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**Electron tunneling rates between an atom and a
corrugated surface**

by

Matt F. Taylor

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

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APPROVED, THESIS COMMITTEE:

Peter J. A. Nordlander, Chairman
Professor of Physics

Carl Rau
Professor of Physics

Gustavo Scuseria
Professor of Chemistry

Houston, Texas

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Abstract

Electron tunneling rates between an atom and a corrugated surface

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We introduce a new method for calculating the broadening of atomic levels as a function of the atom's position outside the surface. The surface is studied using a cluster model, and the adsorbate-cluster eigenproblem is solved using quantum chemistry codes. The resulting density of states is projected on the adsorbate orbitals, revealing the broadening of adsorbate energy levels into resonances. We extract the width of these resonances from the projected density of states to calculate the broadening. Arbitrary lateral adsorbate positions and surface geometries can be explored by specifying different atom-cluster configurations.

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Chapter 1

Introduction

Electron tunneling between a surface and adsorbed atoms is key to many processes studied in surface physics. These charge transfer events are central to understanding chemisorption, catalysis and atom-surface scattering, for example. However, study of atom-surface interactions poses some unique challenges. The tools of chemistry and atomic physics have difficulty with the macroscopic scale of the surface, whereas solid state physics methods are confounded by the breaking of translational symmetry.

Conventional models for atom-surface charge transfer processes treat the substrate as a continuum, with charge density varying only in the surface normal direction (jellium). This approximation is used in the complex scaling approach developed by Nordlander and Tully [1], and in the coupled angular modes (CAM) method of Teillet-Billy and Gauyacq [2]. While these methods accurately predict the variation of the tunneling rate with vertical adsorbate-surface separation, they ignore corrugation of the tunneling rate with lateral adsorbate position.

For small adsorbate-surface distances, tight-binding methods have been applied to the charge transfer problem with some success [3] [4] [5]. These models account for the corrugated surface structure, but cannot be applied when the adsorbate is much

more than one lattice space from the surface. Also, the dependence on semi-empirical tight-binding parameters reduces the generality of these methods.

The present work builds on the tight-binding approach by including self-consistency and correlation effects via the density functional formalism. The surface is modeled as a finite cluster, and the adsorbate-cluster electronic structure is resolved using general-purpose quantum chemistry codes. As these codes are equipped to study an arbitrary arrangement of atoms from first principles, the accessible range of adsorbate positions and surface structures is limited only by computational resources. No modification of the codes or the method is required when approaching a new system.

Chapter 2

Theory

This chapter presents a theoretical overview of atom-surface charge transfer and the cluster method we have developed to study it. The first section describes charge transfer in quantum mechanical terms and relates it to the electronic structure of the atom-cluster system. The second section summarizes limitations of the method, primarily due to cluster size effects, and it is followed by a systematic study of those size effects using a semi-empirical tight-binding model. Next, the method for calculating the tunneling rate is described in detail, and finally that method is tested for some small clusters to verify its accuracy.

2.1 Electronic Structure and Tunneling Rate

Each charge transfer calculation begins by resolving the electronic structure of a crystalline cluster and nearby adsorbate atoms. The electronic structure and tunneling rate are connected through the adsorbate-resolved density of states (JDOS), i.e. the adsorbate level's spectral density. In the macroscopic limit, the JDOS is a continuous curve. For small adsorbate-surface interactions, this curve forms a Lorentz distribution:

$$A_{l\sigma}(\omega) = \frac{\Gamma/2\pi}{(\omega - \epsilon_{l\sigma})^2 + (\Gamma/2)^2} \quad (2.1)$$

Here $A_{l\sigma}$ denotes the adsorbate level's spectral function, $\epsilon_{l\sigma}$ is the noninteracting eigenvalue for the level, and Γ is the width. Once the adsorbate spectral function has been obtained from the electronic ground state, the width of the primary peak is measured numerically.

It has been demonstrated in prior work that this width is directly proportional to the tunneling rate [1].

2.2 Limitations

Computational constraints and approximations in the model impose limits on the adsorbate-cluster configurations that can be effectively studied with the present method. When the adsorbate is extremely close to the cluster (3 a.u. or less), the resonance width approaches the scale of features in the bulk substrate's energy spectrum. In this case, the spectral function is distorted from a perfect Lorentzian curve, and the width of the JDOS is significantly different from Γ .

On the other hand, when the adsorbate is far from the cluster (8 a.u. or more), the adsorbate-cluster separation distance is on the same scale as the cluster itself. At this range, cluster state wavefunctions are significantly different from their macroscopic counterparts, resulting in quantum size effects that distort the JDOS.

Calculation of an adsorbate level shift is much more strongly size-dependent than calculation of level broadening. This is because the adsorbate's image charge in a finite cluster is significantly different from its image in a surface, even at modest distances from the cluster. Furthermore, these image charge effects are not well-represented in the density functional method used for electronic structure calculation. Since the much larger clusters and more complex formalisms needed for accurate shift determination are not computationally accessible with current technology, the present work has only approached resonance width calculations.

2.3 Cluster Size Effects

When an adsorbate interacts with a metal surface, its energy levels are broadened into resonances. A similar effect is observed when the surface is replaced by a finite cluster, but the width of the resonance may not be the same.

Within the intermediate range of separation distances, cluster boundary effects will be the largest source of size-dependence in the calculated resonance width. Therefore, each width calculation has been repeated for at least two clusters of similar composition, but different size. The variation of Γ with cluster size gives us some idea of the accuracy of these calculations.

The effect of finite cluster size can be modeled with the scattering method developed by Krueger and Pollmann [6]. The cluster boundary is treated as a potential

barrier that perturbs the semi-infinite surface. We construct an infinite array of such barriers, dividing the surface into a superlattice of clusters. The scattering method gives the resulting green's function, projected onto any atom in the cluster:

$$G_{nn} \approx G_{nn}^{(0)} - \sum_m \frac{|G_{nm}^{(0)}|^2}{G_{mm}^{(0)}} \quad (2.2)$$

where n is any atomic level and m are only those levels that fall inside the potential barrier. It can be shown that the square modulus of the inter-site green's function, $|G_{nm}^{(0)}|^2$, decays as r_{nm}^{-2} in a free electron metal. This relation is not surprising, as it is already known that the inter-site density matrix decays with the inverse-square of distance in a metal [7].

The distance to the barrier varies linearly with cluster diameter, L , so $|G_{nm}^{(0)}|^2$ is proportional to L^{-2} . However, the sum over m will include fewer atoms as the cluster size increases, since the ratio of cluster surface area to enclosed volume goes as L^{-1} . Therefore, the total sum is proportional to L^{-3} .

Applying this result to the golden rule expression for Γ , we find that the deviation of Γ from its macroscopic limit is proportional to the inverse of the cluster's volume.

$$G_{ll} \approx G_{ll}^{(0)} (1 + \sum_n V_{ln} G_{nn} V_{nl}) \quad (2.3)$$

$$\Delta\Gamma_{size} = \sum_n |V_{in}|^2 \Delta G_{nn} \propto \frac{\Gamma}{L^3} \quad (2.4)$$

2.4 Tight-Binding Study of Cluster Size Effects

For intermediate atom-surface separation distances (2-8 au), quantum size effects are the largest source of uncertainty in calculating resonance widths from finite clusters. To study these size effects, we have constructed a semi-empirical tight-binding model of aluminum according to the method of Slater and Koster [8]. Tight-binding parameters developed by Krueger and Pollmann were used [9], and the Hamiltonian eigenproblem was solved using the ARPACK library developed at Rice University [10].

The tight-binding study was conducted to meet two primary goals: qualitative understanding of the size dependence of the density of states, and quantitative estimates of the cluster size necessary to calculate Γ with acceptable accuracy. We begin by discussing the qualitative part of these results.

Fig. 2.1 shows the total density of states for aluminum cubes of various sizes. In each case, the DOS follows the general form of the macroscopic distribution, but is modulated by the size quantization of energy states. The distribution of one-electron eigenstates is quite analogous to a deep, three-dimensional square well with approximately the same geometry as the cluster.

Figure 2.1 Total density of states for semi-empirical tight-binding models of four cubic aluminum clusters. As cluster size increases, the density of states approaches that of macroscopic aluminum.

Next, we added an idealized alkali adsorbate to each cluster to simulate the interaction of a free lithium atom with its surface. The adsorbate energy levels were set to the experimental values for Li 2s and 2p orbitals [11], but the adsorbate-surface interaction parameters were left as scalable variables to simulate changes in adsorbate position. The adsorbate is assumed to be at the center of the cluster's top face, and near enough that only its interaction with the nearest cluster atom is significant. While this model is not expected to be numerically accurate in representing the Li-surface interaction, it provides a realistic qualitative picture of the relationship between cluster size and the adsorbate-resolved density of states (JDOS).

In addition to the cubes described previously, two new cluster shapes were added; they included tall columns of fixed surface area but variable depth, and flat squares of fixed depth but variable width. This revealed a key difference between depth variation and width variation of the JDOS.

Fig. 2.2 shows the adsorbate 2s JDOS for a series of aluminum columns of increasing depth. As the column depth increases, the JDOS changes in a fairly uniform manner; the eigenstates become more closely spaced, but follow the same general pattern.

Fig. 2.3 shows the adsorbate 2s JDOS for a series of aluminum squares, each one three layers deep but of increasing lateral dimension. The JDOS of the squares

Figure 2.2 The adsorbate-projected density of states (JDOS) for four aluminum columns of increasing depth, as calculated via a tight-binding model. A Lorentzian with the extracted width is superimposed on the raw JDOS.

changes much more unpredictably with cluster size than the columns. Even a small change in width can result in a radically different distribution of eigenstates.

The difference between depth-based and width-based size effects can be generally understood in terms of the square well model. If we match each square well eigenstate with a similar Bloch state in the cluster, its wavefunction will be as follows, up to a normalization constant:

$$\psi_{k\sigma}(\vec{r}) = \sum_i \sin(\vec{R}_i \cdot \vec{k}) \phi_\sigma(\vec{r} - \vec{R}_i) \quad \vec{k} = \frac{\pi n_x}{L_x} \hat{x} + \frac{\pi n_y}{L_y} \hat{y} + \frac{\pi n_z}{L_z} \hat{z}$$

The wavefunction used above is written in a coordinate system where the origin lies at one corner of the cluster, therefore the cluster atom nearest the adsorbate has coordinates $(L_x/2, L_y/2, 0)$. Accordingly, we can write the Hamiltonian matrix elements involving the adsorbate and a cluster eigenstate as follows:

$$H_{l\sigma,k\sigma} = \sin\left(\frac{\pi n_x}{2} + \frac{\pi n_y}{2}\right) V_\sigma \quad H_{k\sigma,k\sigma} = E_\sigma + \frac{\pi^2}{2} \left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2} \right)$$

where E_σ is an energy level of the cluster atoms, and V_σ is the matrix element between the adsorbate orbital and an orbital of the nearest cluster atom. The form of this matrix element explains why JDOS changes with cluster width are more irregular than with cluster depth. It is as if the adsorbate is interacting with several bands, each labeled by one (n_x, n_y) pair. Within each band, the states are spaced uniformly and have the same interaction matrix element with the adsorbate; increasing the depth of the cluster packs the eigenvalues more closely, but doesn't fundamentally

Figure 2.3 The adsorbate-projected density of states (JDOS) for four aluminum squares of increasing width, as calculated via a tight-binding model. A Lorentzian with the extracted width is superimposed on the raw JDOS.

change the shape of the band or its adsorbate interaction. On the other hand, a change in width rearranges all the bands and the strength of their interactions with the adsorbate, resulting in a radically different JDOS.

Fig. 2.4 shows the change in JDOS with cluster size. The density axis is scaled logarithmically so that states with very small components in the JDOS are still visible. The data seems to confirm the aforementioned difference between width effects and depth effects. Each of the curves formed by the JDOS points corresponds to one of the (n_x, n_y) bands. As the cluster depth increases, the bands have the same structure, but are more densely populated with eigenstates. When the depth is held constant but the cluster width increases, more bands are added and the structure of those bands is completely rearranged.

The results of this study suggest trends in the cluster size consistency of Γ calculations. As cluster depth increases, the JDOS keeps roughly the same structure but is better resolved, therefore we would expect the calculated Γ to converge fairly smoothly toward some limit. As cluster width increases, however, the JDOS changes unpredictably. Therefore, we expect Γ to vary somewhat randomly as the cluster width changes, making its convergence more difficult to recognize.

In Fig. 2.5, the resonance width, Γ , is plotted versus cluster depth. Each curve represents clusters with the same lateral cross-section, i.e. the same L_x and L_y dimensions. A broadening of $\beta = 2.0$ eV was used to extract Γ in all cases. Though

Figure 2.4 Raw adsorbate-projected density of states (JDOS) from tight-binding models of aluminum. The upper two plots show that increasing a cluster's vertical depth adds more points to the JDOS, but doesn't alter its fundamental structure. The lower two plots show that, in contrast, a change in width radically rearranges the JDOS.

each curve converges clearly toward a limiting value of Γ , it would be misleading to conclude that any one of these is the semi-infinite limit. Each lateral cross-section produces a different large-depth limit for Γ , and these limits will only agree when the lateral dimensions are large.

The second goal of the tight-binding study is to estimate the cluster size necessary to accurately determine Γ . First of all, a cluster depth must be chosen. In all the depth versus Γ plots shown above, Γ rises up to a critical depth, then rapidly decays to its large-depth limit. At five layers deep, all clusters are past their critical depth and Γ is within approximately 10% of its limit. At six layers, Γ is within 2% of its large-depth limit, regardless of lateral dimensions.

Once a cluster depth is selected, lateral dimensions must be chosen. From the clusters studied, it appears that the smaller of the two lateral dimensions determines the accuracy of Γ . In Fig. 2.6, Γ is plotted versus each cluster's minimum lateral dimension. Five-layer deep clusters are within 10% of the macroscopic Γ , even for very small lateral dimensions. Increasing their lateral size beyond three or four atomic planes will gain little accuracy in Γ . Six-layer deep clusters should be somewhat wider; clusters about five atomic planes wide are necessary before the uncertainty in Γ is 2% or less.

Figure 2.5 Tunneling rate vs. vertical cluster depth for tight-binding models of aluminum. All clusters converge toward a constant tunneling rate as depth increases, but the converged value depends strongly on the cluster's lateral dimensions.

Figure 2.6 Tunneling rate vs. shortest lateral cluster dimension for tight-binding models of aluminum. Clusters five and six layers deep were studied, and the deeper clusters show much faster convergence with lateral size.

2.5 Width Extraction

The JDOS for a discrete system, such as a cluster, consists of individual delta function "spikes" rather than a smooth spectrum. To extract Γ , we must first transform the JDOS into a continuous function with a single recognizable peak. To make this transformation, we apply a Lorentzian broadening of width β :

$$A'_l(\epsilon) = \sum_k |C_{lk}|^2 \frac{\beta/2\pi}{(\epsilon - \epsilon_k)^2 + (\beta/2)^2} \quad (2.5)$$

When the energy level spacing is much less than Γ , the resonance width can be unambiguously determined by minimally broadening the JDOS and measuring its FWHM. Unfortunately, the range of interest for Γ corresponds to such closely spaced energy levels that extremely large clusters would be required. For example, if $\Gamma \approx 0.05 \text{ eV}$ or $\tau \approx 6.582 \times 10^{-15} \text{ sec}$, a relatively large width, the energy level spacing in the JDOS approaches Γ at a cluster size of 500 atoms. The range of interest for Γ could extend as much as four orders of magnitude lower, requiring clusters of millions of atoms for clear resolution of the Lorentzian.

To circumvent this limitation, it was necessary to devise another way of extracting Γ from the projected density of states. A number of statistical methods were first attempted, treating the JDOS as a set of data points to be fitted to a probability distribution. However, because these methods are often sensitive to outlying points, secondary features in the JDOS frequently distorted the best-fit distribution, result-

ing in unreliable estimates for Γ . The time-dependent population of the adsorbate level was also examined, but there was no clear method for matching the periodic population function of a finite system to the aperiodic exponential decay found in the macroscopic system.

The most reliable way to estimate Γ turned out to involve Lorentzian broadening of the JDOS, but instead of a minimal broadening parameter, we apply a very large broadening, $\beta \gg \Gamma$. The FWHM of the resulting peak is directly related to Γ , due to an algebraic property of the Lorentzian distribution. This distribution can be represented as the Fourier transform of an exponential:

$$A^\Gamma(\epsilon - \mu) = \frac{\Gamma/2\pi}{(\epsilon - \mu)^2 + (\Gamma/2)^2} = \int e^{i\omega t} d\omega \exp(-it\mu - \frac{\Gamma}{2}|t|) \quad (2.6)$$

The convolution of this Lorentzian with another of width β can be rewritten using a product of Fourier transforms.

$$\begin{aligned} A^\Gamma(\epsilon - \mu) * A^\beta(\epsilon) &= \int e^{i\epsilon t} dt \exp(-it\mu - \frac{\Gamma}{2}|t|) \exp(-\frac{\beta}{2}|t|) \\ &= \int e^{i\epsilon t} dt \exp(-it\mu - \frac{\Gamma + \beta}{2}|t|) \end{aligned} \quad (2.7)$$

But this is just another Lorentzian of width $\Gamma + \beta$. Therefore, if we know the full width at half-maximum (FWHM) of the broadened spectrum, we can extract the original width, Γ by subtracting the broadening parameter:

$$\Gamma = FWHM - \beta \quad (2.8)$$

2.6 Width for Small Clusters

The above expression for Γ is exact in the macroscopic limit, but may not be exactly true for a finite system. As an extreme example, consider an adsorbate that interacts with only a single cluster state. If the cluster state energy is very near the adsorbate energy, then there are two eigenstates represented in the JDOS:

$$A_l(\epsilon) = \frac{1}{2}\delta(\epsilon - \epsilon_l + v) + \frac{1}{2}\delta(\epsilon - \epsilon_l - v) \quad (2.9)$$

A Lorentzian broadening of width β results in two superimposed Lorentz distributions of width β , with their centers separated by $2v$. The FWHM of this double-Lorentz function depends on v and β as follows:

$$FWHM = \sqrt{8v^2 + \sqrt{80v^4 + 8v^2\beta^2 + \beta^4}} \quad (2.10)$$

This formula looks very unlike the macroscopic expression for the broadened FWHM. However, if we take β to values much larger than v and expand in powers of v/β , a simpler expression emerges.

$$FWHM - \beta = \frac{6v^2}{\beta} + O\left(\frac{v^4}{\beta^4}\right) \quad (2.11)$$

For sufficiently small v , the resonance width is proportional to v^2 as per the golden rule. Therefore, the difference $FWHM - \beta$ is still proportional to Γ , even for the smallest possible cluster. As cluster size increases, one would expect the constant of proportionality to approach unity.

To verify this trend, the large-broadening method was applied to a semi-empirical tight-binding model of lithium near the (001) aluminum surface. Fig. 2.7 shows the relationship between $FWHM - \beta$ and v^2 for a range of cluster sizes. A relatively large broadening of 5 eV was used to demonstrate the large β behavior. As expected, $FWHM - \beta$ is proportional to v^2 , and the constant of proportionality converges to its macroscopic value in the limit of large cluster size.

This result can be used to determine the relationship between Γ and adsorbate position, even for very small clusters. If the cluster diameter, L and broadening parameter, β are held fixed, then Γ can be reliably determined up to a constant factor:

$$FWHM - \beta \approx f(L, \beta)\Gamma \quad (2.12)$$

The size-dependent factor can be estimated by accurately calculating Γ at a single adsorbate position. A high symmetry position may be chosen for this calculation to allow the largest possible cluster size.

Figure 2.7 The accuracy of the present work's width extraction method is tested against several aluminum tight-binding calculations. The extracted resonance width is plotted versus the tunneling rate, calculated directly from the adsorbate-cluster tight-binding parameters.

Chapter 3

Results

The method described in the previous section was applied to two clusters interacting with an alkali atom, one representing a metallic surface and one a semiconducting surface. In both cases, the density functional method was used to determine the ground state electronic structure of the adsorbate-cluster system, and project its density of states on an adsorbate level.

A range of lateral adsorbate positions was explored for each cluster, and the resulting resonance widths were extracted using the broadening method previously described. In each case, results for two different broadening parameters and two different cluster sizes are presented, showing the accuracy of the results.

3.1 Density Functional Method

The density functional method provides a much more physically accurate calculation of electronic structure than our tight-binding model. It is an *ab initio* method, requiring no semi-empirical parameters, and it includes charge redistribution and correlation effects. The disadvantage is its computational cost, so that cluster sizes must be smaller than in the tight-binding study.

The first step in determining resonance widths is to find the ground state electronic structure of the adsorbate-cluster system. For this purpose we used CMOL [12], an electronic structure code previously developed at Rice. CMOL uses the density functional formalism under the local spin density approximation, so both charge self-consistency and some correlation effects are taken into account. CMOL is also optimized for the conditions found in many surface physics problems: large numbers of atoms and interatomic distances much greater than the equilibrium bond lengths.

In each calculation, the surface is represented by a cluster of the same chemical composition as the substrate. These clusters are not relaxed, but instead fixed in the substrate's bulk geometry. While a relaxed cluster would be more physical in isolation, it may be less similar to the macroscopic surface. The primary disadvantage of unrelaxed clusters is the slow convergence of the electronic structure; however, in the systems we studied convergence was sufficiently fast for our needs.

An important goal of the present work is to allow calculation of resonance widths for arbitrary adsorbate positions. Therefore, restricting the atom-cluster configuration to high symmetry positions is undesirable. However, it is possible to take advantage of symmetry in the surface normal direction without restricting the adsorbate position. For each system in the present study, all atoms were reflected across the crystal plane furthest from the adsorbate. This generates a cluster approximately twice as large with two identical adsorbate atoms on opposite faces, but with very

little increase in computational cost. Interactions between the twin adsorbates are very small due to their large separation distance, and in any case they are screened from one another by the cluster. Therefore, the results will be nearly the same as for a single adsorbate.

It is also possible to take advantage of lateral symmetry, and still explore adsorbate positions over most of the surface unit cell. For example, on the (001) surface of an fcc crystal, continuous adsorbate trajectories can be constructed along the (100), (010), and (110) directions, while maintaining a plane of symmetry parallel to the direction of motion and normal to the surface. Similar paths of symmetry can be found for other crystal structures, though some may be inverted across the lateral symmetry plane rather than reflected.

From each electronic structure calculation, the projected density of states (JDOS) must be available. CMOL allows the JDOS to be easily extracted from its results, but any electronic structure calculation that generates eigenvectors (i.e. molecular orbital coefficients) can be used:

$$A_l(\epsilon) = \sum_k |C_{lk}|^2 \delta(\epsilon - \epsilon_k) \quad (3.1)$$

where A_l is the JDOS or spectral function, ϵ_k are the eigenvalues and C_{lk} are the corresponding eigenvector coefficients in the adsorbate level, l . Note that both occupied and unoccupied eigenstates contribute to the JDOS.

3.2 Li on Al(001)

We have applied the density functional method to the interaction of lithium with the (001) surface of aluminum. A great deal of experimental and theoretical work has been concentrated on alkali atom scattering off aluminum, and especially on lithium due to the relative simplicity of its atomic structure. See ref. [13] for a review of this field.

Five different cluster geometries were studied. The first two clusters are three layers deep and five layers wide along their shortest lateral dimension. These broad, shallow clusters are designed to allow adsorbate positioning anywhere along the longest lateral axis while keeping four-fold symmetry to reduce computational cost.

The second and third clusters have similar size to the first two, but their lateral axes are rotated 45 degrees from the crystal axes. These clusters are also designed to allow lateral adsorbate movement, but along a different direction than the first two. Fig. 3.1 shows the shape of all five aluminum clusters and the planes or lines of symmetry along which the adsorbate is placed.

The Γ values obtained from these clusters are sensitive to the broadening parameter, β , with which Γ is extracted. To compensate, Γ is rescaled so that its minimum value along the trajectory is unity. Since both trajectory orientations have their minimum Γ at the center site, where they intersect, the results of the two orientations can be directly compared.

Figure 3.1 Aluminum clusters used in the density function study of lithium on the Al(001) surface.

Fig. 3.2 shows the change in this rescaled Γ as the lithium adsorbate moves across the first two clusters at 8.5 au above the top aluminum layer. For both of these clusters, the adsorbate is placed along a trajectory that passes over the center and top sites. After the rescaling, the corrugation of Γ is relatively insensitive to cluster size, especially in the central part of each cluster surface. One would therefore expect that the corrugation of Γ accurately reflects the macroscopic result.

Fig. 3.3 shows the lateral dependence of Γ for the third and fourth clusters. For these clusters, the adsorbate is placed along a trajectory that passes over the center and bridge sites, at a 45 degree angle to the previous trajectory. Again, Γ is rescaled to equal one at the center site, and after rescaling it is nearly independent of cluster size.

The fifth aluminum cluster is somewhat larger, measuring nine layers deep and five layers wide in both lateral dimensions. This cluster is designed for a more restricted range of adsorbate positions along the vertical axis, where the system has eight-fold symmetry. The Γ values calculated from this cluster are expected to be fairly accurate, as the cluster is well within the size guidelines developed from the tight-binding study.

The results obtained from the large cluster are plotted in Fig. 3.4, revealing the decay of Γ with increasing adsorbate-cluster separation. The two solid curves in the figure were obtained with different broadening parameters, 1.0 eV and 2.0 eV, showing that the results are relatively insensitive to β . For this reason, the calculated

Figure 3.2 Lithium (2s) level broadening as a function of the atom's lateral position over Al(001), including top and center sites. Solid lines represent data from cluster (2), and dashed lines represent cluster (1). For both clusters, broadening parameters of 1.0 and 2.0 eV were used to extract resonance widths.

Figure 3.3 Lithium (2s) level broadening versus lateral position over Al(001), including center and bridge sites. Solid lines represent data from cluster (4), and dashed lines represent cluster (3). For both clusters, broadening parameters of 1.0 and 2.0 eV were used to extract resonance widths.

Γ values can be used directly, avoiding the rescaling that was required with the smaller clusters.

At adsorbate-cluster distances greater than about 8 au, the tunneling rate calculated from these results is not reliable. In this range, the separation distance approaches the length scale of the cluster diameter, and the cluster's electron wavefunctions decay much faster than the wavefunctions from a macroscopic surface. As previously discussed, the matrix element, V_{ik} is mainly determined by conditions near the adsorbate and in the cluster interior. At large separation distances, the cluster wavefunctions near the adsorbate decay very rapidly, and the component of V_{ik} representing the cluster interior dominates.

Fig. 3.4 shows the tunneling rate calculated from the largest aluminum cluster for adsorbate distances up to 15 au from the interface. For comparison, the figure includes two other sets of data. First, it includes the results predicted by analytic complex scaling theory for a lithium adsorbate on bulk aluminum [1]. Second, we have estimated Γ from the overlap of a hydrogenic 2s wavefunction with a simplified step function surface potential. The cluster data clearly follows the latter pattern, indicating that cluster size effects are primarily due to changes in the cluster wavefunctions near the adsorbate.

Figure 3.4 Lithium (2s) level broadening versus vertical distance above the Al(001) top site, as measured from the jellium edge. The solid lines represent widths extracted from the density functional study of aluminum cluster (5) using broadening parameters of 1.0 eV and 2.0 eV. The dashed lines show comparable results from complex scaling theory (a) and from the overlap of a hydrogenic 2s wavefunction with a simple step potential (b).

3.3 Li on Si(110)

Charge transfer between an adsorbate and a semiconducting surface is not as well understood as for a metal surface. In a semiconductor, the density of states is very different from a free-electron metal, and electron eigenstates can be more localized. Both of these factors make it difficult to apply analytic theories to semiconducting or insulating surfaces. However, they should not be significant obstacles to the present work, because it is primarily a numerical method.

Two cluster models were studied to simulate a lithium atom on the silicon (110) surface. As with the aluminum study, the clusters were not relaxed so that they would more accurately represent the macroscopic surface. Surface reconstruction was not taken into account, but its effect should not be qualitatively significant, especially for the 110 surface, which has relatively few dangling bonds per surface unit cell. To speed convergence of electronic structure calculations, dangling silicon bonds along the sides of the clusters were terminated with hydrogen. The top and bottom faces, where the adsorbates interact, were left clean.

Both clusters have the same depth, but one has larger lateral dimensions to test cluster size convergence of the results. In both cases, the lithium adsorbate was positioned in a plane parallel to the surface normal vector, and parallel to the cluster's longest dimension. The resulting system had four-fold symmetry regardless of adsorbate position in that plane.

Figure 3.5 Silicon clusters used in the density function study of lithium on the Si(110) surface.

The geometry of these silicon clusters is shown in Fig. 3.5. The corresponding lithium 2s resonance widths are in Fig. 3.6, covering a range of adsorbate positions along a lateral trajectory. For each cluster, only the innermost unit cell was selected for calculation of Γ to minimize edge effects. As with the aluminum study, Γ is rescaled, in this case so that it is unity at its maximum, and widths are extracted with broadenings of both 1.0 and 2.0 eV.

The lateral variation of Γ shows stronger, less sinusoidal variation than for the aluminum clusters. This is in part because the silicon surface corrugation is deeper, and has longer length scales than aluminum's corrugation. However, it may also result from greater localization of electron eigenstates. As the adsorbate encounters these

Figure 3.6 Lithium (2s) level broadening versus lateral position over Si(110). Solid lines represent data from cluster (1), and dashed lines represent cluster (2). For both clusters, broadening parameters of 1.0 and 2.0 eV were used to extract resonance widths.

localized states, the matrix elements between adsorbate and surface wavefunctions increase exponentially, resulting in an increased tunneling rate.

The corrugation of Γ is also more sensitive to the broadening parameter with which it is extracted. This may simply be due to the small cluster size, but it is also possible that the spectral function is more non-Lorentzian due to the band structure of silicon. Theoretical advances in charge transfer at semiconducting surfaces may be needed before these issues can be explored further.

3.4 Outlook

The results presented above are meant only as a demonstration of the proposed method for electron tunneling calculations. In the near term, applications of the method will be limited to similar demonstrations, as computational technology is not yet capable of the demands posed by very large cluster calculations.

Nonetheless, a number of interesting systems may be studied qualitatively, even with current processing capabilities. For example, charge transfer near localized surface features may be studied, such as vacancies, step edges and multiple adsorbates. The adatom may even be replaced by a molecule; since the density of states can be projected on molecular orbitals (MOs), tunneling rates can be obtained between the MOs and the surface. Various molecular orientations would also be accessible.

A possible improvement to the method would be the addition of diabatic charge states to the electronic structure codes. Currently, only the total charge of the atom-cluster system may be controlled, and the results reflect that system's adiabatic ground state. If the adsorbate charge could be separately controlled, ionic adsorbates could be studied as well as neutral atoms and molecules. Further examination is needed to determine whether these charge states can be simulated with existing codes, or if new development is required.

Chapter 4

Conclusions

In this work, we have demonstrated a new method for calculating the electron tunneling rate between a surface and an incident, low-energy adsorbate. The surface is represented by a finite cluster reflecting the composition and lattice structure of the macroscopic substrate. To find the tunneling rate, the electronic structure of the adsorbate-cluster system is calculated numerically, and the density of states is projected on chosen adsorbate orbitals. This projected density of states is then convoluted with a broad Lorentzian distribution, and the resulting full width at half-maximum of the result is extracted. The difference between this width and the broadening parameter is a good approximation for Γ , which becomes exact in the limit of large cluster size and small adsorbate-cluster interaction.

The method's most significant limitation is the restricted range of separation distance between the adsorbate and the cluster interface. When this distance approaches the length scale of the cluster, the cluster wavefunctions begin to decay much faster than for a semi-infinite surface. This distorts the Hamiltonian matrix elements between adsorbate orbitals and cluster states, which in turn changes Γ as predicted by the golden rule.

On the other hand, the method present here can be applied to surfaces of arbitrary geometry and composition, including semiconductors, insulators and heterogeneous systems. The accuracy of the results is limited only by computational resources, and even the separation distance limit can be increased by modeling larger clusters. We anticipate that as computing technology advances, this method can be applied up to the longest separation distances where charge transfer is significant.

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