# Vacuum Tunneling Current from an Adsorbed Atom

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The tunneling current density is computed in the vacuum region between two planar metal electrodes, on one of which is an adsorbed atom. The calculation uses self-consistent wave functions for each electrode; the effects of adatom valence resonances are fully taken into account. This study leads to a better understanding of important aspects of the current flow in the scanning tunneling microscope. Its emphasis is not so much on the question of resolution discussed in earlier theoretical work, but on the characteristic signatures of chemically different atoms at a surface.

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This Letter is a discussion of the distribution of tunneling current in the vacuum region between two planar metallic electrodes with a small bias voltage between them, in the instance in which there is an adsorbed atom at its equilibrium distance on one of the electrodes. The analysis is designed to illuminate certain important aspects of the current flow in the scanning tunneling microscope.[1–5] It is the first study to calculate the total additional current due to a real atom (rather than a simple potential well intended to represent a small but unspecified number of atoms), and to show that the additional current from a single atom is of the order of that measured experimentally. Some of the questions to be addressed are what are the characteristic differences in the current distributions from different atoms, what are the effects of resonances near the Fermi level, and how spatially localized is the current.

The jellium model for the metal surface will be used; it can be expected to be adequate for a general discussion of many of the properties that depend on the wave function well outside the surface. Now the wave functions that arise in a self-consistent density-functional calculation are available for a jellium surface with and without an atom,[6] but are not available for the combined two-electrode system. Finding such wave functions for the combined system is a difficult problem, and in future work, where it would be useful to study the case in which there is an atom on each of the two electrodes (in which case one could be scanned past the other), the determination of such a wave function would be still harder. In view of this, it would seem useful to consider the Bardeen tunneling-Hamiltonian formalism,[7] which gives the *total* tunneling current in terms of wave functions determined separately for each electrode in the absence of the other. However, the purpose of this discussion is to exhibit the current density distribution (putting aside questions of the direct measurability of this quantity), and therefore the tunneling-Hamiltonian formalism as it stands cannot be used. It proves possible, though, via a derivation analogous to that of Bardeen, to obtain an expression for the current density in terms of the separate wave functions for the two electrodes. [Were we to have the wave function for the combined system, we could, of course, obtain the current density immediately from Eq. (2) below, as is done, e.g., for the simple model wave function of Ref. 5.]

Let us begin by sketching the derivation of the formula to be used for the current density. Atomic units, $\hbar = m = |e| = 1$, are employed. The Hamiltonian for the left (right) electrode considered separately is $H_{L(R)} = -\frac{1}{2}\nabla^2 + V_{L(R)}$; $H_{L(R)}$ has eigenfunctions $\psi_\mu^L$ ($\psi_\nu^R$) and eigenvalues $E_\mu$ ($E_\nu$). The Hamiltonian for the combined (two-electrode) system is $H = H_L + V_R$. The wave function $\Psi_\mu(\mathbf{r},t)$ for the combined system (whose form we need only in the vacuum region) is taken to coincide with $\psi_\mu^L$ at $t = -\infty$ and to differ from it subsequently because of the adiabatic addition to $H_L$ of $V_R$, regarded as a perturbation.[8] For finite $t$ in such a continuum perturbation problem[9]

$$\Psi_\mu = \left[\psi_\mu^L + \int d\nu \left\{ \mathrm{P}\frac{1}{E_\mu - E_\nu} - i\pi\delta(E_\mu - E_\nu)\right\} \langle \nu | V_R | \mu\rangle \psi_\nu^R \right] \exp(-iE_\mu t), \tag{1}$$

where $\int d\nu$ is an integration over energy and a sum or integration over the other state labels as well, and the P indicates that the principal value is to be taken in the integral over energy.

For small bias $\mathscr{V}$ and zero temperature, the current density is

$$\mathbf{j}(\mathbf{r}) = 2\mathscr{V} \int d\mu\, \delta(E_\mu - E_\mathrm{F}) \operatorname{Im} \Psi_\mu^* \nabla \Psi_\mu. \tag{2}$$

(The factor 2 is for spins, which we do not include in our labels $\mu$ and $\nu$.) Now let us write

$$\mathbf{j}_{\nu\mu}(\mathbf{r}) = -\tfrac{1}{2} i (\psi_\nu^{R*} \nabla \psi_\mu^L - \psi_\mu^L \nabla \psi_\nu^{R*}). \tag{3}$$

If we substitute (1) into (2), neglect $O(\langle \nu | V_R | \mu \rangle^2)$, and take account of the fact that there is, of course, no current in the ground state of one electrode taken as an isolated system, then we see that (using an obvious notational simplification)

$$\mathbf{j}(\mathbf{r}) = 4\mathscr{V} \int d\mu\, \delta(E_\mu - E_\mathrm{F}) \left[ \pi\, \mathrm{Im} \int d\nu\, \delta(E_\mu - E_\nu) + \mathrm{Re}\, \mathrm{P} \int d\nu \frac{1}{E_\mu - E_\nu} \right] \langle \nu | V_R | \mu \rangle\, \mathbf{j}_{\nu\mu}^*(\mathbf{r}). \tag{4}$$

Now we could have used the stationary state $\psi_\mu^{L*}$ instead of $\psi_\mu^L$ just as well in the above discussion (and similarly for $\psi_\nu^{R*}$). It proves convenient to in fact extend the meaning of $\int d\mu$ to include a sum over these two cases (similarly for $\int d\nu$). We will then include a factor $\frac{1}{2}$ with each of these integrals. When we do this, the second term in Eq. (4) drops out. We then use the fact, demonstrated by Bardeen,[7] that $\langle \nu | V_R | \mu \rangle = i J_{\nu\mu}$, where $J_{\nu\mu} = \int d\mathbf{S} \cdot \mathbf{j}_{\nu\mu}(\mathbf{r})$ with $S$ a surface in the vacuum region, to obtain

$$\mathbf{j}(\mathbf{r}) = \pi \mathscr{V} \int d\mu \int d\nu\, \delta(E_\mu - E_\mathrm{F}) \delta(E_\nu - E_\mathrm{F}) J_{\nu\mu} \mathbf{j}_{\nu\mu}^*(\mathbf{r}). \tag{5}$$

Note that if this is integrated over the surface in the vacuum region, we recover the usual tunneling-Hamiltonian expression for the total current[4] (recall the factor $\frac{1}{4}$ here due to the redefinition of $\int d\mu$ and $\int d\nu$).

Now let us discuss briefly the computation of the wave functions $\psi^L$ and $\psi^R$. In the case of the bare metal in the jellium model (which we take as the right electrode)[6]

$$\psi_{Em\kappa}^R(\mathbf{r}) = e^{im\phi} J_m(\kappa\rho)\, u_{E\kappa}(z), \tag{6}$$

where we use cylindrical coordinates with $z$ along the surface normal and where $u_{E\kappa}(z)$, which is computed self-consistently using the density-functional formalism, is oscillatory deep in the metal and decays exponentially in the vacuum [with inverse decay length given asymptotically by $(2\Phi)^{1/2}$ in atomic units; $\Phi$ is the electrode work function]. This is discussed by Lang and Williams in Ref. 6. Also described there are the self-consistently computed density-functional wave functions for the atom-jellium model (our left electrode) but only within a sphere of $\sim 7$ bohrs in radius about the atom. These wave functions must be propagated further into the vacuum, which is done with the bare-metal Green's function described in Ref. 6 (details of this will be given elsewhere).[10] Note that in evaluating Eq. (5) to obtain the current density, the integrand (summand) is diagonal in $m$ (because of the cylindrical symmetry of our system) but not in $\kappa$, and so we must integrate over both $\kappa_L$ and $\kappa_R$.

Let us now turn to a discussion of the results. The two metallic electrodes are taken to have the same high electron density (corresponding to $r_s = 2$, which is broadly representative of many metals[11]). We begin with the case in which a Na atom is adsorbed on the left electrode. The current density for this case is shown in Fig. 1. The left and right edges of the box correspond to the positive background edges for the two electrodes. The presence of the Na atom is indicated schematically by two dashed circles with a cross which gives the computed equilibrium distance of the nucleus. Results are shown only in a strip in the center of the vacuum barrier; much closer to the surfaces, the representation of Eq. (1) is not adequate. At each point of a grid in this strip, the current density is represented by an arrow. The length (and thickness as well) of the arrow is made proportional to $\ln(ej/j_0)$, where $j$ is the magnitude of the current density and $j_0$ is the current density that would be present without

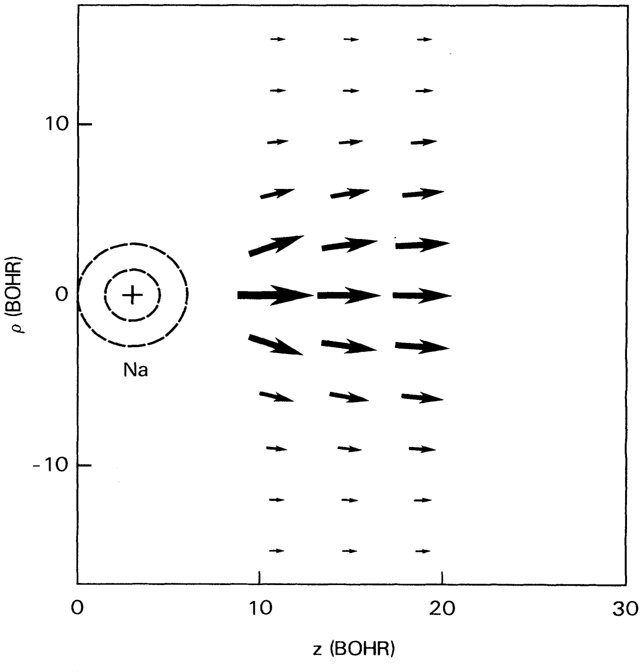

FIG. 1. Current density for case in which a Na atom is adsorbed on left electrode. Length (and thickness) of arrow is proportional to $\ln(ej/j_0)$ evaluated at the spatial position corresponding to the center of arrow.

the atom. The factor $e = 2.718$ is included so that at large lateral distances $\rho$, where $j = j_0$, a unit length arrow is shown, instead of simply a blank space. Note that for example along the right edge of the strip, the largest arrow represents roughly a factor 20 in current density compared with the smallest arrow (which corresponds approximately to $j_0$). We see that the current distribution is quite sharp, and shows a large enhancement due to the atom. The plate separation of 30 bohrs (16 Å) is larger than the tip-to-surface separations presently typical of scanning tunneling microscope experiments. If the plate separation is reduced to, e.g., 16 bohrs (8.5 Å), which is more typical, the current pattern (now computable reliably only in a narrower strip) is in fact quite similar to that seen in Fig. 1. The additional tunneling conductance at this latter separation that is caused by the presence of the atom is $0.3 \times 10^{-8}\ \Omega^{-1}$ (which is not too far from the experimental range). Figure 2 shows a contour map of $j_z/j_0$ for the case given in Fig. 1.

The dashed curve in the left half of Fig. 3 shows the additional eigenstate density due to the presence of the Na atom on the metal surface which we have taken as the left electrode; that is, it is the state density for the metal-adatom system, minus that of the bare metal. The fact that the resonance, which corresponds to the $3s$ valence level of the free atom, is mostly above the Fermi level indicates that the $3s$ electron of the Na has been largely lost to the metal.[6] In the present low-bias case only states in the immediate vicinity of the Fermi level contribute to the current; the density of such states is reduced because the peak of the resonance is significantly above $E_F$. (Nonetheless there is still an appreciable density of $3s$ states at $E_F$.)

We can study the effect of having the Fermi level further up in the $s$ resonance by considering atoms in the next column of the periodic table. Instead of discussing Mg, which follows Na, let us consider Ca, because it has the same calculated equilibrium metal-adatom separation as Na and thus comparisons will not be complicated by effects of changes in this separation. In the free atom, of course, the Ca $4s$ valence shell is filled, but in the adsorption case there is loss of electronic charge to the solid, with the result that the Fermi level is near the peak of the $4s$ resonance, as seen in the left half of Fig. 3 (solid curve).

The calculations for the current distributions done here include wave functions of all $m$ values [$m$ is the azimuthal quantum number; see Eq. (6)]. Wave functions with $m \neq 0$ (e.g., $p_{xy}$ states), however, have a node on the $z$ axis, and as a consequence their main weight lies closer to the left-electrode surface, and hence further from the right electrode. Their contributions to the current are thus much smaller than those for $m = 0$ (e.g., $s$ and $p_z$ states) since the current decreases exponentially with separation; in fact, these $m \neq 0$ wave functions make only a small contribution to the atom-induced current enhancement. For this reason, just the $m = 0$ contributions to the state densities are shown in the left part of Fig. 3.

It is seen that the $m = 0$ Fermi-level state density for Ca is approximately 4 times that for Na; and a compu-

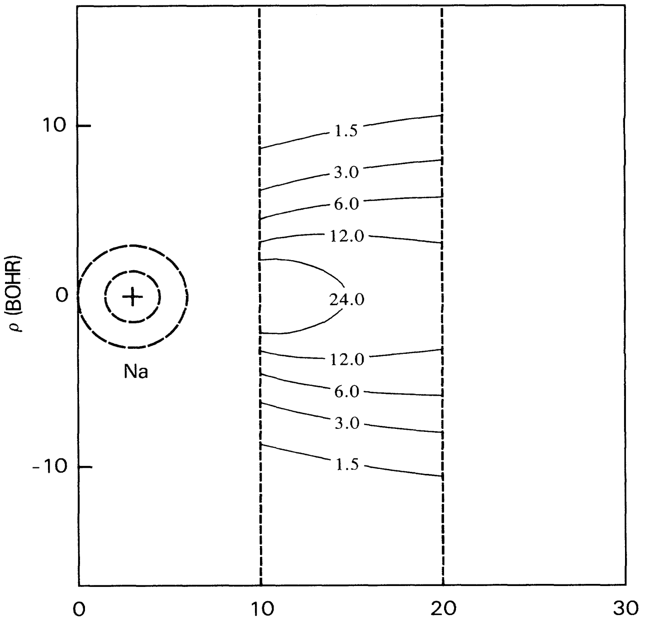

FIG. 2. Contour map of $j_z/j_0$ for case in which a Na atom is adsorbed on the left electrode.

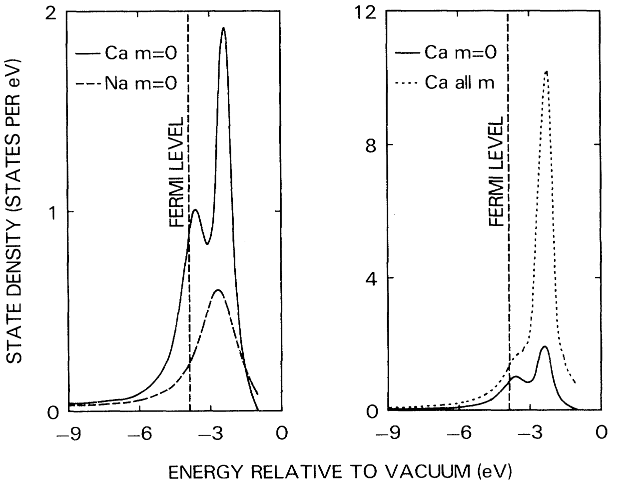

FIG. 3. Curves of difference in state density between metal-adatom system and bare metal. The lower-energy Ca peak correponds to $4s$, the upper to $4p$ (and some $3d$). The azimuthal quantum number is denoted by $m$.

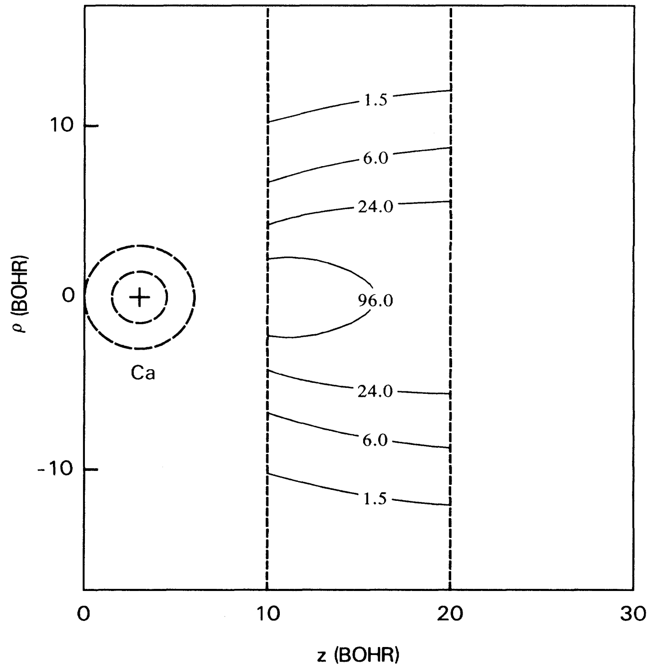

FIG. 4. Contour map of $j_z/j_0$ for case in which a Ca atom is adsorbed on the left electrode.

tation shows that the total additional current due to the presence of the atom is about 4 times as large. A contour map of $j_z/j_0$ for Ca is shown in Fig. 4. The right half of Fig. 3 compares the state density computed for the Ca case including contributions from all $m$ values with that for $m=0$ only. It is clear that the total state density (all $m$ included), as might be measured in an angle-integrated photoemission experiment, is quite misleading in a discussion of the tunneling current. This would clearly be yet more true for a case in which the Fermi level were to lie higher up, where it would sample an even greater density of $p_{xy}$ states.

Now it turns out that if we continue calculations for atoms in the sodium row of the periodic table where the $p$ shell is partly filled, then the current distribution as a function of Fermi level position in the resonance shows a behavior more complicated that that described above. The additional current density due to the presence of the atom, $\delta \mathbf{j}(\mathbf{r}) = \mathbf{j}(\mathbf{r}) - \mathbf{j}_0$, goes through a change in sign, and for an electrode separation the same as that shown in Figs. 1 and 2, with, e.g., a S atom on the left electode, the total current density is seen to be reduced from $j_0$ by $\sim$ 20%–30% in the atom region. In contrast to the Na case described above, decreasing the electrode separation does not fully preserve the basic features of the current distribution, but rather (for distances less than $\sim$ 16 bohrs) leads to a very small region about the $z$ axis in which the current density is increased over $j_0$, although laterally further away there continues to be a current density decrease. This behavior will be discussed in more detail elsewhere.

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[10] Note that image effects are omitted in the calculation, and that density-functional eigenfunctions are used as if they were *bona fide* single-particle wave functions.

[11] The calculated work function is 3.9 eV, which is appropriate for an $s$-$p$ metal of this density.