is likely to occur, the lifetime of the atomic state is greater than $\tau_p$, however, excitation of a surface plasmon through this mechanism is improbable. This conclusion is consistent with the use of the adiabatic image potential. Surface plasmons and bulk excitations are therefore not included explicitly in the model of the atom-surface interaction.

Finally, for external charge velocities comparable to the Fermi velocity of the metal the true potential deviates somewhat from the inverse first power distance dependence of equation (2.5.7). For this reason, we limit the ion velocity in these studies to $v = 0.5$ a.u., above which corrections to the image potential are substantial.$^{29,30}$

As an atom approaches a metal surface the atomic energy levels tend to rise in response to the metallic screening charge (image charge). The configuration interaction among these (discrete) states may decrease this effect somewhat, however, the general trend is an elevation. This variation is especially important in the resonant ionization and neutralization process, where the relative level of the energy of the atomic state and the Fermi level of the metal determine what type of charge transfer event can occur.

The apparent Coulombic component of the energy is legitimately included in the state energy when we discuss
the ionization (and neutralization) process, but not in the calculation of the configuration interaction of discrete states. In the ionization process, which is really the configuration interaction between discrete and continuum states, the final state consists of an electron at infinity and a charged atomic core in the vicinity of a metal surface. The real Coulomb energy between the core and the screening charge in the metal (after ionization) is the source of the energy shift of the ionized state. (For neutralization the screened core exists in the initial state, the electron in the metal is unscreened.)

The leading Coulomb term in the series expansion of the potential is not included in the description of the configuration interaction of discrete states because the neutral atom induces no net surface charge. There can be no Coulombic distortion of the atom in response to a neutral metal. For this reason the matrix elements of the atom-surface potential between discrete states $j$ and $k$ is taken to be

$$V_{jk} = \langle j \mid V_{\alpha-m} \mid k \rangle = \langle j \mid \frac{1}{R} - \frac{1}{q_d} - \frac{1}{q_s} \mid k \rangle. \quad (2.5.13)$$

This form of the potential function, however, diverges at the image plane and in the vicinity of the core image (if the core is close to the surface). This unphysical behavior can be eliminated if the effects of screening by the metal are included in the model.
2.5.C Screening

The divergence of the bare electron-(self-image) potential at the image plane suggests that some modification of the potential must be made in the surface region. Both the screening of the atomic core and the particulate nature of the screening charge itself are involved. There are three cases which must be considered: two are modifications of the image potential which take the form of screening functions (the electron-self-image and the electron-core image for \( z \geq -s \)), and the third is the actual screening of the atomic core (when \( z \leq -s \)).

The screened potential for a unit charge in an homogeneous electron gas can be written as \( e^{-\lambda r}/r \) (the Friedel oscillations are ignored since they cannot be realistically included in the model). This function approaches the Coulomb potential at short distances and vanishes at large distances, as the magnitude of the total screening charge approaches unity. In an inhomogeneous gas in which the screening charge is not spherically symmetric there may be residual multipole moments. For an electron near a metal surface we expect the situation to be reversed: as the electron penetrates the surface and approaches the image position the potential vanishes (as it must more than a few Bohr radii within the bulk of the metal), but outside the surface screening layer it attains its full image value.
Accordingly, the electron- (self-image) interaction potential is represented by the approximate function (cf. fig. 2.3 ),

\[ V_{e-si} = \begin{cases} \frac{-1}{4(s+z)} \left[ 1 - \exp \left( -\lambda^o (s+z) \right) \right] ; & z > -s \\ V_{p} ; & z < -s. \end{cases} \]

(2.5.14)

\( \lambda^o \) is the constant inverse screening length taken to have the value given by Fermi-Thomas theory at the reduced surface density. (Park, Houston and Laramore have suggested however, that the existence of surface plasmon response modes may lessen the screening length at the surface in spite of the low electron density. No calculation has been carried out.) \( V_{p} \) is a function the choice of which is discussed below.

Modification of the electron- (core image) potential is slightly more troublesome since it is nonlocal, depending explicitly on both the core and electron positions. We assume that it can be approximated by the expression

\[ V_{e-ci} = \frac{1}{R} \left[ 1 - \exp \left( -\bar{\lambda}(s,z) R \right) \right] \]

(2.5.15)

where \( R \) is the electron- (core image) distance. \( \bar{\lambda} \) is some function of atom-surface distance, \( s \), and axial component of electron position, \( z \), which takes into account, in an
Figure 2.3 The electron-(self image) potential in its bare and modified form near the image plane.

Figure 2.4 Potential of the atomic core in the surface region with and without screening. Asymmetry is caused by the change in (s,r) with r, which approximates inhomogeneity of screening charge.
approximate fashion, the inhomogeneous distribution of charge at the surface. Calculations of the matrix elements in the surface region for several choices of \( \lambda(s,z) \) are presented below.

Finally, when the electron is within the surface layer the atomic core is screened by the conduction electrons. Since the full unscreened energy for this region is included in the eigenenergies of the unperturbed hydrogenic functions, the unrealized energy contribution must be deducted (cf. fig. 2.4'). The negative potential term subtracted from the Hamiltonian is

\[
V_{e^{-sC,C}} = -\frac{1}{r} \left[ 1 - \nu \rho \left( \lambda(s, \hat{r}) \hat{r} \right) \right] \tag{2.5.16}
\]

The function \( \lambda(s,r) = \lambda(u(s,r)) \) is taken to have the simple form

\[
\lambda(u) = \begin{cases} 
\rho \left[ 1 - \nu \rho \left( q \left( u - u_0 \right) \right) \right]^{-1} & ; u < u_0 \\
\infty & ; u > u_0
\end{cases} \tag{2.5.17}
\]

where \( \rho, q, \) and \( r \) are parameters chosen such that \( \lambda \) has the values appropriate to the bulk and surface densities as predicted by Fermi Thomas screening model. Parameter \( u_0 \) is the distance outside of which electron density is negligible. (The values we have used appropriate to a metal of unit electron radius \( r_s = 2 \) are: \( \rho = 0.931, \)
q = 0.2248 a_o^{-1}, h = 5. a_o, and u_o = 4.85 a_o.) With these screening functions, the interaction potential is

\[ V_{int} = \begin{cases} 
\left[ \frac{-1}{4(s+z)} \left(1 - \exp(-\lambda^0(s+z))\right) + \frac{1}{r} \left(1 - \exp(-\lambda(s,z))\right) \right]; & z > -S \\
\left[ V_p^0 + \frac{1}{r} \left(1 - \exp(-\lambda(s,z))\right) \right]; & z < -S 
\end{cases} \]

(2.5.18)

The term \( V_p^0 \) is a pseudopotential component of the electron- (self-image) potential effective inside the metal. The need for this term arises from the requirement that electrons enter the metal at or above the Fermi level \( \epsilon_F \). Such electrons must have a wave function orthogonal to the occupied continuum levels. Actually, the exclusion principle requires that the overlap integral of the continuum with the discrete state, integrated over all space, be zero. Suppose region A is inside the surface plane and region B is outside, then the orthogonality requirement is

\[ \langle \kappa_c | \psi_d \rangle_A = -\langle \kappa_c | \psi_d \rangle_B \]  

(2.5.19)

The pseudopotential is that energy term which, when added to the potential function in region A, insures that the wave function of the external electron is orthogonal to that of the metallic electrons. The size of pseudopotential \( V_p \) obviously depends on the angular form and parity of the wave functions.
This argument is similar in spirit to that made by Levine\textsuperscript{32} and Gdzu\k{e}k\textsuperscript{33} concerning the geometry of possible states of an adsorbed atom at a semiconductor or metal surfaces, respectively. Gdzu\k{e}k concludes that for atomic states at metal surfaces, the angular momentum must obey the selection rule, $(m_z + l) = 0$, and the state have odd parity, to exist in the presence of the surface potential discontinuity. The variation of the surface potential is gradual enough that this is more a trend than a rule.

Determination of the function, $V_p$, is complicated by the screening of the atomic core by the conduction electrons. Consider a single atomic state; the wave function for that state should, in principle, be orthogonal to the (perturbed) wave functions of the metallic electrons. The increased density of screening charge near the atomic core causes $V_p$ to be greater in the perturbed case than if the core were not screened. The value of $V_p$, however, affects the occupancy of the atomic state, which, in turn, determines the magnitude of the screening charge. The whole problem must therefore be solved self-consistently. Instead of trying to solve the full multiaatomic-state chemisorption problem, we choose to set the potential inside the metal to a simple constant, $V_p = V_p^0$, independent of state.

This approximation is supported by the following arguments. The contribution to the matrix elements from the region within the metal are probably overestimated if
a WKB type metallic wave function is used (cf. Section 2.6) since the rapid oscillations of the wave function near the metal cores are not represented. These rapid oscillations tend to reduce the value of the matrix elements.

Finally, the use of a constant $V_p^0$ is a better approximation for states which lie below the Fermi level than for states which lie above it (in the unperturbed metallic model) since there is no requirement that those atomic states be orthogonal to empty metallic states. Such atomic states have very short lifetimes in the region in which $V_p$ is important (near the surface) and decay very quickly regardless of their detailed atomic structure there. We can think of them, in this region, as approximate atomic states which serve to provide a proper environment (via equation 2.4.3) for the determination of the structure of the lower lying states.
II.6 Metallic Wave Function

The metal surface consists of a symmetrical array of charged cores which may have a narrow quasi-bound band of filled localized directional orbitals (e.g., d-orbitals of transition metals) and a broad non-localized band of weakly- or non-interacting conduction electrons. The lattice of ion cores plays an obviously important role in the scattering of ions from the surface, but we assume that the effect of the lattice on the time development of the valence electrons of an atom near the surface can be adequately represented by a continuum positive background charge (jellium approximation), as it often can for the valence electrons of the metallic atoms themselves. That is, the surface represented in this model is unstructured.

The narrow d-electron band clearly has very important effects in the chemisorption process and can, if it falls in the appropriate energy range, cause the neutralization (to the ground state) of incident scattered ions through a near resonant nonadiabatic transfer. As important as the d-band may be in chemisorption and neutralization at the surface, its relevance to the present calculation is less certain. In the transition metals the absence of nodal surfaces in the d-state wave function combined with the long-range excursions of the s-p electrons make the d-wave function fall off very rapidly at large radius (cf. figure 2.5). In the surface region the
Figure 2.5 Radial extension of the 4s and 3d states of a transition metal atom (schematic). Ref. 36 p341.
atomic (rather than the nonlocalized) character of the d-states is probably more pronounced than in the bulk. The severe asymptotic decline of the atomic d-wave functions supports the belief that even in the presence of a narrow d-band near the Fermi level the neutralization process outside the surface layer is dominated by the s-p band. For this reason we do not pursue any calculation which includes the d-band density explicitly.

The metallic wave function, then, is simply that for a three dimensional finite potential well. The Sommerfeld wave function, employed by Gadzuk\textsuperscript{37} and Remy\textsuperscript{38} in calculating resonant ionization rates, has a reasonable form along the surface normal, but has an unrealistic angular dependence. A better choice seems to be a modified form of the WKB solution.

\[
K_{mn} = \begin{cases} 
\frac{1}{k_r} \left[ \frac{3}{2} \right] \exp \left( i \left( k_x x + k_y y \right) \right) \sin \left[ k_z (z + s) + \gamma^0 \right] ; & z < -S \\
\frac{1}{k_r} \left[ \frac{2}{2} \right] \exp \left( i \left( k_x x + k_y y \right) \right) \exp \left( -\sqrt{2V_0 - k_z^2} \right) \cdot (z + S) ; & z > -S 
\end{cases}
\]

(2.6.1)

where box normalization is used, for cube of extent L; $\gamma^0$ is a phase angle; and $V_0$ is the bottom of the conduction band of the metal (cf. fig. 1.1.1).
The prime on $k_z$ in the second expression indicates that it represents the wave number taken with respect to the band bottom. This wave function is identical to the Sommerfeld function for $k_x = k_y = 0$. 
References - Chapter II

1. Ref. 11 (Ch. I).
5. Ref. 24 (Ch. I).
6. Ref. 16 (Ch. I).
10. \( \psi \) must have a translation factor to do so exactly. cf. ref. 9.
20. Ref. 5 (Ch. I).
21. Ref. 6 (Ch. I).
34. Ref. 26 (Ch. II).
37. Ref. 6 (Ch. I).
38. Ref. 7 (Ch. I).
Chapter III. Dynamics

3.1. State Function

The time development of the system is, from our point of view, that of the atom as it moves along its outward trajectory. The atom may undergo electronic transitions both to and from the adiabatic states. Such transitions may be caused by both the coupling of the electronic and nuclear motion and an actual exchange of electrons with the metal. We ignore the possibility of creation of plasmon\(^1\) or other exciton\(^2\) states within the metal which may provide an energy loss mechanism in collisions with the surface. Furthermore, we do not include two electron de-excitation or neutralization mechanisms, such as the Auger process\(^3\) (although the effect of these processes could be included phenomenologically in the time development equations).

We assume that the regions in which the Auger and resonant processes are dominant do not overlap. That is, we concentrate on those ions which have traversed the region of high Auger transition probability without undergoing neutralization.

Within the limitations of this model, the total time dependent wave function for the system can be written as

\[
\Psi(t) = \sum_n a_n(t) \psi_n(R(t)) e^{-i\int_0^t \omega_n(R(t)) dt} + \sum_x b_x(t) \chi_x e^{-i\omega_x t}
\]  

(3.1.1)
where \( \{ \psi_n^a \} \) is the truncated set of adiabatic atomic states (2.4.1) of energy \( w_n \) and \( a \) is summed over all other states which are allowed to participate in the interaction. This sum could include conduction band, localized core and surface states, or the localized states of some atom or molecule adsorbed on the surface; but we limit this discussion to inclusion of the modified WKB states (2.5.1) for free conduction electrons. The sum over these quasi-continuum functions is effectively an integration over the wave vector \( \vec{k} \),

\[
\sum_\alpha b_\alpha \kappa_\alpha e^{-i \omega_\alpha t} = \int \int \int b_{\vec{k}}(t) \kappa_{\vec{k}} e^{-i \omega_{\vec{k}} t} d^3 \vec{k} \quad (3.1.2)
\]

For the isotropic free electron model used here the energy and wave vector are simply related (cf. Appendix 3.3), so that

\[
\Psi(t) = \sum_{n=1}^{N} a_n(t) \psi_n(R(t)) e^{-i \int_0^t \omega(R(t')) dt'}
\]

\[
+ \int \int \int b_{\vec{\epsilon}}(t) \kappa_{\vec{\epsilon}} \rho_{\vec{\epsilon}} e^{-i \omega_{\vec{\epsilon}} t}
\]

where the superscript \( \Omega \) is inserted to emphasize the dependence on angle.

We make the approximation that only processes for which \( b_{\vec{\epsilon}}(t) = b_{\vec{\epsilon}}(t) \), independent of angle, are included in the expansion (3.1.3). This is possible since the
metal is expected to act as a source or sink, but not a reservoir, of electrons. That is, the metal (in the absence of the atom) is isotropic in its half space, and, consequently, as long as we are interested only in the final occupancy of the atomic state, the angular dependence of \( b_\epsilon(t) \) is irrelevant.

If the metal were to act as a temporary reservoir, an electron jumping from atomic state \( \psi_n \) to metallic state \( \kappa_\epsilon \left( \omega_n = \omega_\epsilon \right) \) at time \( t \), for example, might be prevented from jumping back to atomic state \( \psi_n' \left( \omega_n' = \omega_\epsilon; t \neq t' \right) \) by the angular variation of \( b_\epsilon(t) \) which we have dropped. Such processes, nonlocal in time and difficult to include in a numerical computation, probably don't exist for continuum states of a real metal for finite \( \Delta t = t-t' \) because of relaxation phenomena.

Substitution of the total wave function, 3.1., into the time dependent Schrödinger equation results in the expression

\[
\sum_n \left( \hat{a}_n \psi_n + a_n \dot{\psi}_n - i \omega_n(t)a_n\psi_n \right) e^{\int_0^t \omega_n(R(t'))dt'}
\]

\[
+ \iiint d\Omega d\epsilon \left( b_\epsilon \kappa_\epsilon \rho_\epsilon + b_\epsilon \kappa_\epsilon \dot{\rho}_\epsilon + b_\epsilon \kappa_\epsilon \rho_\epsilon - i \omega_\epsilon b_\epsilon \rho_\epsilon \kappa_\epsilon \right) e^{-i \omega_\epsilon t}
\]

\[
= -\sum_n a_n H_{\text{el}} \psi_n e^{\int_0^t \omega_n(R(t'))dt'} - i \iiint d\Omega d\epsilon b_\epsilon \kappa_\epsilon \rho_\epsilon e^{-i \omega_\epsilon t}.
\]

(3.1.4)
The $K_e^{\Omega}$ and $\dot{\rho}_e$ terms are dropped, under the assumption that neither the metallic wave functions nor the density of states is changed much by the presence of a single external ion. This restriction also excludes the possibility of excitation of surface or bulk plasmons or bulk excitations.

### 3.2 Partition of the Hamiltonian

The electronic Hamiltonian function $H_{el}$ for a single electron is

$$H_{el} = T + V_a + V_m + V_i \tag{3.2.1}$$

where $T$ is the kinetic energy operator, $V_a$ and $V_m$ the unperturbed atomic and metallic potential functions, respectively, and $V_i$ is the interaction potential

$$V_i = \begin{cases} V_{e\text{-image}} + V_{e\text{-core image}} ; |z| > s \\ 0 ; |z| < -s \end{cases} \tag{3.2.2}$$

A collision in which the particle grouping is different in the final state is different from that in the initial state is referred to as a rearrangement collision.\textsuperscript{4,5} Such particle exchange collisions have the typical feature that the Hamiltonian functions for the initial and final states have different dominant potential interactions. The term which in the initial state was a perturbation may cause binding in the final state, for example. No single term must remain small throughout the interaction.
The Hamiltonian function $H_{el}$ can be partitioned as

$$H_{el} = T + V_a + V_m + V_i = \begin{cases} H_a^{(o)} + V_m + V_i \\ H_a + V_m \\ H_m + V_a + V_i \end{cases}$$

(3.2.3) (3.2.4) (3.2.5)

The terms "prior" and "post" are arbitrarily assigned to the atomic and ionic states respectively. Equations (3.2.3) and (3.2.4), then, are the prior forms of the Hamiltonian. Eigenfunctions of $H_a^{(o)}$ are the unperturbed atomic wave functions, those of $H_a$ are the adiabatic atomic wave functions; the perturbation is caused by the presence of the metal. Equation (3.2.5) corresponds to the post partitioning of the Hamiltonian. Eigenfunctions of $H_m$ are metallic wave functions, the ionic potential is the perturbation.

3.3 Time Development

The state of the entire physical system is fully described by the amplitudes $a_n(t)$ and $b_\xi(t)$ (of equation 3.1.3), which relate to the atom and metal, respectively. A set of coupled first order differential equations for the time development of $a_n(t)$ [$b_\xi(t)$] can be found by multiplying equation 3.1.4 by $\Psi_n^*(t)$ [$K_\xi^*,\Omega^*$] and integrating the product over all space. The form of the resulting equations depends on the way in which the Hamiltonian function, 3.2.1, is partitioned. Substitution of the
post form, 3.2.5, in the matrix element coupling the atomic and metallic states produces the following equation for the atomic state coefficients.

\[
\dot{a}_{n'}(t) = -\sum_{n=1}^{N} a_n(t) \langle \psi_{n'}(t) | \dot{\psi}_{n}(t) \rangle e^{-i \int_0^t \Delta_{nn'}(R(t')) dt'} \\
- \int \int d\Omega d\epsilon \, b_{\epsilon'}(t) \langle \psi_{n'}(t) | k_{\epsilon'}^{n'} \rangle \rho_{\epsilon} e^{-i \int_0^t \Delta_{\epsilon n'}(R(t')) dt'} \\
- i \sum_{n=1}^{N} a_n(t) \langle \psi_{n'}(t) | V_m | \psi_{n}(t) \rangle e^{-i \int_0^t \Delta_{nn'}(R(t')) dt'} \\
- i \int \int d\Omega d\epsilon \, b_{\epsilon}(t) \rho_{\epsilon} \langle \psi_{n'}(t) | V_{a} + V_{i} | k_{\epsilon}^{n'} \rangle e^{-i \int_0^t \Delta_{\epsilon n'}(R(t')) dt'} ; \\
\quad n = 1, \ldots, N 
\tag{3.3.1}
\]

where,

\[
\Delta_{\epsilon n} (R(t)) = (\omega_{\epsilon} - \omega_n (R(t))) 
\tag{3.3.2}
\]

and \( N \) is the number of discrete atomic states in the expansion. The corresponding equation for the time development of the metallic coefficient is

\[
b_{\epsilon'}(t) = -\sum_{n=1}^{N} \dot{a}_{n} (t) \langle k_{\epsilon'}^{n} | \dot{\psi}_{n}(t) \rangle e^{-i \int_0^t \Delta_{n\epsilon'}(R(t')) dt'} \\
- \sum_{n=1}^{N} a_n(t) \langle k_{\epsilon'}^{n'} | \dot{\psi}_{n}(t) \rangle e^{-i \int_0^t \Delta_{n\epsilon'}(R(t')) dt'}
\]
\[
-i \sum_{n=1}^{N} a_{n}(t) \left[ \left( \omega_{e'} - \omega_{n}(t) \right) \left\langle \kappa_{e'}^{n'} | \Psi_{n}(t) \right\rangle + \left\langle \kappa_{e'}^{n'} | V_{a} + V_{i} | \psi_{n} \right\rangle \right] e^{t \int_{0}^{t} \Delta(n_{e'}^{(R(t'))}) dt'}
\]

\[
-i \int_{\Omega} \int d\Omega d\epsilon b_{\epsilon}(t) \rho_{\epsilon} \left\langle \kappa_{e}^{n'} | V_{a} + V_{i} | \kappa_{\epsilon}^{n} \right\rangle e^{-i \Delta_{\epsilon \epsilon'} \epsilon} t
; \]

all \( \epsilon' \).  \hspace{1cm} (3.3.3)

The second term on the right side of equation 3.3.3 contains the factor

\[
a_{n}(t) \left\langle \kappa_{e'}^{n'} | \hat{\Psi}_{n}(t) \right\rangle = a_{n}(t) \nu(R(t)) \frac{\partial}{\partial R} \left\langle \kappa_{e'}^{n'} | \Psi_{n}(t) \right\rangle \hspace{1cm} (3.3.4)
\]

This factor represents the variation of metallic amplitude caused by the time variation of occupied atomic states. This effect is not one that we wish to follow, except insofar as it affects the final atomic state. Because of the high density of metallic electrons the variation of \( b_{\epsilon} \) caused by this term is probably slight; it is deleted from the equation.

Furthermore, the fourth term to the right in equation 3.3.3 contains a factor

\[
\left( \omega_{e'} - \omega_{n}(t) \right) e^{\nu(R(t)) \int_{0}^{t} \Delta(n_{\epsilon}(R(t'))) dt'}
\]

(3.3.5)

According to the usual stationary phase condition\(^6\) the term contributes a nonvanishing component to the integrated \( b_{\epsilon',}(t) \) only when
\[ \frac{\partial}{\partial t} \int_0^t \Delta_{n', \epsilon'}(R(t')) dt' \left( = \left( \omega_n(t) - \omega_{\epsilon'} \right) \right) = 0. \] \hspace{1cm} (3.3.6)

Since \((\omega_n(t) - \omega_{\epsilon'})\) appears as a prefactor, the net contribution of this term must be zero.

The equation for \(\dot{a}_n(t)\), 3.3.1, can be rearranged so that it contains no time derivative of the \(b_\epsilon(t)\) amplitude. 7 Substitution of equation 3.3.3 into equation 3.3.1 results in the expression

\[ \dot{a}_n(t) = -\sum_{n=1}^N a_n(t) \langle \psi_{n'}(t) | \psi_n(t) \rangle e^{-i \int_0^t \Delta_{nn'}(R(t')) dt'} + \sum_n \int \int \int d\Omega d\epsilon \left( \dot{a}_n(t) b_\epsilon \right) \langle \psi_{n'}(t) | \psi_n(t) \rangle e^{-i \int_0^t \Delta_{nn'}(R(t')) dt'} + i \sum_n \int \int \int d\Omega d\epsilon a_n(t) \langle \kappa_{\epsilon'} | \psi_n(t) \rangle \langle \psi_{n'}(t) | \kappa_{\epsilon} \rangle e^{-i \int_0^t \Delta_{nn'}(R(t')) dt'} + i \int \int \int \int \int d\Omega d\epsilon \int \int d\Omega' d\epsilon' \left( \dot{b}_{\epsilon'} b_\epsilon \right) \langle \kappa_{\epsilon'} | \psi_n(t) \rangle \langle \psi_{n'}(t) | \kappa_{\epsilon} \rangle e^{-i \int_0^t \Delta_{\epsilon n'}(R(t')) dt'} - i \sum_n a_n(t) \langle \psi_{n'}(t) | \psi_n(t) \rangle e^{-i \int_0^t \Delta_{nn'}(R(t')) dt'} - i \int \int \int d\Omega d\epsilon \left( \dot{b}_\epsilon b_\epsilon \right) \langle \kappa_{\epsilon} | \psi_n(t) \rangle \langle \psi_{n'}(t) | \kappa_{\epsilon} \rangle e^{-i \int_0^t \Delta_{\epsilon n'}(R(t')) dt'} \]

\hspace{1cm} (3.3.7)
The second term on the right side looks as if it should be contracted over \( \rho_\epsilon |K_\epsilon^{\Omega}\rangle \langle K_\epsilon^{\Omega'}| \). If we do so, the \( \hat{a}_n(t) \) dependence of equation 3.3.7 vanishes entirely. This is an example of the overcompleteness problem discussed by Grimley. In practice we integrate only over some subset of the, in principle, complete set \( \{K_\epsilon\} \). In fact, the set of metallic functions 2.6.1 is not complete, and, even if it were made so it would be an inappropriate basis set for the construction of localized atomic functions.

Taking only diagonal elements of the second term on the right and rearranging the last term equation 3.3.7.

\[
(1 - \Delta_{\epsilon n}^2) \hat{a}_n(t) = \sum_n a_n(t) \langle \psi_{n'} | \dot{\psi}_n \rangle e^{-i \int_0^t \Delta_{\epsilon n'}(R(t')) dt'}
\]

\[-i \sum_n a_n(t) \left[ \langle \psi_{n'}(t) | V_{\epsilon} | \psi_n(t) \rangle - \iiint d\Omega d\epsilon \langle K_\epsilon^{\Omega} | V_{\epsilon} | \psi_n(t) \rangle \right] e^{-i \int_0^t \Delta_{\epsilon n'}(R(t')) dt'} - i \iiint d\Omega d\epsilon b_{\epsilon}^{n'}(t) \rho_\epsilon \cdot \]

\[
\left[ \langle \psi_{n'}(t) | V_{\epsilon} | K_\epsilon^{\Omega} \rangle - \iiint d\Omega' d\epsilon' \rho_\epsilon' \langle K_\epsilon^{\Omega} | V_{\epsilon} | K_\epsilon^{\Omega'} \rangle \langle \psi_{n'}(t) | K_\epsilon^{\Omega'} \rangle \right] e^{-i \int_0^t \Delta_{\epsilon n'}(R(t')) dt'}
\]

(3.3.8)
where \( \Delta_{\epsilon n}^2 \equiv \iint d\Omega d \epsilon \rho_\epsilon \left| \langle \psi_n(t) | \kappa_{\epsilon n}' \rangle \right|^2 \). The first term on the right represents nonadiabatic coupling of atomic states, the second modifies the phase development of the amplitude \( a_n(t) \) to allow for the perturbation presence of the metal, and the third allows for the transfer of electrons to and from the metal.

The \( \dot{b}_\epsilon(t) \) equation, 3.3.3, can be rearranged in the same way to yield the expression

\[
(1 - \Delta_{\epsilon n}^2) \dot{b}_\epsilon(t) = -i \sum_m a_m(t) \left[ \langle \kappa_{\epsilon m}' | V_a | \psi_n(t) \rangle \right. \\
- i \sum \langle \psi_n(t) | V_m | \psi_m(t) \rangle \langle \kappa_{\epsilon n}' | \psi_n(t) \rangle e^{-i \int_0^t \Delta_{n e'}(R(t')) dt'} \\
- i \iint d\Omega d \epsilon \langle \kappa_{\epsilon n}' | V_a | \kappa_{\epsilon n} \rangle \sum_m \langle \psi_n | V_a | \kappa_{\epsilon m} \rangle.
\]

\[ \langle \kappa_{\epsilon n}' | \psi_n(t) \rangle e^{-i \Delta_{\epsilon n} t} \]  \hspace{1cm} (3.3.9)

A term containing the factor \( \langle \psi_n | \psi_n \rangle \langle \kappa_{\epsilon n}' | \Omega' | \psi \rangle \) has \( \hbar \) dropped for reasons discussed above and the indices have been changed. The secular term in this equation serves to modify the phase development of the \( b_\epsilon(t) \) amplitudes. Even if we were to retain this term the resultant phase modification would not be realistic since we have ignored screening effects in the metal which tend to reduce the strength of potential \( V_a \). It seems most reasonable to set
the coefficient of the secular term equal to zero and allow the metallic states to develop as unperturbed states.

Suppressing the normalization coefficient, equation 3.3.9 without the secular term or coupling of metallic states by the atomic core becomes

\[
\begin{align*}
\frac{b_{\epsilon}(t)}{a_{n}(t)} &= -i \sum_{n=1}^{N} a_{n}(t) \left[ \langle \kappa_{\epsilon}^{n'} | V_a | \psi_n(t) \rangle \langle \psi_n(t) | V_{mn} | \psi_m(t) \rangle \right] \left( \kappa_{\epsilon}^{n} \right) \\
&= -i \int_0^t \Delta_{n\epsilon} (R(t')) dt' \langle \psi_n | \psi_n \rangle.
\end{align*}
\]

(3.3.10)

Let

\[
\Gamma_1(\epsilon, n, t) = \left[ \langle \kappa_{\epsilon}^{n} | V_a | \psi_n \rangle \langle \psi_n(t) | V_{mn} | \psi_m(t) \rangle \langle \kappa_{\epsilon}^{n} | \psi_m(t) \rangle \right]
\]

and

\[
\Gamma_2(\epsilon, n, t) = \left[ \langle \kappa_{\epsilon}^{n} | V_a | \psi_n \rangle \langle \psi_n(t) | V_{mn} | \psi_m(t) \rangle \langle \kappa_{\epsilon}^{n} | \psi_m(t) \rangle \right]
\]

(3.3.11)

Equation 3.3.8 must be solved for \(a_{n}(t)\). To do so, an expression for amplitude \(b_{\epsilon}(t)\) in terms of \(a_{n}(t)\) must be found. Formally, such an expression is the result of the integration of equation 3.3.11 over time

\[
\begin{align*}
\frac{b_{\epsilon}(t)}{a_{n}(t)} &= -i \sum_{n=1}^{N} \int_0^t dt' a_{n}(t') \Gamma_1(\epsilon', n, t) \\
&= -i \int_0^t \Delta_{n\epsilon} (R(t'')) dt'' + b_{\epsilon}(0).
\end{align*}
\]

(3.3.13)
In this expression \( b_{\varepsilon}(t) \) is taken to consist of the initial amplitude for the metallic state, \( b_{\varepsilon}(0) \) (cf. Appendix 3.1), and a component representing transfer of amplitude from the atom.

For brevity, let

\[
F_2(\varepsilon, n, t) \equiv \int \int d\Omega \Gamma_2(\varepsilon, n, t)
\]

and similarly for \( \Gamma_1 \). Further, whenever two such factors appear together, it is to be understood that the angular integration is carried out over the product of the \( \Gamma \)'s.

Substitution of equation 3.3.13 for \( b_{\varepsilon}(t) \) into equation 3.3.8 for \( \dot{a}_n(t) \) results in the expression

\[
\dot{a}_{n'}(t) = -\sum_{n} a_n(t) \langle \psi_{n'}(t) | \psi_n(t) \rangle e^{-i\int_0^t \Delta_{nn'}(R(t')) dt'} - i\int_{-\infty}^t \int_{-\infty}^t d\varepsilon F_2(\varepsilon, n, t) P_\varepsilon \int_0^t d\tau' a_{n'}(t') F_1(\varepsilon, n, t) e^{-i\int_0^{t'} \Delta_{nn'}(R(t'')) dt''} + \omega \int_{-\omega}^{\omega} e^{-i\int_{-\infty}^t \Delta_{\varepsilon n'}(R(t'')) dt''} - i\int_{-\infty}^t d\varepsilon P_\varepsilon b_{\varepsilon}(0) F(\varepsilon, n, t) e^{-i\int_0^t \Delta_{\varepsilon n'}(R(t'')) dt''}
\]

(3.3.15)

The prime on the first summation sign indicates that \( n \neq n' \).

Let the nonadiabatic coupling term be represented by

\[
V_{n'n}(t) \equiv a_n(t) \langle \psi_{n'}(t) | \psi_{n'}(t) \rangle e^{-i\int_0^t \Delta_{nn'}(R(t')) dt'}
\]

(3.3.16)
The time and energy integrals in the second term to the right in equation 3.3.15 lead to a Dirac delta-function, \( \delta(\omega_n - \omega_{n'}) \), for atomic states \( n \) and \( n' \). For the process that is local in time \( (t = t') \) the possibility of exact energy degeneracy of distinct states is excluded by the Pauli principle. The process (nonlocal in time) in which atomic state \( n \) loses an electron to a metallic state (at time \( t' \)) which later (at \( t \)) loses the electron to the then degenerate atomic state \( n' \), is highly unlikely, for reasons discussed above (cf. Section 3.1).

For these reasons, we retain only the diagonal element of the second term in equation 3.3.15, leaving

\[
\ddot{a}_{n'}(t) = \sum_n V_{n'n}(t) - \int_\infty^\infty d\varepsilon F_z(\varepsilon, n, t) \rho_\varepsilon \int_0^t dt' a_{n'}(t') F_1(\varepsilon, n, t')
\]

\[
\begin{align*}
-i &\Delta_{\varepsilon_{n'}}(\mathcal{R}(t'')) dt'' \\
- &\mathcal{E} &\int_\infty^\varepsilon d\varepsilon \rho_\varepsilon b_\varepsilon(\varepsilon) F_z(\varepsilon, n, t')
\end{align*}
\]

(3.3.17)

The terms of this equation for amplitude \( a_{n'}(t) \) represent nonadiabatic coupling of atomic states, loss of amplitude from atomic state \( n' \) to the metal, and gain into state \( n' \) from the unperturbed electron distribution within the metal, respectively. Temporarily, the nonadiabatic coupling term \( V_{n'n}(t) \) is deleted since it is not affected by the following mathematical manipulations. It is reinstated in equation 3.3.33.
In order to solve this equation we introduce the Fourier transform pair

\[ a_{n'}(t) = \int_{-\infty}^{+\infty} d\beta f(\beta) e^{-i\beta t} \tag{3.3.18} \]

\[ f(\beta) = \frac{1}{2\pi} \int_{t'}^{\infty} dt' a_{n'}(t) e^{i\beta t'} \tag{3.3.19} \]

Multiplying equation 3.3.17 by \( e^{i\beta t - \eta t} \) (where \( \eta \) is a small convergence factor which we shall eventually assume to be negligible), and integrating over \( t \) \((0 \leq t \leq \infty)\), we find, after an integration by parts, that the left side of equation 3.3.17 becomes

\[ a_{n'}(0) = 2\pi i \beta f(\beta) \tag{3.3.20} \]

If \( F_1(\epsilon, n', t') \) is sufficiently slowly varying in \( t' \) with respect to the variation of the exponential term, it can be taken out of the integral and evaluated at time \( t \). An integration by parts of the second term to the right in equation 3.3.17 yields the result (the nonintegral term vanishes at both limits)

\[ -2\pi i \int_{-\infty}^{+\infty} d\epsilon \frac{a_{n'}(t) F_1(\epsilon, n', t) F_2(\epsilon, n', t) \rho_\epsilon f(\beta)}{(\omega_{n'} - \epsilon) - \beta - i\eta} \tag{3.3.21} \]

in terms of the Fourier transform \( f(\beta) \). Performing the integration in the last term in equation 3.3.17 we find that
\[ a_n'(0) - 2\pi i\beta f(\beta) = -2\pi i \int_{-\infty}^{+\infty} d\epsilon \frac{F_1(\epsilon, n', t) F_2(\epsilon, n', t)}{\epsilon - (\omega_n + \beta) + i\eta} \]
\[ - i \int_{-\infty}^{+\infty} d\epsilon \frac{b_\epsilon(0) P_\epsilon}{\epsilon - \omega_n - \beta - i\eta} F_2(\epsilon, n', t) \]

(3.3.22)

For times \( t > 2\pi \) the \( \beta \) factor in the denominator of the first term on the right side of equation 3.3.22 can be set equal to zero. We cannot set \( \beta = 0 \) in the second term since it lacks an \( f(\beta) \) factor. Thus,

\[ 2\pi i f(\beta) = \left[ a_n'(0) + i \int_{-\infty}^{+\infty} d\epsilon \frac{b_\epsilon(0) P_\epsilon}{\epsilon - \omega_n - \beta + i\eta} F_2(\epsilon, n', t) \right] \]
\[ + \left[ \beta + \int_{-\infty}^{+\infty} d\epsilon \frac{F_1(\epsilon, n', t) F_2(\epsilon, n', t)}{\epsilon - \omega_n + i\eta} \right] \]

(3.3.23)

To get back to the more easily interpreted \( a_n(t) \) amplitudes we take the inverse Fourier transform by multiplying equation 3.3.23 by \( e^{-i\beta t} \) and integrating over \( \beta \) \((-\infty \leq \beta \leq \infty\)).

The result of this integration is the expression

\[ 2\pi \int_{-\infty}^{+\infty} d\beta f(\beta) e^{-i\beta t} = a_n'(0) \int_{-\infty}^{+\infty} d\beta \frac{e^{-i\beta t}}{\beta - \gamma} \]
\[ + i \int_{-\infty}^{+\infty} d\epsilon \frac{b_\epsilon(0) P_\epsilon}{\epsilon - \omega_n + i\eta} F_2(\epsilon, n', t) \int_{-\infty}^{+\infty} d\beta \frac{e^{-i\beta t}}{(-\beta + \gamma)(\beta - \epsilon + \omega_n + i\eta)} \]
\[ \equiv (A) + (B). \]

(3.3.24)
where

\[ \gamma = \int_{-\infty}^{+\infty} \frac{d\epsilon}{\pi} \frac{F_{1}(\epsilon, \omega'_{n}, t) F_{2}(\epsilon, \omega'_{n}, t)}{-(\epsilon - \omega'_{n}) + i\eta} \]  \hspace{1cm} (3.3.25)

The first integral, (A), is easily evaluated by a contour integration along the real \( \beta \) axis and a semicircle at infinity in the lower half complex \( \beta \) plane, with the result

\[ (A) = 2\pi i \ a_{n}(0) \ e^{-i\gamma t} ; \ \gamma > 0 \]  \hspace{1cm} (3.3.26)

The second integral (B) is more interesting and is evaluated in Appendix 3.2, with the result

\[ (B) = -2\pi^{2} i \ b_{n}(0) \ \rho_{n} F_{2}(\bar{\epsilon}, \omega'_{n}, t) e^{i\gamma t} \]  \hspace{1cm} (3.3.27)

where,

\[ \bar{\epsilon} = \omega'_{n} - \gamma \]

We have yet to deal with the integral \( \gamma \) in the exponential. Now, using the identity 11

\[ \lim_{n \to 0} \frac{1}{(\epsilon' - \omega_{n} \pm i\eta)} = \mathcal{P} \left( \frac{1}{\epsilon' - \omega_{n}} \right) + i\pi \delta(\epsilon' - \omega_{n}) \]  \hspace{1cm} (3.3.28)

we have, upon substituting equation 3.2.33 into equation 3.3.25, and integrating,

\[ \lim_{n \to 0} \int_{-\infty}^{+\infty} d\epsilon \frac{F_{1} F_{2}}{(\epsilon' - \omega_{n} - i\eta)} = \mathcal{P} \int_{-\infty}^{+\infty} d\epsilon \frac{F_{1} F_{2}}{\epsilon' - \omega_{n}} + i\pi \rho_{n} F_{1} F_{2} \]  \hspace{1cm} (3.3.29)
where \( \mathcal{P} \) denotes the Cauchy "principal part" of the integral.

Let

\[
\alpha = \mathcal{P} \int_{-\infty}^{+\infty} \frac{F_1 F_2}{(\epsilon' - \omega_n')}. \tag{3.3.30}
\]

Then, substituting equations 3.3.29, 3.3.27, and 3.3.26 into equation 3.3.24, we have

\[
a_{n'}(t) = a_{n'}(0) \exp \left[ i \alpha t - \pi \left( F_1 F_2 t \right) \right] - \pi b_{\epsilon}(0) F_{\epsilon} \\
F_2(\epsilon, n', t) \exp \left[ i \alpha t - \pi \left( F_1 F_2 t \right) \right] \cdot t \tag{3.3.31}
\]

where \( F = F(\epsilon, n', t) \). This result is valid for large \( t \) only if \( F_1 \) and \( F_2 \) are constant in \( t \), however, the time derivative of \( a_n(t) \) remains correct provided that these terms vary sufficiently slowly with respect to the exponential term.

Now, the term in \( \alpha \) in both exponents modifies the phase development of the adiabatic state \( \psi_n \), to allow for the presence of a degenerate continuum. Since the effect is small and almost certainly has no influence on this calculation, \( \alpha \) is set equal to zero.

The first term in equation 3.3.29 represents the exponential decay of state \( n' \) into an empty continuum, consequently, it is effective only if \( \omega_n > \phi_w \), the work
function. States for which the first term is active cannot be replenished by a resonant process. The second term represents the simultaneous input into amplitude \( a_{n'}(t) \) from the metal and its exponential decay into the continuum. Transfer of amplitude from the metal is possible only if the energy level of state \( n' \) is degenerate with a filled metallic state. Since the energy levels of the adiabatic states are constantly moving there is no depletion of the metallic states. Again, the Pauli principle precludes transitions back to the metal. The effective value of the exponent is thus zero, that is, the atomic state either loses amplitude if above the Fermi level or gains amplitude if below.

Equation 3.3.31 is then reduced to

\[
a_{n'}(t) = a_{n'}(0) e^{-\pi \int \frac{F_1}{F_2} t} - \pi b_\epsilon(0) \rho_\epsilon \left| F_2(\epsilon, n', t) \right| t \tag{3.3.32}
\]

Reintroducing the nonadiabatic coupling term, \( v_{n' n} \), and explicitly including the energy condition for the loss and gain terms,

\[
\dot{a}_{n'}(t) = \sum_{n' \neq n} \nabla_{n' n} -\pi F_1(\epsilon, n', t) F_2(\epsilon, n', t) \rho_\epsilon \, a_{n'}(t) \, \Theta(\epsilon - \epsilon_F)
\]

\[
-\pi b_\epsilon(0) \rho_\epsilon \, F_2(\epsilon, n', t) \, \Theta(\overline{\epsilon_F} - \epsilon), \tag{3.3.33}
\]

where the step function is defined as

\[
\Theta(x) = \begin{cases} 
1 & ; \ x > 0 \\
0 & ; \ x < 0 
\end{cases} \quad (3.3.34)
\]
In numerical computation a function with continuous first derivative is used in place of \( \theta \) (cf. Appendix 3.5).

Equation 3.3.23 exhibits some single-electron properties which are not relevant to the atom-metal interaction. Since we do not allow for changes in the metallic occupancies, the third term to the right in 3.3.33 must cause an incoherent gain in probability of occupancy of the atomic state. The ambiguity in phase arises only if \( a_n > 0 \) when the gain term becomes effective. To compensate for this unphysical behavior, multiply the gain term by \( \text{sgn} (a_n(t)) \). This is consistent with the discussion following equation 3.3.3.

The Pauli exclusion principle for metallic states has been satisfied by deleting the loss term in equation 3.3.23 for states of energy below the Fermi level. The corresponding requirement for the atomic state has yet to be considered. As the theory stands at this point, amplitude \( a_n(t) \) can increase without bound. In fact, the atom core, which is the source of the potential \( V_a \) which causes the metal-atom transition, is screened as charge accumulates in the atomic states. As the atom approaches neutrality, this potential vanishes. To include this occupancy dependence in the model, we multiply the core potential by the factor

\[
Q(t) = \sum_{\infty} \left( 1 - |a_n(t)|^2 \right), \tag{3.3.35}
\]
which is the effective charge of the core (this approximation is discussed in more detail in Appendix 3.1).

With these revisions, the set of equations which is solved numerically for (complex) atomic state amplitudes is

\[
\dot{a}_{n'}(t) = -\sum_{n=1}^{N} a_{n}(t) \langle \psi_{n'}(t) | \dot{\psi}_{n}(t) \rangle e^{-i \int_{0}^{t} \Delta_{n,n'}(R(t')) dt'}
- \pi F_{1}(\epsilon, n', t) F_{2}(\epsilon, n, t) \rho_{\epsilon} a_{n'}(t) \theta(\epsilon - \bar{\epsilon}_{F})
+ \pi b_{\epsilon}(0) \rho_{\epsilon} | F_{2}(\epsilon, n', t) | \theta(\epsilon_{F} - \epsilon) \text{sgn}(a_{n'}(t)) Q(t),
\]

(3.3.36)

where \( N \) is the number of basis functions from which the adiabatic states are formed, and \( N' \) is the number of adiabatic states which interact. These equations are non-linear because of the effective charge term, \( Q(t) \).

For a single channel \( \lambda \) of energy \( \epsilon \) below the Fermi level the nonadiabatic coupling and loss terms of equation 3.3.36 vanish, leaving

\[
\dot{a}_{\epsilon}(t) = -\pi b_{\epsilon}(0) \rho_{\epsilon} F_{2}(\epsilon, \lambda, t) (\sqrt{-|a_{n}(t)|^{2}}).
\]

(3.3.37)

This first order equation can be solved analytically,

\[
a_{\epsilon}(t) = \frac{A_{\epsilon}^{\sigma} \exp(-2\pi b_{\epsilon}(0) \rho_{\epsilon} \int_{0}^{t} dt' F_{2}(\epsilon, \lambda, t'))}{\overline{A_{\epsilon}^{\sigma} \exp(-2\pi b_{\epsilon}(0) \rho_{\epsilon} \int_{0}^{t} dt' F_{2}(\epsilon, \lambda, t')) + 1}}
\]

(3.3.38)
where $A_\lambda$ is the initial condition

$$A_\lambda = \ln \left[ \frac{1 + a_\lambda(t)}{1 - a_\lambda(t)} \right]$$  \hspace{1cm} (3.3.39)

In equation 3.3.38 subscript $\lambda$ refers to the adiabatic state, but we can, as a first approximation, take $a_\lambda(t)$ to be the coefficient of an unperturbed hydrogenic state and explore the dependence of neutralization probability on velocity, initial ion-surface separation and metal occupancy $b_\lambda(0)$. The coupling term $F_2$ for the unperturbed state has a much simpler form than that for the adiabatic state and can be reasonably well represented by a simple exponential. In this case the integrals in expression 3.3.38 can be done analytically.

Finally, the effect of a narrow d-band in the metal could be represented by inclusion of a second gain term in equation 3.3.36. Such a term could model the directional properties of the d-band electrons in an approximate fashion through the $F_2$ factor, although explicit inclusion of these effects introduces a nonaxial asymmetry which may couple atomic states of different magnetic sublevel $m_z$. 
References - Chapter III

1. Ref. 27,28 (Ch. II).
2. Ref 19 (Ch. I).
8. T.B. Grimley, in Electronic Structure and Reactivity of Solid Surfaces ed. E.G. Derovune et. al. (Plenum, New York,1976)p.113, also ref. 26 (Ch. II).
9. Such factors can be considered to appear implicitly in the denominator of each matrix element.
11. ibid. p.85.
Chapter IV. Results and Discussion

4.1 Introduction

The adiabatic state problem is essentially the chemisorption problem posed for all atom-surface separations and as such it is intrinsically a many body problem which must be solved ultimately in a self-consistent manner. Rather than concentrate on this aspect of the scattering problem we have chosen to accept a one electron model which includes the perturbing effect of the interaction potential on the atom and the transition of electrons to and from the atom. The use of the screened image potential itself includes some correlation effects, as the Hartree Fock method alone does not reproduce the image potential.\footnote{1}

The specific results of this adiabatic state calculation, then, cannot be accepted as absolute in the near-surface region. We have included screening and potential variation in this region because of the belief that a model which produces plausible results, or those that compare reasonably with experiment, in the full interaction region is more likely to be correct in the region of weaker interaction than is some other model.

On the other hand, description of the excited state structure is, in some ways, less obscure than that of the ground state. For instance, screening of a highly localized state can be accomplished effectively only by those
conduction electrons in the metal which are characterized by wavelengths comparable to or less than the size of the localized state. The excited states of an atom are much larger than the ground state, because of the nature of the Coulomb potential, and are screened by a wider band of conduction electrons. (The distinction is caused by the radial polynomial factor in the hydrogenic wave function.) Because of this property of the excited states, the exponentially screened potential function, 2.5.18, is probably a better approximation for the screening of the excited than the ground state. Finally, the detailed interaction of the higher excited states becomes important only as the atom leaves the surface, since in the metal they are almost certainly unfilled. The strong asymmetry of metallic charge in the surface region itself may then be the prime factor in determining the structure of the adiabatic excited states.

The dependence of the detailed energetic structure of the adiabatic states on certain features of the model of the potential interaction is quite strong. The most realistic aspect of the approximate potential function is probably the use of the image potential for an electron outside the metal surface. This approximation has been shown\textsuperscript{2,3} to be rather accurate, even for external charge velocities a large fraction of the Fermi velocity. Fortunately, this part of the interaction potential is the
full asymptotic interaction, since all other terms vanish at large atom-surface distances.

The least reliable part of the model is probably the use of a constant, energy independent potential, \( V_p^0 \), for the electron-metal interaction term within the metal. The influence of this term on the matrix elements which determine the adiabatic state structure is large when the overlap between the atomic function and the internal region of the metal is large. For excited states, this overlap can remain large over an appreciable distance from the surface. The net effect of this term is either to promote accumulation of charge within the surface, if \( V_p^0 \) is numerically less than the averaged value for the Coulomb interaction in this region,\(^4\) or repel charge into the vacuum if \( V_o \) is greater than this averaged value. Because of the necessity of antisymmetrizing the total many-electron wave function (which results in the exclusion force), \( V_p^0 \) is taken in the calculations described here to be greater than the average Coulomb value. To facilitate the numerical computation (since no reliable guide exists for its choice), it is taken to be zero.

The matrix elements for coupling of the hydrogenic wave functions have been calculated using floating Gaussian wave functions. Use of these wave functions rather than Slater type orbitals is economically advantageous if the numerical form of the final expression for the matrix
element can be reduced to a simple combination of transcendent functions or if the matrix elements vary smoothly enough so that they need be found at relatively few atom surface separations. If a final numerical integration is required, as it is in this calculation (cf. Appendix 2.2) use of Gaussian functions composed of a large set of \( n \) exponential parameters \( \alpha \) \((n = 8, 9\) provides very good accuracy for these functions) is prohibitively expensive since the number of numerical integrations in the \( i^\text{th} \) matrix element is \( kpqn^2 \) where \( p \) and \( q \) floating ctnters comprise the \( i^\text{th} \) and \( j^\text{th} \) wave functions, respectively, and \( k \) is the number of integrations required for each matrix element. We have found, however, that even a small set of Gaussian parameters \( \alpha \) \((n = 2,3)\) gives reasonably accurate results for the matrix elements provided that we perform the rest of the calculation allowing explicitly for the nonorthogonality of the basis. The advantage of the floating Gaussian orbitals in this case is that it is necessary to find the form of the numerically integrated function for only two displaced Gaussian centers; one can then find the matrix elements for any wave function simply by summing over the proper sets of centers and exponential parameters (assuming that the parameters are available).

The metal is completely characterized in this model by four parameters, the energy of the bottom of the conduction band, \( V_o \), the pseudopotential, \( V_p^0 \), the Fermi energy,
\( \varepsilon_F \), and the density of states function, \( \rho_\varepsilon \). Explicit dependence on structure is absent, although there are small variations in Fermi energy \( \varepsilon_F \) at different crystal faces. This characterization of the metal is probably inadequate for comparison of the theory with experiment. The ion trajectory, in particular, which has not been included in the model in any detailed way, is strongly dependent on the crystal structure of the metal through the mechanism of channeling. The Auger neutralization probability may also have a strong dependence on crystal structure at the surface. Both of these factors must be known before the number and direction of ions emergent from the surface can be calculated. Observed excited state population must, therefore, depend on the more detailed characterization of the bulk metal and crystal face at least through those factors.

4.2 Adiabatic States of Hydrogen

The individual contributions to the matrix element \( \langle 2s | V_{\text{int}} | 2s \rangle \) of unperturbed hydrogenic wave functions with interaction potential \( V_{\text{int}} \), 2.5.18, are shown in figure 4.1. For this diagonal matrix element, the attractive electron-(self-image) and repulsive electron-(core image) terms are almost equal in magnitude, although the electron-(core image) term contains the \( 1/4s \) component which does not enter into the calculation of adiabatic states (cf. discussion of Section 2.5). The electron-(screened core)
Figure 4.1 Individual contributions to the matrix element $\langle 2s | v_{\text{int}} | 2s \rangle$ of unperturbed hydrogenic wavefunctions with the interaction potential $v_{\text{int}}$. 
energy is positive to compensate for the negative Coulombic component already present in the unperturbed hydrogenic eigenenergies but which has been diminished by the screening effect of the metallic electrons when the core is close to the surface.

Several forms of function $u(s, r)$ of equation 2.5.17 have been considered. The goal is to find a function of core position, $S$, and electron position, $r$, which in an approximate fashion compensate for the variation in density of screening charge surrounding the atomic core in the surface region. In principle, the potential of the atomic electron depends on the integrated value of contributions from the core and inhomogeneously distributed screening charge. Since the distribution of screening charge at the surface is not readily calculable it seems reasonable to make the assumption that the effect of screening depends only on the two planes, parallel to the surface, in which the core and electron are found. The function $u(s, z)$, where the second argument is the $z$ component of $r$, then determines how the importance of the planes is weighted.

Representative matrix elements for screening length corresponding to the core, electron, and a variety of intermediate positions have been calculated. The results indicate that weighting the screening function toward the electron position emphasizes the spatial variation of the wave function, producing kinks in the matrix elements. Since such kinks might constitute an unphysical
nonadiabatic kinematic coupling of adiabatic states, and in view of the rapidity of electron motion compared to the response time of the metal, such solutions are rejected. Functions weighted toward the core, although smooth, do not account for the nonlocality of the potential function, and, especially for excited states of $m \neq 0$, must be a poor approximation. As a compromise the screening length is taken to be that relevant to the unperturbed electron density of the plane midway between the core and electron planes. Furthermore, the matrix elements are smoothest if parameter $p$ (inverse screening length) of equation 2.5.23 is taken to have the same value as $\lambda^0$ of 2.5.20. The use of smoothness as a criterion in choosing these functions is reasonable since the screening charge of the metal is not allowed to respond to the presence of the atom. In a self-consistent model, rapid variations in screening charge distribution with changes in core position are probably avoided.

Solution of the matrix equation 2.4.3 using hydrogenic wave functions, interaction potential 2.5.24, and the free space eigenenergies of hydrogen yields the eigenfunctions and eigenenergies of the adiabatic states of hydrogen near a metal surface. The adiabatic eigenenergies as a continuous function of atom-surface distance $s$ are shown in figure 4.2. The basis of hydrogenic states is restricted to the $m_z = 0$ states of $n = 1,2,3$ which are mixed by this (cylindrically symmetric) potential. The
Figure 4.2 Adiabatic state energies for the $m_z=0$ magnetic sublevels of hydrogen in the vicinity of a metal surface.
metal surface (defined by the image plane) is at \( S = 0 \), the metal occupies the half space to the left of the surface. The energy is given in units of Hartrees with zero defined as the \( z = \infty \) vacuum level. These curves contain the \( 1/4s \) component (cf. Section 2.5B) so that the resonant ionization and neutralization conditions are more easily identified.\(^7\)

The structure of the adiabatic eigenfunctions which determines the eigenenergies of figure 4.2 can be described in the following way. The eigenfunction which asymptotically correlates with the hydrogenic \( 1s \) wave function (hereafter called the adiabatic \( 1s \) eigenfunction of \( 1s \) eigenfunction) is not changed much by the interaction and remains largely an unperturbed hydrogenic \( 1s \) function for all values of \( s \); the energy variation is caused mostly by the \( 1/4s \) term.

The \( n = 2 \) adiabatic eigenfunctions change character abruptly at the strong avoided crossing at \( S \approx 4.8 \ a_0 \). Within that distance from the surface the \( 2s \) function is comprised mostly of the \( n = 3 \) hydrogenic functions which form a long-range dipole with charge repelled from the surface. In the same region the \( 2p \) function represents a shorter range dipole in the same direction. The \( 3s \) function has strong components of the reversed dipole, with charge accumulated within the surface. At the avoided crossing it becomes energetically favorable for the dipole character of the \( 3s \) state to pass to the \( 2s \) state so that the atomic electron has a high probability of being found between the
metal and atomic core. The 2s and 2p states retain this dipolar until \( s > 20 \ a_0 \) where they begin to approach their asymptotic unperturbed limits (although there is still a significant \( n = 3 \) component in both states).

The adiabatic \( n = 3 \) eigenfunctions undergo a similar transformation. At \( s = 1 \ a_0 \) the 3p and 3d states have a strong quadrupolar character, with charge shifted away from the core. As the atom goes through the avoided crossing at \( s = 6 \ a_0 \) a short-range dipole is formed in the 3s state (involving the 2p, 3s, and 3d functions). As \( s \) increases the 2p function has less effect on the 3s state and by \( s = 15 \ a_0 \), the 3s state is mostly quadrupolar with charge shifted toward the core (compression), similarly, the 3d state is quadrupolar with charge shifted away from the core.

The 3p function is not effectively coupled to any other for \( s > 6 \ a_0 \), so that the 3p and 3p states are very similar in that region. This effect may be caused by the presence of the \( 2p_z \) state and the strong tendency for a compression of charge toward the core to reduce the total energy. If more hydrogenic states were added to the basis, it is probable that the 3p state would couple strongly with the \( s \) and \( d \) functions of higher \( n \) in some intermediate distance region.

The configuration interaction which most effectively lowers energy seems to be that which causes formation of a dipole with charge accumulation between the core and
surface, and compression of the charge around the core. This general tendency is also observed through the density functional theory. 8

4.3 Atom-Metal Coupling Terms

Solution of the time development equation, 3.3.36, requires evaluation of the coupling term \( p_\varepsilon F_1 F_2 \), which is relevant to the loss process, and \( b_\varepsilon(0) p_\varepsilon F_2 \), which determines the gain rate. \( F_1(\varepsilon, n, t) \) and \( F_2(\varepsilon, n, t) \) are given by expressions 3.3.11 and 3.3.12 integrated over all angles,

\[
F_1(\varepsilon, n, t) = \int d\Omega \left[ \langle \kappa_\varepsilon^n | V_\alpha | \psi_n(t) \rangle - \sum_{m'} \langle \psi_{m'} | V_m | \psi_n \rangle \langle \kappa_\varepsilon^n | \psi_{m'} \rangle \right] (4.3.1)
\]

\[
F_2(\varepsilon, n, t) F_1(\varepsilon, n, t) = \int d\Omega \left[ \Gamma(\varepsilon, n, t) \left[ \langle \kappa_\varepsilon^n | V_\alpha | \psi_n(\varepsilon) \rangle - \int d\Omega' d\varepsilon' p_{\varepsilon'} \langle \kappa_\varepsilon^n | V_\alpha | \kappa_{\varepsilon'}^{n'} \rangle \langle \psi_n | \kappa_{\varepsilon'}^{n'} \rangle \right] \right] (4.3.2)
\]

Following the choice of the electron-metal potential, \( V_\alpha \), within the metal as zero, the second term in the integrand of 4.3.1 is taken to be zero. The calculation of \( F_1 \) and \( F_2 \) from the metallic wave function, 2.6.1, and Slater orbitals is described in detail in Appendix 3.4; occupation amplitude \( b_\varepsilon(0) \) is evaluated in Appendix 3.3. Let

\[
\Gamma_1 = p_\varepsilon F_1(\varepsilon, n, t) \quad (4.3.4)
\]

\[
\Gamma_2 = p_\varepsilon F_2(\varepsilon, n, t) F_1(\varepsilon, n, t) \quad (4.3.5)
\]
$T_1$ and $T_2$ represent integrals of the products of decaying exponential functions with centers displaced by a distance $S$. They can be approximated, at least asymptotically, by a simple exponential function,

$$W_1^a = c_1^a \exp(c_2^a S), \quad (4.3.6)$$

as is typically done in the literature for matrix elements of the ground state. The coupling terms for excited states, however, are not as well represented by this function because of the overlap component of equation 4.3.2 and saturation of the exponential behavior at small $s$, where the atomic wave function penetrates the surface.

The spatial integration for $P_1$ and $P_2$ has been performed only for the region outside the metal, where the metallic wave function is a decaying exponential. As the atom approaches the surface the largest spherical maximum of the $3s$ wave function, for instance, intersects the surface plane at $S = 13.5 \ a_0$. Thereafter the contribution of that peak to the matrix element diminishes, which leads to a maximum and, possibly, an eventual decline in the value of the matrix element. While an approximation function consisting of a single exponential cannot describe such behavior, the exponential of a quartic polynomial, however is sufficient. (Variations from the (discrete) values of the coupling terms introduced by use of this (continuous) function are much smaller than those introduced by the displacement of the image plane from the half density plane.)
The approximation function has the form

\[ T_{1,2} \equiv \exp \left( \sum_{n=0}^{\infty} C_{n}^{(1,2)} S_{n} \right) \]  (4.3.7)

For the \( n = 3 \) states the assumption that the spatial integration in the coupling matrix elements be carried out only over the region outside the metal causes the matrix elements to fall off rapidly near the surface. Integration of these matrix elements over all space using metallic wave function 2.6.1, however, would overestimate the actual values since the real metallic wave functions are orthogonal to the metallic core functions, and the external potential, \( V_{a} \), is scattered within the metal.

Rather than try to calculate this contribution to the coupling matrix elements directly, we assume that the uncalculated component is sufficient to maintain the matrix elements at their calculated maximum values from that point to the surface plane. The approximation functions 4.3.7 are then found by a least squares procedure. This approximation would limit the accuracy of the branching ratios for the \( n = 2 \) and \( n = 3 \) states if the dominant mode of population of the \( n = 3 \) states were resonant neutralization. Since the \( n = 3 \) states lie above the Fermi level in every case we have studied, however, no resonant transitions to the \( n = 3 \) states occur. Nonadiabatic excitation from the \( n = 2 \) states is the dominant population mechanism for these states. Since the loss term from the \( n = 3 \) states
is not effective close to the surface the ratios of final state probabilities are relatively insensitive to the details of this approximation.

The calculated atom-metal coupling terms for ionization (T2) and neutralization (T1) unperturbed hydrogenic states are presented in figures 4.3 and 4.4 respectively. The presence of a maximum in the n = 1 and n = 2 atoms near the surface is an artifact of the method used to find the coefficients in equations 4.3.7 and 4.3.8 and has no significance. Since these functions are never used for S < 1 a_0 the variation is not important.

The analogous coupling terms for loss from the adiabatic states of hydrogen are shown in figure 4.5 for the 2s, 2p_z, and 3s states (where the arrow denotes asymptotic correlation) and in figure 4.6 for the 3s, 3p_z, and 3d_z states. Here the variation with distance is much stronger than for unperturbed hydrogenic states since the curves represent the product of the linearly varying state coefficients with the exponentially varying coupling terms.

4.4 Single Channel Resonant Neutralization

The description of the time evolution of the adiabatic states of hydrogen in an outgoing trajectory is complicated by the large number of simultaneous interdependent processes. In order to demonstrate the sensitivity of the results to variation of the initial distance parameter, S_o, the single channel equation for resonant neutralization of
Figure 4.3 Atom-metal coupling terms $T_2/2k'_0$ (where $k'_0$ is the wavenumber of the metallic state degenerate with the atomic state) for hydrogenic wavefunctions ($m_z = 0$).
Figure 4.4 Atom-metal coupling terms $T_1/2\pi k_0^1$ for hydrogenic wavefunctions ($m_2=0$).
Figure 4.5 Atom-metal coupling terms for the adiabatic states of hydrogen ($m_z=0$) near a metal surface.
Figure 4.6 Atom-metal coupling terms for the adiabatic states \( (m_z=0) \) near a metal surface.
hydrogen into the unperturbed hydrogenic 2s state is solved. The form of the solution is given by equation 3.2.43. If $P_2$ is represented by a simple exponential function, 4.3.6, the integration can be done analytically, with the result (cf. equation 3.2.43)

$$A_{2s}(t) = \frac{A_{2s}^0 \exp \left[ \frac{-2C_0}{\alpha \sqrt{v}} \left( \exp(-\alpha v t) - \exp(-\alpha v t_0) \right) - 1 \right]}{A_{2s}^0 \exp \left[ \frac{-2C_0}{\alpha \sqrt{v}} \left( \exp(-\alpha v t) - \exp(-\alpha v t_0) \right) + 1 \right]} \quad (4.4.1)$$

Figure 4.7 shows the variation of $P_{2s}(t)$, as calculated from equation 4.4.1, with initial distance $S$. The dependence on $S_0$ displayed in these curves is overemphasized because of the simple form of $P_2$. (The solution refers to the hydrogenic 2s state.)

4.5 Solution of the Time Development Equations

The solution of the time development equations, 3.3.36, is strongly dependent on a number of parameters which characterize the system under study and the way in which the system is modeled. In this section these parameters are listed and a number of illustrative solutions of the time development equations is discussed.

The metal is taken to be a simple free electron gas characterized by the Fermi energy and the work function. Some variation from free electron behavior could be included in the metallic occupancy term $b_\varepsilon(0)$ if reliable data were available, however, we have restricted these studies to the free electron $b_\varepsilon(0) = 1$ case.
Figure 4.7 Occupation probability $P_{2s}(t)$ for several values of starting distance $s_0$. The $^2s$ state referred to is the hydrogenic state.
Figure 4.8 Occupation probability for the $2s$ adiabatic state of hydrogen with no coupling to the other atomic states. $\epsilon_f = .138$ a.u. for Mg.
The atomic trajectory is completely described by the velocity, \( v \), and angle of the trajectory with the surface normal, \( \theta \). The velocity is taken to be a constant and the trajectory to be a straight line. This assumption is good at high velocities, but must fail at some low velocity where the electronic excitation energy becomes an appreciable fraction of the core translational energy.

Some parameters in the calculation are more explicitly model dependent. The sensitivity of the results to variation of the distance between the image and half density planes has been explored. Displacement of the image plane has the general effect of reducing the loss and gain rates between the atom and metal. The initial state of the system as it leaves the metal is also a model parameter in this calculation. We have not attempted to follow the neutralization process for excited states of an atom within the metal surface but compare final probabilities and branching ratios for some range of initial values. Finally, the number of adiabatic states which are included in the solution of the time dependent equations is varied to determine which effects and trends present in the truncated basis calculation might reasonably be expected to be observed were an infinity of states present.

In the following series of figures, which pertain to hydrogen, the state occupation probabilities as a function of atom-surface distance are shown as velocity, image plane displacement, number of adiabatic states, initial amplitudes,
and Fermi level are varied. As an example of the neutralization process without nonadiabatic coupling, the single state solution of the rate equation for the adiabatic $2s$ state is presented in figure 4.8. The shape of the curve is simply related to the energy level of the $2s$ adiabatic state with respect to the Fermi level of the metal. Occupation probability increases until the energy of the state crosses the Fermi level (at $S \approx 4 \ a_0$). Subsequently there is an exponential decay with a loss of probability to the metal.

Inclusion of nonadiabatic coupling with the $2p$ and $3s$ states (these adiabatic states are composed of the $n = 1, 6$ hydrogenic functions) results in an effective excitation mechanism (cf. figure 4.9). The total probability follows the same general pattern as seen in the single state case (figure 4.8). The strongest coupling of states occurs at the avoided crossing of the energy curves (figure 4.2).

Figures 4.8 and 4.9 pertain to the neutralization process for image plane displacement $d_S = 0 \ a_0$. The following calculations are done with $d_S = 2 \ a_0$ which is probably a better value for the single-electron radius $r_s = 2 \ a_0$. Variation of this parameter, which is strictly model dependent, produces an appreciable change in the final results, but qualitative features remain unchanged (compare figure 4.9 with figure 4.12). The difference is attributable mainly to the change in the gain and loss rates (which
Figure 4.9 Occupation probabilities for the $2s$, $2p_z$, and $3s$ adiabatic states of hydrogen.

$H = Mg$
$v = .5$
$d_s = 0$
$\Theta = 0$
$s_o = 1a_o$
$a_n(0) = 0; \text{ all } n$
Figure 4.10 Occupation probabilities for the 2s, 2pz, and 3s adiabatic states of hydrogen.
Figure 4.11 Occupation probabilities for the $2s$, $2p_z$, and $3s$ adiabatic states of hydrogen.
Figure 4.12 Occupation probabilities for the $2s$, $2p_z$, and $3s$ adiabatic states of hydrogen.
Figure 4.13 Occupation probabilities for the $2s$, $2p_z$, and $3s$ states of hydrogen.

\[ H = Mg \]
\[ \nu = 0.5 \]
\[ d_s = 2a_0 \]
\[ \Theta = 0 \]
\[ s_0 = 1a_0 \]
\[ a_n(0) = 0; \text{ all } n \]
Figure 4.14 Occupation probabilities for the $\overrightarrow{2s}$, $\overrightarrow{2p_z}$, and $\overrightarrow{3s}$ adiabatic states of hydrogen.
depend on distance from the half density plane) and the adiabatic state structure (which is found with respect to the image plane).

Figures 4.10 through 4.13 show state occupation probabilities as a function of atom-surface distance for several velocities in the range $0.05 \leq v \leq 0.5$. The work function assumed in these calculations is that of magnesium, and the trajectory lies along the surface normal ($\theta = 0$).

The initial condition to the solution of the Schrödinger equation is $a_u(t = 0) = 0$; all $n$. That is, the ion is bare as it leaves the surface. This is an arbitrary assumption, in that the lowest excited adiabatic state is below the Fermi level at the surface (cf. figure 4.2). Higher excited states must be unoccupied. In order to explore the sensitivity of the structure of the state interaction and ratios of final state probabilities to changes in the initial values, the solution of the time development equation, 3.3.36, has been calculated for $a_{\rightarrow 2s}(t = 0) = 1$. The results of this calculation are shown in figure 4.14. The term in equation 3.3.36 which causes the largest departure from exact scaling is the nonlinear effective charge factor $Q_n(t) = \sum \frac{1}{n} \left[ 1 - |a_n(t)|^2 \right]$, which is effectively a constant if the excited states are sparsely populated. Thus, the absolute final state probabilities in figures 4.10-4.13, indicate a lower limit on the predicted value. An approximation to the upper limit can
be found by transposing the entire set of curves in each figure upward to the point at which the highest peak touches the unit probability axis.

The results of a series of calculations such as those presented in figures 4.10-4.13 are summarized in figure 4.15. Predominance of the $2p$ state at low energies is caused by the very strong avoided crossing of the $2s$ and $2p$ energy levels, which may make this nonadiabatic behavior evident even at thermal core velocity. Calculations have not been carried out in this low velocity region because of the computational expense. The relative constancy of the total probability is a result of the compensatory relationship of the gain and loss terms.

The nonadiabatic coupling term of equation 3.3.36 contains a factor $\langle \psi_n, (t) | \dot{\psi}_n (t) \rangle$. In the semiclassical approximation, perpendicular atom-surface distance $S(t)$ is treated as a parameter rather than a dynamical variable. For the time derivative, then,

$$\frac{d}{dt} \psi_n (t) = \frac{\partial S}{\partial t} \frac{\partial \psi_n}{\partial S} = v(t) \frac{\partial \psi_n}{\partial S} \cos \theta$$

where $\theta$ is the angle of the (straight line) trajectory with the surface normal. For a given velocity, $v$, the nonadiabatic coupling strength is reduced by a factor of $\cos \theta$ along nonnormal trajectories. The gain and loss terms depend only on the amount of time the atom spends near the surface, and are therefore effectively augmented.
Figure 4.15 Occupation probabilities for the $2\text{s}$, $2\text{p}_2$, and $3\text{s}$ adiabatic states of hydrogen (asymptotic) as a function of core velocity.

\begin{align*}
\text{H - Mg} \\
d_s &= 2a_0 \\
\Theta &= 0 \\
s_0 &= 1a_0 \\
a_n(0) &= 0; \text{ all } n
\end{align*}
Some indication of these trends is evident in figure 4.16, which is the analog of figure 4.10 for a scattering angle of 30°. The variation of final state probabilities as a function of angle is shown in figure 4.18 for constant velocity \( v = .5 \). Occupation probability of the \( 2p_z \) state declines with increasing angle, \( \theta \), because of the longer time during which it is subject to ionization.

The calculations which have been described up to this point have all employed basis sets of three adiabatic states (each of which is composed of the \( n = 1, 6 \) hydrogenic wave functions). A series of calculations with four state basis sets has been performed. Again, the results are relatively insensitive to the initial occupation probability of the \( 2s \) state (compare figures 4.19 and 4.20). Both figures refer to the high velocity limit (\( v = .5 \)) where the dependence on \( a_n (t = 0) \) must be strongest.

Final state probabilities (as a function of velocity), are presented in figure 4.21. The structure of the curves for the \( 2s, 2p_z \), and \( 3s \) states is similar to that calculated without the \( 3p_z \) state, with a high \( 2p_z \) probability at low velocity, intermediate interaction between \( 2s \) and \( 2p \) states and central peak for the \( 3s \) state, but the \( 3p_z \) dominates at high velocities. In fact, the depressed value of the \( 3p_z \) probability at low velocity is not caused by a lack of nonadiabatic coupling, but rather by the very high loss rate for the \( 3p_z \) state (cf. figure 4.7), for \( 10 < s < 30 a_0 \).
Figure 4.16 Occupation probabilities for the $2s$, $2p_z$, and $3s$ adiabatic states of hydrogen for an exit trajectory $30^\circ$ from the surface normal.
Figure 4.17 Occupation probabilities for the $2s, 2p_z$, and $3s$ adiabatic states of hydrogen versus surface normal exit angle $\theta$. 

H = Mg  
$\nu = 0.5$  
$d_s = 2a_0$  
$s_o = 1a_0$  
$a_n(0) = 0; \text{ all } n$
Figure 4.19 Occupation probabilities for the $2s$, $2p_z$, $3s$, and $3p_z$ adiabatic states of hydrogen.

H = Mg
v = .5
d_s = 2a_0
$\theta = 0$
s_o = 1a_0
$a_{2s}(0) = 1$
a_n(0) = 0; n \neq 2s
Figure 4.19 Occupation probabilities for the $2s$, $2p_z$, $3s$, and $3p_z$ adiabatic states of hydrogen.
Figure 4.20 Occupation probabilities for the $\overrightarrow{2s}$, $\overrightarrow{2p_z}$, $\overrightarrow{3s}$, and $\overrightarrow{3p_z}$ states of hydrogen versus core velocity.

$\text{H - Mg}$

$d_s = 2a_0$
$\theta = 0$
$s_o = 1a_0$
$a_n(0)=0; \text{ all } n$
This is why the total probability is lower in this velocity range for the four state than the three state calculation (figure 4.16).

Inclusion of the $3d_z$ state might actually increase the total probability somewhat, since it has a lower loss rate than the $3p_z$ state (figure 4.6). This calculation has not been carried out because of the large requirements in computer time. Furthermore, calculation of an accurate $3d_z$ adiabatic state requires a larger basis set than has been employed here. The limiting factor in including higher states is the computational expense in computing matrix elements of the electronic Hamiltonian. Such matrix elements might be approximated through use of the extended Hückel theory\(^3\) (guided by the calculated results for lower states) and included in the solution of matrix equation 2.4.3. This procedure would provide, at least, a proper environment for the $n = 3$ states.

A single three state calculation for hydrogen ion reflection by a potassium surface has been performed (cf. figure 4.21). In this case, the $2s$ state lies asymptotically below the Fermi level; the neutralization probability for that state is large. A discussion relevant to this calculation is presented in Section 4.8.
Figure 4.21 Occupation probabilities for the $\vec{2s}$, $\vec{2p_z}$, and $\vec{3s}$ adiabatic states of hydrogen.

$H - K$
$v = .5$
$d_s = 2a_0$
$\theta = 0$
$s_0 = 1a_0$
$a_n(0) = 0$; all $n$
4.6 Adiabatic States of Helium

All calculations reported here have been performed using an atomic basis of hydrogenic wave functions exclusively. A zeroth order approximate description of the behavior of helium in the same environment can be found by inserting the energy splittings relevant to helium in the secular equation 2.4.3. Since the wave functions of helium resemble those of hydrogen, at least, asymptotically, this substitution is reasonable. A more accurate set of discrete-discrete and discrete-continuum matrix elements could be found by fitting floating Gaussian orbitals to some approximate form of the excited state wave functions for helium\(^{11}\) and using the Morse, Young, Haurwitz\(^{12}\) functions in a scheme such as is described in Appendix 3.4. The results of the calculations reported here, however, support the contention that the energy levels of the adiabatic states influence the final state probabilities more than does the detailed spatial structure of the adiabatic state wave functions.

The adiabatic state eigenenergies for the helium singlet and triplet spectra are shown in figures 4.22 and 4.23, respectively. These diagrams are quite similar to the analogous results for hydrogen. The main difference is that for helium the zeroth order energy splitting acts to dilute the strength of the state interactions, the avoided crossings are somewhat weaker.
Figure 4.22 Adiabatic state energies for the helium singlet system.
Figure 4.23 Adiabatic state energies for the helium triplet system.
4.7 Atom-Metal Coupling Terms for Helium

The coupling coefficients for the unperturbed states of helium, which correspond to those shown in figures 4.3 and 4.4 for hydrogen, differ from the corresponding hydrogenic values through only the relatively weak dependence on energy. (There is a large variation only for the 1s state.)

The loss rates for the \(2s\), \(2p_z\), and \(3s\) adiabatic states are presented in figures 4.24 for the singlet and 4.25 for the triplet state of helium. Again, the only factor which distinguishes the two spin states is energy. (The secular equations are solved separately.) The curves in these figures show the same kind of structure as is displayed by hydrogenic states (cf. figure 4.5).

4.8 Solution of the Time Development Equations for Helium

The addition of the spin index \(\sigma\) to equation 3.3.36 for amplitudes \(a_{n',\sigma}(\varepsilon)\) forces us, in principle, to extend the summation over \(n'\) to include \(2N'\) states (which requires solution of \(4N'\) coupled equations). As equation 3.3.36 is written, the two spin systems would then be coupled only through the nonlinear effective charge factor \(Q(t)\). The form of the Anderson Hamiltonian for this system, equation 2.5.15, suggests that the energy level of each state should also be dependent on the amount of "other spin" electron in that state through the term \(U_{\text{eff}} n_{\sigma} n_{a-\sigma}\), or the Hartree Fock approximate form of this term. Inclusion of
Figure 4.24 Atom-metal coupling terms for the $2s$, $2p_z$, and $3s$ adiabatic states of helium.
### Figure 4.25
Atom-metal coupling terms for the $2s$, $2p_z$, and $3s$ adiabatic states of helium.
this effect would raise the energy level of each state by
the Coulomb energy associated with the presence of other
electron.\textsuperscript{13}

This variation of the energy levels is difficult to
include in an actual calculation. The energy $U_{\text{eff}}$ for
hydrogen is taken to be the difference between the electron
affinity and ionization potential (multiplied by a
screening factor). For helium, since there is no bound
negative ion, no such simple guide exists. Furthermore,
the Hartree Fock approximation with its omission of the
correlation energy frequently predicts the wrong products
in molecular dissociation calculations and, therefore,
seems inappropriate here.

The effect of this variation of the energy levels
on the neutralization process may be predictable under cer-
tain circumstances if the initial energy levels of the two
spin states of some atomic level are split in energy.
Suppose that one excited state, $a$, is degenerate with the
metallic continuum. The spin states $a^\dagger$ and $a^\dagger$ are charac-
terized by zero-occupation energies $\varepsilon_{a^\dagger}$ and $\varepsilon_{a^\dagger}$, respec-
tively. A possible mechanism for the depopulation of the
energetically higher spin state is suggested. As the ion
leaves the surface (cf. figure 4.26) each energy level
begins to rise in response to the increasing occupation of
the other. Eventually, if the gain rates are comparable,
the $a^\dagger$ level crosses the Fermi level and begins to lose
amplitude. The energy level $\varepsilon_{a^\dagger}$ returns to its initial
Figure 4.26 Possible variation in energy of two spin levels of state 'a' during a resonant neutralization process (schematic).
value as the down spin state is depopulated. Under these conditions, neutralization of the lower spin state is dominant. Of course, the assumption that $U_{\text{eff}}$ is large enough to force one state above the Fermi level has not been demonstrated.

Following this argument, the following calculations for helium are performed primarily for the triplet state, which lies energetically below the singlet. The assumption is made that both spin states are equally represented in the metal and that the singlet state is asymptotically above the Fermi level (or is driven above it by the occupation of the triplet state), although some results are reported for the uncoupled singlet state. The results for scattering of helium by a clean magnesium surface should be characteristic of metals which meet those criteria. (In hydrogen the spin states are very nearly degenerate, however, for magnesium the occupation probabilities are small.)

Representative solutions of the time development equations for the singlet states of helium passing through a magnesium surface (with no coupling to the triplet system) have been found (figures 4.7 and 4.28). In this case, it is probable that where the adiabatic state energy crosses the Fermi level the energy shift caused by the occupation of the triplet state is small.
Figure 4.27 Occupation probabilities for the $2s$, $2p_z$, and $3s$ adiabatic states of the helium singlet system.
Figure 4.28 Occupation probabilities for the \(2s\), \(2p_z\), and \(3s\) adiabatic states of the helium singlet system.

\( ^1\text{He} - \text{Mg} \)
\( v = .5 \)
\( d_s = 2a_o \)
\( \theta = 0 \)
\( s_0 = 1a_o \)
\( a_n(0)=0; \text{ all } n \)
Results for the triplet state are presented in figures 4.29-4.31 for the three state and 4.34-4.35 for the four state adiabatic basis. The dominant feature is the large asymptotic $\bar{2}s$ state probability caused by the failure of the adiabatic state energy to rise above the Fermi level of the metal (magnesium). No coupling to the singlet spectrum is included. The development of state probabilities for a metal characterized by a Fermi level lying above the energy levels of the $\bar{2}s$ and $\bar{2}p$ states is displayed in figure 4.32. Such results are tentative since, again, the energy levels of the states may be dependent on their occupancies.
Figure 4.29 Occupation probabilities for the 2s, 2p\(_z\), and 3s adiabatic states of the helium triplet system.
Figure 4.30 Occupation probabilities for the $\overrightarrow{2s}$, $\overrightarrow{2p_z}$, and $\overrightarrow{3s}$ adiabatic states of the helium triplet system.

$^3$He - Mg

$\nu = 0.5$

$d_s = 2a_o$

$\Theta = 0$

$s_o = 1a_o$

$a_n(0) = 0$; all $n$
Figure 4.31 Occupation probabilities for the $2s$, $2p_z$, and $3s$ adiabatic states of the helium triplet system versus core velocity.

$^3\text{He} - Mg$

$d_s = 2a_0$

$\Theta = 0$

$s_\omega = 1a_0$

$a_n(0) = 0;\ all\ n$
Figure 4.32 Occupation probabilities for the 2s, 2p_z, 3s, and 3p_z adiabatic states of the helium triplet system.
Figure 4.33 Occupation probabilities for the $\vec{2}s$, $\vec{2}p_z$, $\vec{3}s$, and $\vec{3}p_z$ adiabatic states of the helium triplet system.

$^3$He - Mg

$v = 0.5$

$d_s = 2a_o$

$\theta = 0$

$s_o = 1a_o$

$a_n(0) = 0$; all $n$
Figure 4.34 Occupation probabilities of the 2s, 2p_z, 3s, and 3p_z states of the helium triplet system versus velocity.
Figure 4.35 Occupation probabilities for the \( \vec{2s} \), \( \vec{2p_z} \), and \( \vec{3s} \) adiabatic states of the helium singlet system.

\[ ^1\text{He} - K \]
\[ v = 0.5 \]
\[ d_s = 2a_o \]
\[ \theta = 0 \]
\[ s_o = 1a_o \]
\[ a_n(0) = 0; \text{ all } n \]
Figure 4.36 Occupation probabilities for the $\bar{2}s$, $\bar{2}p_z$, and $3s$ adiabatic states of the helium triplet system.

$^3\text{He} - K$

$v = .5$

$d_s = 2a_o$

$\theta = 0$

$s_o = 1a_o$

$a_n(0)=0; \text{ all } n$
4.9 Connection to Experimental Studies

The theory developed here is not intended as an analysis of any single experiment, but addresses questions which are relevant to several theoretical and experimental studies. The measured quantities in ion-surface scattering are typically Auger (or secondary-) electron current, sputtered particle mass, product charge fraction, or radiation spectrum. Of the first two, the theory presents no new information.

In the charge fraction experiments the neutral and positive and negative ion currents of the reaction products are measured. We have not calculated the background neutral (ground state) current or the negative ion fraction (for hydrogen). The calculated fraction of emergent ions which are resonant neutralized shows a tendency to be constant and fairly small (cf. figure 4.15, 4.20) even in the presence of strong variations of the final states if the excited states are asymptotically above the Fermi level. If one state is asymptotically below the Fermi level, the probability of its occupation is large at low velocity and decreases exponentially with velocity (cf. figure 4.34). The charge fraction is thus not very sensitive to the inclusion of nonadiabatic coupling of states in the model. Direct comparison with experiment requires an evaluation of the Auger rate, but experimental results seem to favor a weak variation of charge fraction with velocity.
Radiation from the excited states of backscattered\textsuperscript{15,16} and sputtered\textsuperscript{17} atoms has also been observed. Since the radiative lifetime of these states compared to the collision time at the surface is long, observed radiation comes mostly from free space atoms. The variation of final state probability with velocity calculated here is quite strong, especially for hydrogen. It should be possible to find limits to this variation experimentally through measurement of radiation lineshape.\textsuperscript{15}

Provision for the neutralization of magnetic substates of nonzero angular momentum projection, $m_z \neq 0$, has not been included in this calculation. Since the geometry of these states does not allow much distortion of the atomic charge at the surface the adiabatic state energies probably rise monotonically as the atom approaches the metal. For this reason, resonant transitions into these states are precluded if the Fermi level falls below the asymptotic $2p_z$ value. Since the nonadiabatic coupling (for a smooth surface) connects only states of the same magnetic sublevel, under these conditions, only the $m_z = 0$ excited states should be filled.

The relative population of magnetic substates is observable in an experiment through the polarization of that component of the observed radiation caused by intra-atomic transitions in the backscattered beam. Under the conditions described above, the theory predicts that plane
polarized radiation,\textsuperscript{18} emitted in a dipolar pattern parallel to the surface, should be observed. Such polarization effects might be effectively masked if a gas overlayer were present (the neutralization process is much more efficient under these conditions), or if there were filled surface states above the conduction band. Some experimental studies of the polarization of light emitted by fast hydrogen and helium ions which have passed through a thin carbon foil have been carried out.\textsuperscript{20} The observations indicate that the $m_z = 0$ magnetic sublevel is preferentially populated (at least in the absence of a large surface field\textsuperscript{21}).

The adiabatic states which have been calculated are also relevant to the electron induced desorption problem,\textsuperscript{22} wherein an adsorbed atom is excited from the ground state by electron impact. The equilibrium adsorption distance for the excited state may be different from that for the ground state. The excited atom may therefore gain sufficient kinetic energy to surmount any potential barrier which might otherwise prevent it from leaving the surface. The adiabatic state energies shown in figures 4.2, 4.22, 4.23 do not contain the core-core and core-image energy which, at small $s$, is highly repulsive, and which compensates for the $1/4s$ term, as discussed in Section 2.5. If these terms were added the curves would have a minimum near the surface. Detailed description of the electron induced desorption process probably requires a rather careful treatment of the electronic structure of the ground state adsorption phase.
4.10 Conclusions

The diversity of physical processes possible in a collision between a fast ion and a metal surface is large. One effect which has not been included in this discussion, for example, is the sputtering of the surface atoms themselves. The relative degree to which the ion-(surface core) interaction or the ion-(conduction electron) interaction determine the final state of the projectile atom is unclear. In this work, we have dealt exclusively with the latter. Fortunately, the projectiles which are easiest to describe theoretically are also the lightest, and which must, at a given velocity, cause the least disruption of the surface.

One goal of this work has been to determine the probable role of one nonadiabatic excitation process on the final state spectrum of an atom leaving a metal surface. Regardless of the details of the model used to describe the surface, it seems clear that the excited states of an atom near the surface must be strongly perturbed by its presence; the nonadiabatic excitation mechanism seems inevitable.

If the calculation were performed with a localized atomic basis for the metallic states the adiabatic state structure for the external atom would be a function of crystal structure, face, and orientation of the trajectory. Some averaging procedure would be necessary to find the
observable probability versus velocity relation. The extent to which the averaging process might wash out the structure of this relation or couple magnetic sublevels is unclear.

The extension of this work to lower velocities requires a more careful treatment of the ion trajectory. A semiclassical analysis of this problem has been discussed by Weenas and Howsman.23
References - Chapter IV

1. Ref 8 (Ch. III).
2. Ref. 18 (Ch. II).
3. Ref. 17 (Ch.II).
4. i.e. $\int_{z<-s} d\tau \psi_i^* \psi_2/\tau > V_0 \int_{z<-s} d\tau \psi_i^* \psi_2$
5. Ref. 22 (Ch.II).
6. Ref 6 (Ch.II).
7. cf. figure 1.1.
14. Ref. 6 (Ch. ii).
19. Ref 16 (Ch. I).
21. Ref. 16 (Ch. IV).
Appendix 2.1 Floating Gaussian Orbitals

Use of Gaussian orbital wave functions\textsuperscript{1,2} facilitates the evaluation of certain integrals which arise in atomic and molecular calculations. Floating gaussian orbitals are employed in the present calculation. They have the form

\[
\Phi_i(\mathbf{r}) = \sum_{j=1}^{N} \sum_{k=1}^{M} A_{kj} \exp\left[ -\alpha_{kj} (\mathbf{r} - \mathbf{R}_{kj})^2 \right] \tag{A2.1.1}
\]

where the sum on \( j \) is over the gaussian centers displaced from the atomic core by \( \mathbf{R}_{kj} \) and index \( k \) is over the parameters \( A \) and \( \alpha \) relevant to center \( j \). Values for \( A^{(ij)} \) and \( \alpha^{(ij)} \) for the excited states of hydrogen have been calculated by Sambe\textsuperscript{3} for \( M = 2, 3, 4 \) and \( N = 1s, ..., 3d_z \).

Briefly, the results of Boys' work used here are as follows. Let the single \( j, k^{th} \) component of A2.1.1 with exponential parameter \( \alpha(\mathbf{r}_A) \) be written as \( |\alpha, A\rangle \). Then the overlap matrix element is just

\[
\langle \alpha_A | \alpha_B \rangle = \left( \frac{\pi}{\alpha} \right)^{3/2} \exp\left[ -\frac{AB^2 \alpha_1 \alpha_2}{\alpha} \right] \tag{A2.1.2}
\]

where \( \alpha = \alpha_1 + \alpha_2 \), and \( AB^2 = \sum_{x, y, z} (A_x - B_x)^2 \) is the square of the distance between centers \( A_1 \) and \( A_2 \). The interaction between two gaussian elements and an external charge at \( C \) is given by
\[ \langle \alpha_1 A | V_c | \alpha_2 B \rangle = \frac{2\pi}{\alpha} \exp \left( \frac{-AB_{\alpha_1, \alpha_2}}{\alpha} \right) F(CP^2 \alpha) \]  

(A2.1.3)

in which,

\[ F(z) \equiv z^{-\frac{1}{2}} \int_0^\infty e^{-u^2} du, \]  

(A2.1.4)

\[ CP^2 = \sum_{x,y,z} \left( C_x - P_x \right)^2 \]  

(A2.1.5)

\[ P_x = \frac{\alpha_1 A_x + \alpha_2 B_x}{\alpha_1 + \alpha_2} \]  

(A2.1.6)

(The exchange and Coulomb integrals are listed in reference 1.)
Appendix 2.2 Matrix Elements $\langle \varphi_{a}^{(u)} | V_{\text{int}} | \varphi_{b}^{(u)} \rangle$

The integral $\langle \varphi_{a}^{(u)} | V_{e-c_{i}} | \varphi_{b}^{(u)} \rangle$ of the $i^{th}$ and $j^{th}$ single exponential parameter elements of gaussian wave functions $\varphi_{a}^{(u)}$ and $\varphi_{b}^{(u)}$, respectively, over the electron-(core image) potential is just (cf. Appendix 2.1),

$$
\langle \varphi_{a}^{\nu} | V_{e-c_{i}} | \varphi_{b}^{\nu} \rangle = A_{i} A_{2} \exp \left( -\frac{\lambda B z^{2}}{\alpha} \right) \cdot \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} dx \, dy \, dz \, \frac{e^{-\lambda \left( x^{2} + y^{2} + \left( z - p_{z}^{2} \right)^{2} \right)}}{\sqrt{x^{2} + y^{2} + (2s + z)^{2}}} \cdot \left[ 1 - \exp \left( -\lambda(s) \sqrt{x^{2} + y^{2} + (2s + z)^{2}} \right) \right]
$$

(A2.2.1)

The integral is most easily evaluated in cylindrical coordinates. Let $v = x^{2} + y^{2} + (2s + z)^{2}$, then,

$$
A_{2.2.1} = A_{i} A_{2} \pi e^{\frac{\lambda B z^{2}}{\alpha}} \int_{-\infty}^{\infty} \frac{e^{-\lambda \left( z - p_{z}^{2} \right) \frac{v}{\sqrt{v}}}}{(2s + z)^{2}} \cdot \left[ 1 - \exp \left( -\lambda(s) \sqrt{v} \right) \right] \, dv \, dz
$$

(A2.2.2)

from which point we can integrate each of the two terms in the $v$ integral separately to get

$$
A_{2.2.1} = A_{i} A_{2} \pi \frac{\lambda y_{2}}{\sqrt{y_{2}}} \left[ \exp \left( -\frac{\lambda B z^{2}}{\alpha} - \frac{\alpha p_{z}^{2}}{\alpha} + 4 \alpha s \right) \int_{-\infty}^{\infty} e^{\frac{\lambda B z^{2}}{\alpha}} \right] \left[ \exp \left( -\frac{\lambda B z^{2}}{\alpha} - \frac{\alpha p_{z}^{2}}{\alpha} + 4 \alpha s \right) \right] \left[ \exp \left( -\lambda(s) \sqrt{v} \right) \right] \, dz
$$

(A2.2.3)
This expression, A2.2.3, is inconvenient for actual calculation because of the $4x^2$ factor in the exponential.

The standard methods for calculating the complementary error function all contain an $\exp(-4x^2)$ factor. Define

$$\text{erfc}(x) \equiv e^{x^2} \text{erfc}(x). \quad (A2.2.4)$$

The appropriate manipulations of A2.2.3 yield the result

$$A2.2.1 = \frac{\lambda}{\alpha \lambda^2} e^{-\frac{A^2}{\alpha^2 \lambda^2}} \int_{-s}^{\infty} dZ e^{-\alpha Z^2 + 2\alpha P Z} \left[ \tilde{\text{erfc}} \left( \sqrt{\alpha} (2s + Z) \right) - \exp (-\lambda (s, z) \cdot (Z + s)) \right. \tilde{\text{erfc}} \left( \frac{\lambda (s, z)}{2 \sqrt{\alpha}} + \sqrt{\alpha} (2s + Z) \right) \right] \quad (A2.2.5)$$

where the $\tilde{\text{erfc}}(x)$ is computed as a polynomial for $0 < x < 1.5$, as a continued fraction for $1.5 < x \leq 6.0$, and as an asymptotic approximation for $x > 6$. For $z < -s$ (the case in which the electron is within the surface plane, but the core is not) the matrix element reduces by the same series of manipulations to
\[ \langle \Phi^u_{a_i} | V_{e-c} | \Phi^u_{a_j} \rangle = \frac{A_1 A_2}{\sqrt{\alpha}} \prod_{i=2}^{3} \exp \left( -\frac{A B^2}{\alpha} \frac{\alpha}{\alpha_{2}} - \alpha P_z^2 \right) \]

\[
\int_{-\infty}^{s} e^{-\alpha z^2 + 2 \alpha P_z z} \left[ \text{erfc} \left( \sqrt{\alpha} \left| z \right| \right) - \exp (-\lambda(s,z)) \cdot \left| z \right| \right. \left. \text{erfc} \left( \frac{\lambda(s,z)}{2 \sqrt{\alpha}} + \sqrt{\alpha} \left| z \right| \right) \right] dz
\]

(A2.2.6)

The electron-(self-image) integral for two single gaussian exponential parameters is, for \( z > -s, \)

\[ \langle \Phi^u_{a_i} | V_{e-c} | \Phi^u_{a_j} \rangle = A_1 A_2 \exp \left[ -\frac{A B^2}{\alpha} \frac{\alpha}{\alpha_{2}} \right] \]

\[
\left\{ \begin{array}{l}
-\pi^{3/2} \frac{V_0}{\alpha} \text{erfc} \left( \sqrt{\alpha} \left| F \right| \right) ; F > 0 \\
-\pi^{3/2} \frac{V_0}{\alpha} \left( 1 + \text{erf} \left( \sqrt{\alpha} \left| F \right| \right) \right) ; F < 0 \\
\end{array} \right.
\]

\[ -\lim_{T \to 0^+} \left[ \frac{V_0 A_0}{\alpha} \pi \int_{-\infty}^{\infty} e^{-\alpha \chi^2} \left( 1 - e^{\lambda(F-\chi)} \right) d\chi - \frac{\pi}{4} \int_{-F}^{F} \int_{-F}^{F} e^{-\alpha \chi^2} \left( 1 - e^{-\lambda(\chi+F)} \right) d\chi \right]
\]

(A2.2.7)
where the electron-(self-image) potential has the form

\[ V_{e-Si} = -V_0 \left[ 1 + \frac{A_0 (1 - e^{-\lambda(z + s)})}{z + s} \right] \theta(s - z) - \frac{(1 - e^{-\lambda(S + z)})}{4(z + s)} \]  \hspace{1cm} (A2.2.8)

and,

\[ F \equiv s + p_z \cdot \theta(s + z) \]  \hspace{1cm} (A2.2.9)

The last term in expression A2.2.7 is that caused by the image potential when the electron is outside the surface, and is consequently the dominant term. It can be expressed in the form of an infinite series rather than an integral of the term \((1 - e^{\lambda v})/v\) is written as a series and integrated term by term.

\[ 1 - \frac{e^{-\lambda v}}{v} = \lambda \sum_{n=0}^{\infty} \frac{(-\lambda v)^n}{(n+1)!} \]  \hspace{1cm} (A2.2.10)

The last term in A2.2.7 is then

\[ -\frac{\lambda}{4} e^{-\alpha t^2} \sum_{n=0}^{\infty} \frac{(\lambda)^n}{(n+1)!} \int_0^\infty v^n \exp(-\alpha v^2 - 2\alpha vt) dv \]  \hspace{1cm} (A2.2.11)

which can be expressed in terms of the parabolic cylinder functions\(^5\) \(D_{-\nu}(z)\) as

\[ -\frac{\lambda}{4} e^{-t^2/2} \sum_{n=0}^{\infty} \frac{(\lambda)^n}{(n+1)(2\alpha)^{n+1/2}} D_{-\nu}(\sqrt{2} \cdot t') \]  \hspace{1cm} (A2.2.12)

where,
\[ t' = \sqrt{\alpha'} (s + P_z) \]  

(A2.2.13)

Then,

\[ \langle \Phi_{\alpha_1}^u | V_{e^{-s\lambda}} | \Phi_{\alpha_1}^u \rangle = \frac{-\pi \lambda^0}{4\alpha} e^{2AB^2 \alpha \lambda_0} \sum_{n=0}^{\infty} \frac{(-\lambda)^n}{(n+1)(2\alpha)^{n+1}} f(-\sqrt{2} \cdot t') \]  

(A2.2.14)

where the series of values

\[ f(-\sqrt{2} \cdot t') \equiv e^{-t'/2} D_{\frac{t'}{2}} \]  

(A2.2.15)

can be found from the \( n = -1, -2 \) values of \( D_{-n} \) and the recursion relation.\(^6\)

The corresponding series solution for the terms arising from the contribution to the integral from within the surface plane is

\[ \langle \Phi_{\alpha_i}^u | V_{e^{-s\lambda}} | \Phi_{\alpha_i}^u \rangle = \frac{-\pi V_o}{5 + z} e^{\frac{-AB^2 \alpha \lambda_0}{\alpha}} \left[ \frac{1}{2} \sqrt{\frac{\pi}{\alpha}} e^{-t'} \right] \]

\[ -A_0 \sum_{n=0}^{\infty} \frac{(-\lambda)^n}{(n+1)(2\alpha)^{n+1}} f(-\sqrt{2} \cdot t') \]

(A2.2.16)

where \( V_o \) and \( A_0 \) are defined by expression A2.2.8. The utility of these series expansions, as they are written, is limited to the case of large \( \alpha \) and small \( \lambda \), otherwise convergence is slow.
Appendix 2.3 Asymptotic Form of the Atomic Matrix Elements

The asymptotic form of the electron-(self-image) matrix element differs from the general form in that the integration is carried out over all space and there is no screening of the image charge. Under these conditions,

\[
\langle \alpha_1 A_1 | V_{e-si} | \alpha_2 A_2 \rangle \xrightarrow{\text{large } S} \]

\[
-\frac{\pi}{4} \frac{e^{-\frac{\alpha}{\lambda}(z-p_z)^2}}{\sqrt{\pi}} \int_{-\infty}^{+\infty} \frac{e^{-\frac{\alpha}{\lambda}(S+z)^2}}{(S+z)} \, dz \quad (A2.3.1)
\]

Let \( x = \sqrt{\alpha}(z-p_z) \) and \( t' = \sqrt{\alpha}(S+p_z) \). To avoid convergence difficulties at \( z = -S \) let \( -t'^2 \rightarrow -t'^2 + i\eta \approx z \) and let \( \eta \rightarrow 0 \) at the end of the calculation. Then, after some manipulations, equation A2.3.1 can be expressed in terms of elementary functions as

\[
-\frac{\pi}{4} \frac{e^{-\frac{\alpha}{\lambda}(z-p_z)^2}}{\sqrt{\pi}} \Re \left[ \lim_{\eta \rightarrow 0} \int_{-\infty}^{+\infty} e^{-\frac{\alpha}{\lambda}(S+z)^2} \, dz \right] \quad (A2.3.2)
\]

Using the series expansion for the error function of complex argument, we get, finally,

\[
\langle \alpha_1 A_1 | V_{e-si} | \alpha_2 A_2 \rangle \xrightarrow{\text{large } S} \]

\[
-\frac{\pi}{4} A_1 A_2 \exp \left( -\frac{\alpha}{\lambda}(z-p_z)^2 \right) \left[ \frac{t'}{2} + \sum_{n=1}^{\infty} \frac{e^{-(\frac{n}{2}+t')^2}}{n} - e^{-(\frac{n}{2}+t')^2} \right] \quad (A2.3.3)
\]
The electron-(core image) asymptotic matrix element is found quite easily by application of Boys' formula A2.1.3 for the interaction of two concentric atomic orbitals with an external charge. The final result for the sum of the two contributions is

\[
\langle \alpha_1 A_1 | V_{e-S} + V_{e-A} | \alpha_2 A_2 \rangle \xrightarrow{\text{large } \alpha} \frac{\pi^{\frac{1}{4}} A_1 A_2}{\alpha} \exp\left(\frac{-\alpha B_2^2 \alpha_1 \alpha_2}{\alpha}\right)
\]

\[
\left[ \sqrt{\frac{\pi}{\alpha c P z}} \text{erf} \left(\sqrt{\frac{\alpha c P z}{T}}\right) - \frac{t' e^{-t'^2}}{4} - \frac{1}{4} \sum \frac{e^{-\left(\frac{n}{z} - t'\right)^2}}{n} - \frac{e^{-\left(n - t'\right)^2}}{n} \right]
\]

(A2.3.4)

where \(\alpha = \alpha_1 + \alpha_2\), \(t' = \sqrt{\alpha(S+P_z)}\), and CPZ is defined in Appendix 2.1.
Appendix 2.4  Computational Details - Adiabatic States

The adiabatic atomic states are represented by eigenvector solutions of the matrix equation (2.2.3). To find these states the matrix elements of unperturbed atomic states, \( \langle \phi_{i}^{(u)} | V_{\text{int}} | \phi_{j}^{(u)} \rangle \), are required as a continuous function of atom-surface distance \( s \). Since these matrix elements are smoothly varying functions of \( s \) and are either monotonic or have a single maximum they can be represented quite accurately with a simple approximation function. A grid of twenty points is taken from \( s = 1 \) to \( 30 \ a_0 \) and a cubic spline approximating procedure is used to find the approximate values of the matrix elements between grid points. The asymptotic form of the matrix elements is itself a polynomial so that relatively few grid points in the asymptotic region are needed, the highest density of points is placed in the near-surface region. Once the approximating function is found, the matrix elements are available as a continuous function of \( s \).

The diagonalization of matrix equation 2.2.3 can then be carried out by standard techniques on a grid of \( n \) points, each corresponding to some distance \( s_n \). The eigenenergies \( \epsilon_i(s_n) \) and coefficients \( C_{ij}(s_n) \) of the adiabatic states vary much more rapidly with \( S \) than the matrix elements. Again, a cubic spline approximation is used to obtain \( \epsilon_i \) and \( C_{ij} \) between grid points. The orthonormality
of the adiabatic eigenstates between grid points is used as a test of the accuracy of the fit and to determine where the highest density of grid points must be placed. A maximum relative error of $10^{-8}$ has been obtained using $n = 165$ points, at highest density $\Delta s = 0.025 \ a_0$.

A second consideration in the choice of a fitting function is the need for the spatial derivative $\partial c_{ij}/\partial s$ in equation 3.3.36. Polynomial approximating functions, for instance, oscillate about the exact function with $m$ intersections, where $m$ is the order of the polynomial. This behavior introduces an unrealistic contribution to the kinematic coupling parameter $\Lambda$. One can limit this effect qualitatively, when using a cubic spline function, by spacing the mesh points close enough so that straight lines between the points reproduce all the basic features of the represented function.

Finally, the adiabatic wave function, 3.1.1, contains an integral $\int \psi_1'(S)v dS$. This set of integrals is evaluated analytically prior to solution of differential equation 3.3.36 at each grid point. The component of the integral from the nearest lower grid point on is then evaluated using the spline coefficients at the time of solution of 3.3.36.
Appendix 3.1 Relation of Single Particle and Many Particle Theory

The somewhat phenomenological interpretation of $b_\epsilon(0)$ in equation 3.3.18 as the unperturbed many electron occupancy of the metal can be reinforced by comparison of the single and many electron formalisms. For simplicity we consider a system comprised of one atomic state $d$ and a large number of quasi discrete metallic states $c_i; i=1,n$. Let the state vector be

$$\Psi^{(\epsilon_{\beta})} = | d, c_1, \ldots, c_n \rangle \quad \text{(A3.1.1)}$$

and the creation and destruction operators for the $i^{th}$ state be $a_i^\dagger$ and $a_i$, respectively. In the Heisenberg picture we can express any Hamiltonian operator containing one and two particle operators as

$$\hat{H} = \sum_{k, l} a_{k}^\dagger \langle k | H_0 | l \rangle a_{l} + \frac{1}{2} \sum_{q, r, s, t} a_{q}^\dagger a_{r}^\dagger \langle q r | V | t s \rangle a_{s} a_{t}, \quad \text{(A3.1.2)}$$

where $H_0$ is the one particle operator, which in our case consists of the kinetic energy operator plus the isolated metal and ion potential functions, and $V(t=0)$ is the electron-electron Coulomb interaction $1/r_{12}$. The equation of motion for the operator $a_j$ is

$$\dot{a}_j(t) = -i \sum_{l} \langle j | H_0 | l \rangle a_l(t) - i \sum_{r, s, t} a_{r}^\dagger(t)a_{s} a_{t}(t) \langle j r | V | t s \rangle \quad \text{(A3.1.3)}$$
Suppose $H_o = H_o^{(u)} + V(t)$ where the $|j\rangle$ are eigenstates of $H_o^{(u)}$. Then,

$$\dot{a}_j(t) = -i\sum_L (\omega_j \delta_{jl} + \langle j|V|l\rangle) a_L(t) - i\sum_{r,s,t} a_r^+ a_s a_t \langle j_r|V|l_s\rangle \tag{A3.1.4}$$

which is

$$\dot{a}_j(t) + i \left( (\omega_j + \langle j|V|l\rangle) \right) a_j(t) =$$

$$-i\sum_L \langle j|V|l\rangle a_L(t) - i\sum_{r,s,t} a_r^+ a_s a_t \langle j_r|V|l_s\rangle,$$

where the prime on the summation symbol indicates that $l \neq j$.

We make the unitary transformation

$$a_j = \sum_q b_q c_{qj}^*, \quad a_j^+ = \sum_q b_q^* c_{qj},$$

where

$$c_{qj} = e^{i\tilde{\omega}_q t} \delta_{qj}, \quad \tilde{\omega} \equiv \omega_q + \langle q|V|q\rangle. \tag{A3.1.5}$$

This eliminates the secular term. The transformed Heisenberg operator then satisfies the equation

$$\dot{b}_j(t) = -i\sum_L \langle j|V|l\rangle b_L(t) e^{-i(\tilde{\omega}_j - \tilde{\omega}_l)t}$$

$$-i\sum_{r,s,t} b_r^+(t) b_s(t) b_t e^{-i(\tilde{\omega}_r + \tilde{\omega}_j - \tilde{\omega}_s - \tilde{\omega}_t)t} \langle j_r|V|l_s\rangle \tag{A3.1.6}$$
For the continuum case the sum on \( j \) goes over to an integral and field operators are introduced in place of the creation and annihilation operators. For the \( j = 1 \) atomic state the first term on the right hand side of equation A3.1.6 resembles the \( b_\epsilon \rangle \langle 0 \rangle \) term in equation 3.3.15. The formal connection can be made at the level of the transition rate, an observable quantity.

\[
\langle w_j \rangle = \langle a_j^+ a_j^+ a_j + a_j^+ a_j \rangle = \langle b_j^+ b_j \rangle \langle b_j^+ b_j \rangle.
\]  
(A3.1.7)

For an initial state occupation number \( b_\epsilon \rangle \langle 0 \rangle \) for \( c_1, \ldots, c_n \) in A3.1.1 the expression resulting from integration of equation A3.2.6 over \( t \) and substitution of the result along with A3.2.6 into A3.2.7 is identical in form to that found in the single particle formalism. The coefficients \( a(t) \) in the single particle case are complex numbers whereas the \( b \)'s are operators. We get the same result for the transition rate in the two cases if we always take \( b_\epsilon \rangle \langle 0 \rangle \) to be a real number in the single electron calculation.

The last term in equation A3.2.6 is also relevant to the model we use. It represents, among other things, the electron-electron Coulomb interaction which prevents more than one negative charge from accumulating in the atom upon neutralization. The general form of the term is illustrated in Figure A3.2.1, the same diagram as that for single step or direct Auger neutralization if level \( r \) lies in the continuum. If \( r \) equals \( s \), an atomic orbital
Figure A3.1.1

Figure A3.1.2
(≠ j), in the second inhomogeneous term in A3.1.6 (figure A3.1.2) the term becomes

\[ -i \sum_{s_i, \xi} n_s(t) b_\xi(t) e^{-i(\tilde{\omega}_j - \tilde{\omega}_\xi)t} \langle j s | V | t s \rangle \]  \hspace{1cm} (A3.1.8)

In terms of wave functions the matrix element is

\[ \langle j s | V | t s \rangle = \int d\tau_1 \int d\tau_2 \frac{\Phi_j^*(z) \Phi_s^*(l) \Phi_s(z) \Phi_\xi(l)}{r_{12}} \]  \hspace{1cm} (A3.1.9)

Since only index \( \xi \) refers to a metallic function the integrand is appreciable only for \( r_2 > r_1 \), then expanding \( 1/r_{12} \) in a power series we have

\[ \langle j s | V | t s \rangle = \langle j | \frac{1}{r_2} | t s \rangle + \int d\tau_1 | \Phi_s^2 | \int d\tau_2 \frac{\Phi_j^*(z) \Phi_\xi(z)}{r_2^2} + \ldots \]  \hspace{1cm} (A3.1.10)

This is the one-electron matrix element plus a correction term which is small at large atom-surface separations.

Substituting this result into A3.1.8 (and including the \( s = j \) term) we can combine the two one-electron terms,

\[ b_j(t) = -i \sum_{l, s} \langle j l V_c | l t \rangle b_\xi(t) e^{-i(\tilde{\omega}_j - \tilde{\omega}_\xi)t} (1 - n_s) + \ldots \]  \hspace{1cm} (A3.1.11)

Index \( \xi \) refers to metallic orbitals, \( s \) refers to atomic orbitals, and \( n_s \) is the number operator for the \( s \) state.

In the Hartree-Fock approximation this is written as
\[
\dot{b}_j(t) = -i \sum_{\lambda, s} \langle j | V_c | \lambda \rangle b_\lambda(t) e^{-i(\tilde{\omega}_j - \tilde{\omega}_\lambda)t} (1 - \langle n_s \rangle) \tag{A3.1.12}
\]

where the expectation value of the occupancy of the s state is substituted for the operator. This expression has the same physical origin as the effective charge factor \(Q(t)\) which we have introduced phenomenologically in equation 3.3.36.
Appendix 3.2 Evaluation of Equation 3.2.29

The integral (B) of equation 3.2.29 which is to be evaluated is

\[ -i \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \rho_{\beta} b_\epsilon(0) F_2(\epsilon, \eta, t) \frac{e^{-i\beta t}}{(\beta-\gamma)(\beta-\epsilon+\omega_n+i\eta)} \]  \hspace{1cm} (A3.2.1)

The integral \( \gamma \) is complex; separate its real and imaginary parts

\[ \gamma = \int_{-\infty}^{+\infty} d\epsilon \frac{F_1 F_2}{(\epsilon-\omega_n)^2 + \eta^2} + i \int_{-\infty}^{+\infty} d\epsilon \frac{F_1 F_2 \eta}{(\epsilon-\omega_n)^2 + \eta^2} \hspace{1cm} (A3.2.2) \]

Let

\[ -i b_\epsilon(0) \int_{-\infty}^{+\infty} d\epsilon F_2(\epsilon, \eta', t) \equiv h(\epsilon) \hspace{1cm} (A3.2.3) \]

Then,

\[ \Delta_{3.2.1} = \int_{-\infty}^{+\infty} d\epsilon h(\epsilon) \int_{-\infty}^{+\infty} d\beta \frac{e^{-i\beta t}}{(\beta-\epsilon+\omega_n-i\eta)(\beta+\gamma+\eta') + i Y'} \hspace{1cm} (A3.2.4) \]

Allowing \( \epsilon \) to be complex and making the coordinate transformation
\[ \varepsilon' = \varepsilon - y_r + w_n' - i(y_i' + \eta), \]

\[
A 2.3.4 = \int_{-\infty}^{+\infty} d\varepsilon' h(\varepsilon' + y_r - w_n' + i(y_i' + \eta)) \int_{-\infty}^{+\infty} d\beta e^{-i\beta t} \frac{e^{-i\beta t}}{(\beta - \varepsilon' + \gamma_r + i\gamma_i)(\beta + \gamma_r + i\gamma_i)} \]

\[ \int_{-\infty}^{+\infty} d\varepsilon' h(\varepsilon' + y_r - w_n' + i(y_i' + \eta)) g(\varepsilon') \tag{A3.2.5} \]

If we make the coordinate transformation \( \beta' = \beta + \frac{\varepsilon'}{2} \), the analytic properties of the function \( g(\varepsilon') \) become clear.

\[
g(\varepsilon') = e^{i\frac{\varepsilon'}{2} t} \int_{-\infty}^{+\infty} d\beta' e^{-i\beta' t} \frac{e^{-i\beta' t}}{(\beta' - \frac{\varepsilon'}{2} + \gamma_r + i\gamma_i)(\beta' + \frac{\varepsilon'}{2} + \gamma_r + i\gamma_i)}. \tag{A3.2.6} \]

The expression \( g(\varepsilon') \) can be evaluated by integration over a closed semicircular contour on the lower half complex \( \beta' \) plane (cf. fig. A3.2.1). The real \( \varepsilon' \) axis is included in the diagram. As we integrate \( g(\varepsilon') \) over \( \varepsilon' \) the points \( \beta_1' \) and \( \beta_2' \) move along the \( R(\beta') - i\gamma_i \) axis from the left and right, respectively, "pinching" the real \( \varepsilon' \) axis at \( \varepsilon' = 0 \). The coalescence of these points on the \( \varepsilon' \) axis gives rise to a second order singularity in the \( g(\varepsilon) \) function.

A theorem of Hadamard\(^{10,11}\) states (in our notation) that it is sufficient that if \( \beta' \neq \beta'(\varepsilon') \), the function

\[
g''(\varepsilon') = \int_{a}^{b} d\beta' f(\beta', \varepsilon') \tag{A3.2.7} \]
\[ \beta_i' = -\gamma + \frac{\varepsilon_i'}{2} - i \varepsilon_i \]
\[ \beta_2' = -\gamma - \frac{\varepsilon_i'}{2} - i \varepsilon_i \]

Figures A3.2.1, A3.3.3
has a true pinching or coincidence singularity if:

1. \( f(\beta', \varepsilon') \) has no end point singularity, i.e., \( f^{-1}(\beta', \varepsilon') \rvert_{a,b} \neq 0 \);
2. \( f^{-1}(\beta, \varepsilon_o') = 0 \) and \( [f'(\beta, \varepsilon_o')]^{-1} = 0 \) for some \( \beta \) on the contour;
3. the singularities approach the \( \varepsilon' \) contour from opposite sides. In the present case, each of the conditions is fulfilled, which indicates that the second order nature of A3.2.6 cannot be removed by a coordinate transformation.

The \( \varepsilon' \) integral in equation A3.2.5 can be integrated over the contour \( L \) shown in figure A3.2.2. For \( \varepsilon' \neq 0 \), the function \( g(\varepsilon') \) has two first order poles at the points \( \beta_1' \) and \( \beta_2' \) of figure A3.2.1. Evaluating the residues at these points and using the Cauchy integral theorem we find that

\[
g(\varepsilon') = -2\pi i e^{i \frac{\varepsilon'_t}{2}} e^{i \frac{\varepsilon'_t}{2}} \left[ \frac{e^{-i \frac{\varepsilon'_t}{2}} - e^{i \frac{\varepsilon'_t}{2}}}{\varepsilon'} \right]
\]

(A3.2.8)

On the contour \( L \) of figure A3.2.2 we have

\[
A3.2.5 = \lim_{\delta \to 0} \int d\varepsilon' \quad h(\varepsilon' + \delta, -\omega_n' + i(\gamma_r + \eta)) \cdot 2\pi i e^{i \frac{\varepsilon'_t}{2}} e^{i \frac{\varepsilon'_t}{2}} \left[ \frac{e^{-i \frac{\varepsilon'_t}{2}} - e^{i \frac{\varepsilon'_t}{2}}}{\varepsilon'} \right]
\]

(A3.2.9)

which consists of a Cauchy principal part and the integral around the small semicircle at \( \varepsilon' = 0 \). The integral along the part at infinity vanishes. The principal part of the integral may not be zero but it does not interest us since
its contribution to the coefficients $a'_n(t)$ via equation 3.3.36 vanishes rapidly with $t$. (This is the origin of what appears to be a delta function $\delta(t)$ in equation 3.3.1.) If we attempt to move the singularity in A3.2.9 off the real $\varepsilon'$ axis through a coordinate transformation the second order nature of the singularity vanishes. This manipulation is not permissible; limits and integrations cannot be commuted if doing so changes the analytic nature of the integrand.

Dropping the principal part of the integral,

$$A_{3.2.9} = 2\pi i \ h(\delta_r - \omega_n^i + i(\nu + \eta)) e^{i\nu t}$$

$$\lim_{\delta \to 0} \int_0^\pi d\theta \left( \frac{1 - e^{-i\delta t} e^{i\theta}}{\delta e^{i\theta}} \right)$$

$$= -2\pi i \ b_{\varepsilon}(0) \ F_{\varepsilon}(\varepsilon, \nu', t) e^{i\nu t}$$

which is the desired result 3.3.27.
Appendix 3.3  Metallic Density of States, the $b_\varepsilon(0)$ Term

In the transition from a sum over $\vec{k}$ to an energy integral in 3.1.3 we use the relation,\textsuperscript{12} for arbitrary function $f(\vec{k})$,

$$\sum_{\tilde{i}} f(\tilde{k}_i) = \iiint f(\tilde{k}) \rho_\varepsilon d\Omega d\varepsilon \quad (A3.3.1)$$

For a spherical Fermi surface with two electrons per energy level to allow for spin degeneracy the density of states in the free electron model is

$$\rho_\varepsilon = \frac{\sqrt{\varepsilon}}{4 \pi^3}$$

To determine $b_\varepsilon(0)$ of 3.3.36 we require that the total number of electrons in the atom metal system be $N+1$, where $N$ is the number of conduction electrons in the metal.

Then,

$$N+1 = \langle \Psi(o)|\Psi(o)\rangle = \sum_{n, n'} a_{n'}^\dagger(o) a_n(o) \delta_{n n'} + \iiint \left[ b_\varepsilon^{n'}(o) \right]$$

$$\rho_\varepsilon \iiint b_{\varepsilon'}^{n'} \rho_\varepsilon \langle \kappa_{\varepsilon'}^{n'} | \kappa_{\varepsilon}^{n} \rangle d\varepsilon' d\Omega' d\varepsilon d\Omega$$

(A3.3.2)

but,

$$\langle \kappa_{\varepsilon}^{n} | \kappa_{\varepsilon'}^{n'} \rangle = \frac{\delta(\varepsilon - \varepsilon')}{\rho_\varepsilon} \frac{\delta(\Omega - \Omega')}{\rho_\varepsilon}$$

(A3.3.3)

and $b_\varepsilon(0)$ and $\rho_\varepsilon$ are isotropic, so that
\[ N + 1 \approx 1 + 4\pi \int_{-\infty}^{+\infty} d\epsilon \, b_\epsilon^{*}(0) b_\epsilon(0) \frac{\sqrt{|k_o|}}{4\pi^3} \]

(A3.3.4)

\[ N = \frac{V}{\pi^2} \int_{-\infty}^{+\infty} d\epsilon \, |b_\epsilon(0)|^2 |k_o| \]

(A3.3.5)

Further, we assume that \( b_\epsilon(0) \) is constant within the zero temperature limits of the conduction band \((-|V_o| < \epsilon < -|V_o| + \epsilon_F)\). The variation of \( b_\epsilon(0) \) with temperature is restricted to a narrow band about \( \epsilon_F \); \( b_\epsilon(0) \) could more accurately be represented by the Fermi-Dirac function, but the difference for this calculation is negligible. The resultant expression is

\[ |b_\epsilon(0)|^2 = \frac{9\pi}{8\sqrt{2}} \frac{\epsilon_F^{3/2}}{\varepsilon_s^3} \]

(A3.3.6)

where \( n \) is the number density, and \( r_s \) the single electron radius. Values of several relevant parameters are listed in Table A3.3.7. Since the Fermi energy \( \epsilon_F \) is calculated in the free electron model with number density a function of crystal structure and valence, the occupancy term \( b_\epsilon(0) \) is unity (or 0.5 per spin) for each of the metals listed in the table.
<table>
<thead>
<tr>
<th>Metal</th>
<th>$r_s(a_o)^{13}$</th>
<th>$\varepsilon_F$(a.u.)</th>
<th>$\phi$(a.u.)$^{14}$</th>
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<tbody>
<tr>
<td>Li</td>
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<td>.177</td>
<td>.0875</td>
</tr>
<tr>
<td>Na</td>
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<td>.119</td>
<td>.0864</td>
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<td>.158</td>
</tr>
<tr>
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<td>.405</td>
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</tr>
<tr>
<td>Sn</td>
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<td>.377</td>
<td>.161</td>
</tr>
</tbody>
</table>

Table A3.3.1 Some relevant parameters for selected metals. Single-electron radius $r_s$ and Fermi energy $\varepsilon_F$ are calculated using the free electron model, work function $\phi$ is an experimental result.
Appendix 3.4 Evaluation of the Transition Matrix Elements

The matrix element 3.3.12,

\[
F_2 (\epsilon, n, t) = \left[ \langle \psi_n (\epsilon) | V_a | k_\epsilon^n > \right] \int d\Omega' d\epsilon' \rho_{\epsilon'} \left[ \langle k_{\epsilon'}^n | V | k_{\epsilon}^n > \psi_n (\epsilon) \langle k_{\epsilon}^n | \right]
\]

appears in expression 3.3.33 for time dependent state amplitudes a_n (t). Evaluation of A3.4.1 requires the computation of the three matrix elements (A) \( \equiv \langle \psi_n (t) | V_a | k_\epsilon^\Omega > \), (B) \( \equiv \langle \psi_n | k_\epsilon^\Omega > \), and (C) \( \equiv \sum \int d\Omega' d\epsilon' \rho_{\epsilon'} \langle k_{\epsilon'}^\Omega | V_a | k_\epsilon^\Omega, \Omega' > \).

The region of integration for each of these matrix elements is the half space outside of the surface plane, so that \( k_\epsilon^\Omega \) has the form of the second part of equation 2.6.1,

\[
k_{\epsilon}^\Omega = \frac{1}{k_r} L^{\frac{3}{2}} 2 k_z^\frac{1}{2} \exp (i (k_x x + k_y y)) \exp (- \sqrt{2 V_o - k_z^2} | (s + z) >)
\]

\( z > -s \) \hspace{1cm} \text{(A3.4.2)}

where the energy values are measured from the bottom of the conduction band. In the half space within the metal potential V_a is effectively screened; the contribution to the matrix elements is small and is not calculated (cf. discussion in Section 4.3).

Then, the first integral is

\[
(A) = \frac{2 k_z^\frac{1}{2}}{k_r} L^{\frac{3}{2}} \int_0^\infty dz \left\{ \exp ( - \sqrt{2 V_o - k_z^2} (s + z)) \right\} \int_0^\infty dx \int_0^\infty dy \left[ \exp (i (k_x x + k_y y)) \psi_n (t) / \tau \right]
\]

\( \text{(A3.4.3)} \)
Such integrations can be done in a systematic way by decomposing the adiabatic wave function $\psi_n(t)$ into a sum of products of single exponentials and radial and angular factors as,

$$\psi_n(t) = \sum_{j,k} C_{nj}(R(t)) d_{jk} f_k \exp(-a_k r) \quad (A3.4.4)$$

where $C_{nj}$ are the elements of the $n^{th}$ adiabatic state eigenvector, $d_{jk}$ is that matrix of constants and $f_k$ that vector of radial and angular functions which, in the matrix sum, form the appropriate wave function, and $a_k$ is the exponential parameter. In this way the matrix elements for the hydrogenic wave functions or for some approximate atomic wave function can be found by changing only $d_{ij}$ and $a_k$.

Thus,

$$\langle A \rangle = \langle \text{const.} \rangle \sum_{i,j} C_{nj}(R(t)) d_{ij} \int \int \int d\rho d\theta d\phi \exp(-\sqrt{Z e^{-k^2} r})$$

$$f_L(z) \left[ \int \int \int d\rho d\theta d\phi \exp(i(k_x \rho + k_y \theta + k_z \phi)) f'_L e^{-a_k r} \right] \quad (A3.4.5)$$

where, for example, the $m_z = 0$ hydrogenic functions are constructed from the set

$$f_L(z) f'_L = \left\{ 1, \rho, \rho \cdot \rho, \rho \cdot \rho, \rho \cdot \rho, \rho \cdot \rho, \rho \cdot \rho, \rho \cdot \rho \right\}, \quad l=1, \infty.$$
As suggested by Sternberg,\textsuperscript{15} integrals of the form of those in square brackets can then be done by a contour integration technique.

Introduce the Fourier transform

\[
\frac{e^{-ar}}{r} = \frac{1}{2\pi^2} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \frac{e^{i\beta \cdot r}}{a_i^2 + \beta \cdot \beta} \, d\beta \, d\beta \, d\beta \quad (A3.4.6)
\]

The corresponding Fourier transforms of $e^{-ar}$, $r e^{-ar}$ and so on can be found by repeatedly differentiating equation A3.4.6 with respect to $a_i$. For the $f_{\lambda}^\prime = 1$ term of A3.4.5 the integral in square brackets becomes

\[
\frac{1}{2\pi^2} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \frac{e^{i[(k_x + \beta_x) x + (k_y + \beta_y) y] + \beta \cdot z}}{a_i^2 + \beta \cdot \beta} \, dy \, dx \, d\beta \, d\beta \, d\beta \quad (A3.4.7)
\]

The $x$ and $y$ integrals act as Dirac delta functions,

\[
\int_{-\infty}^{+\infty} e^{ik_x \gamma} \, d\gamma = 2\pi \delta(k_x + \beta_x) \quad (A3.4.8)
\]

so that the $\beta_x$ and $\beta_y$ integrations can be done immediately. This process leaves terms like

\[
\int_{-\infty}^{+\infty} \frac{e^{i\beta \cdot z}}{a_i^2 + \beta \cdot \beta} \, d\beta \quad (A3.4.9)
\]

which can be done by contour integration over a semicircle in the upper (lower) half complex $\beta_z$ plane for $z$ greater (less) than zero. The necessary results for the $n = 2$ hydrogenic functions are
\[
\int_{-\infty}^{\infty} \frac{e^{i\beta_z z}}{a_i^2 + \beta_z^2} \, d\beta_z = \frac{\pi \exp(-a_i |z|)}{a_i} \quad (A3.4.10a)
\]

\[
\int \frac{e^{i\beta_z z}}{(a_i^2 + \beta_z^2)^2} \, d\beta_z = \frac{\pi}{Z a_i^2} \left[ \frac{1}{a_i} + \frac{1}{|z|} \right] \exp(-a_i |z|) \quad (A3.4.10b)
\]

\[
\int \frac{e^{i\beta_z z}}{(a_i^2 + \beta_z^3)^3} \, d\beta_z = \frac{\pi}{8 a_i^2} \left[ \frac{3}{a_i^2} + \frac{3 |z|}{a_i} + z^2 \right] \exp(-a_i |z|) \quad (A3.4.10c)
\]

for the e^{-ar}/r, e^{-ar}, and re^{-ar} integrals, respectively.

With these results A3.4.10a,b,c, equation A3.4.5 for matrix element (A) reduces to a single tedious, but elementary, z integration which must be done for each of these functions \( f_z \). Furthermore, the matrix elements (B) which is like (A) except for the potential term \( V_a \) can be found by an exactly analogous procedure. This process produces expressions for (A) and (B) which are functions of angle \( \theta \) of the metallic state (over which a numerical integration is eventually performed).

The remaining integral is

\[
(C) = \iiint d\Omega \, d\epsilon' \, P_{\epsilon'} \left( \langle \kappa_{\epsilon'}^{N'} | V_a | \kappa_{\epsilon}^N \rangle \right) \quad (A3.4.11)
\]
where $d\Omega'$ is an increment of solid angle. We must introduce a screening length $\alpha$ to insure convergence of the integral. Explicitly, the integral is

$$(C) = \int \int \int d\Omega' d\epsilon' \rho_{\epsilon'} \int \int \int dz dx dy \exp \left[ i (k_x' + k_x) x ight. $$

$$+ i (k_y' + k_y) y \left. \left( \sqrt{2 \left| V_0 \right| - k_z'^2} + \sqrt{2 \left| V_0 \right| - k_z^2} \right) z - \alpha r \right] / r.$$  

(A3.4.12)

Once again, introducing Fourier transform A3.4.6 and integrating over the resultant delta functions, equation A3.4.12 reduces to

$$(C) = 2 \int \int \int d\Omega' d\epsilon' \rho_{\epsilon'} \int \int \int dz \exp \left[ i \beta_z \right.$$  

$$+ \left. i \left( \sqrt{2 \left| V_0 \right| - k_z'^2} + \sqrt{2 \left| V_0 \right| - k_z^2} \right) z \right] / \left( F^2 + \beta_z^2 \right)$$  

(A3.4.13)

where,

$$F^2 = \alpha^2 + k_x'^2 + k_x^2 + k_y'^2 + k_y^2$$  

(A3.4.14)

The $\beta_z$ integration has already been done, A3.4.10a, and the resultant $z$ integration is elementary. Then,

$$(C) = \frac{8\pi k_x'}{k_r' \Lambda^3} \exp \left( - \sqrt{2 \left| V_0 \right| - k_z'^2} S \right) \int \int \int d\Omega' \rho_{\epsilon'} \int \int \int d\Omega \frac{k_x'}{F} \exp \left( - \sqrt{2 \left| V_0 \right| - k_z'^2} S \right) \left\{ \frac{1 - e^{(F-\eta)S}}{F-\eta} + \frac{1}{F+\eta} \right\}$$  

(A3.4.15)
where,

\[ \eta = \sqrt{2|\nu_0| + \frac{k_z^4}{F}} + \sqrt{2|\nu_0| + \frac{k_z^2}{F}} \]  

where, \( \frac{k_z^2}{F} \) varies slowly with \( \theta \) compared to the exponential term; it is evaluated at \( \theta = \theta_{ave} \) and brought out of the integral. Then, the integral is

\[ \iint d\Omega \cos \theta \exp\left[-\sqrt{2|\nu_0| - k_o^2 \cos^2 \theta}\right] \]  

which can be integrated analytically, this leaves

\[ (C) = \frac{16\pi^2 k_z^2}{k_o^2 L^3} \exp\left(-\sqrt{2|\nu_0| - k_z^2} S\right) \int_{-\infty}^{+\infty} d\epsilon' \frac{k_o'}{p^2} \]

\[ \cdot \left[ \frac{1}{F} \left\{ \frac{1 - e^{(F-\eta)s}}{F - \eta} + \frac{1}{F + \eta} \right\} \right] \left\{ \left( e^{\frac{\sqrt{qq - 1}}{2} - 1} \right) e^{\frac{\sqrt{qq - 1}}{2} - \left( \frac{\sqrt{qq - 1}}{2} \right) e} \right\} \]  

where

\[ p = -k_o' S \]  

\[ q = \frac{2|\nu_0|}{k_o'^2} \]  

The second exponential term in curly brackets in 3.4.18 is much smaller than the first term and is dropped. Furthermore, the term in square brackets varies much more slowly with energy than the exponential term; it is evaluated at \( \epsilon = \epsilon' \). The remaining integral can be done
analytically, resulting in a series of three exponentials, the first of which is a factor of more than \( s (s^2) \) times the second (third). Keeping only this first term we have the result

\[
(C) = \frac{32}{k^2 \sqrt{S}} \exp \left( -\sqrt{2|V_0|} - k_2 S \right) \cdot \left[ \frac{1}{F} \left\{ \frac{1-e^{(F-\beta)s}}{F-\beta} \right\} + \frac{1}{F+\beta} \right] \cdot \left[ V_0 \left( e^{-2s\sqrt{V_0}} - e^{-2s\sqrt{V_0}-\varepsilon F/2} \right) \right. \\
\left. + \frac{\varepsilon F}{2} e^{-2s\sqrt{V_0}-\varepsilon F/2} \right] 
\]

(A3.4.20)

which is used in the calculation. (The contribution to \( F_2 \) is usually small.) The sum of elements (A), (B), and (C) is integrated numerically over angle \( \theta \).
Appendix 3.5  Computational Details Solution of Time Dependence Equations

Equation 3.3.36 describes the time evolution of the atomic states. It represents a system of $n$ coupled first order differential equations for the complex amplitudes $a_n(t)$, where $n$ is the number of adiabatic basis states. The equations are nonlinear in the term $\sum_{n} (1-|a_n(t)|^2)$ which inhibits transfer of more than unit charge to the ion (cf. Appendix 3.2).

For all but the simplest (uncoupled) cases, analytic solution of the equations is impossible. A numerical integration procedure must be used. We use as the criterion of accuracy that the probability of a state with unit initial amplitude stays constant if the loss and gain terms are eliminated. The exponential energy factor in the nonadiabatic coupling term makes it the largest inhomogeneous term; even in the absence of coupling between states it couples the real and imaginary parts of $a_n(t)$. The IMSL routine DREBS$^{16}$ was found to be sufficiently accurate to maintain the normalization to within a cumulative relative error in probability of less than $10^{-4}$ for a reasonable expenditure of execution time.

To aid in the numerical solution of the equations it is desirable to have a smooth "turn on" function at the Fermi level to avoid a discontinuity in the gain and loss terms. This smooth transition between occupied and
unoccupied states is present in a real metal because of the
temperature dependence of occupancy at the Fermi level
and the probable narrowing of the band width in the surface
region. For this reason we multiply the loss and gain
terms by the additional factor
\[
\left[ 1 - \exp(-c \cdot |\epsilon_i - \epsilon_f|) \right]
\]
where \( \epsilon_i \) is the energy of the \( i^{th} \) adiabatic state and \( c \) is
taken to be 250, a value chosen because it causes a
relatively smooth transition over a range of energy which
is small compared to the average energy difference between
states. The value of \( c \) might become important if one of
the adiabatic states were very close in energy to the
Fermi level for a long time, but this is a situation in
which the results are unreliable in any case.
References - Appendices

1. Ref. 14 (Ch. II).
2. Ref. 15 (Ch. II).
6. Expression 9.254.2 of ref. 5 for D^-2(z) has the wrong sign.
7. Ref. 4 eq. 7.4.9.
8. Ref. 4 eq. 7.1.29.
15. International Mathematical and Statistical Libraries, 7500 Bellaire, Houston, Tex.