Effect of parallel velocity on the formation of a Kondo resonance in the atom-surface interaction

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(Received 31 August 1998; revised manuscript received 8 December 1998)

We investigate the effect of parallel velocity on the formation of a Kondo resonance when an atom is scattered against a surface. It is shown that the structure of the Kondo resonance depends sensitively on the parallel velocity of the atom. It is shown that this dependence can be probed by studying charge transfer in atom-surface scattering experiments. [S0163-1829(99)07219-7]

I. INTRODUCTION

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 there appear resonances 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. Recently, direct experimental evidence for the formation of a Kondo resonance when a magnetic atom is chemisorbed on a metal surface has been presented.[3,4] The analogous collective many-body effects will also occur in the problem of an atom moving outside a metal surface,[5–7] provided that the motion of the atom is slow enough.

In a recent paper,[7] we demonstrated that in an atom-surface scattering experiment involving appropriately chosen atoms and substrates, there will be time for such a correlated state to form when the atom is near the surface. Some of the characteristics of this state will survive as the atom leaves the surface and can be detected. Specifically, we have shown that it is possible to probe the dramatic temperature dependence of the population of the atomic level when the atom is in the strongly correlated mixed-valent state near the surface. This phenomenon can simply be detected by measuring the ionization probability (charge-transfer probability) of atoms scattered against a substrate as a function of substrate temperature.[7] This prediction has also been verified using an alternative calculational method.[8] Indeed, these findings indicate that measuring charge transfer in atom-surface scattering experiments may provide an ideal way to probe these states, because of the wide range of parameters that can be varied.

The dramatic temperature dependence of the population of the atomic level in the mixed-valent regime arises from the formation of a Kondo resonance located just above the Fermi energy. This resonance is typically very narrow. Energy fluctuations larger than the width of this resonance are expected to weaken its contribution to the population of the atomic level and thus reduce the temperature dependence of the charge transfer between the atom and the substrate. Such energy fluctuations can come from recoil caused by electron tunneling, large amplitude vibrations of the substrate atoms, or the Doppler smearing, $\vec{v}_\parallel \cdot \vec{k}_\parallel$, of the Fermi-Dirac distribution caused by parallel velocity $\vec{v}_\parallel$ of the scattered atom.[9] Simple estimates of the two first mechanisms show that they can be neglected in the relevant hyperthermal scattering experiments.[7] However, due to the construction of the instruments used in typical atom-surface scattering experiments, it is not always possible to keep the parallel velocity of the scattered atom low.

The purpose of this paper is to investigate quantitatively how the effects of parallel velocity will influence the proposed temperature dependence of charge transfer. The present calculation shows that the temperature dependence is considerably less sensitive to the effect of parallel velocity than our previous crude estimates indicated. However, more importantly, the present calculation shows that, by measuring the parallel velocity dependence of the charge transfer while keeping the substrate temperature constant, it is also possible to probe the mixed-valent state formed when the atom is close to the surface.

II. MODEL

As a model system we adopt the same system used in our previous investigation, i.e., a single N-fold degenerate level shifting below the Fermi level as the surface is approached. The energy of each of the N degenerate atomic states is assumed to depend on atom-surface separation Z as $\epsilon_\sigma(Z) = E(\infty) - \frac{1}{4}(Z-1)^{-1}$ and the width of each of the atomic states is taken as $\Gamma(Z) = (3/2N)e^{-0.65Z}$. Atomic units will be used throughout the paper unless otherwise indicated. This is a realistic parametrization that approximates the results of electronic structure calculations,[10,11] except at very small atom-surface separations. The Fermi energy is assumed to be at zero energy and we will assume that $E(\infty) = (1/27.2) = 1$ eV.

The charge transfer can be calculated using a time-dependent Anderson model that takes the form:

$$H(t) = \sum_\sigma \epsilon_\sigma(Z(t)) n_\sigma + \sum_{\vec{k}} \epsilon_{\vec{k}} n_{\vec{k}} + \sum_{\sigma \neq \sigma'} U_{\sigma\sigma'}(Z(t)) n_\sigma n_{\sigma'} + \sum_{\sigma \vec{k}} [V_{\sigma,\vec{k},\vec{Q}}(\vec{R}(t)) c^+_{\vec{k}} c_\sigma + \text{H.c.}], \quad (1)$$

where $\vec{Q}$ is the electronic momentum shift associated with the projectile velocity $\dot{\vec{R}}$. In atomic units, $\vec{Q}=\dot{\vec{R}}$. The new feature associated with parallel velocity that we wish to study is that the matrix element $V_{\sigma,\vec{k},\vec{Q}}$ in the presence of a parallel velocity $\dot{R}_\parallel = Q_\parallel$ has a time-dependent and k-dependent phase. This gives a $\vec{k}$ dependent energy smearing, which should be expected to weaken the effects associated with the Kondo resonance.

The inclusion of parallel velocity represents a generalization of the method developed earlier.[5] It is now necessary to consider its effects on the atom-metal interaction matrix $V_{\sigma,\vec{k},\vec{Q}}[\vec{R}(t)]$. We first write the matrix element for an atom at rest, a distance Z from a noncorrugated surface

$$V^{(S)}_{\sigma k}(Z)=\int d^3r\,\psi^*_{\vec{k}}(\vec{r})v(\vec{x}_\parallel,z-Z)\phi_\sigma(\vec{x}_\parallel,z-Z). \quad (2)$$

Here $\psi_{\vec{k}}(\vec{r})=u_{\vec{k}}(\vec{r})e^{i\vec{k}_\parallel\cdot\vec{r}_\parallel}$ is the Bloch function of the conduction electrons near the surface, $v(\vec{r})$ is the metal-atom interaction, and $\phi_\sigma(\vec{r})$ is the wave function for the atomic level σ. This is the usual ''static'' matrix element describing the electron scattering in and out of the atomic (impurity) level. The phase of $V^{(S)}$ is independent of time or $\vec{k}$ and only contributes a static energy shift. In the case of a moving atom, the matrix element becomes

$$V_{\sigma,\vec{k},\vec{Q}}(\vec{R}(t))=\int d^3r\,\psi^*_{\vec{k}}(\vec{r})v(\vec{r}-\vec{R}(t))\phi'_\sigma(\vec{r}), \quad (3)$$

where now $\phi'_\sigma(\vec{r})$ is the wave function for the atomic level σ as viewed from the metal surface. This wave function is related through a coordinate transformation to the solution in the frame in which the atom is at rest

$$\phi'_\sigma(\vec{r})=\phi_\sigma(\vec{r}-\vec{R}(t))\exp\left[i\vec{Q}(t)\cdot(\vec{r}-\vec{R}(t))+\frac{i}{2}\int^t Q^2(\tau)d\tau\right]. \quad (4)$$

We have assumed that $|\dot{\vec{Q}}|$ is much smaller than the atom's energy-level spacings divided by its size, so that the force induced by $\dot{Q}$ in the atom's rest frame can be neglected.

The time-varying magnitude and phase of the matrix element each have qualitatively different effects and it is useful to exhibit them explicitly

$$V_{\sigma,\vec{k},\vec{Q}}(\vec{R}(t))=|V_{\sigma,\vec{k},\vec{Q}}(\vec{R}(t))|e^{i\theta_{\vec{k},\vec{Q}}(t)}. \quad (5)$$

Throughout this work we assume that the surface is uncorrugated in the region important to the matrix element and that the projectile has sufficient symmetry for the perpendicular and parallel motion to be decoupled. Then the Bloch state $\psi_{\vec{k}}(\vec{r})$ is of the form $\psi_{\vec{k}}(\vec{r})=u_{k_z}(z)e^{i\vec{k}_\parallel\cdot\vec{x}_\parallel}$. It follows from Eqs. (3) and (4) that the phase $\theta_{\vec{k},\vec{Q}}$ can be written as

$$\theta_{\vec{k},\vec{Q}}(t)=-\vec{k}\cdot\vec{R}_\parallel(t)+\tfrac{1}{2}\int^t Q^2(\tau)d\tau+\tilde{\theta}_{\vec{k},\vec{Q}}(t), \quad (6)$$

and its time derivative

$$\dot{\theta}_{\vec{k},\vec{Q}}(t)=-\vec{k}\cdot\vec{Q}_\parallel(t)+\tfrac{1}{2}Q^2(t)+\dot{\tilde{\theta}}_{\vec{k},\vec{Q}}(t). \quad (7)$$

Here $\tilde{\theta}_{\vec{k},\vec{Q}}(t)$ is the phase and $|V_{\sigma,\vec{k},\vec{Q}}(\vec{R}(t))|$ is the magnitude of the integral $\int d^3r u^*_{k_z}(z+Z(t))e^{-i(\vec{k}-\vec{Q}_\parallel)\cdot\vec{x}_\parallel}v(\vec{r})\phi_\sigma(\vec{r})e^{iQ_zz}$.

In the velocity regime investigated here, the predominant term affecting the Kondo state at low velocities in Eq. (7) is the first one. It represents an energy smearing of the Fermi level, which has an effect comparable to temperature in destroying the narrow correlated state. This term only needs to be of order of the narrow energy width γ of the correlated state to be effective. The second term, represents an energy shift, whose first effect is a velocity dependent renormalization of the Kondo temperature. However, for this to happen, its value would have to reach a noticeable fraction of the ''large'' parameters like ϵ_σ. In fact the contributions of this term are not noticeable even at the highest velocities considered here. The third term is also of order Q^2 (and higher), and represents another contribution from the *perpendicular* motion to $\dot{\theta}$. In the Appendix, we present a simple approximation that suggests that this term ($\tilde{\theta}_{k,Q}$) would appear to make a contribution to $\dot{\theta}$ of the same order as the previous term. In fact, since this term can give a $\vec{k}$-dependent energy smearing, not just an energy shift, it may well be the most important of the terms formally of order Q^2 in their effect on the correlated state. The investigation of their effect will have to await a future work. Here, we work with approximations valid at slow velocities.

By following the notation of Ref. 5, the effect of the conduction-band electrons on the noncrossing approximation equations is fully expressed in terms of the quantities

$$K^{\gtrless}_\sigma(t,t')=\sum_{\vec{k}} V^*_{\sigma,\vec{k},\vec{Q}}(\vec{R}(t))G^{\gtrless}_{\vec{k}}(t-t')V_{\sigma,\vec{k},\vec{Q}}(\vec{R}(t')) \quad (8)$$

where $G^{\gtrless}_{\vec{k}}(t-t')$ is the conduction-band electron propagator. Using Eq. (5), we find

$$K^{\gtrless}_\sigma(t,t')=\sum_{\vec{k}} |V_{\sigma,\vec{k},\vec{Q}}(Z(t))V_{\sigma,\vec{k},\vec{Q}}(Z(t'))| \times e^{-i[\epsilon_k(t-t')+\theta_{\vec{k},\vec{Q}}(t)-\theta_{\vec{k},\vec{Q}}(t')]}f^{\gtrless}(\epsilon_{\vec{k}}), \quad (9)$$

where we have explicitly noted that in the absence of surface corrugation the magnitude of the matrix element is independent of $\vec{R}_\parallel$. The quantity $f^<(\epsilon)$ is the Fermi-Dirac function and $f^>(\epsilon)=1-f^<(\epsilon)$.

There are two cases where Eq. (9) simplifies substantially. The first occurs when the motion is purely parallel to a jellium surface at constant velocity. Then $Q_z=0$, $\epsilon_{\vec{k}-\vec{Q}_\parallel}=\epsilon_k-\vec{k}\cdot\vec{Q}_\parallel+\frac{1}{2}Q^2_\parallel$, and $\theta_{\vec{k},\vec{Q}}(t)=-\vec{k}\cdot\vec{Q}_\parallel t+\frac{1}{2}Q^2_\parallel t$. Furthermore, $|V_{\sigma,\vec{k},\vec{Q}}(Z(t))|\equiv|V_{\sigma,\vec{k}-\vec{Q}_\parallel}(Z)|$ becoming a function of $\vec{k}-\vec{Q}_\parallel$ alone. Using Eqs. (5) and (6) one finds that Eq. (9) becomes

$$K^{\gtrless}_\sigma(t,t')=\sum_{\vec{k}} |V_{\sigma,\vec{k}}(Z)|^2e^{-i\epsilon_k(t-t')}f^{\gtrless}(\epsilon_{\vec{k}+\vec{Q}_\parallel}), \quad (10)$$

thus formulating this particular case for the correlated system in the same manner as was done earlier[9] for the uncorrelated one. Evaluation of Eq. (10) is straightforward, and we have

used it in our many-body theory to check on the range of validity in parallel velocity for our theory.

The second case where Eq. (9) simplifies substantially is for small velocities. We are interested in the question of assessing the effect of the parallel velocity on the formation of the correlated electron states, which should occur on the scale of $Qk_F \sim \gamma \ll 1$, where γ is the width of the many-body resonance at the Fermi level (or the Kondo temperature). Since $k_F \sim 1$ this means $Q \ll k_F$. One simplification that follows is that, as implied earlier, we keep only the leading term in the phase $\theta_{\vec{k},\vec{Q}}(t) = -\vec{k}\cdot\vec{R}_\parallel(t)$ and neglect all the higher order contributions from $\vec{Q}$ to the phase. In this case, one can also set $\vec{Q}=0$ in $V_{\sigma,\vec{k},\vec{Q}}(Z)$ and write it in terms of the static matrix element $\lim_{\vec{Q}\to 0} V_{\sigma,\vec{k},\vec{Q}}(Z) = V^{(S)}_{\sigma,\vec{k}}(Z)$ [see Eq. (2)]. These approximations are adequate for studying the formation of the correlated electron state. They avoid the necessity of introducing additional parameters into our model, but limit the range of velocities that can be treated. However, our calculations were checked under the assumption of isotropic $|V_{\sigma,\vec{k}}(Z)|$ for the special case of parallel motion near a jellium surface, where Galilean invariance affords considerable simplification [see Eq. (10)]. In this case, no small velocity approximation was made. In this paper, we only present results for velocities where the two calculations agreed. We do not know of a similar simple check for the corresponding terms arising from the perpendicular motion, but we assumed in cutting off our plots that the effect would be comparable.

We continue to make the assumption made in previous studies that the strength of $V^{(S)}$ (and not its $\vec{k}$ dependence) is time independent, i.e.,

$$V^{(S)}_{\sigma,\vec{k}}(Z(t)) \equiv u_\sigma(Z(t)) v_{\vec{k}}, \tag{11}$$

where the functions u and v are real and positive. We now write $K^{\gtrless}_\sigma(t,t')$ using the same form as we used in our treatment of the perpendicular motion

$$K^{\gtrless}_\sigma(t,t') = \sqrt{\Gamma(Z(t))\Gamma(Z(t'))}\, f^{\gtrless}(t,t'), \tag{12}$$

with $\Gamma(Z)$ being the usual $(Q=0)$ tunneling rate at the Fermi level. The generalization of the earlier formalism thus appears entirely in the definition of $f^{\gtrless}(t,t')$ which, in the presence of parallel velocities, takes the form

$$f^{\gtrless}(t,t') = \int \frac{d\epsilon}{2\pi} \xi(\epsilon) f^{\gtrless}(\epsilon) e^{-i\epsilon(t-t')} \left\langle e^{-i[\theta_{\vec{k},\vec{Q}}(t) - \theta_{\vec{k},\vec{Q}}(t')]} \right\rangle_\epsilon, \tag{13}$$

with $\xi(\epsilon) = \langle 1 \rangle_\epsilon / \langle 1 \rangle_{\epsilon_F}$, where the band average for an arbitrary function $g_{\vec{k}}$ is defined by

$$\langle g_{\vec{k}} \rangle_\epsilon \equiv \frac{\sum_{\vec{k}} g_{\vec{k}} v^2_{\vec{k}} \delta(\epsilon - \epsilon_k)}{\sum_{\vec{k}} v^2_{\vec{k}} \delta(\epsilon - \epsilon_k)}. \tag{14}$$

We still need to solve the problem of how to treat the angular dependence of $v_{\vec{k}}$, hopefully in a parameter free manner. The angular dependence of $v_{\vec{k}}$ in Eq. (11) can also introduce a significant parallel velocity dependence to the charge transfer.[9,12,13] We appeal to the fact that a principal purpose of this work is to show that reasonable deviations from normal incidence will not prevent a correlated state, that otherwise would form, from forming, as predicted in Ref. 7. Therefore we want to make an approximation that will not underestimate the destructive effect of parallel velocity. The largest effect of parallel velocity on the correlated state occurs when $\vec{k}$ is parallel to the surface, leading to the largest value of $|\dot{\theta}_{k,Q}|$. On the other hand, the matrix element $v_{\vec{k}}$ will be larger for $\vec{k}$'s normal to the surface. Therefore, taking an isotropic $v_{\vec{k}}$ will lead to an error in the appropriate direction. It also leads to the cancellation of the matrix element from the average (14), satisfying our wish to avoid extra parameters, where possible.

Putting the pieces together, one finds that

$$\left\langle e^{-i[\theta_{\vec{k},\vec{Q}}(t) - \theta_{\vec{k},\vec{Q}}(t')]} \right\rangle_\epsilon \approx \left\langle e^{i\vec{k}\cdot\vec{Q}_\parallel(t-t')} \right\rangle_\epsilon \approx \frac{\sin qQ_\parallel(t-t')}{qQ_\parallel(t-t')}, \tag{15}$$

where q is the wave vector corresponding to the energy ϵ. For a parabolic ϵ vs q dispersion beginning a distance D below the Fermi level ($\epsilon_F \equiv 0$), one has simply $q = k_F\sqrt{(1+\epsilon/D)}$. The band average of the phase of the atom-metal interaction [Eq. (15)] thus reduces to an average over occupied band energies. Moreover, the weight of the averaging is constrained to the vicinity of the Fermi energy. In fact, we found at low temperatures and velocities that q in Eq. (15) can be replaced by k_F with very high accuracy. The value of k_F enters our theory as an additional parameter whose value we choose to be $k_F = 0.8$ a.u. throughout this paper. This is a realistic value for simple metals.

For our numerical calculations we take $\xi(\epsilon) = 1 - \epsilon^2/D^2$ for $|\epsilon| < D$, with $D = 5$ eV, and $N = 4$. The model of strongly correlated electron system (large U) was solved within the so-called noncrossing approximation[14,15] (NCA), which is a well-established self-consistent approximation[1,2] known to give better than qualitatively correct results[15,16] except at very low temperatures. The NCA has been generalized to the time-dependent nonequilibrium situation a while ago;[17] the nonequilibrium calculations reported here use the exact (numerical) solution[5] to the time-dependent equations.

III. RESULTS

We now turn to the discussion of our results. The calculated temperature dependence of the final populations is shown in Fig. 1. In typical charge-transfer experiments, the memory of the charge-transfer processes occurring during the incoming trajectory is lost. The final charge transfer is determined by the nonadiabatic effects that occur during the outgoing trajectory.[18,19] We therefore model the charge transfer here using a trajectory with an atom starting in equilibrium at $Z=3$ and proceeding outward with a speed v for various temperatures. We kept the normal component of the velocity constant in our calculations when comparing the charge transfer at different scattering angles such as in Fig. 1.

It can be seen that the proposed temperature dependence is weakened when the scattering angle is increased. How-

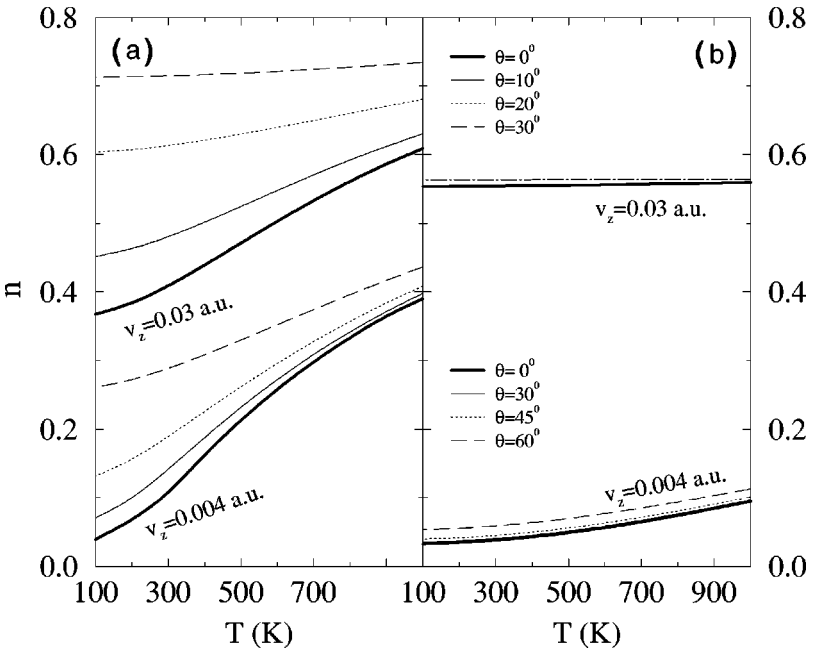

FIG. 1. Calculated population of the atomic level as a function of temperature for several different scattering angles. (a) $U=\infty$, $N=4$; (b) $U=0$, $N=1$.

ever, for low normal velocities the effect persists even for as large scattering angles as 45°. The principal effect of the parallel velocity is an increase in the final population of the atomic level. This increase is caused by the kinetic population of the mixed-valent resonance discussed below. The increase is larger for low temperatures than for the high temperatures, where thermal fluctuations cause a population of the resonance even at slow parallel velocities. In contrast, virtually no temperature or angular dependence of the charge transfer is observed in the absence of electron-electron interactions, i.e., $U=0$. We show the $U=0$, $N=1$ system in Fig. 1(b).

In Fig. 2(a), we show the calculated final population of the atomic level at $T=100$ K as a function of perpendicular velocity for several different scattering angles. The same is shown for $T=10^3$ K in Fig. 2(b). The shape of the curves depends on the scattering angle. For normal incidence, we recover the shape expected when the charge-transfer dynamics involve two mechanisms with different time constants,

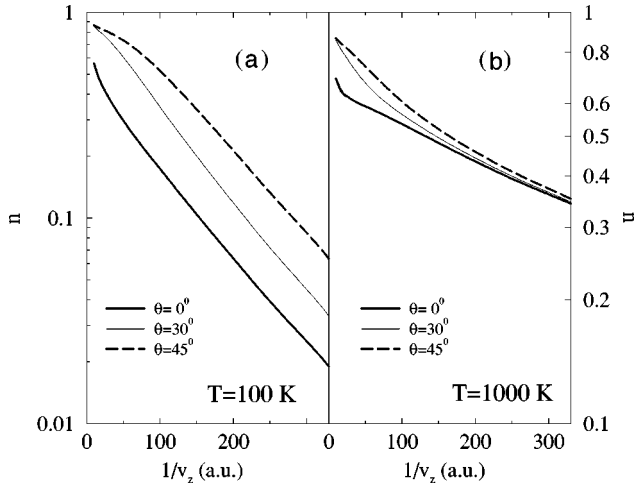

FIG. 2. Final nonequilibrium population vs $1/v$ for different scattering angles at (a) $T=100$ K and (b) $T=1000$ K.

i.e., Γ and γ discussed earlier.[6] The relatively fast decrease of n as a function of $1/v$ for large velocities is due to nonadiabaticity associated with the width of the atomic resonance, i.e., Γ and the slow decrease of n at large $1/v$ is caused by the nonadiabaticity associated with the formation of the mixed-valent peak.

We suggest that the involvement of the two electronic time scales be studied experimentally by monitoring the dependence of the final population on the scattering angle (at a fixed normal velocity). As we have shown, the Doppler smearing of the Kondo resonance becomes important when $v_\parallel k_F \sim \gamma$, where γ is the width of the Kondo peak. Since the width of the Kondo resonance is affected by the substrate temperature, and the ability of the Kondo peak to form depends on the normal velocity, different angular dependence should be expected as these conditions are varied.

For instance, at low temperatures [$T=100$ K in Fig. 2(a)], the effect of parallel velocity is significant for all, except the highest, velocities shown. This is because the width γ is small and the parallel velocity thus produces relatively large effects. Only at large velocities when the resonance does not have enough time to form does the effect of parallel velocity disappear. On the other hand, at large temperatures [$T=10^3$ K in Fig. 2(b)], the angular effects are small at low velocities because the Kondo (mixed valent) resonance is broadened by temperatures, i.e., $\gamma \geqslant T$ and thus $v_\parallel k_F < \gamma$.

In order to explain the dependence of the charge transfer on the parallel velocity, we show, in Fig. 3, the spectral function for an atom moving at different parallel velocities at a constant atom-surface separation ($Z=4$ a.u.). Although the charge transfer in scattering experiments is mostly determined by regions closer to where the resonance ϵ_σ crosses ϵ_F, i.e., somewhat farther away from the surface, the spectral functions in Fig. 3 clearly demonstrate the involvement of the two time scales. The first panel shows the spectral function for an atom at rest. The broad resonance at an energy $\epsilon=\epsilon_\sigma \approx -2.5$ eV is the hybridized atomic level. The width of this feature is Γ. The narrow peak at the Fermi level

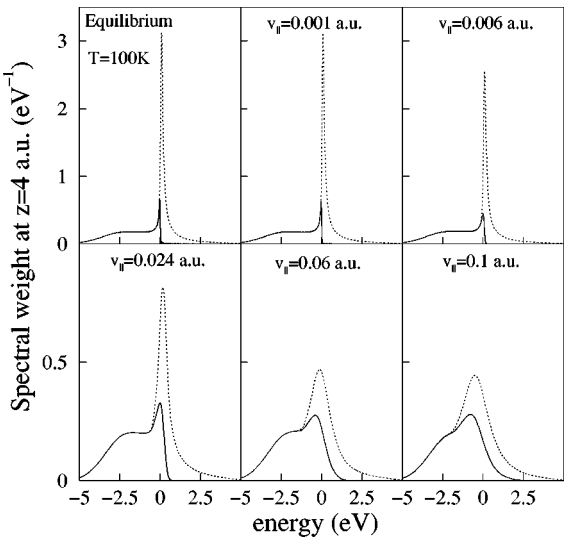

FIG. 3. Spectral functions of an atomic level for an atom moving with different velocities parallel to the surface. The dotted lines are the total spectral functions and the solid lines are the occupied part of the spectral functions. The atom surface separation is $Z=4$ a.u. The lower panel has a different scale than the top one.

is the Kondo resonance. The width of this feature, γ, is proportional to the Kondo temperature.[1] The Kondo resonance is not present in treatments where the intra-atomic correlation is neglected. It is this feature, which in the mixed-valent regime is called the mixed-valent resonance, which is responsible for the temperature dependence of the atomic population. As the parallel velocity is increased, it can be seen that the Kondo resonance becomes smaller and broader until it disappears altogether (here at about $v_{\parallel}\sim 0.1$ a.u.). The atomic level resonance remains unaffected by the parallel velocity. The reason why the Kondo resonance is influenced by $v_{\parallel}$ is the Doppler smearing of the Fermi surface for finite parallel velocities. As the atom moves along the metallic surface, substrate electrons with the momentum antiparallel to the velocity of the atom appear to have a larger kinetic energy than substrate electrons with their momentum in the same direction. At the Fermi energy, the energy difference between two such electrons is $\epsilon_{\vec{k}_{\parallel}+Q_{\parallel}}-\epsilon_{\vec{k}_{\parallel}-Q_{\parallel}}=2\vec{Q}_{\parallel}\vec{k}_{\parallel}=2\vec{v}_{\parallel}\vec{k}_{\parallel}$. This energy smearing is similar to the effect of thermal excitations caused by increasing the substrate temperature. It dampens the fluctuations responsible for the Kondo and mixed-valent resonances. In Fig. 3, we also show the occupied part of the spectral functions. The total population of the atomic level is given by the area under the occupied spectral function. As the parallel velocity of the atom is increased, it can be seen that the occupied spectral function extends to larger energies ϵ. This kinetic population of the Kondo resonance increases the population of the atomic level.

This can also be seen in Fig. 4, where we show the steady-state population of the atomic level as a function of parallel velocity for several constant surface separations. The interacting system shows an initial increase in the level occupation with increasing $v_{\parallel}$. The reason for this is the parallel velocity-induced kinetic population of the resonance at ϵ_F. The increase is partially offset by the decrease of the

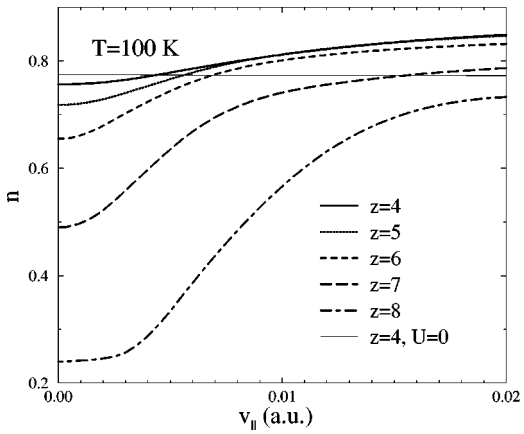

FIG. 4. Calculated steady-state atomic population for an atom moving parallel to the surface at several surface separations z and at the substrate temperature $T=100$ K.

magnitude of the Kondo resonance with increasing parallel velocity.

The above steady-state results are useful in interpreting the charge transfer in the actual atom-surface scattering situation, which we show in Fig. 5 as a function of the parallel velocity $v_{\parallel}$. We modeled the charge transfer the same way as we did in Fig. 1.

Depending on the normal velocity, the final charge distribution carries information about different spatial regions on the trajectory. For instance, at the slow velocity $v_z=0.003$ a.u., the tunneling is still efficient beyond the point where ϵ_{σ} crosses the Fermi energy ($z=7.25$ a.u.), and the final population thus resembles that of the steady-state system at $z=8$ a.u. (Fig. 4). At larger normal velocities, a region closer to the surface determines the final charge distribution as the tunneling rate Γ near the Fermi level crossing is too small to have significant effect on the outcome of the experiment. The onset of the parallel velocity dependence occurs at almost an order of magnitude slower $v_{\parallel}$ in the presence of electron correlations than in their absence. This is because the effect of parallel velocity is governed by the

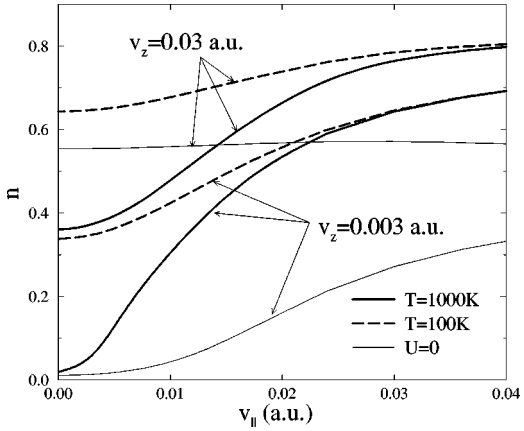

FIG. 5. Calculated population of the atomic level as a function of $v_{\parallel}$ for two substrate temperatures $T=100$ K and $T=1000$ K and two different values of the perpendicular velocity ($v_z=0.003$ a.u. and $v_z=0.03$ a.u.). We also show the $U=0$ system that shows negligible temperature dependence in this temperature range.

relation between the relevant level width and $v_\parallel k_F$. For the noninteracting system, this is the width of the broad atom-induced resonance near the point where ϵ_σ crosses the Fermi energy, which is of the order of 0.5 eV here. For the correlated system, this is the Kondo and mixed-valent resonances with their width of order T_K, typically much smaller than 0.5 eV.

Finally, we would like to point out that as the projectile velocities increase, memory effects may become important. When this happens, the charge transfer should be calculated using a realistic scattering trajectory and appropriate level shifts and broadenings. For large parallel and perpendicular velocities, one may then find that the final charge transfer may depend also on the initial state of the atom. We could not address the question of the memory effects within the current formalism, because the approximations employed here break down before the memory on the initial state becomes significant. A more general theory that will allow us to look into the issues relevant at higher velocities is currently being developed.

IV. CONCLUSION

In conclusion, we have investigated the effect of parallel velocity on the formation of a Kondo resonance when an atom is scattered against a surface. It is shown that the structure of the Kondo resonance depends sensitively on parallel velocity of the atom. It is shown that this dependence can be probed by studying charge transfer in atom-surface scattering experiments. Nevertheless, the anomalous temperature and velocity dependence persist to larger angles of incidence than the back-of-envelope estimates of Ref. 7 indicated, which should simplify the experimental detection of these effects.

ACKNOWLEDGMENTS

This work was supported in part by the National Science Foundation under Grants Nos. DMR 97-08499 (M.P.,D.C.L.) and DMR 95-21444 (P.N.).

APPENDIX: SIZE OF $\dot{\vec{\theta}}$

Here we give a simple expansion, which is not necessarily meant to be a working approximation, but is rather presented to suggest the magnitude of $\dot{\vec{\theta}}_{k,Q}$ relative to the the other terms in Eq. (7). Assuming as always that the surface is uncorrugated in the region important to the matrix element, the matrix element (3) may be written in the form

$$V_{\sigma,\vec{k},\vec{Q}}(\vec{R}) = \exp\left[-i\vec{k}\cdot\vec{R}_\parallel(t) + \frac{i}{2}\int^t Q^2(\tau)d\tau \right] \int dz h_{\vec{k}-\vec{Q}_\parallel}(z,Z)e^{iQ_z z}, \tag{A1}$$

where

$$h_{\vec{k}-\vec{Q}_\parallel}(z,Z) = \int d^2x_\parallel \psi^*_{\vec{k}-\vec{Q}_\parallel}(\vec{x}_\parallel, z+Z)v(\vec{r})\phi_\sigma(\vec{r}) \tag{A2}$$

may be taken real. We make a cumulant expansion of the matrix element (A1) in Q_z times the size of the region contributing to the matrix element. The lowest order term in this expansion, after comparison with Eq. (6), gives

$$\tilde{\theta}_{\vec{k},\vec{Q}} = Q_z \overline{z}_{\vec{k}-\vec{Q}_\parallel} \tag{A3}$$

with

$$\overline{z}_{\vec{k}} = \frac{\int dz z h_{\vec{k}}(z,Z)}{\int dz h_{\vec{k}}(z,Z)}, \tag{A4}$$

and $|V_{\sigma,\vec{k},\vec{Q}}(\vec{R})| = \int dz h_{\vec{k}-\vec{Q}_\parallel}(z,Z) \equiv V_{\sigma,\vec{k}-\vec{Q}_\parallel}(Z)$. The magnitude thus only depends on the distance Z from the surface and on the parallel velocity $\vec{Q}_\parallel$. Since $\dot{\bar{z}}_{\vec{k}} \propto Q_z$ (plus higher order terms), $\dot{\tilde{\theta}}$ makes a contribution to $\dot{\theta}$ of the same order as the preceeding term in Eq. (7).

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