Electronic bath approach to thermal effects in ion-surface scattering

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McDowell's 1985 electronic bath theory of charge transfer is used to investigate the effect of varying surface temperature on the process of ion scattering from a solid surface. As a specific example, the system of Na^+ scattered from W is modeled. The neutralization probability is found to have a significant temperature dependence only if the ion orbital energy is fairly close (within 1 eV) to the Fermi level, at closest approach. As well, the temperature effect is greatest when the ion's incident energy is small (on the order of a few eV). © *2000 American Institute of Physics.* [S0021-9606(00)70305-9]

I. INTRODUCTION

The mechanisms of charge transfer during ion scattering from solid surfaces have been extensively studied for a number of years.[1–3] However, most theoretical studies have considered only the situation of zero temperature, although experimental evidence indicates that charge-transfer probabilities are temperature dependent, at least under some conditions. In one investigation, Overbosch et al.[4] measured the neutral flux of Na atoms scattered from W(110) as a function of temperature. At relatively low incident energies (30 eV), a "huge" effect was observed, diminishing with increasing incident energy. The neutral fraction was always seen to increase with temperature. In another set of experiments, Bu et al.[5] measured the ion yields formed from scattering Na, K, and Cs atoms from a Si(111) surface. For small incident energies (< 3 eV), the ion yield was observed to rise with increasing temperature. However, when the incident energy was greater than 15 eV, the ion yield was seen to be effectively independent of temperature.

From a theoretical perspective, several approaches have been used. Overbosch et al.[4] used the rate equation approach to analyze their experimental data, and they found reasonable agreement between theory and experiment, except at low incident energy. Brako and Newns[6] worked with the equations of motion for the time-dependent Anderson–Newns Hamiltonian. The theory was found to be compatible with experiment, except at low temperatures.

Very recently, Merino and Marston[7] used the dynamical $1/N$ expansion method, primarily to study the Kondo effect, but also obtained ion fractions as a function of temperature. In looking at the situation of Ca atoms scattered from a Cu(001) surface, the ion yield was seen to increase with temperature. The drawback to their approach is that there is a very large set of differential equations to be solved numerically, which is computationally intensive. The above studies all modeled temperature effects by varying the occupancies of excited electronic states with temperature. One may speculate that thermal motion of substrate atoms may also make a contribution, but recent calculations[8] indicate that such effects are negligibly small.

The current study adopts the electronic bath approach of McDowell[9] to investigate the influence of temperature on the resonant charge-transfer process occurring during ion/atom scattering from a solid surface. The one-electron theory ignores nuclear motions in the solid, and is devised analogously to generalized Langevin theory. The specific system under study is that of Na ions, with incident energies of a few eV, scattered from a W surface, whose work function is varied to simulate partial covering by adatoms.

II. MODEL

The model used here is that formulated by McDowell,[9] with parameters chosen in order to simulate the scattering of Na^+ or Na^0 from W, with varying work function and surface temperature, at low incident kinetic energies. For brevity, we present here only the highlights of the method, and refer the reader to McDowell's paper[9] for the details of the derivations.

The starting point is the assumption that the system may be described by a one-electron Hamiltonian of the form

$$H(t) = \varepsilon_0 c_0^+(t) c_0(t) + V(t)[c_0^+(t) c_1(t) + c_1^+(t) c_0(t)]$$
$$+ \alpha \sum_{m=1}^{N} c_m^+(t) c_m(t) + \beta \sum_{m=1}^{N-1} [c_m^+(t) c_{m+1}(t)$$
$$+ c_{m+1}^+(t) c_m(t)], \tag{1}$$

where $c_m(t)[c_m^+(t)]$ is an annihilation (creation) operator for atomic orbital m, in the Heisenberg representation. The subscript 0 labels the sole orbital on the projectile, and subscript

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m labels those on the solid (with N large), with $m=1$ designating the target atom on the surface. It is assumed that the projectile orbital interacts only with that on the target atom. The Heisenberg equations of motion for the annihilation operators are

$$\frac{dc_m(t)}{dt}=i[H(t),c_m(t)]. \tag{2}$$

A direct approach is to attempt to solve Eq. (2) either analytically or numerically. As an alternative, McDowell proposed an ''electronic bath'' approach in which the Eq. (2) is reworked into a form similar to that seen in generalized Langevin theory. The idea is to separate the orbitals into those for the ion (which here consists of just one orbital), a primary zone (containing the p solid orbitals nearest the surface), and an electron bath (consisting of the remaining $N-p$ solid orbitals). The key feature of the method is that the differential equations for the orbitals in the bath are removed from the system (2), being replaced by a memory kernel and a driving term (which typically must be approximated).

McDowell's approach ultimately formulates equations of motion for ensemble-averaged number operators on the ion and in the primary zone, and these take the following form:

$$\frac{dn_{00}}{dt}=i\sum_{k=1}^{p}[H_{k0}(t)n_{k0}(t)-H_{0k}(t)n_{0k}(t)], \tag{3a}$$

$$\frac{dn_{i0}}{dt}=i(\varepsilon_i-\varepsilon_0)n_{i0}(t)+iH_{0i}(t)n_{00}(t)$$

$$-i\sum_{k=1}^{p}H_{0k}(t)n_{ik}(t)-\frac{1}{2}\sum_{k=1}^{p}w_{ki}^* n_{k0}(t), \tag{3b}$$

$$\frac{dn_{ij}}{dt}=i(\varepsilon_i-\varepsilon_j)n_{ij}(t)+i[H_{0i}(t)n_{0j}(t)-H_{j0}(t)n_{i0}(t)]$$

$$-\frac{1}{2}\sum_{k=1}^{p}[n_{ik}(t)w_{kj}+w_{ki}^* n_{kj}(t)]+w_{ij}N_{\varepsilon_{ij}}(T), \tag{3c}$$

with $n_{ji}^*=n_{ij}$. The initial conditions for (3) are

$$n_{00}(-\infty)=0, \tag{4a}$$

$$n_{0i}(-\infty)=n_{i0}(-\infty)=0, \tag{4b}$$

$$n_{ij}(-\infty)=\delta_{ij}N_{\varepsilon_{ij}}(T), \tag{4c}$$

where the Fermi–Dirac distribution is denoted by

$$N_{\varepsilon_{ij}}(T)=\{1+\exp[(\varepsilon_{ij}-\varepsilon_f)/bT]\}^{-1}. \tag{5}$$

In (5), b is the Boltzmann constant, ε_f is the Fermi level, and

$$\varepsilon_{ij}=(\varepsilon_i+\varepsilon_j)/2, \tag{6}$$

ε_i being the energy of the ith zone orbital. The set of equations (3) may be solved numerically. The main quantity of interest is the neutralization probability $P=n_{00}(\infty)$, representing the occupancy of the projectile orbital after scattering, with $P=0$ corresponding to positive ionization, and $P=1$ to neutralization.

The coefficients H_{0i} take the form

$$H_{0i}=H_{i0}=v_iV(t). \tag{7}$$

For the Huckel-type chain of length p, one obtains[9,10]

$$v_i=\left(\frac{2}{p+1}\right)^{1/2}\sin\left(\frac{i\pi}{p+1}\right), \tag{8}$$

$$w_{ij}=\frac{-4\beta}{(p+1)}\sin\left(\frac{pi\pi}{p+1}\right)\sin\left(\frac{pj\pi}{p+1}\right)\left[1-\left(\frac{\varepsilon_{ij}-\alpha}{2\beta}\right)^2\right]^{1/2}, \tag{9}$$

$$\varepsilon_i=\alpha+2\beta\cos\left(\frac{i\pi}{p+1}\right). \tag{10}$$

As indicated earlier, the system to be modeled here is Na^+-W. To this end, the parameters α and β are chosen to have values of -5 and -1.75 eV, respectively, to reproduce the band edges of W.[11] The interaction potential is taken to have the form[12]

$$V(t)=V(z(t))=Fz(t)\exp(-\mu z(t)), \tag{11}$$

where F is a constant force, given by (13) below, and $z(t)$ is the projectile trajectory, assumed to have Born–Mayer form[13] given from

$$\exp(2az(t))=(A/K)\cosh^2(avt), \tag{12}$$

with $K(v)$ the initial kinetic energy (speed) of the projectile. The Born–Mayer inverse-length and energy parameters have the values[14] $2a=1.9232$ a.u. and $A=517.63$ a.u., respectively. The interaction parameters in (11) have values given from the rules

$$F=(I_0I_1)^{1/2}, \tag{13}$$

$$2\mu=(2I_0)^{1/2}+(2I_1)^{1/2}, \tag{14}$$

where the ionization potentials are $I_0=0.1889$ a.u. for Na and $I_1=0.2933$ a.u. for W. These give $F=0.162$ a.u. and $\mu=0.69$ a.u. To simulate image effects, the ion orbital energy ε_0 is given a dependence on the ion-surface separation z, namely

$$\varepsilon_0(z)=\frac{1}{4z}-I_0. \tag{15}$$

For the calculations reported here, a primary zone of size $p=20$ was found to be large enough to produce convergent results. The results were found to be independent of the value of the initial condition (4a), namely 0 for Na^+ or 1 for Na^0, which shows the ''memory-less'' nature of the system.

III. RESULTS AND DISCUSSION

Several calculations were made using the model of Sec. II, and some representative results are presented here. The surface temperature T was varied in the range 0 to 2000 K. The Fermi level ε_f was varied from -6 to -1.5 eV, to simulate partial coverages of the surface by adsorbates. Several incident kinetic energies K were used, although the most noticeable effect was observed for the lowest ($K=5$ eV in this work).
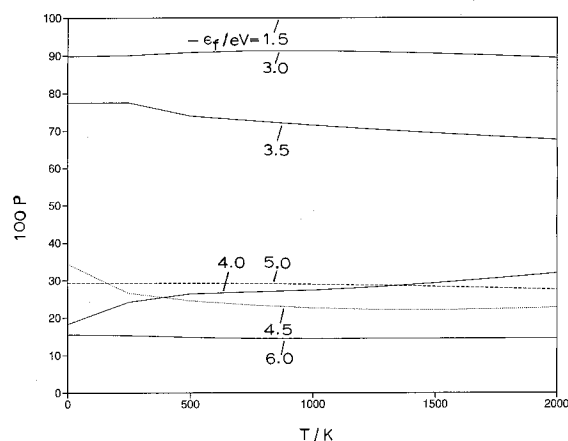
FIG. 1. Neutralization probability P, expressed as a percentage, versus temperature T, with projectile kinetic energy $K=5$ eV, for various Fermi levels ε_f as marked.

FIG. 2. As in Fig. 1, but with $K=25$ eV.

Figure 1 shows the neutralization probability P, expressed as a percentage, as a function of temperature, for several values of ε_f, and with $K=5$ eV. Most immediately obvious is the fact that P is essentially independent of T, for most values of ε_f. The exceptions occur when $\varepsilon_f=-4$ and -4.5 eV, where it is seen that P is a more strongly varying function of T. (More precisely, the variation in P is about 12% to 14%.) For other values of ε_f, the variation in P is less than 2%. Another obvious feature is that, for low Fermi levels ($\leqslant-4$ eV), the neutralization probability is small (less than 40%), while, for high Fermi levels ($\geqslant-3$ eV), it is large (greater than 90%). Thus, as ε_f is varied from -4 to -3 eV, P increases rapidly, regardless of temperature.

In order to understand these features, it is important to recognize that the ion orbital interacts mainly with solid orbitals of approximately the same energy. As the ion scatters from the surface, its orbital energy ε_0 (15) varies between -5.14 and -3.5 eV, so states in the solid in that energy range need to be considered. We look first at the situation where $T=0$. When the Fermi level is low (e.g., -6 eV), the states with energies in the most interactive range are unoccupied and, since $\varepsilon_0 > \varepsilon_f$, the tendency for any electron on the projectile is to transfer into a (lower-energy) orbital in the solid, so the neutral fraction tends to be low. As the Fermi level is raised (e.g., -5 eV), the most interactive states start to become filled, thereby dampening this effect, and raising P. When the Fermi level has become high (e.g., -3 eV), the states in the interactive range are all filled; then, if the projectile orbital is empty, there is a high probability that an electron from the solid will transfer to it, thereby neutralizing it, and P is expected to be large.

We turn now to the case where $T>0$. Here, the location of the Fermi level is of the utmost importance. This is because, as T increases, only states near the Fermi level have their occupancies change appreciably [as may be seen from the Fermi–Dirac distribution (5)]. States not near the Fermi level will have the same occupancies (either 0 or 1) at all temperatures under consideration here. Therefore, a temperature effect is expected to occur only when the states near the Fermi level are heavily involved in the charge-transfer pro-
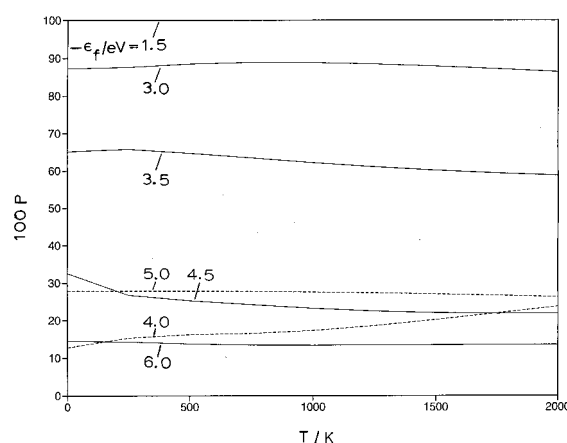
cess, that is to say, strongly interacting with the ion orbital. As we have seen, this situation occurs when $|\varepsilon_f-\varepsilon_0|$ is small. When $|\varepsilon_f-\varepsilon_0|$ is large, the ion orbital has little interaction with the states near the Fermi level, and so the charge-transfer process should be essentially independent of the temperature. This is clearly seen to be the case in Fig. 1, for both $\varepsilon_f \geqslant -3$ eV and $\varepsilon_f \leqslant -5$ eV.

In the case where $|\varepsilon_f-\varepsilon_0|$ is fairly small, the ion orbital interacts strongly with states near the Fermi level (whose occupancies change considerably with T), and thus a noticeable temperature effect should be observed. The results in Fig. 1 confirm this expectation ($\varepsilon_f=-3.5, -4, -4.5$ eV), as the neutralization probability P is seen to change by 10% or more, as T varies from 0 to 2000 K. Interestingly, it is seen that P may be either an increasing or decreasing function of T, depending upon the value of ε_f. As T increases, states just above the Fermi level have their occupancies increased, while those just below the Fermi level have theirs decreased. All these states are interacting strongly with the ion state: the occupied states tend to increase P and the unoccupied ones tend to decrease P; the states which prove to be dominant determine the final value of P.

The effect of increasing the projectile's kinetic energy K to 25 eV is shown in Fig. 2. It is seen that the situation is qualitatively the same as for $K=5$ eV, although the variation in P with temperature is somewhat smaller. Increasing K further, e.g., to 100 eV (not shown), produces a further decrease in the temperature effect.

It may be noticed that the values of P in Fig. 2 are about the same as, or slightly lower than, the corresponding values in Fig. 1, except for the cases $\varepsilon_f=-3.5$ and -4 eV, where they are substantially lower. To understand this feature, we must keep in mind the earlier point about the value of P being determined by the size of $|\varepsilon_f-\varepsilon_0|$, and also note that (15) implies that ε_0 depends on K, because the trajectory $z(t)$ does. When $\varepsilon_0(\infty)$ is well below the Fermi level (as happens when $\varepsilon_f=-1.5$ eV, for example), then $\varepsilon_0(z)$ also stays well below the Fermi level throughout the interaction, and a high neutralization probability results. If $\varepsilon_0(\infty) \ll \varepsilon_f$, then this occurs essentially independently of the value of K, so P does not vary much with K. A similar argument may be

made when $\varepsilon_0(\infty) \gg \varepsilon_f$ to conclude that here also P should not depend strongly on K. It is only when $\varepsilon_0(z)$ is close to ε_f, for at least part of the interaction, that the value of P has a stronger dependence on ε_0, and hence on K, resulting in significant variation of P with K. This situation occurs for the intermediate values of ε_f (-3.5 and -4 eV in our figures).

We can make a comparison to the experimental results of Overbosch et al.[4] (specifically their Fig. 3), although a quantitative comparison is hampered by the fact that their detector could measure the neutral flux in only arbitrary (not absolute) units. The experiments[4] suggest that the temperature effect is quite large for $K = 30$ eV, and becomes smaller for larger K. On the other hand, the theory here shows a more modest-sized effect, even for smaller K, but agrees with experiment regarding the decrease of the effect for larger K. In the experiments,[4] the neutral fraction always increases with T, but they were done with a fixed Fermi level (about -5.2 eV). The theory here suggests that a richer variety of behavior is possible, depending on the position of the Fermi level.

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