Apparent Size of an Atom in the Scanning Tunneling Microscope as a Function of Bias

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In order to determine how the sample density of states is reflected in topographic images obtained in the scanning tunneling microscope, the apparent size of an adsorbed atom is studied as a function of bias voltage for several different atoms. This quantity is found to reflect state-density features that lie well above the Fermi level, but it shows a striking absence of any trace of *d*-state peaks below the Fermi level.

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We consider here the way in which topographic images obtained with the scanning tunneling microscope are affected by the sample density of states. We study the case in which the sample is a single atom adsorbed on a surface, and find in particular that the higher-energy portion of the adatom state-density spectrum is reflected in the apparent vertical size of the adatom as a function of bias.[1]

For this analysis, we calculate the vacuum tunneling current between two planar, parallel, metallic electrodes, each with an adatom, as a function of the bias between them; one of these electrodes represents the tip, the other the sample. The tunneling-Hamiltonian formalism[2] is used to compute the total current in terms of the wave functions determined separately for each electrode in the absence of the other[3]; these wave functions are calculated as described earlier.[4] The jellium model with $r_s = 2$ is used for each of the metal surfaces.

Let us take s to be the z-axis separation (i.e., that along the surface normal) between the center of the tip atom and the center of the sample atom, and Y to be the lateral separation (i.e., that parallel to the surface) between the tip and the sample atoms. Let us hold the current fixed; then the z-axis separation will be a function of the lateral separation and the applied bias voltage: $s = s(Y,V)$. For any given Y, the separation s will increase substantially as V is increased from the millivolt range to several volts, in order to maintain the current at its fixed value. The measure of z-axis displacement due to scanning laterally over the atom on which we will focus our attention is $\Delta s(V) = s(0,V) - s(\infty,V)$. We can call this quantity the apparent vertical size (or displacement above the surface) of the adatom. It is the most important piece of information in the topograph.[5]

Consider an atom S adsorbed on one electrode (sample) and an atom T adsorbed on the other electrode (tip). Let I_{ST} be the current flowing between the two electrodes with their adatoms, and let I_S (I_T) be the current flowing for this same arrangement in the absence of atom T (S), but with the bare-metal electrode on which the absent atom had been adsorbed remaining in place. We will always exclude from these calculated currents the current that would flow between the two bare metal surfaces in the absence of both atoms (which is infinite because of the infinite surface area).[6] We model the current that flows between tip and sample in the experiment by $\delta I = I_{ST} - I_S$. For large lateral separations Y, this difference excludes the current flow between atom S and the metal surface on which atom T is adsorbed, which is necessary in order that our model yield results appropriate for a sharp tip.[7] For $Y = \infty$ (and a given value of s), $\delta I = I_T$. For $Y = 0$, I_S is in general very small compared with I_{ST}, and so we take $\delta I \approx I_{ST}$. We therefore construct a table of values of I_T, and $I_{ST}(Y=0)$, for various values of s, and by interpolation find the quantity Δs defined above. This is done for each bias V that we consider, with the current δI kept at the same fixed value for all V.[5,8] The calculations of the currents are done in the same way as those described elsewhere,[9] with the same approximation, in which the stationary-state wave functions are computed in the absence of the electric field. It will be recalled that this approximation leads to a rather small error for biases (typically ~1 eV) that are not too large on the scale of the work function. We include only wave functions with azimuthal quantum number $m = 0$ (i.e., s and p_z for example, but not p_{xy}), because $m \neq 0$ components make a much smaller contribution to the tunneling currents considered here—cf. discussion in Refs. 4 and 7.

We will consider three different sample atoms: Na, Mo, and S, as prototype alkali metal, transition metal, and nonmetal. A Na atom is used for the tip in all calculations, but the results are rather independent of the tip atom used.[10] We show in Fig. 1 the additional eigenstate density due to the presence of each of the three sample atoms on a metal surface; that is, we give the total eigenstate density for the metal-adatom system, minus that of the bare metal. Only the $m = 0$ component is shown. For Na, 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. In the case of Mo, the large peak just below the Fermi level corresponds to the 4d state of the free atom, and the smaller peak about 1 eV above the Fermi level corresponds to the 5s state. For S, the 3p peak is seen well

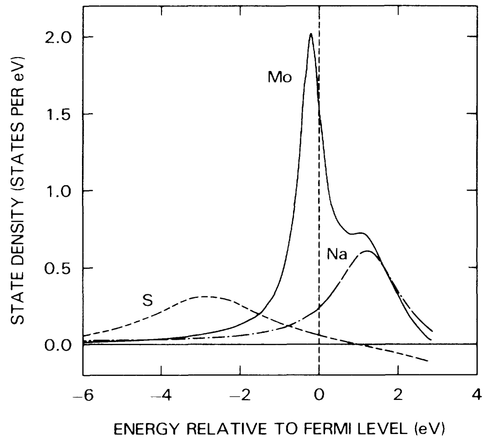

FIG. 1. Difference in eigenstate density between the metal-adatom system and the bare metal ($r_s=2$) for adsorbed Na, Mo, and S. Only the $m=0$ component is shown.

below the Fermi level. Note that past about 1 eV above the Fermi level, the additional state density due to the presence of the S atom is negative; that is, some of the metal states that were present in this energy region are pushed out of it.

We show the curves of $\Delta s(V)$ for these atoms in Figs. 2–4, for V in the range -2 to $+2$ eV. Positive V corresponds to the polarity in which electrons tunnel into *empty* states of the sample. At the top of each figure, the corresponding state-density curve for energies in the range -2 to $+2$ eV is given for comparison.

Figure 2 shows the computed $\Delta s(V)$ for the case of the Na sample atom[11]; it clearly reflects the mostly empty 3s resonance. The relation between the shape of the peak in the $\Delta s(V)$ and the shape of the state-density peak is explored in the Appendix (see discussion of the δ-function state-density case). The curvature of the $\Delta s(V)$ graph up toward the left in the negative-bias region is simply an effect of the exponential barrier-

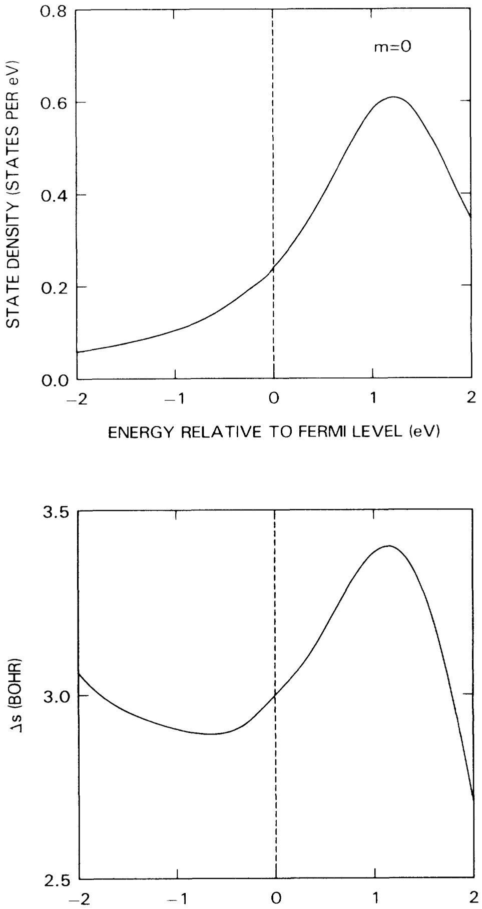

FIG. 2. Top: Na eigenstate density difference. The 3s resonance is clearly evident. Bottom: $\Delta s(V)$ for Na sample adatom.

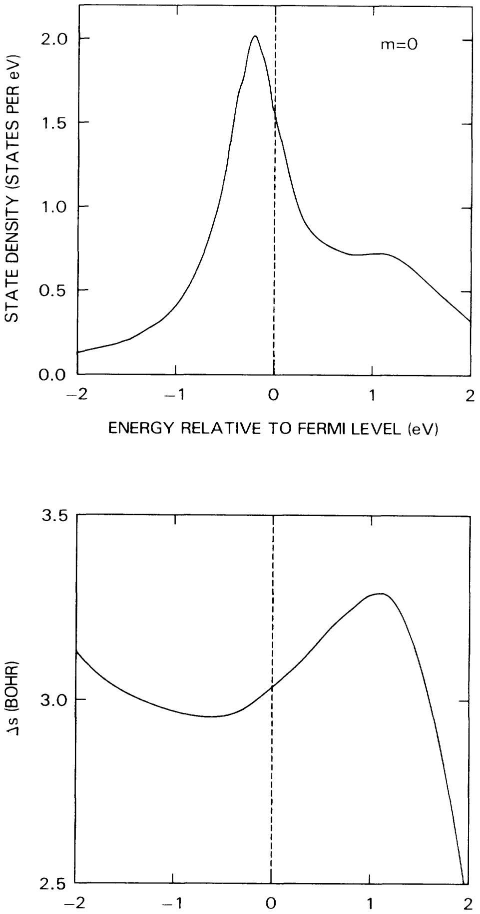

FIG. 3. Top: Mo eigenstate density difference. The lower-energy Mo peak corresponds to 4d; the upper, smaller peak to 5s. Bottom: $\Delta s(V)$ for Mo sample adatom.

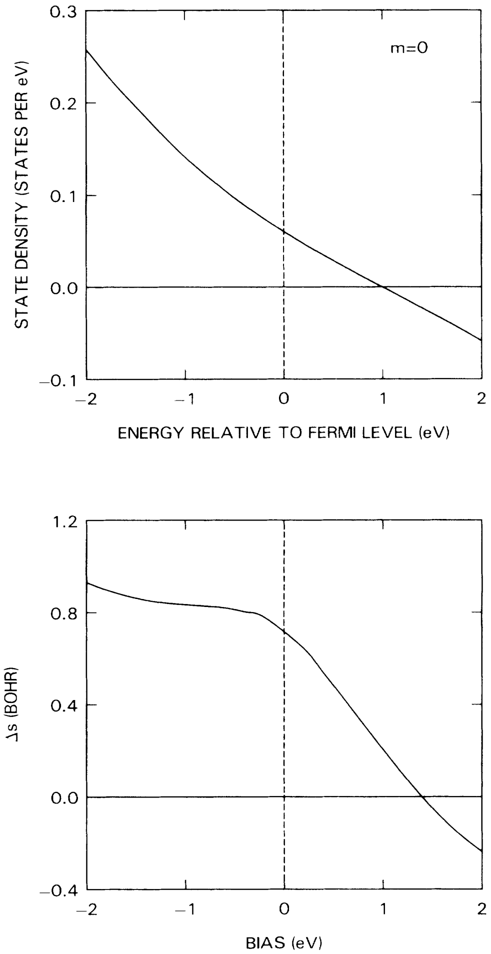

FIG. 4. Top: S eigenstate density difference. Bottom: $\Delta s(V)$ for S sample adatom.

penetration factor, and would be present even if the state density of the sample, and tip as well, had no structure whatsoever. (Cf. discussion of constant-state-density case in Appendix.)

The graph of $\Delta s(V)$ for Mo shown in Fig. 3 is very similar to that for Na, with the large peak at positive bias associated with the mostly empty $5s$ state of the adsorbed Mo atom. It is striking how little evidence there is of the $4d$ state in this graph. The reason for this is that the valence d orbitals in the transition elements are in general quite localized relative to the valence s orbitals, and will thus have a much smaller amplitude at the tip. This greater localization can be loosely thought of as being due to the effect of the centrifugal barrier; also, of course, the d orbital lies in a shell of smaller radius than the s orbital, since its principal quantum number is lower by 1 (e.g., $4d$ compared with $5s$). The only exception to the behavior seen in Fig. 3 occurs for adatoms at the far left of the periodic table, where the d states lie at relatively higher energies, such as Ca studied in Ref. 9 with its d resonance ~ 1.5 eV above the Fermi level. In this case, $\Delta s(V)$ does show a corresponding peak.

We can explore this behavior further by looking at a curve of dI/dV for Mo as a function of V, as in Ref. 9, and again no peak is evident at the position corresponding to the $4d$ resonance; the curve looks very similar to that for a Na sample. We can alternatively compute the local density of states due to the Mo at positions well into the vacuum, and we also see practically no trace of the $4d$ resonance. A similar effect has been observed experimentally in the scanning tunneling microscope by Demuth, van Loenen, and Tromp,[12] who found no evidence of the d-band of Ag adsorbed on Si in spectroscopic data, although in this case the fact that the d states lie well below the Fermi level would alone be enough to give this result.[13]

Figure 4 gives $\Delta s(V)$ for S. We note the rather striking fact that for a bias just above $+1$ eV, the S atom is essential invisible, that is, causes no displacement of the tip, and for biases much above this, the tip moves *closer* to the atom as it passes over it (negative displacement). The negative displacement is a direct consequence of the fact noted earlier that the additional state density due to the presence of the S atom is negative in the relevant energy region. Since the total (metal plus atom) state density at these energies is then lower than it is for the bare metal, the tip must move closer to the surface when it is over the atom in order to maintain a constant tunneling current. A more complete discussion of the shape of this curve is given in the Appendix (see the linear-state-density case).

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Appendix.— For qualitative discussion, we use a very crude model for the tunneling current (following Ref. 9), in which the current is given as an energy integral over sample and tip state densities, with the simplest barrier penetration factor. If we take the tip state density to be constant for convenience, then equating the currents for lateral separations $Y=0$ and $Y=\infty$ implies equating the energy integrals which approximate these currents (using atomic units, $|e| = \hbar = m = 1$):

$$\int_0^V d\varepsilon[\rho_S(\varepsilon)+C]\exp\{-2s(0,V)[2(\Phi-\varepsilon)+V]^{1/2}\} = \int_0^V d\varepsilon\, C\exp\{-2s(\infty,V)[2(\Phi-\varepsilon)+V]^{1/2}\},$$

where $\rho_S(\varepsilon)$ is the $m=0$ component of the sample density of states due to the adatom, with ε the energy relative to the Fermi level. We simply use a constant C to indicate the bare-metal state density (neglecting among other things that the barrier thickness seen by electrons from the bare metal should be larger than that seen by electrons from the adsorbed atom by roughly the metal-adatom bond length). We furthermore put $s(Y,V)$ for the barrier thickness, even though the actual barrier thickness will be smaller (since s is a center-to-center z distance).

We now give the results of evaluating $\Delta s(V) = s(0,V) - s(\infty,V)$ using this equation for several simple model state densities. We exhibit only the most important dependence of Δs on V in each case, retaining in particular only the leading power in s^{-1}, and considering $|V|$ smaller than Φ but large enough to neglect $\exp[-2s(2\Phi + |V|)^{1/2}]$ relative to $\exp[-2s(2\Phi - |V|)^{1/2}]$. We denote by a and b quantities that are *positive,* and are either constant or slowly varying as a function of V (they represent different expressions in each case).

If $\rho_S(\varepsilon)$ is constant, then $\Delta s(V) \sim a(2\Phi - |V|)^{-1/2}$. This shows the upturn seen for $V \sim -2$ eV in the curves given above for Na and Mo. If $\rho_S(\varepsilon) \propto \delta(\varepsilon - \varepsilon_0)$, then $\Delta s(V) \sim \theta(V - \varepsilon_0)[a - b(V - \varepsilon_0)]$ for $\varepsilon_0 > 0$ and $V - \varepsilon_0$ small, with θ the step function. This gives an abrupt increase in $\Delta s(V)$ at the position of the state-density peak, with a linear decrease for higher bias; in a realistic case (e.g., Fig. 2) this becomes an asymmetric peak. If $\rho_S(\varepsilon) \propto \varepsilon_0 - \varepsilon$ (with $\varepsilon_0 > 0$), as is roughly the case for S in Fig. 4, then $\Delta s(V) \sim a \ln\{1 + b[\varepsilon_0 - V\theta(V)]\}$. For $V < 0$ this gives a constant displacement $\Delta s(V)$; for $V > 0$ it gives a displacement that decreases with V, crossing zero at $V = \varepsilon_0$. This is approximately the behavior seen in Fig. 4.

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[1] Cf. G. Binnig, H. Fuchs, Ch. Gerber, H. Rohrer, E. Stoll, and E. Tosatti, Europhys. Lett. **1**, 31 (1986); J. Tersoff, Phys. Rev. Lett. **57**, 440 (1986); J. M. Soler, A. M. Baro, N. Garcia, and H. Rohrer, Phys. Rev. Lett. **57**, 444 (1986).

[2] J. Bardeen, Phys. Rev. Lett. **6**, 57 (1961).

[3] All image effects are omitted.

[4] N. D. Lang, Phys. Rev. Lett. **55**, 230, 2925(E) (1985), and IBM J. Res. Dev. **30**, 374 (1986).

[5] Consider a periodic array of adsorbates on the surface with lattice spacing l. Then for tip distance $s \gg l$, we expect an exponential decrease of Δs with increasing tip distance ("smoothing")—see J. Tersoff and D. R. Hamann, Phys. Rev. B **31**, 805 (1985). However, for $l \gg s$, which is essentially the single-atom case we consider here, Δs is much less strongly distance dependent. A simple analysis taking a spherical s-wave for the atom and a decaying plane wave for the metal leads to a correction to Δs of $-\kappa^{-1}\ln\kappa z$, with κ the dominant vacuum inverse decay length (which is the same for both waves) and z the distance between the tip and the *metal.*

[6] The current *density* in the absence of both atoms is $\sim 10^{-3}$ of the current density on the axis in the presence of the atoms (taking two Na atoms as an example).

[7] N. L. Lang, Phys. Rev. Lett. **56**, 1164 (1986).

[8] We hold the current constant at the value it has for a bias of 10 meV when the distance between the nucleus of the Na tip atom and the positive background edge of the sample surface, with no sample adatom, is 19 bohrs.

[9] N. D. Lang, Phys. Rev. B **34**, 5947 (1986).

[10] This is not the case if we look at dI/dV vs V, as in Ref. 9.

[11] The calculated *lateral* size of the atom is found to vary by $\sim 10\%$ over the same bias range (cf. results in Ref. 7).

[12] J. E. Demuth, E. J. van Loenen, and R. M. Tromp, to be published.

[13] The difficulty of seeing low-lying occupied states has been discussed by R. M. Feenstra, J. A. Stroscio, and A. P. Fein, to be published.