Thermal effects on charge transfer in atom-surface scattering

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(Received 26 June 2000; accepted 16 November 2000)

This paper studies the effect of varying substrate temperatures on the resonant charge-transfer process between a scattered particle and a solid surface. Two possible mechanisms for an effect are considered: (1) coupling of the transferring electron to the thermal motion of the target atom on the surface, and (2) changing occupancies of electron orbitals in the solid as temperature varies. Only the latter is found to give a noticeable effect, occurring when the electronic energy level on the projectile is favorably positioned relative to the Fermi level of the target solid. However, even though this effect is noticeable, both mechanisms we consider give very small thermal effects. All other mechanisms, for example those leading to the Kondo (or mixed-valent) effect, are neglected.
 [DOI: 10.1063/1.1339283]

I. INTRODUCTION

Charge-transfer processes occurring between ions (or atoms) and solid surfaces during scattering have received considerable attention recently.[1–5] In one experiment,[6] Overbosch *et al*. investigated the ionization of Na atoms scattered by a W(110) surface as a function of incident kinetic energy K and of surface temperature T. The main observation was that the fraction of surviving neutrals increases with T, with the effect being largest for lower values of K ($\sim$30 eV). Theoretical treatments of this phenomenon have been given, using the rate equation[6] and one-electron equations of motion,[7] and discrepancies with the experimental results were found for low K in the former calculations and for low T in the latter. In another experiment,[8] Bu *et al*. studied the ionization of alkali atoms scattered by the Si(111) and Pt surfaces, also as a function of K and T. They found that the ionic yields have very little dependence on T for K greater than about 15 eV, while, for lower values of K (less than about 3 eV) the ion yields increase with increasing T. They presented a classical model of the process, finding good agreement with their experiments.

The calculations of Brako and Newns, referred to above,[7] incorporated temperature effects by allowing substrate electron states above the Fermi level to become occupied according to the usual Fermi–Dirac distribution. Sulston and Goodman[9] have recently used an electronic bath approach to study thermal effects. They found that the ion neutralization probability has a significant temperature dependence only if the ion orbital energy is close (within 1 eV) to the Fermi level, at closest ion-surface approach; they also found the thermal effects to be greatest when the ion's incident energy is small (a few eV). A different candidate for a contribution was suggested by Sulston and Davison,[10] and that is from the coupling of the thermal motion of the substrate atoms to the substrate electrons. Their preliminary estimates indicate that the motion of the target atoms, due to recoil, may have a measurable effect on charge-transfer probabilities.

A rigorous, many-body treatment of temperature effects is intractable, and even a good approximation to such a treatment would be very difficult to formulate. It is the purpose of this paper to present a simple theoretical treatment of the two thermal effects mentioned above: we christen the effect of the smoothing out of the band-level distribution around the Fermi level ''the Fermi effect,'' and the effect of the atom–electron coupling ''the recoil effect.'' We begin by building a ''two-level model'' of the charge-transfer process, in which the substrate supports a single electronic level. Effects of the actual substrate band structure are then approximated by averaging the two-level results over the band levels, thus neglecting all in-band electronic processes. Double occupancy of the single level is neglected in this simple treatment, but some account of spin effects is taken [see the extra factors of $2^{1/2}$ in (2.9) below].[11,12] Also neglected here is the intra-atomic Coulombic repulsion, which is the essential ingredient of the Kondo (or, more generally, the mixed-valent) effect.[13–15] The projectile–target interaction is modeled by a head-on collision, and all atomic motion is considered to be one-dimensional.

II. THE TWO-LEVEL MODEL

A. Quantum-mechanical treatment of the oscillator

A point projectile, of mass m_p, speed v, and kinetic energy K, is incident, in a one-dimensional head-on manner, on a substrate target atom, of mass m_t. The thermal properties of the substrate are modeled by joining the target atom to the remainder of the substrate by a spring, forming an oscillator of frequency ω. The phonon occupation number of the oscillator is p, giving it an energy of $(p+\frac{1}{2})\hbar\omega$.

We word the analysis in terms of a ''hole model,'' ''hole'' meaning ''absence of electron'' as usual: we assume that the hole is initially (time $t=t_0$) on the projectile level 0,

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and is able to move to the target level k. States are denoted by $|lp\rangle$, $|lp+1\rangle$, etc., where $l=0$, k means that the hole is on the projectile, target level respectively, and p is a non-negative integer denoting the oscillator state; the notation is that $|lp\rangle$ stands for $|l,p\rangle$ and $|lp\pm1\rangle$ for $|l,p\pm1\rangle$.

Where n_k is the hole occupation number of the (single) level k, our Hamiltonian $\mathcal{H}(t)$ is defined by

$$\mathcal{H}(t)=E+V(t)+\Lambda n_k x-F(t)x, \tag{2.1}$$

where x is the position of the oscillator; the four terms in our Hamiltonian (2.1) arise as follows:

(1) E is the unperturbed energy of the system;
(2) $V(t)$ is the ''hopping'' energy perturbation which allows the hole to move between the projectile and target levels, that is transitions between states $|0p\rangle$ and $|kp\rangle$;
(3) $\Lambda n_k x$ is the perturbation which is the origin of the recoil effect. The presence of the factor n_k means that it acts only when the hole is on the target, and it then allows the phonon occupation number to change (by ±1), that is transitions between states $|kp\rangle$ and $|kp\pm1\rangle$. It corresponds to a force, $-\Lambda n_k$, on the target (presence of the hole on the target tends to force the target to the left, that is away from the solid, if $\Lambda>0$). Alternatively, one may assume that the recoil perturbation acts only when the hole is on the projectile, in which case the n_k in (2.1) is replaced by n_0, the hole occupation number of the level 0. We have done calculations using both assumptions, and there is no qualitative difference between the two;
(4) $-F(t)x$ is a perturbation similar to $\Lambda n_k x$, except that it acts independently of the location of the hole, that is it allows transitions between states $|lp\rangle$ and $|lp\pm1\rangle$ with either value (0 or k) of l. It corresponds to the mutual projectile-target force ($F(t)$ on the target and $-F(t)$ on the projectile), and is usually assumed to be non-negative. Its effect on the projectile is to reverse its momentum in a classical manner, and it is assumed to be given *a priori*, derived from a projectile trajectory, which is in turn derived from a projectile–target interaction potential.

If we define $\phi(t)$ and λ by

$$\phi(t)=(\hbar/2m_t\omega)^{1/2}F(t), \tag{2.2}$$

$$\lambda=(\hbar/2m_t\omega)^{1/2}\Lambda, \tag{2.3}$$

then the nonzero matrix elements of the Hamiltonian (2.1) are obtained from its symmetric property and from the following four results:

$$\langle lp|Fx|lp-1\rangle=p^{1/2}\phi, \tag{2.4}$$

$$\langle kp|\Lambda n_k x|kp-1\rangle=p^{1/2}\lambda, \tag{2.5}$$

$$\langle lp|E|lp\rangle=\varepsilon_0+\varepsilon_k-\varepsilon_l+(p+\tfrac{1}{2})\hbar\omega, \tag{2.6}$$

$$\langle 0p|V|kp\rangle=V, \tag{2.7}$$

with all other matrix elements equal to zero.

The equation of motion for the amplitudes a_{lp} is

$$i\hbar\dot{a}_{lp}=\sum_{l'p'}\langle lp|\mathcal{H}|l'p'\rangle a_{l'p'}, \tag{2.8}$$

where the dot denotes a time derivative.

Using (2.1) with (2.4)–(2.8), we get

$$i\hbar\dot{a}_{0p}=(p\hbar\omega-\varepsilon_0)a_{0p}+2^{1/2}Va_{kp}-\phi(p^{1/2}a_{0p-1}-(p+1)^{1/2}a_{0p+1}), \tag{2.9a}$$

$$i\hbar\dot{a}_{kp}=(p\hbar\omega-\varepsilon_k)a_{kp}+2^{1/2}Va_{0p}-(\phi-\lambda)(p^{1/2}a_{kp-1}-(p+1)^{1/2}a_{kp+1}), \tag{2.9b}$$

where the extra factor of $2^{1/2}$ has been inserted in order to take account of spin effects in the solid;[11,12] also $(\varepsilon_0+\varepsilon_k+\frac{1}{2}\hbar\omega)a_{0p}$ has been subtracted from the right-hand side of (2.9a), and $(\varepsilon_0+\varepsilon_k+\frac{1}{2}\hbar\omega)a_{kp}$ from the right-hand side of (2.9b), for convenience (these subtractions make no difference to any results).

The initial conditions, at $t=t_0$, are such that the hole is on the projectile, and the modal occupancy is p_0, that is

$$a_{lp}(t_0)=\delta(l,0)\,\delta(p,p_0)e^{i\xi}, \tag{2.10}$$

where δ denotes the Kronecker delta function, and ξ is a real, but otherwise arbitrary, phase angle.

Actual calculations proceed as follows. A maximum value, $p_{\max}$, of p is chosen, and the equation (2.9), with (2.10) borne in mind, are integrated numerically over a time interval which contains the interval during which $V(t)$ and/or $F(t)$ are/is non-negligible, with $p_{\max}$ chosen sufficiently large in order that appropriate convergence is obtained. The most useful check on the results is the unitarity check, which is based on the physical requirement that

$$\sum_{l,p}|a_{lp}(t)|^2=1. \tag{2.11}$$

All physical information is contained in the values of $|a_{lp}(\infty)|^2$, that is the values of $|a_{lp}|^2$ after both $V(t)$ and $F(t)$ have finally become negligible. For example, the charge-transfer probability, P_k, that is the probability that the hole has moved from the projectile to the target, is given by

$$P_k=\sum_p|a_{kp}(\infty)|^2. \tag{2.12}$$

If the oscillator is initially in thermal equilibrium at temperature T, then results must be averaged over the appropriate distribution, $f(p_0)$ of p_0

$$f(p_0)=(1-e^{-\hbar\omega/bT})e^{-p_0\hbar\omega/bT}, \tag{2.13}$$

where b is the Boltzmann constant. The oscillator frequency ω is chosen on the basis of some ''characteristic surface vibration temperature,'' Θ_c, say an ''effective Debye temperature,'' using the usual prescription[16]

$$\hbar\omega=b\Theta_c. \tag{2.14}$$

B. Semiclassical treatment of the oscillator

1. Rationale for a semiclassical treatment

Because the phonon energy $\hbar\omega$ is much less than typical vibrational energy transfers in the problem, many phonons participate in the scattering process, which implies that large values of $p_{\max}$ are necessary for convergence in the quantum-mechanical model. As a result, the calculations, while always converging nicely for sufficiently large $p_{\max}$, are sometimes rather time-consuming.

For example, if the mass ratio m_p/m_t is denoted by ρ, then the energy transfer, ΔE, from projectile to target is given approximately, for sufficiently large K, by[17] $\Delta E = 4\rho K/(1+\rho)^2$. The phonon energy (2.14) is $b\Theta_c$, and so we expect that $p_{\max}$ must be considerably larger than $p_{\min}$:

$$p_{\max} \gg p_{\min} = \frac{4\rho K}{(1+\rho)^2 b\Theta_c}. \tag{2.15}$$

For Na^+ incident on a W surface, with $K=5$ eV and $\Theta_c = 250$ K,[18] say, we have[19] $p_{\min} \approx 90$.

2. The model

The position and momentum of the target oscillator are denoted by x and y, respectively. The amplitudes a_{lp} become simply a_l, the oscillator being treated classically, and the equations of motion (2.9) become

$$i\hbar\dot{a}_0 = 2^{1/2}Va_k - \varepsilon_0 a_0, \tag{2.16a}$$

$$i\hbar\dot{a}_k = 2^{1/2}Va_0 - (\varepsilon_k - \lambda x)a_k. \tag{2.16b}$$

These equations of motion must, of course, be supplemented by the classical equations of motion of the oscillator

$$\dot{y} = f - m_t\omega^2 x - \lambda|a_k|^2, \tag{2.17a}$$

$$\dot{x} = y/m_t. \tag{2.17b}$$

The analog of (2.10) for the initial conditions for (2.16) is

$$a_l(t_0) = \delta(l,0)e^{i\xi}, \tag{2.18}$$

and the initial conditions for (2.17) are

$$y(t_0) = Am_t\omega\cos\beta, \tag{2.19a}$$

$$x(t_0) = A\sin\beta, \tag{2.19b}$$

where β is the oscillator phase angle, and A is the oscillator amplitude,

$$A = (2p_0\hbar/m_t\omega)^{1/2}, \tag{2.20}$$

where p_0 is again the ''initial modal occupancy,'' now giving initial modal energy $p_0\hbar\omega$. The averaging over p_0 is now done via

$$f(p_0) = (\hbar\omega/bT)e^{-p_0\hbar\omega/bT} = (\Theta_c/T)e^{-p_0\Theta_c/T}, \tag{2.21}$$

rather than (2.13), and results must also be averaged over β, which is distributed uniformly over the interval $0 \leqslant \beta < 2\pi$.

The charge-transfer probability formula (2.12) becomes

$$P_k = |a_k(\infty)|^2 = 1 - |a_0(\infty)|^2, \tag{2.22}$$

which is also a special case ($t=\infty$) of the analog of the unitarity check (2.11).

C. An (N+1)-level model

When studying the recoil effect, we have done some calculations in which the number of electronic levels on the target is allowed to be large (N), in order to check that the qualitative predictions of the two-level model ($N=1$) are correct. Resulting modifications to the results above are as follows. In (2.9a), a_{kp} is replaced by $\Sigma_{k=1}^N v_k a_{kp}$; in (2.16a), a_k is replaced by $\Sigma_{k=1}^N v_k a_k$; in (2.17a), $|a_k|^2$ is replaced by $\Sigma_{k=1}^N |v_k a_k|^2$. The v_k are the ''level strengths,'' obeying[11,12]

$$\sum_{k=1}^N v_k^2 = 1. \tag{2.23}$$

Our (N+1)-level model (without the phonon terms) is essentially the Brako–Newns ''1/N'' model[20] with ''U'' $=\infty$, ''N'' $=2$ (the physical case), a reduced basis set (no electron–hole pairs), and incorporating a nonzero T.

D. The hopping potential $V(t)$ and the force $F(t)$

We use a standard approximation for $V(t)$,[10–12] that is,

$$V(t) = \bar{F}z(t)\exp(-\mu z(t)), \tag{2.24}$$

where μ and $\bar{F}$ are constants and $z(t)$ is the projectile trajectory, governed by a Born–Mayer potential, $V_{\mathrm{BM}}(z)$, between projectile and target

$$V_{\mathrm{BM}}(z) = A\exp(-2az), \tag{2.25}$$

in which A and $2a$ are the usual BM-potential parameters (we use $2a$ because our a is then the closely related Morse-potential parameter). The trajectory $z(t)$ is given from classical mechanics,[11,12] that is, from

$$\exp(2az(t)) = (A/K)\cosh^2(avt). \tag{2.26}$$

E. The recoil and Fermi effects

The recoil effect is the presence of nonzero λ in (2.9) or (2.16b) and (2.17a), that is, nonzero Λ in the Hamiltonian (2.1); see subsection 3 in Sec. II A above. The Fermi effect is the averaging of the basic two-level results P_k over a realistic density of states, according to the usual Fermi distribution, which is, in some sense, a simplification of the methodology used in Ref. 9. Roughly speaking, the contribution of each level k is governed by the level strength v_k,[10–12] which may be expected to enter a level-averaged probability, P, in the form v_k^2, on account of (2.23). Accordingly, we assume that P may be approximated by the following averaging formula:

$$P = \sum_{k=1}^N v_k^2 P_k[\exp((\varepsilon_k - \varepsilon_f)/bT) + 1]^{-1}, \tag{2.27}$$

where ε_f is the Fermi energy and N is the number of electron levels. The electron band is assumed to occupy the energy region between the band bottom, ε_b, and the band top, ε_t, with $\varepsilon_b < \varepsilon_f < \varepsilon_t$; in other words, the Fermi level lies inside the band, which is of width $B = \varepsilon_t - \varepsilon_b$.

Using several approximations, the authors have obtained an analytical expression for the Fermi effect, in the absence

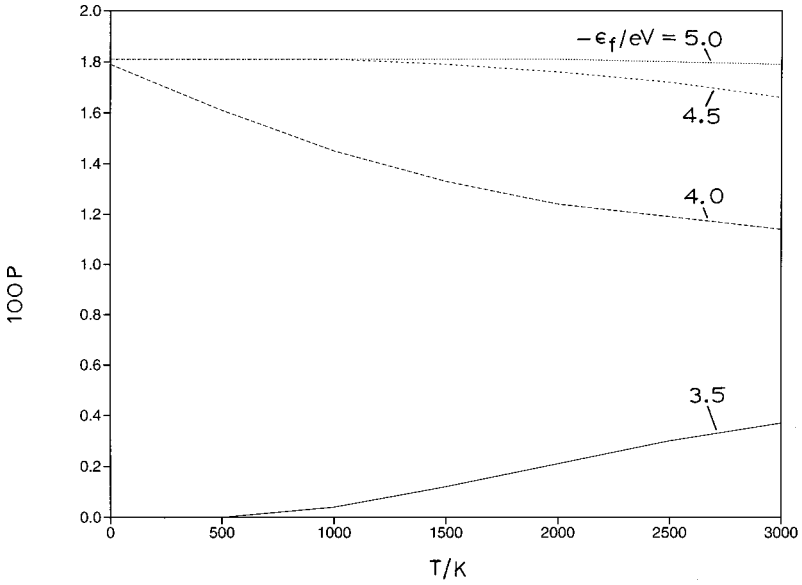

FIG. 1. Charge-transfer probability P (as percentage) versus temperature T for four different values of the Fermi energy ε_f. The kinetic energy of the projectile is $K=25$ eV.

of the recoil effect ($\lambda=0$). Where the T dependence of P is made explicit by writing $P\equiv P(T)$, the result is

$$P(T)-P(0)=\frac{2V^2}{(\epsilon_f-\varepsilon_0)B}\left(1-\frac{\beta}{\sinh\beta}\right)\frac{\sin\alpha}{\alpha}, \quad (2.28a)$$

where α, β are defined by

$$\alpha=(\tau/\hbar)((\varepsilon_f-\varepsilon_0)^2+4V^2)^{1/2}\gg 1, \quad (2.28b)$$

$$\beta=\frac{\pi(\tau/\hbar)(\varepsilon_f-\varepsilon_0)bT}{((\varepsilon_f-\varepsilon_0)^2+4V^2)^{1/2}}<\pi. \quad (2.28c)$$

In (2.28), V is the maximum value of V from (2.24), and τ is the interaction time which would result if the projectile–target repulsive force were constant and equal to the maximum Born–Mayer force from (2.25). The validity of (2.28) is restricted to the conditions written explicitly therein.

Both inequalities in (2.28) are generally valid in our applications. Typically, τ is several hundred times the atomic time unit (about 2.4×10^{-17} s), which validates (2.28b); values of T are very small compared to the atomic temperature unit (about 3.2×10^5 K), which serves to overcome the effect of large τ in (2.28c).

III. PARAMETERS AND CALCULATIONS

A. Parameters

We fix our parameters generally as described in Refs. 10–12 so as to model Na^+ scattered from W. The band energies are $\varepsilon_b=-8.09$ eV and $\varepsilon_t=-1.47$ eV, and the Fermi energy, when not being varied, is $\varepsilon_f=-4.55$ eV. (Note that ε_f is controllable, to some extent, due to the fact that the work function may be changed by partially covering the surface with impurity adatoms.) We sometimes fix ε_0 at -4.11 eV, and sometimes let it be a function of t, to capture some image effects, as described in Ref. 11. The Na–W Born–Mayer parameters A,a are calculated from those for the Na–Na and W–W interactions using standard combination rules,[21] and we get $A=14.1$ keV, $2a=3.63$ Å^{-1}.

We estimate the parameters μ and $\bar{F}$ as before[10–12] from empirical formulas of Ref. 22

$$2\mu l_c E_c^{1/2}=(2I_0)^{1/2}+(2I_k)^{1/2}, \quad (3.1)$$

$$\bar{F}=\mu(I_0I_k)^{1/2}, \quad (3.2)$$

where I is ionization potential and l_c, E_c are atomic units of length (≈0.53 Å) and energy (≈27 eV). Using[23] $I_0=5.14$ eV, $I_k=7.98$ eV, we get $\mu=1.304$ Å^{-1}, $\bar{F}=8.35$ eV/Å.

Suggested values[18] for Θ_c cover a large interval, and we generally use either $2^{1/2}\Theta_c=320$ K or $2^{1/2}\Theta_c=380$ K, the factor $2^{1/2}$ originating from the empirical rule that characteristic bulk vibration temperatures are expected to be about $2^{1/2}$ times their surface counterparts.

The recoil parameter Λ is difficult to estimate. When not being varied, $\Lambda=64$ meV is chosen, the same value as used in Ref. 10 for the Li–W system. The important point here is not so much finding an accurate value for Λ, but rather using values of the correct order of magnitude. Tsukada's[24] parameter η corresponds essentially to our Λ, but we regard his chosen value $\eta=E_c/10^{1/2}\approx8.6$ eV to be a considerable overestimate.

B. Calculations

Results for the charge-transfer probabilities, and for the energy transfers, from the quantum-mechanical model of Sec. II A and the semiclassical model of Sec. II B always agree closely (well within $\pm1\%$). Because both models give essentially the same results, the semiclassical model is of course used the most.

With both the recoil and Fermi effects ''turned on,'' typical results for kinetic energies K in the tens of eV range, over the range of all possible values of T, are shown in Fig. 1, for which $K=25$ eV. Partly in order to make sure that the small resulting values of P were not due merely to a choice of Fermi level ε_f, several such levels were chosen, and results for four typical ones are shown.

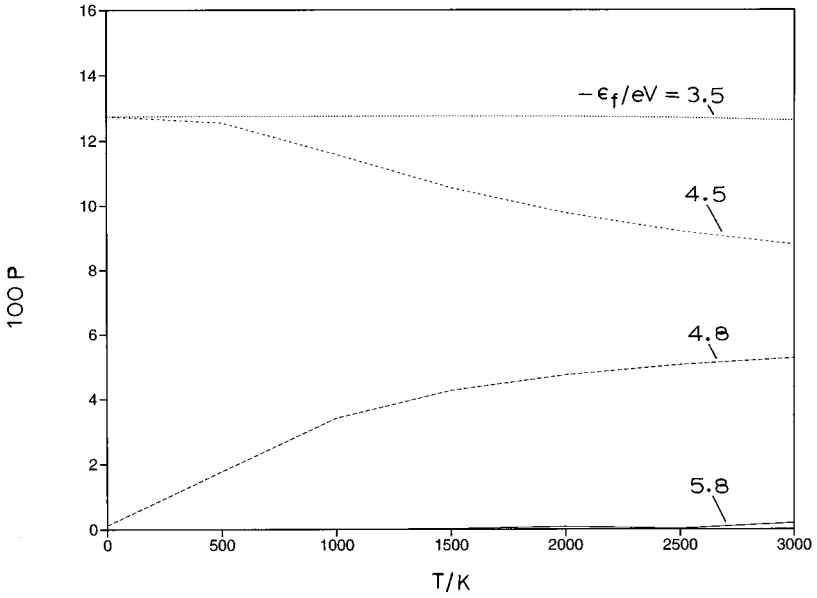

FIG. 2. As in Fig. 2, except that $K=5$ eV.

One may guess on intuitive grounds that smaller values of K should lead to larger temperature effects, so we studied effects of reducing K. Intuition is borne out, particularly for K less than 1 eV. However, the lowest reasonably accessible experimental values of K are probably around 2 eV, and results for $K=5$ eV, again for four typical values of ε_f over the range of all possible values of T, and with both effects in operation, are shown in Fig. 2.

The recoil effect, in the absence of the Fermi effect, was investigated next, with typical results for $K=5$ eV, with $T=0$ and 3000 K, shown in Fig. 3. Our estimates of Λ are of order 60 meV (Sec. III A), and we show results over a somewhat wider range of values. Qualitatively similar results are obtained for all reasonable parameter choices. Tsukada's choice[24] $\Lambda \approx 8.6$ eV leads to a much larger difference between the results at these two temperatures, as may be expected, but, as we have said above, we regard this choice as a considerable overestimate.

Figure 4 serves two purposes, that is to present results for the Fermi effect, in absence of the recoil effect, and to investigate the accuracy of the analytical approximation (2.28). Because of the form of (2.28), we present the results in terms of the difference between the two values of P at $T=0$ and $T=3000$ K, shown as a function of the Fermi energy ε_f; $K=2$ eV has been chosen in order to essentially maximize the effect while still remaining in a feasible parameter space.

IV. CONCLUSIONS

A key parameter in determining the importance of the Fermi effect is the position of ε_f relative to that of ε_0 (at or near closest approach). Only states with energies ε_k close to ε_f will have their occupancies changed appreciably as T increases, echoing similar conclusions already made in Ref. 9. Therefore, it is these states, near the Fermi level, which must

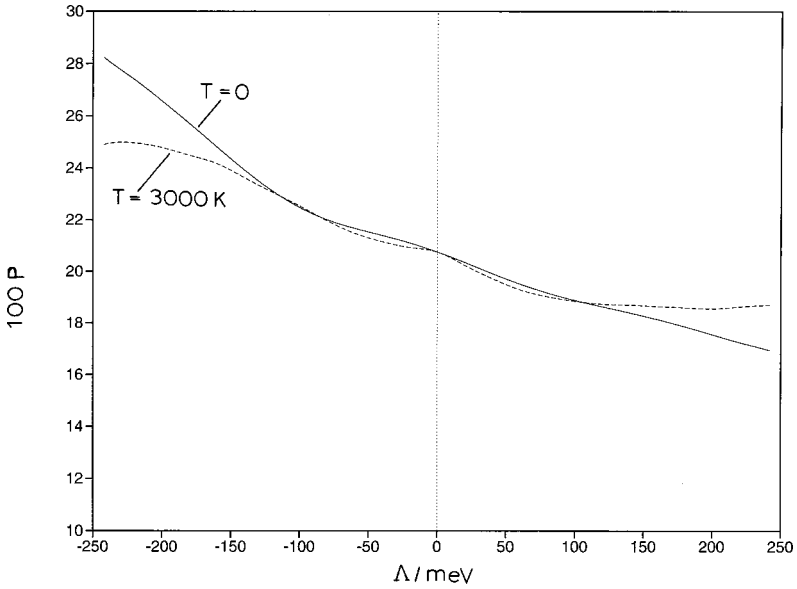

FIG. 3. Charger-transfer probability P (as percentage) versus the recoil parameter Λ for $T=0$ and 3000 K. The kinetic energy of the projectile is $K=5$ eV.

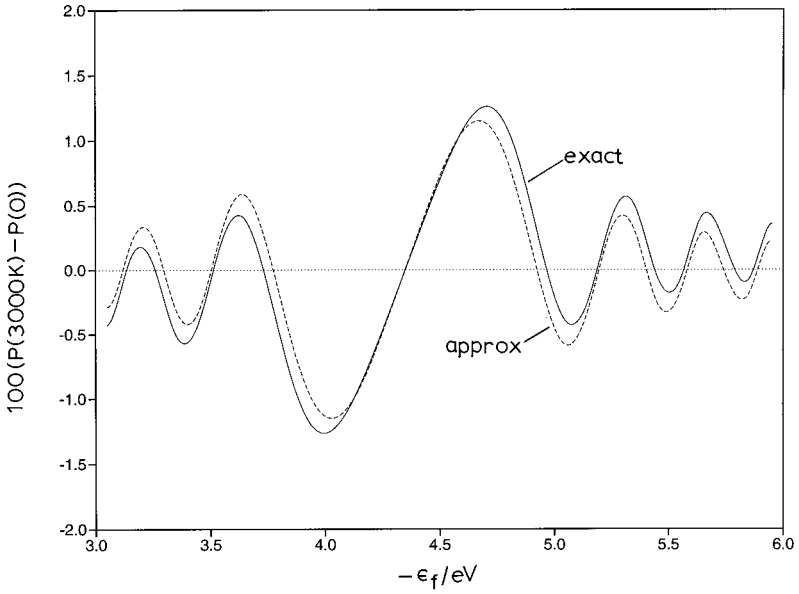

FIG. 4. Charge-transfer probability difference $P(3000\,\mathrm{K})-P(0)$ (as percentage) versus Fermi energy ε_f. The analytical approximation (2.28) is compared with ''exact'' results. The kinetic energy of the projectile is $K=2$ eV.

be responsible for any temperature effect. If $|\varepsilon_f-\varepsilon_0|$ is too large, then the interaction between the projectile state and those near the Fermi level will be small for the parameters used here, and little charge transfer between them will occur at any temperature. It is only when $|\varepsilon_f-\varepsilon_0|$ is small that significant interaction may occur, resulting in the possibility of charge-transfer probabilities with noticeable temperature dependence.

The sign of dP/dT depends on the position of the Fermi level relative to the set of band states which interact most strongly with the projectile (for our parameters, those states lie approximately in the range -4.7 to -4.6 eV). When ε_f is below the ''interactive state levels,'' those states are unoccupied at $T=0$ and thus contribute nothing to P: as T increases, some occupation of those states occurs, and they start to contribute to P. When ε_f is above the interactive state levels, this mechanism is reversed: at $T=0$ they are fully occupied, making their maximum possible contribution to P; as T increases, the occupancy drops, as does their contribution to P. In any event, the Fermi effect is small for the parameters used here, as is clear from Figs. 1 and 2, and most particularly Fig. 4, being at most a few percent, even for the smallest studied values of K. Our analytical approximation (2.28) for the Fermi effect is clearly qualitatively excellent (Fig. 4), although the smallness of the effect itself must be borne in mind. The recoil effect is very small, even smaller than the Fermi effect, as is clear from Fig. 3, the variations being of order 0.1%, even for the small values of K.

Our main conclusion is that the two mechanisms which we have considered in this paper give very small, but noticeable in the case of the Fermi effect, effects on charge-transfer probabilities during atom-surface scattering. Any larger thermal effects must originate from mechanisms other than the two considered here.

ACKNOWLEDGMENT

The work was supported by the Natural Sciences and Engineering Research Council of Canada.

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[17] Reference 16, Sec. 10.5.2.
[18] Reference 16, Sec. 10.7.5.
[19] Initial average phonon occupation numbers, $\langle p_0\rangle=(e^{\Theta_c/T}-1)^{-1}\approx T/\Theta_c$, are negligible compared to this value of $p_{\min}$; even at $T=3000$ K, $\langle p_0\rangle$ is only about 12.
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