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Field-induced transfer of an atom between two closely spaced electrodes

N. D. Lang
IBM Research Division, Thomas J. Watson Research Center, Yorktown Heights, New York 10598

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The transfer of an adsorbed atom from one electrode to another in close proximity, with a potential difference between the electrodes, is analyzed theoretically. Calculations for the case of a Si atom are in accord with results on the transfer of Si atoms in the scanning tunneling microscope under ultrahigh-vacuum conditions at room temperature. Most of the activation-barrier lowering that permits a measurable transfer rate at this temperature is a chemical effect due to the proximity of the electrodes, but the bias provides an additional barrier lowering and a directional driving force. For conditions relevant to experiment, the atom acquires a distance-dependent charge no larger than several tenths of a unit charge ($|e|$).

I. INTRODUCTION

There have recently been several experiments in which an atom is transferred between tip and sample in the scanning tunneling microscope (STM), under the influence of an applied bias of several volts. One example is the transfer between tip and sample of an adsorbed xenon atom, done in vacuum, by Eigler, Lutz, and Rudge.[1] Another is the transfer of silicon atoms from a silicon surface, also done in vacuum, by Lyo and Avouris.[2] A third example is the transfer of gold atoms from a gold tip to the sample surface, done in air, by Mamin, Guethner, and Rugar.[3]

We will analyze this process using a model employed earlier to study aspects of current flow in the STM:[4] two planar metallic electrodes, represented using the jellium model,[5] with a single atom in the region between them. Our solution proceeds in the same way as that given in Ref. 6: First, within the framework of the density-functional formalism, we find the single-particle wave functions and self-consistent density distribution for the pair of bare metallic electrodes, assuming them for simplicity to be identical ($r_s=2$ jellium model), in the presence of the bias voltage. We next use the method of Lang and Williams[7] to find the wave functions and density distribution for the total system, consisting of the two electrodes plus the atom. It will be recalled that this method was originally used to study an atom adsorbed on a single bare metallic surface, and proceeded by solving a Lippmann-Schwinger equation that involved a Green's function for the bare metal. The significant difference here is that the Green's function is appropriate to the biased bimetallic junction, instead of the single surface. From the density distribution, we can determine the force on the atom for various values of the bias.

II. BIMETALLIC JUNCTION

To obtain the density distribution and potentials for the pair of bare metallic electrodes, we follow in outline the procedure of McCann and Brown,[8] using, however, the self-consistency method described by Lang and Kohn.[9] Some results have already been given in Ref. 6, in the context of a different problem. Several additional details are included in the Appendix.

Figure 1 gives an example of results for these potentials. (The term "potential" here really denotes the potential energy of an electron, or in units where $|e|=1$, the potential governing the motion of an electron.) The total effective potential v_{eff}, which appears in the single-particle wave equations of the density-functional theory, is the sum of the electrostatic and exchange-correlation potentials

$$v_{\mathrm{eff}}(z)=v_{\mathrm{es}}(z)+v_{\mathrm{xc}}(z)\ , \tag{1}$$

where v_{xc} is taken in the local-density approximation.[5,10] Figure 1(a) gives v_{eff} for biases $\mathcal{V}$ of 0, 3, and 6 V, for an electrode spacing (distance between the positive background edges of the jellium models for the two electrodes) of 8.5 bohrs, and with the left electrode taken positive. Figure 1(b) gives just the electrostatic part v_{es}. Now the electron density decays roughly exponentially, moving away from either surface (with some decay length α). This has the effect of causing v_{es} to decay over this same length, toward the linear behavior it must have in the central part of the barrier region. For the case of a large spacing between the electrodes, the slope in this region, i.e., the electric field, would be just the bias divided by the distance between the image planes of the electrodes (the image plane is $\sim 1\frac{1}{2}$ bohrs in front of the positive-background edge of each electrode[11]).

Now the dominant behavior of v_{xc} as a function of electron density n is given by $v_{\mathrm{xc}}\sim n^{1/3}$, which means that if the exponentially decaying part of v_{es} varies as $e^{-\alpha z}$, then the exponentially decaying part of v_{xc} will vary as $e^{-1/3\alpha z}$. This is a much slower decay, which is the reason why the v_{eff} curves in Fig. 1(a) show essentially no linear region near the center. (Of course, if the distance between the electrodes were substantially larger, such a linear region would be present.)

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III. FORCE ON THE ATOM

We consider the particular case of a silicon atom. We introduce the atom into the region between the electrodes, and perform the self-consistent density-functional calculation for the charge distribution.[12] The electrode spacing used was 8.5 bohrs (as in Fig. 1), which is in the range relevant to experiment (see below). The polarization of all core orbitals on the Si atom is included in order to obtain an accurate value for the total electrostatic force F on the nucleus,[13] which will be a quantity of central interest to us. It is also convenient to define an energy for discussion purposes as[14]

$$E(z) = -\int_{z_0}^{z} dz' F(z') \, , \qquad (2)$$

where z is the coordinate along the surface normal, and z_0 is arbitrary. (The usual density-functional expression for the energy is difficult to define for this nonequilibrium problem, where the Fermi levels of left and right electrodes are unequal.)

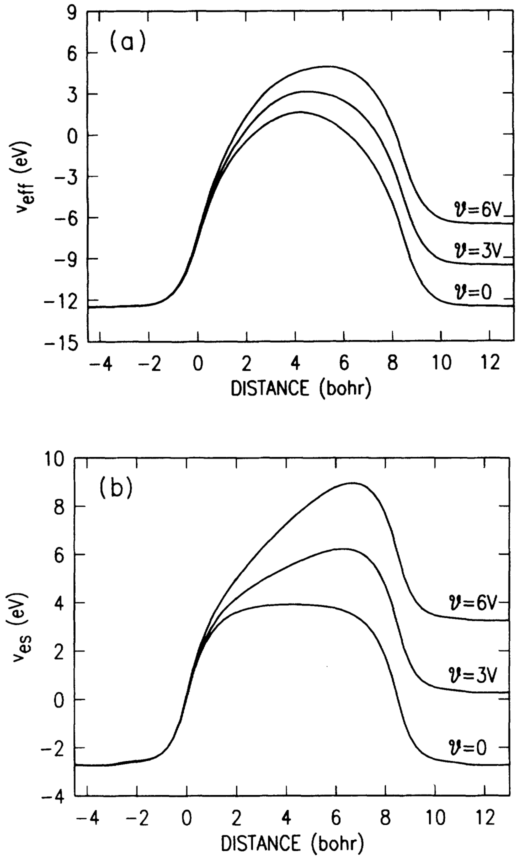

FIG. 1. Potentials for two bare jellium-model electrodes ($r_s = 2$) with left electrode positive-background edge at distance 0, and right electrode background edge at distance 8.5 bohrs. (1 bohr $= 0.529$ Å.) The left electrode is at a bias $\mathcal{V}$ relative to the right electrode. Note that the potentials are those appropriate to an electron, which is why they are higher at the right for positive $\mathcal{V}$. (a) Total effective potential v_{eff}, which is the sum of electrostatic (v_{es}) and exchange-correlation (v_{xc}) potentials. Left-electrode Fermi level is at 0 on energy scale, right-electrode Fermi level is at $|e|\mathcal{V}$ (which puts it slightly above the tunneling barrier for $\mathcal{V} = 6$ V). (b) Electrostatic potential v_{es}.

The results for $F(z)$ are shown in Fig. 2 for three values of the bias $\mathcal{V}$: 0, 3, and 6 V, with the left electrode (which we will call the sample) taken to be positive. Each of the force curves crosses the horizontal axis in three places. These crossings, i.e., the z values for which $F(z) = 0$, correspond to minima or maxima in the corresponding $E(z)$ curve obtained using Eq. (2). For each force curve, the center crossing point corresponds to a maximum in $E(z)$, and the other two crossing points correspond to minima.

Consider first just the $\mathcal{V} = 0$ (solid) curve in Fig. 2. Since the two electrodes are identical, this curve is antisymmetric about the midpoint between the electrodes. The energy curve $E(z)$ derived from this force curve using Eq. (2), a symmetric double-well potential, is shown in Fig. 3.

Figure 3 also shows the energy curve for the case of a single electrode and no applied field (i.e., the simple chemisorption case) for comparison. The energy barrier for an atom to leave the surface in the chemisorption case (i.e., the heat of adsorption of Si on a simple metal represented by the $r_s = 2$ jellium model) is 3 eV; bringing up the second electrode to the distance shown lowers the energy barrier to transfer the atom away from the surface to ~ 0.8 eV. It is this activation barrier that will be of primary interest to us in our discussion.

Returning to Fig. 2, we note that the value of the energy barrier to transferring the atom from the left to the right electrode for a particular bias is given by (the magnitude of) the integral of the corresponding force curve between its left and center $F = 0$ points, with an analogous statement for transfer from right to left. That is, for each curve in Fig. 2, the area under the curve between crossing points gives the activation barrier. We see immediately from this figure that raising the bias $\mathcal{V}$ to 6 V decreases the barrier for transfer from the left electrode by about a factor 2.

Table I gives the actual values of the activation barrier

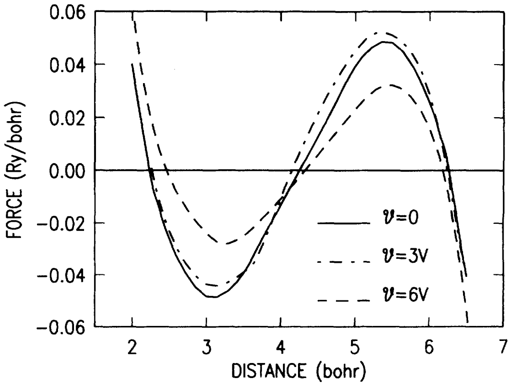

FIG. 2. Electrostatic force on the nucleus of a Si atom placed between the pair of electrodes specified in Fig. 1, as a function of the distance of the atom from the left electrode. Electrode separation held fixed at 8.5 bohrs. Positive force moves atom to the right. (1 Ry $= 13.6$ eV.)

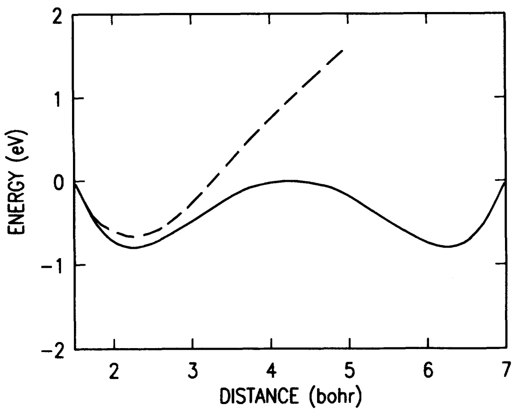

FIG. 3. Solid curve: energy for a Si atom between two electrodes specified in Fig. 1 with zero bias, as a function of the distance of the atom from the left electrode. Electrode separation held fixed at 8.5 bohrs. Zero of energy is taken to be the value at atom distance of 1.5 bohrs [i.e., z_0 in Eq. (2) defining energy is set at this distance]. Dashed curve: same as for solid curve, except right electrode is absent. Energy value far to right is 3 eV above the minimum in the dashed curve (i.e., the heat of adsorption is 3 eV).

Q extracted from these curves. Note the nonlinear dependence of the barrier lowering on bias (for positive sample bias). If we assume that atom transfer is thermally activated, with an Arrhenius form for the transfer rate from left to right, and if we neglect the dependence of the prefactor on the bias, then at room temperature, changing the bias from 0 to +3 V increases the rate by a factor ~ 10, while changing it from 0 to +6 V increases it by a factor $\sim 10^7$.

Since a positive bias here leads to more of an activation barrier lowering than a negative bias of the same magnitude, our simple symmetric model predicts a net transfer of Si atoms from the positive to the negative electrode: the potential energy well on the positive-electrode side of the barrier will not be as deep as that on the negative-electrode side. This is in agreement with the results of Lyo and Avouris.[2] Actually, of course, the usual experimental configuration is quite asymmetric, with the Si atoms in the experiment of Lyo and Avouris being transferred from a Si(111) 7×7 surface to a tungsten STM tip. Even in zero field, the binding energy of the Si adatom in the 7×7 structure is[15] ~ 2 eV, while the binding energy of Si to a simple metal surface[7] is over 3 eV (and is equal to 3 eV in the jellium model[7]), and might be expected to be somewhat higher on a transition metal because of the participation of *d* states in the bonding. Thus, once a Si atom is transferred away from the positive sample surface, it is very unlikely to return without a reverse bias, even more so in the actual experiment than in our model. Note from Table I that putting a negative bias of moderate size ($\lesssim 3$ eV in magnitude) on a given electrode leads in fact to an increase of the activation barrier for atom transfer from this electrode, and it is only for larger negative biases that the barrier starts to decrease.

We note also at this point that the direction of atom transfer in the experiment of Eigler, Lutz, and Rudge[1] for Xe is opposite to that found in the experiment of Lyo and Avouris[2] for Si, i.e., Xe is transferred off of a surface when it has negative polarity. (Another way of stating this is that Si moves in the direction opposite to that of the tunneling electrons, while Xe moves in the same direction.) Both experiments were done in ultrahigh vacuum (the environment for which the present theory is appropriate). This suggests that the direction of transfer for a given polarity can depend on the chemical identity of the atom, or at least that the noble gases as a group may behave differently, since charge-transfer effects (seen below to be important for Si) will be insignificant for these atoms.

The above results indicate that most of the activation-barrier lowering that permits atom transfer between tip and sample results simply from the proximity of the two electrodes (which might be called a chemical effect), and that the effect of the bias for the distances discussed here is smaller. The proximity, in the case shown, decreases the activation barrier from 3 to 0.8 eV, as we have noted, and the positive sample bias decreases it some several tenths of an eV further, in addition to providing a directional driving force. Figure 4 shows the strong dependence of the zero-bias activation energy on electrode separation: a separation change of 2 bohrs (~ 1 Å) leads to a change in activation barrier of more than 1 eV. The ex-

TABLE I. Activation barrier Q for transfer of a Si atom between two jellium-model electrodes. The electrode from which the atom is transferred (denoted the sample in the text) is at a bias $\mathcal{V}$ relative to the other, and the positive-background edges of the two electrodes are separated by 8.5 bohrs. The electrostatic field $\mathcal{E}$ is that midway between the electrodes in the absence of the atom.

$\mathcal{V}$ (V)	Q (eV)	$\mathcal{E}$ (V/Å)
6	0.43	1.8
3	0.78	0.9
0	0.84	0
−3	0.97	−0.9
−6	0.51	−1.8

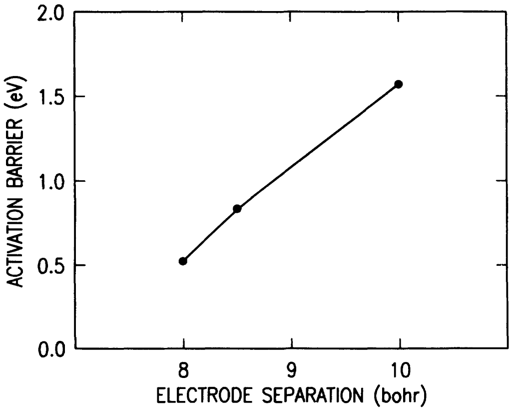

FIG. 4. Activation barrier for transfer of a Si atom from one electrode to another as a function of electrode separation, with $\mathcal{V}=0$. Dots, which have been connected, correspond to the computed values.

periments[2] are in accord with this, in the sense that they show a very sharp dependence of transfer rate on tip-sample separation.

To gain some insight into the force acting on the atom, we consider the related problem of field desorption. The usual explanation for desorption in that case is that due to field-induced charge transfer between atom and surface, the atom becomes an ion whose sign is the same as that of the electric field (taking the direction of the outward surface normal to be positive). This means that the field will exert a force on the ion that tends to move it away from the surface.[16,17] This leads us to consider the charge induced on the atom in our two-electrode problem by the applied bias.

We will define the electron number density $\Delta n(\mathbf{r})$ induced on the atom by the bias in the following way. First we define the change in electron distribution due to the presence of the atom, $\delta n^{\mathcal{V}}(\mathbf{r})$, as the difference between the total electron distribution for the system consisting of the two biased electrodes plus the atom, and the electron distribution for the two biased electrodes without the atom. We then subtract the corresponding quantity for zero bias, thus giving $\Delta n(\mathbf{r})=\delta n^{\mathcal{V}}(\mathbf{r})-\delta n^{0}(\mathbf{r})$. An example of this distribution, corresponding to an atom position for which the force is large, is shown in Fig. 5(a).

Now consider the polarization of the free atom in a uniform electric field. ("Polarization" connotes the difference in electron densities between the atom with and without the field.) It is clear that a major part of $\Delta n(\mathbf{r})$ will be just this free-atom polarization, denoted $\Delta n_{\mathrm{atom}}(\mathbf{r})$. This polarization is of no interest to us here, since it makes no net contribution to the force (i.e., a free atom in a uniform field has no net force on its nucleus because the polarization of the electron cloud cancels the direct effect of the field on the nucleus). For the present purposes, we will take $\Delta n_{\mathrm{atom}}(\mathbf{r})$ to be just the linear part of the relevant free-atom polarization, i.e., the polarization of the free atom that occurs in a small field, scaled up to the field that exists (in the absence of the atom) midway between the electrodes with bias $\mathcal{V}$. This distribution is shown in Fig. 5(b).

The map of primary interest to us therefore is that of $\Delta n(\mathbf{r})-\Delta n_{\mathrm{atom}}(\mathbf{r})$, exhibited in Fig. 5(c). This map clearly shows a transfer of electronic charge away from the atom to the electrodes. Far away from the atom on both surfaces, this difference charge density will have an imagelike form, but it does not have such a form in the immediate vicinity of the atom (the chemical-bond region).[18] The right electrode has more of this difference charge than the left electrode, meaning that the net force on the nucleus due to the presence of the bias is positive. Of course the total bias-induced charge transfer [map 5(a)] is predominantly toward the left electrode, and it is, as shown in map 5(c), only the deviation of this from Δn_{atom} that corresponds to a net transfer toward the right.

It is difficult to define a net charge on the atom from a map such as that of Fig. 5(c), because its value depends on the volume over which the charge distribution is integrated. Another approach, which is well defined albeit approximate, relates to the fact that charge transfer to or

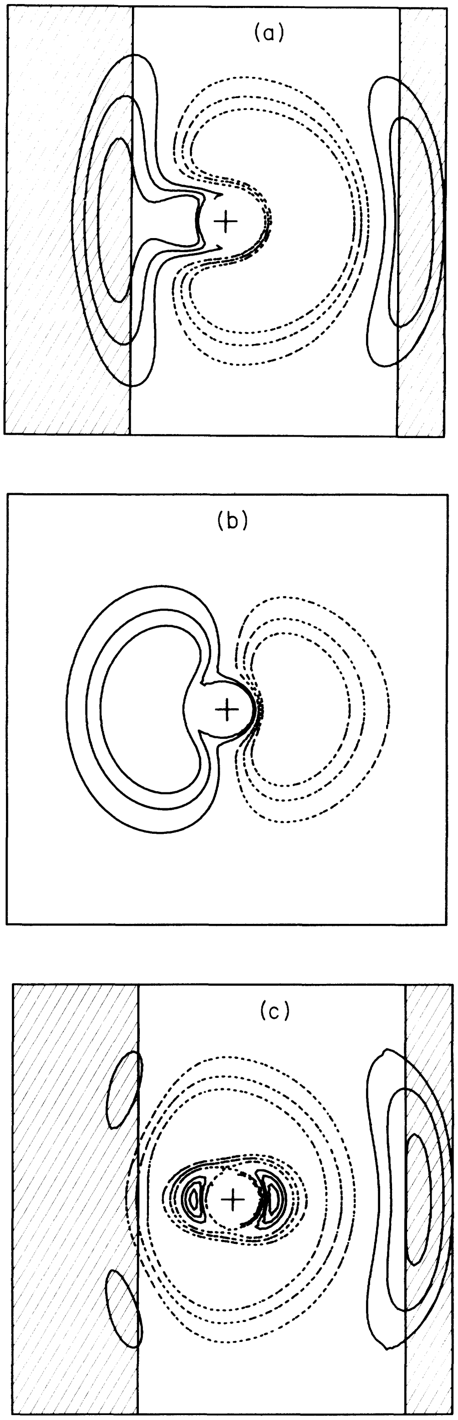

FIG. 5. Contour maps of electron number density differences defined in the text, for a Si atom placed between two jellium model electrodes whose positive backgrounds (shaded areas) are separated by 8.5 bohrs. Left electrode is at a bias of +6 V relative to right electrode; atom nucleus (cross) is 3 bohrs from left background edge. (The atom position chosen is one for which the force is large.) Solid contours are positive (i.e., an electron excess) and broken contours are negative, with values shown ±0.0015, ±0.001, and ±0.0005 electrons/bohr^3. Contours in the immediate vicinity of the nucleus have been deleted for clarity. Map (a): $\Delta n(\mathbf{r})$. Map (b): $\Delta n_{\mathrm{atom}}(\mathbf{r})$. Map (c): $\Delta n(\mathbf{r})-\Delta n_{\mathrm{atom}}(\mathbf{r})$.

from an atom changes the electrostatic potential within the atom, which in turn shifts the core-level eigenvalues.[7] If we compare the difference in core eigenvalues between the atom in our problem and a free atom, with the difference in eigenvalues between a free ion and the free atom, we will have some measure of the net charge on our atom. We therefore define, as in Ref. 16, the excess positive charge q on the atom for a given bias as

$$q_{\mathcal{V}} = [\varepsilon_{\mathcal{V}}(1s) - \varepsilon_{\text{atom}}(1s)]/[\varepsilon_{+\text{ion}}(1s) - \varepsilon_{\text{atom}}(1s)] , \quad (3)$$

where the $\varepsilon(1s)$'s are the $1s$ eigenvalues of, in the order they appear in this equation, the adatom between the electrodes in the presence of the bias $\mathcal{V}$, the free atom, and the free singly charged positive ion. The quantity $\varepsilon_{\mathcal{V}}$ is measured relative to the bare-electrode electrostatic potential at the position of the atom. We will subtract $q_{\mathcal{V}}$, evaluated for zero bias, in order to define the positive charge on the atom induced by the bias: $\delta q \equiv q_{\mathcal{V}} - q_0$. The value of δq for atom positions in the region of primary interest is shown in Fig. 6 for $\mathcal{V}=3$ and 6 V (left electrode positive). Also given is q_0. Note that δq is at most several tenths of a unit charge ($|e|$), and changes sign near the midpoint between the electrodes.

It should not be surprising that $\delta q/|e|$ does not attain values like $+2$ or $+3$ here, as it can at large distances in a field desorption experiment.[17] It is seen in the analysis of field desorption given in Ref. 16 that, for fields comparable with those in the present case (see Table I), the charge on the desorbing atom is also no greater than a few tenths $|e|$ within ~ 5 bohrs of the surface, but in that problem, the charge continues to rise as the atom moves to greater distances. In the present problem, of course, when the atom moves well away from the positive electrode, it encounters the negative electrode, which tends to drive electrons *onto* the atom, giving δq a negative value. The atom never gets very far, on the appropriate distance scale, from a charged surface, as is clear from Fig. 5; this is the reason δq is never very large.

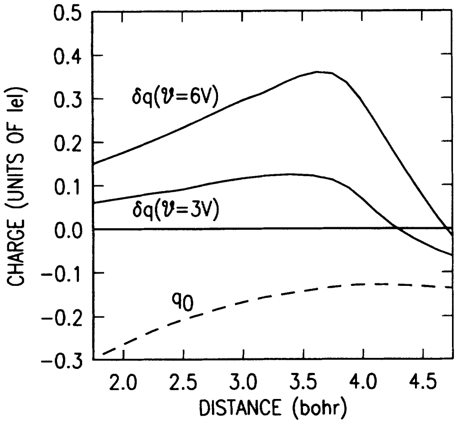

FIG. 6. Charges q_0 and δq, defined in the text, as a function of the distance of the Si atom from left electrode. Atom positions in the left part of the region between the electrodes are shown. Electrode separation held fixed at 8.5 bohrs.

IV. SIMPLE ANALYTIC PICTURE OF BARRIER REDUCTION

Let us now write a very rough expression for the energy as a function of distance, just to facilitate some additional understanding of the above results. Let z be the position of the atomic nucleus relative to the image plane of the left electrode, and let $z=a$ be at the position of the image plane of the right electrode. Let us also say that the equilibrium position of the atom on the left electrode is close enough to the image plane so that we can also take it to be $z=0$.[19]

Then the energy change from its zero-field value as a function of atom position is given very roughly by[3] $\delta E(z) = \tilde{E}_{\mathcal{V}}(z) - \tilde{E}_0(z)$, where

$$\tilde{E}_{\mathcal{V}}(z) = -\int_0^z [q_{\mathcal{V}}(z')\mathcal{E}_{\mathcal{V}}(z') + q_{\mathcal{V}}^2(z') f(z')] dz' . \quad (4)$$

The first term here gives the interaction between the partially charged atom and the applied field, while the second term arises from the interaction between this partially charged atom and the screening charge it induces in the electrodes. For z in the central region between the electrodes, the function $f(z)$ has the form appropriate to the image force on a point charge between parallel plates,[20]

$$f(z) = -(2z)^{-2} - (2a)^{-2}[\psi'(1+z/a) - \psi'(1-z/a)] \quad (5)$$

(ψ' is the trigamma function), but $f(z)$ *stays finite rather than diverging* for z near the electrodes,[21] and tends rapidly to zero inside the electrodes. In the simplified discussion of this section, we omit dipole terms, which can be expected to be relatively less important when there is significant charge transfer.

Now $\delta E(\frac{1}{2}a)$ gives the change in activation barrier due to the bias, if it is assumed that the barrier potential maximum is roughly midway between the electrodes. We see immediately from Eq. (4) that the activation-barrier lowering will be nonlinear in the field (or bias). This is because $q_{\mathcal{V}}$ in general increases with field at a given z, as seen in Fig. 6. The relative importance (and sign) of the two contributions to $\delta E(\frac{1}{2}a)$ corresponding to the two terms in Eq. (4) depends on the bias. For example, for $\mathcal{V}=6$ V, the *magnitudes* of q_0 and $q_{\mathcal{V}}$ ($=q_0+\delta q$) are not too different, leading to the result that for this bias, the second term in Eq. (4) makes a relatively small contribution to $\delta E(\frac{1}{2}a)$, since this contribution is proportional to $q_{\mathcal{V}}^2 - q_0^2$.

V. ACTIVATION BARRIER IMPLIED BY EXPERIMENT

We consider in particular the STM experiment of Lyo and Avouris.[2] It should of course be emphasized that the present calculation is appropriate for Si on a metal surface, but such data are not yet available, and so we confine ourselves only to a qualitative comparison with these measurements.

In this experiment, done in vacuum at room temperature, Si, as noted above, was transferred from a Si surface to the tip only when the sample was positive, and could be transferred back by reversing the polarity of the bias. It was found that for a 10 ms, +3 V pulse, the probability of atom transfer just reached unity when the distance between tip and sample was decreased to a value s_t specified below in terms of the measured apparent tunneling barrier height.

As Müller puts it in his work on field desorption,[17] the time required for an atom at the surface to overcome an energy barrier Q by thermal motions is

$$\tau=\tau_0 e^{Q/kT} , \tag{6}$$

with τ_0 a vibration time for the adsorbed atom, which he takes as 10^{-13} s. For this same choice[22] of τ_0, and with $\tau = 10$ ms, the pulse length in the experiment, this equation implies for $T=300$ K that $Q=0.66$ eV.

Let us now discuss the tip-sample separation s_t that corresponds to this Q value. The apparent tunneling barrier height ϕ_A measured in the microscope was found in Ref. 2 to decrease from its full value to near zero over a range of tip-sample separations of ~3 Å, as has been discussed theoretically.[23] It is convenient to specify separations by the corresponding value of ϕ_A (which provides an absolute scale). The measured ϕ_A was ~2 eV for the separation s_t.

Now ϕ_A can be calculated for our model of two electrodes with the Si atom at equilibrium on one electrode. The atom was kept fixed at the equilibrium distance for the chemisorption case, and ϕ_A was calculated for small bias as $\frac{1}{8}(d \ln I/ds)^2$ atomic units.[23] It was found in this way that $\phi_A \sim 2$ eV when the separation of the electrodes (measured between the two positive background edges) was ~$8\frac{1}{2}$ bohrs. It is for this separation that the numbers in Table I are computed; the fact that the values of the activation barrier given in Table I are comparable to the value extracted from experiment suggests that our calculation of this quantity is reasonable.

VI. CONCLUSIONS

We have seen in this analysis that a large part of the activation-barrier lowering required for transfer of an atom between tip and sample in the STM arises simply from the close proximity of the two electrodes (a chemical-bonding effect). It has been shown that field-induced charge transfer to or from the atom is significant to the force exerted on it, and hence to further changes in the activation barrier. The magnitude of the charge on the atom, however, has been shown to depend strongly on atom position, and to be only a few tenths of a unit charge. The calculated results show the same direction of atom transfer relative to bias polarity as the experiment of Ref. 2, a similarly sharp dependence of activation barrier (or transfer rate) on distance, and a comparable magnitude for the activation barrier. It is thus seen that the calculation described here can provide a reasonable account of atom transfer in the STM under ultrahigh-vacuum conditions.

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APPENDIX

We present here some details in addition to those given in the text and in Refs. 6 and 9, for the self-consistent calculation of the density and potential for the pair of biased metallic electrodes in the absence of the atom. In this appendix and in the associated figure, we will use atomic units, in which $|e|=\hbar=m=1$.

The potential v_{eff} that appears in the single-particle wave equations tends toward an arbitrary constant value v_0 deep in the left-hand electrode, which will be positively biased in our discussion. Deep in the right-hand electrode, v_{eff} tends toward a constant value which we denote $\mathcal{W}+v_0$. This potential is shown schematically in Fig. 7. The Fermi levels for the left and right electrodes are denoted, respectively, E_{FL} and E_{FR}, as shown in the figure, with $E_{\text{FR}}-E_{\text{FL}}=\mathcal{V}$, where $\mathcal{V}$ is the bias. Even though the two electrodes are identical, $\mathcal{W}$ and $\mathcal{V}$ are not exactly equal, as we will discuss in a moment. The eigenfunctions of the wave equations have the form $e^{i\mathbf{K}_{\parallel}\cdot\boldsymbol{\rho}}u_k(z)$, where $\boldsymbol{\rho}$ is the coordinate parallel to the surface and z the coordinate normal to it. The energy eigenvalues E of states that will be of interest to us lie between v_0 and E_{FR}. Deep in the left electrode, $u_k(z)$ has the form of a linear combination of left-moving and right-moving plane waves with wave vector k; here $\frac{1}{2}k^2=E-v_0-\frac{1}{2}K_{\parallel}^2$.

It is convenient to define three energy ranges by the following:

$$\text{(i)}\quad 0<\tfrac{1}{2}k^2<\mathcal{W} ,$$

$$\text{(ii)}\quad \mathcal{W}<\tfrac{1}{2}k^2<E_{\text{FL}}-v_0 ,$$

$$\text{(iii)}\quad E_{\text{FL}}-v_0<\tfrac{1}{2}k^2<E_{\text{FR}}-v_0 .$$

In energy range (i), the wave functions $u_k(z)$ are phase-shifted sine waves deep in the left electrode, which decay exponentially toward the right. In energy range (ii), for

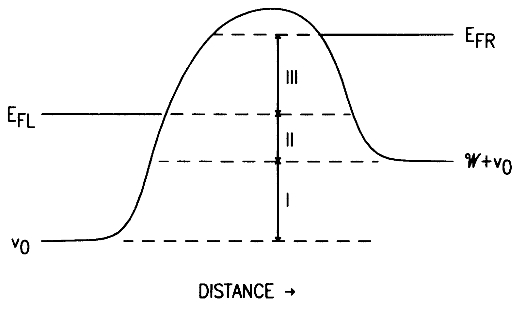

FIG. 7. Schematic diagram of the total effective potential seen by an electron, and the energy regions and energy levels relevant to the problem of two electrodes without the atom, with the left electrode (whose Fermi level is E_{FL}) at a bias $\mathcal{V}$ relative to the right electrode (whose Fermi level is E_{FR}). Note that $\mathcal{V}$ is positive in this diagram, and that there is a net flow of electrons from right to left. The use here of atomic units means that we write $\mathcal{W}$ in the figure instead of $|e|\mathcal{W}$; this quantity differs slightly from $\mathcal{V}$ in general (see text).

each k, there is (1) a plane-wave incident on the barrier region from the left with wave vector k, together with a reflected wave, and a transmitted wave in the right electrode, and (2) a plane-wave incident from the right with wave vector $\sqrt{k^2-2\mathcal{W}}$, together with a reflected wave, and a transmitted wave in the left electrode. In energy range (iii), just as is done by McCann and Brown,[8] we occupy only the state corresponding to the wave incident from the right (of wave vector $\sqrt{k^2-2\mathcal{W}}$) together with its reflected and transmitted parts.

The self-consistent iteration for the two-electrode problem in the absence of the atom is begun with a potential v_{eff}, which is equal to v_0 far to the left and equal to $\mathcal{V}+v_0$ far to the right (i.e., we take $\mathcal{W}=\mathcal{V}$ to start). Now, in energy range (iii) deep in the left electrode, a current flows, so this potential would lead to a slightly larger density of electrons in this electrode than that which would be present in the corresponding unperturbed free-electron metal. Since part of the weight of the occupied energy range (iii) states is shifted to the left electrode when a bias is present, this would also lead to a small density deficiency deep in the right electrode relative to the free-electron value. These changes could be expected to be present within a mean-free-path length of the surfaces.

Of course, a self-consistent solution requires that the electron density neutralize the positive background density deep within the electrodes, and so the Fermi level relative to the bottom of the band in each of the two electrodes will have to change from its free-electron value, with $E_{\text{FL}}-v_{\text{eff}}(-\infty)$ decreasing and $E_{\text{FR}}-v_{\text{eff}}(+\infty)$ increasing. It is easily seen, however, that the constraint $E_{\text{FR}}-E_{\text{FL}}=\mathcal{V}$ implies that the band bottoms $[v_{\text{eff}}\pm\infty]$ must shift relative to each other so that $v_{\text{eff}}(\infty)-v_{\text{eff}}(-\infty)=\mathcal{W}$ is smaller than $\mathcal{V}$. This effect will be negligible for large electrode spacings, for which the current is small, but will be noticeable for small spacings, and must be taken into account. For a bias $\mathcal{V}$ of 6 V, e.g., $\mathcal{W}=5.96$ V for an electrode spacing of 8.5 bohrs.

On each iteration, a small charge density is added in the region of the surfaces so that the computed $v_{\text{eff}}(+\infty)$ has the value of $\mathcal{W}+v_0$, calculated in the previous iteration. The proper self-consistent solution is that for which no such charge density has to be added, and the left and right Fermi levels (whose difference must always equal $\mathcal{V}$) are separated from their respective band bottoms by the amount required to give charge neutrality deep within each electrode.

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[12] It will be recalled from Ref. 7 that the self-consistent calculation is done within a large sphere (of radius ~7 bohrs) centered at the atom. Charge disturbances outside the sphere can be taken into account in an approximate way, but it can be expected that such distant charge disturbances (i.e., changes relative to the charge distribution of the bare bimetallic junction, whose effect is included exactly) could in fact be omitted from the self-consistent calculations for the force. This was confirmed by doing calculations both with and without an image form for the disturbances *outside the sphere;* the difference in the calculated force in the two cases was small on the scale of interest here. Since the atom in general will be fairly close to the image planes of the surfaces, the simple asymptotic (multiple) image formula is not accurate. But for the part of the disturbance that lies outside the sphere of calculation, this formula should be adequate. It was this that was used here; Friedel oscillations were omitted.

[13] It would be possible to freeze the deeper core orbitals, if their effects were properly take into account, but this path was not taken here. Such a procedure is described by R. Yu, D. Singh, and H. Krakauer, Phys. Rev. B **43**, 6411 (1991).

[14] The Hellmann-Feynman theorem allows us to define a total energy for the system in terms of the electrostatic force on the nucleus. This theorem is discussed, for example, in J. I. Musher, Am. J. Phys. **34**, 267 (1966); S. T. Epstein, *The Variation Method in Quantum Chemistry* (Academic, New York, 1974), p. 107.

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[17] E. W. Müller, Phys. Rev. **102**, 618 (1956); R. Gomer, J. Chem. Phys. **31**, 341 (1959). Examples of more recent discussions of field desorption include T. T. Tsong, *Atom-Probe Field Ion Microscopy* (Cambridge University Press, Cambridge, 1990); H. J. Kreuzer and K. Nath, Surf. Sci. **183**, 591 (1987).

[18] The absence in the right-hand map of a charge excess on the left electrode at small lateral distances from the atom arises from the subtraction of the polarized atom density, and does

not necessarily indicate a negligible charge transfer to the left electrode. It could be argued that part of the electronic charge polarized toward the left in the free atom would really be regarded as transferred charge if the electrode were present, even if no further polarization occurred, and that not all of it should therefore have been subtracted in making this map. However, this is difficult to do in a well-defined way.

[19] In fact, the image plane is calculated to be 1.6 bohrs in front of the background edge for the single isolated electrode (Ref. 11), and the equilibrium position, from Fig. 2, is 2.3 bohrs in front of the background.

[20] The infinite series of images for two parallel conducting plates is discussed, e.g., by O. D. Kellogg, *Foundations of Potential Theory* (Springer, Berlin, 1929), p. 230.

[21] A discussion of the interaction between a point charge and a surface, when the point charge is close to the surface, is given in N. D. Lang and A. R. Williams, Phys. Rev. B **16**, 2408 (1977); cf. also R. E. Walkup, Ph. Avouris, N. D. Lang, and R. Kawai, Phys. Rev. Lett. **63**, 1972 (1989).

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