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Nonadiabatic Electron Transfer at Metal Surfaces

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The present article treats the role of the density of electronic states ρ_F at the Fermi level of a metal in affecting the rate of nonadiabatic electron transfer. The rate constant k_{ET} is calculated for the electron transfer across an alkanethiol monolayer on platinum and on gold. The ρ_F of platinum is about 7.5 times that of gold, the difference being mainly due to the d band of Pt. In spite of this difference, the electron transfer rate constant k_{ET} calculated in the present paper increases only by a factor of about 1.8, instead of the factor of about 7.5 expected using ρ_F alone. Implications of these results for present and past experiments are described. Bands which are weakly coupled (e.g., the d-band of Pt in the present case) contribute much less to the rate constant than is suggested by their density of states ρ_F. Thereby, k_{ET} is approximately independent of ρ_F in two cases: (1) adiabatic electron transfer and (2) nonadiabatic electron transfer when the extra ρ_F is due to the d electrons. Experiments which can test the latter are discussed.

1. Introduction

In this paper, we study how the rate of electron transfer is affected by the density (ρ_F) and the nature of electronic states of the metal at the Fermi level, in particular how the exchange current is affected. There have been some experiments performed investigating the variation of the rate constant with the density of states of the metal not using monolayers[1−3] and with monolayers.[4,5] Iwasita et al.[1] measured the electrochemical exchange current i_{ex} for the $Ru(NH_3)_6{}^{2+}-Ru(NH_3)_6{}^{3+}$ couple at several metal electrodes. They found that i_{ex} was the same, even when the density of electronic states differed by an order of magnitude.

The first explanation that comes to mind for such experiments[1−3] is that the electron transfer reaction is adiabatic. The exchange current i_{ex} is expected to be proportional to ρ_F only for nonadiabatic electron transfers, namely, in the limit of weak coupling of the redox agent to the metal. In the adiabatic case, i_{ex} should be independent of ρ_F. However, there is an alternative explanation for the results. The assumption that i_{ex} is proportional to ρ_F in a nonadiabatic process is based on the assumption that the different electronic orbitals in the metal, s, p, and d, which contribute to ρ_F contribute equally to i_{ex}. The large value of ρ_F in metals such as Pt or Pd arises because their d orbitals lie near the Fermi level. If the d electrons are much less coupled to the acceptor than the s electrons (which dominate ρ_F for metals such as Au or Ag), the exchange rate would not be proportional to the total ρ_F even for a nonadiabatic process.

In recent years, there has been much experimental work with monolayers coated on metal surfaces[6,7] (mainly gold). Such experiments have been used to study features such as the distance dependence of the rate of electron transfer, the reorganization energy and the coupling between the redox agent and the metal. When a sufficiently thick monolayer is present, for example, sufficiently long alkyl chains in the case of a thioalkane monolayer, the coupling between the metal and the acceptor is weak and the rate of electron transfer is clearly nonadiabatic. Studies with such a system would help differentiate between the two explanations for the rate constant dependence on the density of states given above, by providing information on the coupling by d versus s electrons.

In this paper, the electron transfer rate constant k_{ET} is calculated for an alkanethiol with 15 methylene units, with the redox agent $Ru(NH_3)_5Py^{2+}$ tethered to it. A monolayer of the alkanethiol ($HS(CH_2)_{15}CONHCH_2PyRu(NH_3)_5{}^{2+}$) is then coated on a metal. We estimate how changing the metal from Pt to Au changes the rate constant and hence the exchange current.

The theoretical model is described in section 2. To treat the metal electrode, a tight binding (TB) approach is used in the calculations. Parameters available from a fit to band structure of the metals[8] are used. The extended-Hückel method[9] is used to treat the alkanethiol bridge and its coupling to the acceptor and to the metal. The bridge part is parametrized to fit experimental band structure of long chain alkanes. In a recent article,[10] it was found that this parametrization was sufficiently accurate for the calculation of the distance-dependence of long-range electron transfer rates in similar systems.

In treating the metal, the Z-transform[11,17] method is used, which facilitates the use of a semi-infinite model for the electrode and allows for easy calculation of metal wave functions with tight-binding parameters. This method is summarized in Appendix A and is applied there to the present problem. In the present paper we use it to explore how k_{ET} changes with a change in ρ_F, namely, how it changes with the metal electrode, and examine particularly the relative contributions of d and s electronic states to the rate constant. The results are discussed in section 3 and compared with available experimental data. The present approach, like that in our earlier papers[12,13] on long range electron transfer, is a pragmatic one, namely, to use an approximate but simple method which has no arbitrarily adjustable parameters and see whether it is in agreement with the trends in the available experimental results.

2. Theoretical Model

The standard expression for the first-order rate constant for a nonadiabatic electron transfer (weak electronic coupling limit)

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for reactants fixed in position is[14]

$$k_{\mathrm{ET}} = \frac{2\pi}{\hbar} FC |H_{\mathrm{DA}}|^2 \tag{1}$$

where FC is the Franck Condon factor and H_{DA} is the electronic coupling between the donor and the acceptor.

We consider a donor (or acceptor) attached to the electrode by a thioalkane bridge monolayer. When a continuum of donor or acceptor levels is involved in the electron transfer, as is the case in a metal electrode, the right hand side of eq 1 is integrated appropriately over these levels. The rate constant for electron transfer can then be written as[14,15]

$$k_{\mathrm{ET}} = \frac{2\pi}{\hbar} \int \mathrm{d}\epsilon \frac{e^{-(\lambda - e\eta + \epsilon)^2/4\lambda k_{\mathrm{B}}T}}{(4\pi\lambda k_{\mathrm{B}}T)^{1/2}} |V(\epsilon)|^2 f(\epsilon) \tag{2}$$

and the units of k_{ET} are s^{-1}. For the Franck–Condon factor we have substituted a classical value (the final ratio of k_{ET}'s for different metals will be insensitive to this approximation),

$$FC = \frac{e^{-(\lambda - e\eta + \epsilon)^2/4\lambda k_{\mathrm{B}}T}}{(4\pi\lambda k_{\mathrm{B}}T)^{1/2}} \tag{3}$$

where λ is the reorganization energy, e is the electronic charge, and η is the overpotential. In eq 2, $f(\epsilon)$ is the Fermi–Dirac distribution with ϵ measured relative to μ, the chemical potential of the electrode,

$$f(\epsilon) = \frac{\mathrm{e}^{\epsilon/k_{\mathrm{B}}T}}{1 + e^{\epsilon/k_{\mathrm{B}}T}} \tag{4}$$

The square of the coupling matrix element, $|V(\epsilon)|^2$ denotes an integral over all the wave vectors **k** which contribute to a given energy,

$$|V(\epsilon)|^2 = \int \mathrm{d}^3\mathbf{k} |H_{kA}|^2 \delta(\epsilon(\mathbf{k}) - \epsilon) \tag{5}$$

$|H_{kA}|$ is $\langle \Psi_{\mathrm{k}} | H | \Psi_{\mathrm{A}} \rangle$ and describes the electronic coupling between the redox agent (A) and a particular electronic state of wave vector **k** of the electrode (which may have contributions from many bands). The integral over wave vectors in eq 5 is intended to include all such states and bands. Ψ_{k} and Ψ_{A} are the wavefunctions of the electrode and the redox agent, respectively. Ψ_{A} is normalized in the usual way and has units of $\mathrm{Å}^{-3/2}$. For Ψ_{k} a box normalization is used, i.e.,

$$\frac{\langle \Psi_{\mathrm{k}}(\mathbf{r}) | \Psi_{\mathrm{k}}(\mathbf{r}) \rangle}{V} = 1 \tag{6}$$

where V is the unit cell volume and $\langle\ \rangle$ implies integration over a unit cell volume. Thus, $\Psi_{\mathrm{k}}(\mathbf{r})$ has no units and $\langle \Psi_{\mathrm{k}} | H | \Psi_{\mathrm{A}} \rangle$ acquires units of eV $\mathrm{Å}^{3/2}$, $|H_{kA}|^2$ has units of eV^2 $\mathrm{Å}^3$ (eV^2wave vector^{-3}), and so $|V(\epsilon)|^2$ has units of eV.

The exchange current can be obtained from the rate constant with η set to 0 and then integrating over a unit area of the metal surface. Equation 2 is readily modified when the redox reagent is not attached to the monolayer.

For a single band case, $\eta = 0$ and $\lambda \gg \epsilon$ (as is typically the case), eq 2 simplifies to[10]

$$k_{\mathrm{ET}} = \frac{2\pi}{\hbar} (4\pi\lambda k_{\mathrm{B}}T)^{-1/2} e^{-\lambda/4k_{\mathrm{B}}T} \overline{|V|^2} \tag{7}$$

where

$$\overline{|V|^2} = \pi k_{\mathrm{B}} T \overline{|H_{kA}|^2} \rho_{\mathrm{F}} \tag{8}$$

the square of the coupling $\overline{|H_{kA}|^2}$ denotes

$$\overline{|H_{kA}|^2} = \frac{\int \mathrm{d}^3\mathbf{k} |H_{kA}|^2\ \delta(\epsilon(\mathbf{k}) - \epsilon_{\mathrm{F}})}{\int \mathrm{d}^3\mathbf{k}\ \delta(\epsilon(\mathbf{k}) - \epsilon_{\mathrm{F}})} \tag{9}$$

and ρ_F is the density of states[16] at the Fermi level,

$$\rho_{\mathrm{F}} = \int \mathrm{d}^3\mathbf{k}\ \delta(\epsilon(\mathbf{k}) - \epsilon_{\mathrm{F}}) \tag{10}$$

We use the volume of the unit cell (with a one atom basis when appropriate as in the present case) as the unit volume and the units of ρ_{F} become eV^{-1} atom^{-1}.

In a multiband case, more than one band contributes to the density of states. If the summation over different bands is included in $\overline{|H_{kA}|^2}$ and ρ_{F} includes densities from all bands, eq 7 is still applicable. $\overline{|H_{kA}|^2}$ has contributions from all bands and depends on how the states are distributed over the bands and how each band couples to the acceptor. Because of this feature, $\overline{|H_{kA}|^2}$ can vary from metal to metal, and so the rate constant is not merely proportional to ρ_{F}, although eqs 7–9 remain valid. Clearly, the electronic states of bands weakly coupled to the redox agent will not contribute as much to the rate constant as those from bands strongly coupled to it.

To obtain k_{ET} (eqs 7–9) a calculation of H_{kA} at the Fermi energy (ϵ_{F}) is needed. This matrix element is the coupling between the metal $\langle \Psi_{\mathrm{k}} |$ and the acceptor $| \Psi_{\mathrm{A}} \rangle$ states. To find the form of the $\langle \Psi_{\mathrm{k}} |$ states of the metal we use the Z-transform method. This method is outlined in Appendix A.

3. Calculation and Results

The metals Au and Pt have very different densities of states at the Fermi level, the difference being largely due to the presence of the d electron band in Pt. The values[8] of $\rho_{\mathrm{F}} = 2.20$/atom/eV for Pt and $\rho_{\mathrm{F}} = 0.29$/atom/eV for Au are used in the present calculation. The Fermi energies[8] of Pt and Au are taken to be 8.68 and 7.32 eV, respectively, and the lattice parameters[24] are 2.77 Å for Pt and 2.88 Å for Au. Literature values[8] of the TB parameters for the metals are used to calculate Ψ_{k}. These parameters were obtained by a fit to accurate band structure calculations. The extended-Hückel theory is used to calculate the energy and overlap matrix elements of the bridge and the acceptor. The structure of the acceptor is estimated from the structure of X-ray data of similar compounds.[25] Only one alkanethiol chain is used instead of the entire monolayer. It was shown by comparison with added alkanethiol molecules that this approximation gave a reasonable and for our purposes adequate description of the coupling.[10] A parametrization of the bridge, and the sequential formula of Hsu and Marcus[10] were used to calculate the coupling element H_{kA}. Some details on the sequential formula, including the key recursion equations used to obtain the matrix elements, are given in Appendix B. The $|H_{kA}|^2$'s were averaged over 60 **k** vectors.[26] These **k** vectors were chosen randomly and included contributions from all bands. Thus, $|H_{kA}|^2$ is averaged over all bands and ρ_{F} is the total density of states. To make the calculations of Hsu one needs the difference in energies of a virtual superexchange state

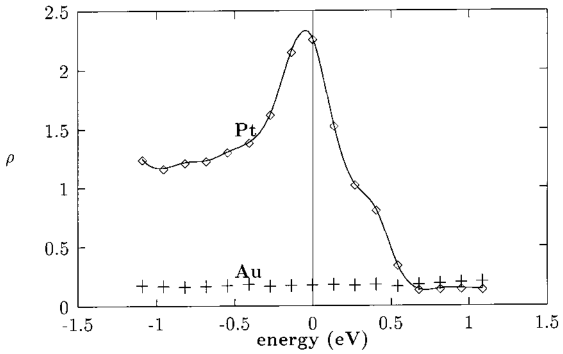

Figure 1. Band structure of Au and Pt with the Fermi energies of each set to 0. ρ is in units of no. of states per atom per eV. (◇) gives the density of states for Pt and (+) gives the density of states for Au.

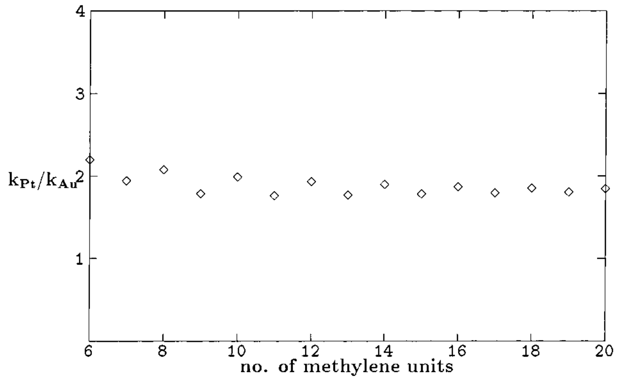

Figure 2. Ratio of rates at zero overpotential vs number of methylene units.

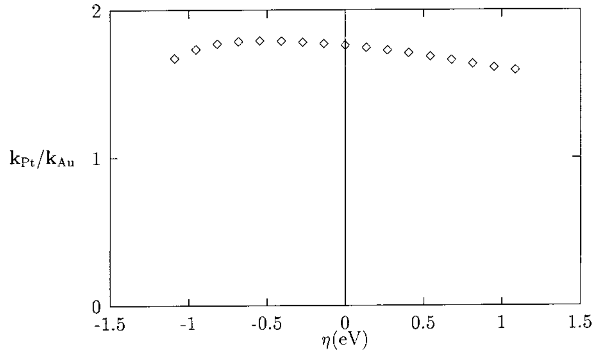

Figure 3. Ratio of k_{Pt} and k_{Au} vs overpotential (η), assuming an equal λ for the two metals.

and the donor/acceptor state at the transition state. This difference can be calculated using a formula[27] given in ref 10.

Our result for the rate constants of the two metals for a 15 methylene unit alkanethiol monolayer gives a value of 1.8 for k_{Pt}/k_{Au}. This result is consistent with unpublished experiments.[4,5] The ratio of the densities of electronic states of the two metals is 7.5.

The ratio of the exchange rate constants as a function of number of methylene units for the two metals is given in Figure 2. The number of methylene units is varied from 3 to 20. This ratio gives the distance dependence of the d orbital coupling. The overpotential dependence of the ratio is also calculated and is plotted in Figure 3. The dependence is found assuming a value of 1.2 eV[28,29] for λ. The same monolayer shields the acceptor in the solution from the metal surface, so we assume that the reorganization energy (λ) does not change on going from Au to Pt. To perform this calculation a value of 0.025 eV for k_BT, and the expression of the rate constant from eq 2 were used.

4. Discussion

It is seen both experimentally and theoretically that the nonadiabatic rate of electron transfer is not simply proportional to the total density of states. It depends, instead, on the density of states modulated by the square of the coupling. Accordingly, it is necessary that the various bands from which the density of states arise be also considered.

A more detailed analysis of the results provides some insight into the nature of the similarity of electron transfer rates for Pt and Au, their large difference in density of states at the Fermi energy notwithstanding. With a density of states at the Fermi energy of 29.9 in no. of states/Rydberg/atom, the density of sp states of Pt is 0.6 and that of d states is 29.3.[8] With a density of states of 4.0 for Au at the Fermi energy, the density of sp states was 1.6 and that of the d states was 2.4.[8] From these results it can be inferred that while the d states in Pt are not ineffective for coupling, their effectiveness is far below that of the sp states. If for a rough estimate the ratio of individual coupling effectiveness of an sp state and of a d state in Pt were taken to be roughly the same as in Au, then the calculated ratio of 1.8 for the rate constants leads from the above figures to a relative effectiveness of sp states to d states of 11.2.

There has been some concern[20] that the extended-Hückel method gives very narrow d-bands, which are more localized than in reality. In the present calculation, the metal is modeled using TB parameters which are not taken from extended Hückel and give good band structure results[8] (Figure 1). The d couplings we used for the Pt−S, Au−S and bridge-acceptor were, however, obtained from an extended-Hückel calculation using the standard parameters available with the program.[9]

The fact that the d orbitals are localized and not strongly coupled to the environment is well-known from field emission experiments.[33] Thus, even though the d electrons are present at the Fermi level, they interact very weakly with external fields or ions and these electrons tunnel out from the metal much less than s electrons at the same energy. This fact has been observed in field emission as well as in ion neutralization experiments.[34] It is thus perhaps, not surprising that this d electron localization also manifests itself in a reduced contribution to the rate constant in electron transfer experiments.

The rate constants were calculated as a function of the number of methylene units for the two metals. Regarding the results in Figure 2 we note that the ratio of the rate constants of Pt and Au changes little with number of methylene units.

We also calculate the overpotential dependence of the ratio of rate constants using eqs 2−5 (Figure 3). We find that the ratio peaks close to the Fermi level and decreases weakly for positive overpotentials. This result is understood using the band structure of the two metals (Figure 1): the density of electronic states of Pt is the highest close to Fermi level (zero overpotential), slopes gradually for negative energies relative to the Fermi energy and decreases sharply for positive energies while the density of states of Au is almost constant over the whole overpotential range. The change in ratio of rate constants with change in overpotential is very small for the anodic and cathodic parts of the curve. This small change should not cause any significant asymmetry in the rate vs overpotential curves, because of the large direct effect of the overpotential in the exponent of eq 2.

The observation of the importance of the type of states for the present study rather than only the density of states has its counterpart in studies of intramolecular vibrational relaxation[31] where the total density of states does not play a direct role in the rate of relaxation. It is rather a local density of coupled vibrational states which is important. In surface physics too, the concept of local density of states is useful to understand spectra where contributions from different layers parallel to the surface might be different.[32]

5. Conclusions

In this paper, we have calculated the effect of the metal density of electronic states on the rate of electron transfer. We find that the rate constant is not simply proportional to the density of states. Instead, we need to consider the individual electronic coupling elements for each of the bands. The coupling matrix elements significantly reduce the effect of the extra density of states of weakly coupled bands, such as the d band. We find, consistent with electron emission results[33] and electron transfer experiments,[4,5] that the d band states couple weakly to the outside environment and, thus, the rate constant for electron transfer does not reflect only the density of states.

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Appendix A: The Z-Transform Model for Semi-Infinite Metals

The Z-transform is a generalization of the discrete Fourier transform and is commonly used in the field of signal processing.[17] The periodicity of crystals makes them very similar to discrete signals and, therefore, the Z-transform can be applied very easily to crystalline solids to obtain their wave functions. It is especially useful in the application of the tight-binding approximation.[11]

We consider a crystal as being built up of planes with two-dimensional translational symmetry. Let $\hat{\mathbf{R}}_{||,1}$ and $\hat{\mathbf{R}}_{||,2}$ be the unit vectors which lie in the plane. Henceforth, we denote any vector[18] lying in the plane by

$$\mathbf{R}_{||} = n_1\hat{\mathbf{R}}_{||,1} + n_2\hat{\mathbf{R}}_{||,2} \qquad \text{(with integer } n_1 \text{ and } n_2) \tag{A1}$$

When we sum over $R_{||}$ we imply a double sum over n_1 and n_2. $\mathbf{k}_{||}$ in the subsequent notation denotes a wave vector conjugate to $\mathbf{R}_{||}$.

Let $\hat{\mathbf{R}}_p$ be the third unit vector for the unit cell, directed from one of the above planes to the next. With this notation each plane has a wave function of the form

$$\Phi_j(\mathbf{r} - \mathbf{R}_p) = \sum_{R_{||}=-\infty}^{+\infty} \exp(i\mathbf{k}_{||}\cdot\mathbf{R}_{||})\Theta_j(\mathbf{r} - \mathbf{R}_p - \mathbf{R}_{||}) \tag{A2}$$

with

$$\mathbf{R}_p = n\hat{\mathbf{R}}_p \tag{A3}$$

where j is an index which labels the orbitals for each atom and $\Theta_j(\mathbf{r} - \mathbf{R}_p - \mathbf{R}_{||})$ denotes the orbital centered at $\mathbf{r} = \mathbf{R}_p + \mathbf{R}_{||}$. The crystals of both Au and Pt have a one atom basis (one atom in the unit cell) and so we use that basis here, but this method is easily generalized to a larger basis.

The wave function of the crystal is

$$\Psi_k(\mathbf{r}) = \sum_{n,j} \Phi_j(\mathbf{r} - n\hat{\mathbf{R}}_p)c_{n,j} \tag{A4}$$

where $c_{n,j}$ is a factor, which we will find using the Z-transform. j is summed over the number of orbitals per unit cell, here numbered 1 to J. n is summed over as many layers as the problem requires, for example, $-\infty$ to $+\infty$ for a bulk crystal, 1 to $+\infty$ for a bulk crystal with a surface, and 1 to a finite m for a slab. The range of n imposes boundary conditions on the wave function, and we will examine later how these conditions affect the wavefunction. For now, we take n to be a problem-dependent quantity.

Using the Schroedinger equation, multiplying by a particular $\Phi_j(\mathbf{r} - n\hat{\mathbf{R}}_p)$ and integrating over $\mathbf{r}$ we obtain

$$\langle \Phi_l(\mathbf{r} - n'\hat{\mathbf{R}}_p)|H|\Psi_k\rangle = \epsilon\langle \Phi_l(\mathbf{r} - n'\hat{\mathbf{R}}_p)|\Psi_k\rangle \tag{A5}$$

For the present problem, where the rate constant is being evaluated at the Fermi level (in the "normal region" for rate constants), ϵ equals ϵ_F and from eqs A2–A5 we have

$$\sum_{n,j}\{\langle \Phi_l(\mathbf{r} - n'\hat{\mathbf{R}}_p)|H|\Phi_j(\mathbf{r} - n\hat{\mathbf{R}}_p)\rangle - \epsilon_F\langle \Phi_l(\mathbf{r} - n'\hat{\mathbf{R}}_p)|\Phi_j(\mathbf{r} - n\hat{\mathbf{R}}_p)\rangle\}c_{n,j} = 0 \tag{A6}$$

The above equation can be written in matrix form,

$$\sum_n \mathbf{M}(n'\hat{\mathbf{R}}_p, n\hat{\mathbf{R}}_p)\mathbf{c}_n = 0 \tag{A7}$$

where $\mathbf{M}$ is a $J \times J$ matrix (J is the number of orbitals per atom) and $\mathbf{c}_n$ becomes a column vector with J components, its jth component being $c_{n,j}$. Using the tight-binding (TB) approximation, we assume that any given plane interacts within itself,

$$\mathbf{M}(n\hat{\mathbf{R}}_p, n\hat{\mathbf{R}}_p) = \mathbf{A} \tag{A8}$$

and with its nearest neighbors,

$$\mathbf{M}(n\hat{\mathbf{R}}_p, (n-1)\hat{\mathbf{R}}_p) = \mathbf{B}^\dagger \tag{A9}$$

$$\mathbf{M}(n\hat{\mathbf{R}}_p, (n+1)\hat{\mathbf{R}}_p) = \mathbf{B} \tag{A10}$$

$\mathbf{A}$, $\mathbf{B}$, and $\mathbf{B}^\dagger$ are $J \times J$ matrices (with J same as above) which can be calculated from TB parameters of the metal.[8,19] $\mathbf{A}$, being the self-interaction of the plane, is Hermitian. When a plane is not at the boundary, and so, both its neighboring planes are present, we have

$$\mathbf{B}^\dagger\mathbf{c}_{n-1} + \mathbf{A}\mathbf{c}_n + \mathbf{B}\mathbf{c}_{n+1} = 0 \tag{A11}$$

Since n is discrete, we use the Z transform[17]

$$\mathbf{F}(z) = \sum_n z^n\mathbf{c}_n \tag{A12}$$

where z is a complex variable and $\mathbf{F}(z)$ a column vector with J components. Only when z is of the form $\exp(i\theta)$ with real θ, does $\mathbf{F}(z)$ reduce to the familiar discrete Fourier transform. From eqs A11 and A12 we see that

$$\mathbf{B}^\dagger\frac{\mathbf{F}(z)}{z} + \mathbf{A}\mathbf{F}(z) + \mathbf{B}\mathbf{F}(z)z = 0 \tag{A13}$$

To obtain a nontrivial $\mathbf{F}(z)$ we set

$$\det\left(\frac{\mathbf{B}^\dagger}{z} + \mathbf{A} + \mathbf{B}z\right) = 0 \tag{A14}$$

This equation has $2J$ roots. Taking the complex conjugate of the above equation to see the symmetry of the roots, we have

$$\det\left(\frac{\mathbf{B}}{z^*} + \mathbf{A}^\dagger + \mathbf{B}^\dagger z^*\right) = 0 \qquad \text{(A15)}$$

Since $\mathbf{A}$ is Hermitian, we see that if z is a root then $1/z^*$ is also a root and so the number of roots with $|z| < 1$ equals the number with $|z| > 1$.

The most general form of $\mathbf{c}_n$ is obtained by inverting the Z-transform (eq A12):

$$\mathbf{c}_n = \sum_m (z_m)^n a_m \mathbf{F}_m(z_m) \qquad \text{(A16)}$$

where the sum is over the number of roots ($2J$), the z_m and $\mathbf{F}_m(z_m)$ are the eigenvalues and eigenvectors of eq A13, and the a_m can be determined from the boundary conditions and the normalization. The boundary conditions are considered next.

(1) Bulk. Any solution to eq A13, $z = z_m$, which has $|z_m| > 1$ or $|z_m| < 1$ will diverge at $+\infty$ or $-\infty$ respectively, and its a_m is set to 0. Therefore only $|z_m| = 1$ roots contribute to eq A16, so $z_m = \exp(ik_m)$ with real k_m,[20] and there is a three-dimensional translational symmetry of the wave function. The final wave function is then of the form

$$\Psi_\mathrm{k}(\mathbf{r}) = \sum_{n,m,j} \exp(ink_m) a_m F_{m,j}(\exp(ink_m)) \Phi_j(\mathbf{r} - n\hat{\mathbf{R}}_\mathrm{p}) \qquad \text{(A17)}$$

where $F_{m,j}$ is the jth component of $\mathbf{F}_m$ and the remaining a_m's can be determined by normalization. The number of Ψ_k equals the number of a_m's found from normalization. The number of Ψ_k also equals twice the number of bands present at that energy. Physically, these Ψ_k represent forward and backward propagating waves.

(2) Surface. The crystal planes are denoted by $n = 1$ to $+\infty$. Two conditions are imposed on Ψ_k: (a) Ψ_k should not diverge at $n = +\infty$ and (b) $\mathbf{c}_0 = 0$, since there is no crystal plane there. Condition (a) requires that only the $|z_m| \le 1$ contribute to Ψ_k. The a_m's associated with the $|z_m| > 1$ roots (the same in number as the $|z_m| < 1$ roots) are set to 0. Condition (b) requires that

$$\sum_{m,j} a_m F_{m,j}(z_m) = 0 \qquad (|z_m| \le 1,\ j = 1 \textit{ to } J) \qquad \text{(A18)}$$

To satisfy (b) we need at least as many solutions of eq A13 (i.e. z_m's) as there are orbitals (i.e., J or components of $\mathbf{c}_0$) and thus J of the a_m's are determined from the boundary condition. The most general form of the wave function is

$$\Psi_\mathrm{k}(\mathbf{r}) = \sum_{n=1}^{\infty} \sum_{m,j} (z_m)^n a_m F_{m,j}(z_m) \Phi_j(\mathbf{r} - n\hat{\mathbf{R}}_\mathrm{p}) \qquad \text{(A19)}$$

Ψ_k has two parts, one with $|z_m| = 1$ which propagates into the bulk, and one with contributions from $|z_m| < 1$, which approaches zero after a few layers.[21] In eq A19, J of the a_m are determined by the boundary condition, eq A18, and the remainder are determined by normalization. If l bands lie at the energy ϵ_F (eq A5) then l solutions Ψ_k exist and l of the a_m need to be determined by the normalization.

Two special cases may arise: (i) Due to the symmetry of the particular crystal (and the particular surface) under consideration none of the decaying solutions contribute to the wave function, e.g., as in the case of Au(111) modeled with only s orbitals.[23] In this situation k and $-k$ (where $z = \exp(ik)$), both contribute to the wavefunction and a $\sin(nk)$-like wave function (n being the nth layer from the origin) satisfies the boundary condition.

(ii) At some particular values of $|\mathbf{k}_\parallel|$ (eq A2) no z with $|z| = 1$ will exist. In this case the boundary conditions may still be satisfied but the resulting wavefunction decays after a few layers, yielding a pure surface state.

In metals with a surface, the most common type of states are of the type given in eq A19. We use such states to calculate $\langle \Psi_\mathrm{k} | H | \Psi_\mathrm{A} \rangle$.

Appendix B: The Sequential Formula

In this appendix we outline the derivation of the sequential formula of Hsu and Marcus[10] and give the key recursion relations which are used in the calculation of H_{kA}. Consider a bridge consisting of n identical units (in the present case of an alkanethiol monolayer the unit would be $-\mathrm{CH_2}-$) each having m molecular orbitals. Let $\mathbf{e}$ be an $m \times m$ diagonal matrix which represents the Hamiltonian of the bridge unit in a basis which diagonalizes it, i.e.,

$$\mathbf{e} = \begin{pmatrix} \epsilon_1 & 0 & \cdots & 0 \\ 0 & \epsilon_2 & \cdots & 0 \\ \vdots & \mathrm{l} & \ddots & \vdots \\ 0 & 0 & \cdots & \epsilon_m \end{pmatrix} \qquad \text{(B1)}$$

Let $\mathbf{v}$ be the coupling between the bridge units in the same basis and $\mathbf{v}^\mathrm{T}$ be its transpose. Both $\mathbf{v}$ and $\mathbf{v}^\mathrm{T}$ are $m \times m$ matrices. With these definitions and the tight-binding assumption the Hamiltonian of the total bridge becomes

$$H^{(n)} = \left(\begin{array}{ccccc|c} \mathbf{e} & \mathbf{v} & \mathbf{0} & \mathbf{0} & \cdots & \mathbf{0} \\ \mathbf{v}^\mathrm{T} & \mathbf{e} & \mathbf{v} & \mathbf{0} & \cdots & \vdots \\ \mathbf{0} & \mathbf{v}^\mathrm{T} & \mathbf{e} & \mathbf{v} & \cdots & \vdots \\ \vdots & \vdots & \vdots & \vdots & \ddots & \mathbf{0} \\ \hline \mathbf{0} & \cdots & \cdots & \mathbf{0} & \mathbf{v}^\mathrm{T} & \mathbf{e} \end{array}\right) \qquad \text{(B2)}$$

The partitions in the above equation splits $H^{(n)}$ into two parts $H_0^{(n)}$ and $H_1^{(n)}$ where

$$H_0^{(n)} = \left(\begin{array}{ccccc|c} \mathbf{e} & \mathbf{v} & \mathbf{0} & \mathbf{0} & \cdots & \mathbf{0} \\ \mathbf{v}^\mathrm{T} & \mathbf{e} & \mathbf{v} & \mathbf{0} & \cdots & \vdots \\ \mathbf{0} & \mathbf{v}^\mathrm{T} & \mathbf{e} & \mathbf{v} & \cdots & \vdots \\ \vdots & \vdots & \vdots & \vdots & \ddots & \mathbf{0} \\ \hline \mathbf{0} & \cdots & \cdots & \mathbf{0} & \mathbf{0} & \mathbf{e} \end{array}\right) \equiv \left(\begin{array}{c|c} H^{(n-1)} & \mathbf{0} \\ \hline \mathbf{0} & \mathbf{e} \end{array}\right) \qquad \text{(B3)}$$

and

$$H_1^{(n)} = \left(\begin{array}{ccccc|c} \mathbf{0} & \mathbf{0} & \mathbf{0} & \mathbf{0} & \cdots & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & \mathbf{0} & \mathbf{0} & \cdots & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & 0 & \mathbf{0} & \cdots & \mathbf{0} \\ \vdots & \vdots & \vdots & \vdots & \ddots & \mathbf{v} \\ \hline \mathbf{0} & \cdots & \cdots & \mathbf{0} & \mathbf{v}^\mathrm{T} & \mathbf{0} \end{array}\right) \qquad \text{(B4)}$$

so that $H^{(n)} = H_0^{(n)} + H_1^{(n)}$. $H_0^{(n)}$ is the Hamiltonian of a bridge with $(n - 1)$ coupled units and 1 uncoupled unit while $H_1^{(n)}$ is the coupling between the $(n - 1)$st unit and the nth unit.

Treating $H_1^{(n)}$ as a perturbation to $H_0^{(n)}$, the Green's function for $H^{(n)}$ can be rewritten exactly as

$$G^{(n)} = (E\mathbf{1} - H^{(n)})^{-1} = (E\mathbf{1} - H_0^{(n)} - H_1^{(n)})^{-1} = G_0^{(n)}(\mathbf{1} - H_1^{(n)}G_0^{(n)})^{-1} \tag{B5}$$

where $G_0^{(n)}$ is the Green's function corresponding to $H_0^{(n)}$, namely,

$$G_0^{(n)} = (E\mathbf{1} - H_0^{(n)})^{-1} = \left(\begin{array}{c|c} G^{(n-1)} & \mathbf{0} \\ \hline 0 & \Delta^{-1} \end{array}\right) \tag{B6}$$

and Δ is the $m \times m$ matrix,

$$\Delta = E\mathbf{1} - \mathbf{e} \tag{B7}$$

where E is the energy of the electron.

The tight binding model is used in this formulation, and so only that block of the Green's function which relates to the transition of the electron from the 1st unit to the nth is needed to calculate H_{kA}. This $m \times m$ block is $G_{(1,n)}^{(n)}$. After some manipulation of eq B5 a recursion relation for $G_{(1,n)}^{(n)}$ can be obtained,

$$G_{(1,n)}^{(n)} = G_{(1,n-1)}^{(n-1)}\mathbf{v}\Delta^{-1}(\mathbf{1} - \mathbf{v}^{\mathrm{T}}G_{(n-1,n-1)}^{(n-1)}\mathbf{v}\Delta^{-1})^{-1} \tag{B8}$$

and

$$G_{(n,n)}^{(n)} = \Delta^{-1}(\mathbf{1} - \mathbf{v}^{\mathrm{T}}G_{(n-1,n-1)}^{(n-1)}\mathbf{v}\Delta^{-1})^{-1} \tag{B9}$$

$G_{(n,n)}^{(n)}$ is the (n,n)th block of $G^{(n)}$. The initial condition of the recursion, namely $G_{(1,2)}^{(2)}$ and $G_{(2,2)}^{(2)}$ can be obtained by directly solving eq B5 as a $2m \times 2m$ matrix equation.

From $G_{(1,n)}^{(n)}$, H_{kA} can be obtained using an equation derived in ref 10:

$$H_{kA} = V_{k,1}G_{(1,n)}^{(n)}V_{n,A} \tag{B10}$$

where $V_{k,1}$ is the coupling of the metal k-states to the bridge and $V_{n,A}$ is the coupling of the bridge to the acceptor.

References and Notes

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(15) This expression for the rate constant includes the assumption that the solvent's dielectric polarization is not "sluggish".

(16) The density of states at a given energy ϵ is

$$\rho = \int \mathrm{d}^3\mathbf{k}\, \delta(\epsilon(\mathbf{k}) - \epsilon)$$

This density can be calculated using the above equation in conjunction with eq A5. A grid is set up in **k**-space to choose **k**-vectors; eq A5 is then solved to obtain eigen energies and a binning technique is used to obtain the density of states from the eigen energies using the above expression for ρ. In the Z-transform formulation a reverse procedure is used, in which for any given energy ϵ, the $\mathbf{k}_{||}$ values are used to find z, by solving eq A13 in Appendix A. (The $\mathbf{k}_{||}$ determine the $\mathbf{B}^{\dagger}$, $\mathbf{A}$, and $\mathbf{B}$ that appear in eq A13.)

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(26) These 60 vectors are chosen randomly. Because of the surface there is no symmetry in the direction perpendicular to the surface. The symmetry in the remaining two directions cannot be exploited either because of the presence of the monolayer. A simpler calculation based on eq 7 was performed with 600 vectors. We find that the ratio $k_{\mathrm{Pt}}/k_{\mathrm{Au}}$ changes from about 1.74 to 1.80 on going from 60 to 600 wave vectors. This seems to be a small enough variation that we use 60 vectors to perform the rest of our calculations.

(27) Using the work functions of the metals[22] (5.7 eV for Pt and 5.31 eV for Au) and the formal potential of $\mathrm{pyRu(NH_3)_5}^{2+}/\mathrm{pyRu(NH_3)_5}^{3+}$ (which is −0.08 eV above SCE[4]) we find that the difference in energy of the two states is

$$\Delta E = E_{\mathrm{metal}} - \Psi_B - \Delta\epsilon_i$$

where E_{metal} is −4.97 eV for Au and −5.16 eV for Pt. Ψ_{B} is the ionization potential of the bridge and $\Delta\epsilon_i$ is the difference in energy of the electronic state of the electron in the bridge and of the HOMO of the bridge.

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