Probing the Highly Correlated Mixed-Valent State via Charge Transfer with Atoms Moving Out from a Surface

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We present physical arguments and quantitative calculations which indicate that under certain conditions atoms moving near metal surfaces exhibit a dramatic temperature and velocity dependence caused by a collective (mixed-valent) state. Charge transfer experiments are proposed to observe this phenomenon. [S0031-9007(96)00799-5]

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The interesting phenomena that may arise in the context of impurity states in a metal are well established [1,2]. In certain parameter ranges there exist collective many-body states, which exhibit unusual low energy behavior. In particular, resonances appear in the electronic spectral functions near the Fermi level associated with the screening of the spin of the impurity (the Kondo effect) or with slow fluctuations between the local charge configurations (mixed-valent behavior) induced by the interactions of the impurity state with the continuum of many-body excitations in the metal. The analogous collective many-body effects should also occur in the problem of an atom outside a metal surface [3,4] provided that the motion of the atom is slow enough. The purpose of this Letter is to propose that, with appropriately chosen systems, the presence of this state should cause dramatic temperature dependence in experiments sensitive to charge transfer in the hyperthermal energy range, such as atom-surface scattering. Indeed, atom-surface measurements may provide an ideal way to probe these states because of the wide range of parameters that can be varied.

Suppose that an atom or an ion is held in a fixed position near the surface. The collective state mentioned above can form if the energy levels of the atom are shifted by the image potential in such a way that the equilibrium configuration of the atom is degenerate, i.e., would have an unfilled subshell (in the absence of wave function overlap with the substrate). We find in the calculations presented below that, in order to freeze in a remnant of such a correlated state, the relevant ionization or affinity level must also cross the Fermi level on the outward trajectory. These conditions are typically not met in experiments to date [5]. Specifically, an alkali metal atom has its unpaired spin state as a neutral atom on the vacuum side of the crossing of the Fermi level, rather than on the surface side. It does not matter, in principle, whether it is the affinity level or the ionization level that crosses the Fermi level during the outgoing trajectory [6]. In the former case, we predict an anomalous temperature dependence in the negative ion yield and, in the latter, an anomalous temperature dependence in the positive ion yield. In the discussion below, we use the negative ion case since it is easier to visualize intuitively. The positive ion case can be obtained simply by reversing the roles of electrons and holes.

Consider a neutral singlet atom held in a fixed position outside a metallic surface. Suppose that its affinity level is about 1 eV above the Fermi level when the atom is held far away, in which case the image potential will shift the level below the Fermi level when the atom is held closer than about 8 a.u. Such a system is characterized by two parameters, the level position E and a width parameter Γ, the latter representing the one-body mixing of the atomic states with those of the metal. Although the degeneracy of the atomic level may be N, where N is at least 2 from spin degeneracy, intra-atomic Coulomb repulsion U will typically prevent more than a single electron from occupying the atomic level. The atom interacting with the surface problem is analogous to the impurity state in the bulk metallic problem, and the fluctuations in and out of this state as a result of the mixing will lead, in the presence of intra-atomic Coulomb interaction, to two qualitatively different regimes: (i) the Kondo-type regime where E is well below the Fermi level and (ii) the mixed-valent regime in which E is within a range $\sim\Gamma$ of the Fermi level. These two situations are illustrated through the associated behavior of the spectral functions in Figs. 1(a) and 1(b), respectively. The peak at the Fermi level in the Kondo region, which is not present in treatments where the intra-atomic correlation is neglected, provides a slow time scale for the problem in addition to the time scale $1/\Gamma$ resulting from the hybridization between the atomic level and the metallic surface. In the mixed-valent case there occurs only a single peak, which can be regarded as resulting from the merging of the Kondo peak and the peak at the atomic level position. Its position, width, and temperature dependence differ qualitatively from what would be expected in a

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one electron theory. In particular, the mixed-valent peak remains just above the Fermi level for a wide range of parameters and hence leads to a marked variation in the thermal average occupancy of the atomic level as the temperature is varied. This is illustrated in Fig. 2 where the thermal population of the atomic level in the mixed-valent regime [Fig. 1(b)] is shown by the solid curve. The temperature dependence can be understood from the fact that, as the temperature is raised, more of the peak's spectral weight is sampled; in addition, the peak becomes broader with increasing temperature, thus moving its effective boundary to lower energies.

There can be no question that the system goes through the mixed-valent regime if E passes through the Fermi level on the atom's trajectory toward or away from the surface. The main question is whether one can find situations in which the system evolves slowly enough to sample the longer characteristic times of the highly correlated state, and hence to be affected by its anomalous temperature dependence. We present a case here that shows the answer might be yes. The ideal thought experiment would be to hold the atom in the position of Fig. 1(b), until it came to thermal equilibrium with the substrate, and then to yank it away so fast that the temperature dependent population probability gets trapped. Although this limiting case is obviously impossible, we argue that a rough approximation to the physics it illustrates probably can be made to occur.

To make things specific, we make a simple model of how E and Γ vary with distance z from the surface: $E = E(z) = E(\infty) - \frac{1}{4}(z - 1)^{-1}$ and $\Gamma = \Gamma(z) = 1.5e^{-0.65z}$, where all quantities are expressed in atomic units (a.u.). This is a realistic parametrization that approximates the results of electronic structure calculations [7], except at the closest distances where the charge transfer rates are so large that the system typically loses memory of what happened there. We will take $E(\infty) = 1/27.2 = 1$ eV in the model calculations presented here.

The curves shown in this Letter are calculated with the above parameter modeling in the large U degenerate Anderson model [8]. This was solved in the so-called noncrossing approximation (NCA) [9,10], which is a well-established self-consistent approximation [1,2] known to give better than qualitatively correct results [10,11], except at very low temperatures [12]. The NCA has been generalized to the time dependent nonequilibrium situation a while ago [13]; the nonequilibrium calculations reported here use the exact (numerical) solution [3] to the time dependent equations. The NCA has recently been shown [11] to be accurate for the functions used here to calculate charge transfer (the so-called auxiliary spectral functions), even in its worst case of $N = 2$ and low temperatures.

We used our solution to make detailed calculations of the average population of the level vs z for a trajectory starting at $z = 3$ and proceeding outward with a speed v for various temperatures. The temperature dependence of the final average populations (in this case, negative ion yield) is shown in Fig. 2 for $v = 0.004$ and 0.03 a.u. It is this unusual temperature dependence for charge transfer that we suggest that experiments look for. We have also made nonequilibrium calculations using the traditional picture neglecting intra-atomic Coulomb interaction, and find, as expected, essentially no temperature dependence. We note that the temperature dependence is similar to that of the *equilibrium* population of a hypothetical atom held fixed in the mixed-valent state, as if this temperature dependence had been frozen in, as speculated earlier. We return to this point below.

The reason for the temperature dependence can be understood from the *equilibrium* spectral functions plus an understanding of the time scales of the problem and how they change with the distance of the atom from the surface. The important features of the spectral density affecting the slow time scale are the position ε and width γ of the narrow spectral feature just above the Fermi level. These are plotted versus distance from the surface z at 200 K in Fig. 3(a). For simplicity, we have not shown results at other temperatures, but simply state that ε shows very little temperature dependence, while γ increases

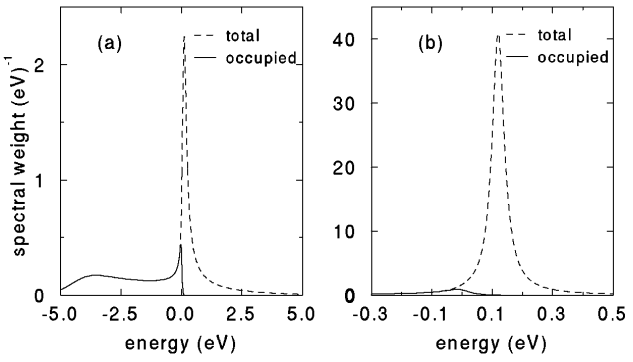

FIG. 1. Equilibrium spectral weights at 200 K for (a) $z = 3.5$ a.u. (Kondo region) and (b) $z = 8$ a.u. (mixed-valence region).

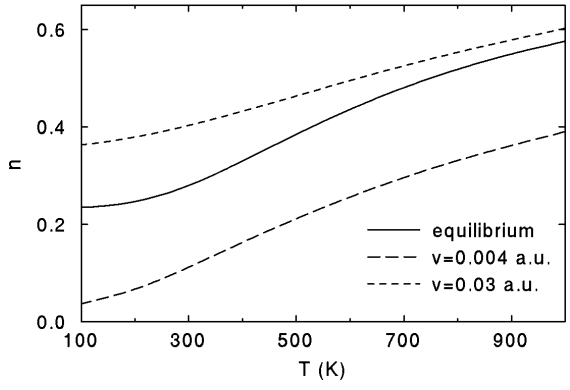

FIG. 2. Solid curve: thermal equilibrium population vs temperature T for $z = 8$ a.u. Dashed curves: final nonequilibrium populations vs T for the indicated velocities v.

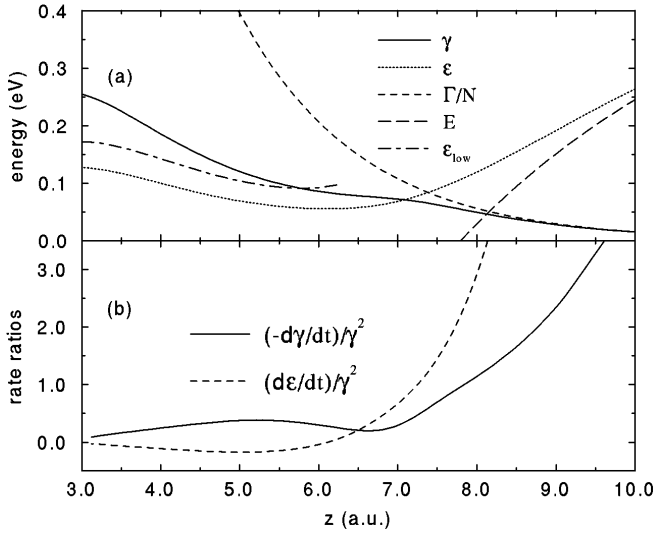

FIG. 3. (a) Widths and energies vs distance. (b) Rate ratios derived from the curves in panel (a).

somewhat with temperature (roughly doubling when the temperature is quadrupled). Also plotted for reference are E and Γ/N, essentially the input parameters, but which also represent the approximate position and width of the only spectral feature present in a noninteracting model. The low energy scale depends sensitively on the ratio of Γ to E (exponentially in the Kondo regime), so that it is important to find systems where the variation in this quantity with z is not too rapid. Here the decrease in Γ with z is roughly offset by the decrease in the magnitude of E with z, leading to low energy scales set by γ and ε that do not change rapidly over the range of z right before E crosses the Fermi level. This low energy scale, $\varepsilon_{\rm low} \equiv k_B T_l$, can be calculated exactly at $T = 0$ in the Kondo regime via Bethe ansatz leading to a simple analytic formula (see Refs. [1] and [10]), which is also plotted in Fig. 3(a). We found the formula useful for making estimates, although it does not correctly give the low energy scale in the mixed-valent regime.

For a qualitative determination of the time scale associated with the formation and decay of the many-body resonance, we estimate that the energy uncertainty γ represents the inverse of this time scale. Similarly, the quantities $|\frac{1}{\gamma}\frac{d\gamma}{dt}|$ and $|\frac{1}{\gamma}\frac{d\varepsilon}{dt}|$ can be taken to be mean field estimates of the inverse time scales for the resonance to be driven out of equilibrium by the time dependence. Thus when $|\frac{1}{\gamma^2}\frac{d\gamma}{dt}|$ and $|\frac{1}{\gamma^2}\frac{d\varepsilon}{dt}|$ are much smaller than unity, we expect local thermal equilibrium to be maintained, while, if they are much larger than unity, we expect that the average populations will be frozen. These quantities [as derived from the curves in Fig. 3(a)] are plotted in Fig. 3(b) for the case of the atom moving uniformly out from the surface with a velocity $v = 0.004$ a.u. The curves suggest that the thermal equilibrium distributions will be roughly maintained until z reaches approximately 8 a.u., at which point they rather suddenly switch to the rapid limit, suggesting that the anomalous temperature dependence similar to that of the solid curve of Fig. 2 will be frozen in. Since the curves in Fig. 3(b) are directly proportional to velocity, one sees that the rapid switching from one regime to the other still occurs for velocities as high as 0.01 a.u. or so. The curves shown are for $T = 200$ K; at higher temperatures, the regime switching continues to occur at even higher velocities.

The above physical arguments provide further support and physical understanding of the predicted temperature dependence, which we plot in a different way in Fig. 4 showing the predicted populations vs velocity at several different temperatures. The fact that these curves are not straight lines on the logarithmic plots reflects the varying time scales as discussed previously [4]. The fact that the curves are quite different for different temperatures is the effect predicted here, which should make the observation of the phenomenon unambiguous.

The effect is robust, in the sense that it does not depend on special sets of parameters. The temperature range in which it occurs, however, is fairly sensitive to $E(\infty)$ relative to the Fermi level, and hence to the work function. For example, when we decreased $E(\infty)$ to 0.75 eV, the low energy scale gets lowered, and the temperature dependence occurred mainly below 300 K. Thus experiments should be tried on several different crystal faces in an attempt to get the temperature dependence to occur in an easily accessible range. Use of alkali coadsorption to modify the work function should be avoided, however, because of the uncertain effect of the dipolar potentials produced by such a procedure. We have also tried different parametrizations for E and Γ, and found that the temperature dependence persists; it is typically seen with varying strength for the range $0.7 < E(\infty) < 2$ eV.

One should note that energy fluctuations of a size comparable to or larger than the width of the mixed-valence resonance near the Fermi level will weaken or destroy the effect. For the case illustrated in Fig. 3 this width is $\sim$50 meV in the critical switching region, but depends on the parameters of the problem such as $E(\infty)$

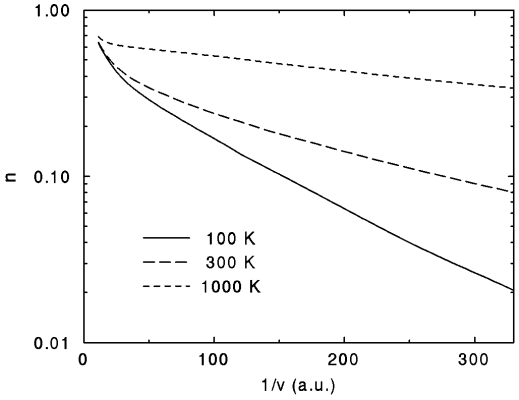

FIG. 4. Final nonequilibrium population vs $1/v$.

as discussed earlier. Even though the energy smearing due to recoil ($\sim q^2/2M$) from the tunneling electron is completely negligible on this scale (~ 1 meV or less), the Doppler smearing $\vec{v}_{\|} \cdot \vec{q}$ due to the parallel component of the atom's velocity $\vec{v}_{\|}$ must be controlled by the experimental geometry, and should be kept less than about 0.0005 a.u. One might also be concerned about the effect of phonons; such thermal vibrations will introduce a modulation of ε or γ. A simple estimate of this effect shows that it is negligible for the temperatures of relevance. Static inhomogeneities are probably even less of a problem, although to the extent that they cannot be minimized in the experiment they will undoubtedly weaken the effect somewhat.

From an experimental point of view, there exist a large number of atom or surface combinations with parameters in a suitable range. The basic situations one should explore involve atoms with affinity levels from about 0.7 to 2 eV above the Fermi level, measuring negative ion yield, or atoms with ionization levels in the above range below the Fermi level, measuring positive ion yield. As mentioned earlier, a necessary requirement is that the image potential shift of the relevant energy level produce a Fermi level crossing such that the atomic species would have degenerate ground state on the surface side of the crossing if all wave function overlap effects with the substrate were turned off [14]. The model problem that we actually solved also assumes that the atom has a nondegenerate ground state when at infinity [15]. The simplest systems that cleanly can be made to satisfy all the above criteria can be chosen from the alkaline earth atoms with noble metal surfaces. The former have ionization energies in the 5–8 eV range, while the latter have almost a continuous range of work functions between 4.3 and 5.5 eV. Therefore one can find a number of combinations where the ionization level's energy is ~ 1 eV below the Fermi level. These would then be examples of $N = 2$ systems which are electron-hole conjugates of those used in the curves and previous discussion. One would look for temperature anomalies in the positive ion yield.

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[14] A critical condition for the selection of systems is that the intra-atomic Coulomb interaction $U(z)$ be sufficiently large at the critical distance z_c, where $E(z)$ crosses the Fermi level, that the doubly ionized state remains empty, i.e., $U(z_c) \approx U(\infty) - e^2/2(z_c - 1) \gg \Gamma(z_c)/N$. In practice, this condition is easily satisfied for systems where $z_c \sim 8$ a.u.

[15] We do not recommend avoiding experimental tests on systems that fail only to meet this latter criterion, because many such systems probably do have correlated states, even though they cannot be described simply by a simple degenerate Anderson model considered here. Particularly, situations involving p-state filling might be expected to have larger effective N's and hence larger temperature effects. Within the simple Anderson model, the strength of the effect roughly doubles as N is increased from 2 to 4.