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One- and Two-Electron Transfer Processes in Ion-Surface Scattering

by

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ONE- AND TWO-ELECTRON TRANSFER PROCESSES IN ION-SURFACE SCATTERING

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Abstract

A phenomenological description of one-electron transfer leading to ion neutralization in ion-surface scattering is summarized. A perturbative treatment using an effective interaction in the Anderson-Newns Hamiltonian is then reviewed, and the conditions under which the perturbative series has fast convergence are explored in terms of the electronic and dynamical properties of the collision system. Computational results are discussed for proton neutralization at different alkali-halide surfaces. In the case of negative-ion formation and hence two-electron transfer to the incoming projectile ion, the Anderson correlation energy U is included in the analysis. Calculations of the probability of negative-ion formation are in qualitative agreement with experiments on the conversion of $H^+ [D^+]$ to $H^- [D^-]$ by scattering from a cesiated W(110) surface. The interplay between temperature effects and U are discussed. Improvements on the calculations by incorporating the image potential into the ionic energy level shift are considered. \rightarrow *not keywords include: see 1473*

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I. Introduction

This paper addresses recent advances which we have made in the theoretical description of charge transfer occurring in ion-surface scattering, where one or two electrons are transferred from the target surface to the incoming projectile positive ion. In Section II we discuss the transfer of one electron from target surfaces to incoming singly-charged ions. We start by giving a phenomenological description of two major features resulting from an ion-neutralization experiment in which the neutralization probability P versus the projectile collision energy E is detected: (i) exponential decrease of P with the increase of E in the high collision energy region and (ii) oscillatory behaviour of $P(E)$ in the low collision energy region. We proceed by outlining a perturbative approach to the chosen ion-surface interaction, stating the rules to compute at any order in the perturbative expansion the neutralization probability and by analyzing the conditions under which the expansion converges rapidly. Finally, we present calculations of the neutralization probability $P(E)$ of protons from various alkali-halide surfaces. For these systems, the fast convergence conditions are met, and the dependence of P on the electronic structure of the collision partners and on the dynamics of the process are critically discussed at the end of Section II.

The transfer of two electrons that leads to the negative-ion formation in ion-surface scattering is discussed in Section III. Within the framework of the time-dependent Anderson-Newns model, we consider the two-electron transfer process in ion-surface scattering, taking into the account the Anderson correlation energy U between the two electrons of opposite spin in the same ionic energy level. The probability of negative-ion formation is calculated by means of the time-evolution operator. The results are in qualitative agreement

with experiments on the conversion of H^+ (D^+) to H^- (D^-) by scattering from a W(110) surface. This unified point of view is further extended to study the temperature effects on negative-ion formation from surface scattering. The interplay between temperature and the correlation energy U is discussed, along with new ideas for improving the calculations by incorporating the image potential into the ionic energy level shift. Finally, Section IV is the summary.

II. One-Electron Transfer

A multiplicity of events are often involved in ion scattering from surfaces, where the neutralization of the ion is one of them. The formation of neutral backscattered particles is studied by monitoring the charge state distribution of the outgoing particles and measuring the ratio of the scattered-neutral flux to the scattered-ion flux. When more information is required on the precise state of the neutralized species, then the photon emission from them is monitored. The mechanism of the charge-transfer process must be understood in order to explain the behavior of the neutralization probability as a function of the collision energy, collision geometry, final state of the atom, nature of the solid target, etc.

A typical result from the experiment of ion neutralization at surfaces shows the following features:¹ The neutralization probability P as a function of the collision energy E exhibits a maximum at some value \bar{E} . For values $E > \bar{E}$, $P(E)$ manifests a rapid decrease to zero, and for $E < \bar{E}$ oscillations are often displaced. A popular phenomenological description of the process is summarized below.²⁻⁴

Let us assume that an ion A^+ is scattered from a surface, where the atomic center of mass follows a classical trajectory $\underline{R}(t)$. The total Hamiltonian of the system can be written as

$$H = H_0 + H_I[\underline{R}(t)] , \quad (1)$$

where H_I is the perturbation created by the incoming ion. If $\underline{R}(t)$ is known, H_I becomes a function of time t . Let $\gamma(t)$ be the rate with which an electron is transferred from the solid to the ion at time t . Therefore, setting $y = 1 - P$, we can write

$$\dot{y}(t) = -\gamma(t) y(t), \quad (2)$$

$$y(t) = \exp \left\{ - \int_0^t dt \gamma(t) \right\} , \quad (3)$$

and if the projectile moves perpendicular to the surface with constant velocity v along the x -axis we have,

$$y(t \rightarrow \infty) = \exp \left\{ - \frac{2}{v} \int_0^\infty dx \gamma(x) \right\} , \quad (4)$$

where $x = v|t|$. Assuming also that $\gamma(x) = \gamma_0 e^{-\alpha x}$, we get

$$y(t \rightarrow \infty) = e^{-2\gamma_0/\alpha v} . \quad (5)$$

This gives the neutralization probability as

$$P = 1 - e^{-2\gamma_0/\alpha v} , \quad (6)$$

which qualitatively describes the high energy portion of experimental results.¹

This simple treatment does not include any oscillatory behavior in $P(E)$. The oscillations are seen to originate from quasi-resonant electron interchange with the core levels.^{5,6} In fact, if we examine a two-(resonant)state time-dependent coupling, the Hamiltonian matrix can be written as

$$H = \begin{vmatrix} \omega & V(t)e^{i\phi(t)} \\ V(t)e^{-i\phi(t)} & \omega \end{vmatrix}. \quad (7)$$

If $\phi(t)$ is assumed to be independent of t so that there is no need to considering time-ordering in computing the evolution operator, and if the phase ϕ of the interaction is taken to be zero, then the state vector of the system is

$$|\psi(t)\rangle = |0\rangle \cos\left[\int_{-\infty}^t dt' V(t')\right] - |1\rangle i \sin\left[\int_{-\infty}^t dt' V(t')\right], \quad (8)$$

where the zero of the energy has been set at the value ω , and where $|\psi(-\infty)\rangle = |0\rangle$. The probability of having $|\psi(\infty)\rangle = |1\rangle$ is

$$|\langle 1|\psi(\infty)\rangle|^2 = \sin^2\left[\int_{-\infty}^{\infty} dt' V(t')\right] = \sin^2\left[\frac{2}{v} \int_0^{\infty} dR V(R)\right], \quad (9)$$

which is an oscillating function whose amplitude decreases with increasing collision velocity v .

A model calculation by Bloss and Hone,⁶ which includes interactions between broad-band delocalized electrons and localized core electrons, exhibits the characteristic oscillations (overimposed on the exponential decay). The Hamiltonian used is an Anderson-Newns type^{7,8} to which is added a core level $|0\rangle$ of the surface atom and an additional state $|2\rangle$ on the ion:

$$H = \sum_k \epsilon_k c_k^\dagger c_k + \epsilon_0 c_0^\dagger c_0 + \epsilon_1 c_1^\dagger c_1 + \epsilon_2 c_2^\dagger c_2 + [v_{01}(t) c_0^\dagger c_1 + \text{h.c.}] \\ + \sum_k [v_{k1}(t) c_k^\dagger c_1 + \text{h.c.}], \quad (10)$$

where k labels the surface delocalized electrons. The following items are excluded from the model: (i) electron-electron interactions (therefore Auger

neutralization and Auger deexcitation); (ii) radiative deexcitation; (iii) negative-ion formation (therefore Coulomb correlation--Coulombic repulsion has been taken to be infinite); (iv) spin dependency [consequence of (iii)]; (v) image forces (therefore the atomic energy levels have been taken as constants); and (vi) overlap integrals of atomic and surface states, which have only a small contribution.

Although several authors^{4,6,9} took the approach of solving the Heisenberg equations of motion for the creation and annihilation operators c^\dagger and c , another possible approach is the use of diagrammatic techniques¹⁰ which are widely applied to time-dependent problems.¹¹ Due to its simplicity, the former approach is more commonly used. On the other hand, a perturbative treatment (with diagrams) allows for a systematic series of approximations to many-body problems, and we shall consider this below.

We consider the following Hamiltonian:

$$H(t) = \sum_k \epsilon_k c_k^\dagger c_k + \epsilon_d c_d^\dagger c_d + H_I(t), \quad (11)$$

where

$$H_I(t) = \sum_k [V_k(t) c_d^\dagger c_k + \text{h.c.}] \quad (12)$$

$$V_k(t) = V_k e^{-\lambda|t|}, \quad (13)$$

and λ is a parameter measuring the duration of the interaction. A single-band/single-atomic level interaction is considered, and we want to explore the consequence of a perturbation expansion of the diagonal elements of the reduced density matrix of the neutralized atom. The vacuum state is the state in which all the band levels $|k\rangle$ are filled with electrons up to the Fermi energy and the ion is in its ground state so that the state $|d\rangle$ is unoccupied. We indicate the state of the system in which one electron has jumped from $|k\rangle$ into $|d\rangle$ by $|1_k 1_d\rangle = c_d^\dagger(t) h_k^\dagger(t) |\psi_0\rangle$, where $|\psi_0\rangle$ is the (unknown) ground interacting vacuum state in

the Heisenberg picture and h_k and h_k^\dagger are hole ladder operators. The charge-transfer probability is therefore

$$P = \sum_k \left| \frac{\langle \psi_0 | h_k^{(\infty)} c_d^{(\infty)} | \psi_0 \rangle}{\langle \psi_0 | \psi_0 \rangle} \right|^2, \quad (14)$$

where the sum over k is nothing more than a partial trace over the state of the unobserved surface. In the interaction picture (in which operators are denoted below by a tilde), the neutralization probability P can be written in terms of the (known) non-interacting ground vacuum state $|0\rangle$ as¹²

$$\frac{\langle \psi_0 | h_k^{(\infty)} c_d^{(\infty)} | \psi_0 \rangle}{\langle \psi_0 | \psi_0 \rangle} = \frac{\langle 0 | T \left\{ \exp \left[-i \int_{-\infty}^{\infty} dt e^{-\gamma|t|} h_k c_d \tilde{V}(t) \right] \right\} | 0 \rangle}{\langle 0 | T \left\{ \exp \left[-i \int_{-\infty}^{\infty} dt e^{-\gamma|t|} \tilde{V}(t') \right] \right\} | 0 \rangle} = \frac{N}{D}, \quad (15)$$

where $\tilde{V}(t)$ is $V(t)$ of Eq. (13) in the interaction picture.

We have computed the neutralization probability P up to third order in the perturbative expansion for several values of the parameter λ [Eq. (13)].¹² This is the only parameter which controls the dynamics of the collision process; in particular, it controls the duration of the interaction and hence the collision energy. We have found that the first-order term gives the main contribution to P provided (i) the duration of the interaction is short enough or (ii) the atomic discrete level is not embedded in the valence band of the solid where the neutralizing electron originates. The maximum exhibited in $P(E)$ in typical experiments¹ is interpreted to result from the interplay between two factors: the resonance and the duration of the interaction factors. As the energy increases, the former makes the neutralization easier because the resonance condition becomes less stringent, but the latter makes the neutralization more difficult because the electron has less time to "jump" into the ion. Another factor which determines the magnitude of the neutralization probability is the relative position between the atomic level and the valence band of the solid. Excluding the case in which the atomic level is embedded in the band (a

situation in which the first few terms of the perturbation expansion are not sufficient to give a converging neutralization probability), the closer the discrete level is to the continuum of the band, the easier the charge transfer occurs. Finally, a wider valence band always enhances the neutralization probability.

It is the interplay of all of the above general rules that determines quantitatively the relative neutralization probability from different solid systems into different atomic states. Therefore, a glance at the electronic structure of the atom-solid pair is often very useful in determining qualitative trends in the neutralization probabilities. As an example, we display in Fig. 1 the electronic structure of the first four hydrogenic shells and of the valence band of some alkali-halide solids. Since these systems have already been discussed at length,¹³ we only want to point out that, for example, both the width of the bromide valence bands and their proximity to the hydrogen ground state would (according to the above rules) favor the trend $\text{LiBr} > \text{NaBr} > \text{KBr}$ for all values of the interaction times. This is indeed what our calculations have shown.¹³ The calculation of the neutralization into the first-excited atomic state from the fluoride systems requires a more exact treatment. At very high values of λ , where the resonance factor does not have any role, the valence band width determines the trend $\text{LiF} > \text{NaF} > \text{KF}$; at low values of λ where its increase makes the neutralization more probable due to the ease of the resonance condition, the proximity of the $n=2$ level to the upper edge of the valence band determines the trend $\text{NaF} > \text{KF} > \text{LiF}$ (see Fig. 2). The absence of the quasi-resonant interaction between the ionic level and discrete inner-core surface states, and of the inclusion of many terms in the perturbative expansion for ionic levels embedded into the solid band, precludes the observation of typical

oscillations on the low-energy side of the neutralization probability plot. The inclusion of long-range image forces, and therefore of a more realistic time dependence of the ionic levels, has been also neglected. We shall address this aspect in the analysis of the two-electron charge-transfer process at the end of the next section.

III. Two-Electron Transfer

For positive-ion scattering from a metal surface, there is considerable experimental evidence for two-electron transfer¹⁴⁻¹⁶ as well. In experimental studies of two-electron surface scattering processes, for example, positive ions such as H^+ , D^+ and Na^+ are scattered from a W(110) surface. As the ions leave the surface, a certain fraction of them are converted into negative ions. For the purpose of increasing this fraction,^{17,16} an overlayer of cesium is deposited on the metal surface to reduce the work function.^{19,20} The formation of negative ions from surface scattering has recently attracted more interest due to its possible use in plasma diagnostics,²¹ the production of high energetic neutral beams²² and heating fusion plasmas.²³

Although theoretical investigations have been made successful for one-electron transfer processes,^{4,6,9,10,13,24-26} based on the time-dependent Anderson-Newns model,^{7,8} the theory for two-electron transfer processes has been basically phenomenological.²⁷ As mentioned before, in the application of that model to the process of ion neutralization, the correlation energy due to the Coulombic repulsion between the two electrons of opposite spin in the same ionic energy level is neglected or implicitly assumed to be infinite. Since such correlation energy has been shown to play a crucially important role in localized magnetization around impurities in transition metals,⁷ in the degree of neutrality of hydrogen atoms chemisorbed on transition metal surfaces⁸ and

in mixed valences occurring in rare-earth compounds,²⁸ we have decided to consider²⁹ negative-ion formation by taking into account the finite Anderson correlation energy U in the time-dependent Anderson-Newns model.^{7,8}

The Hamiltonian under consideration for the negative-ion formation is,

$$H(t) = H_0 + H_I(t) \quad , \quad (16)$$

where

$$H_0 = \sum_{k\sigma} \epsilon_k c_{k\sigma}^\dagger c_{k\sigma} + \sum_{\sigma} \epsilon_d c_{d\sigma}^\dagger c_{d\sigma} + U n_{d\sigma} n_{d,-\sigma} \quad (17)$$

and

$$H_I(t) = \sum_{k,\sigma} [V_k(t) c_{d\sigma}^\dagger c_{k\sigma} + \text{h.c.}] \quad (18)$$

$V_k(t)$ is given by Eq. (13), and $n_{d\sigma}^\dagger = c_{d\sigma}^\dagger c_{d\sigma}$. The probability of negative-ion formation at time t , $P(t)$, can be calculated with the help of the time-evolution operator, $T(t)$. To lowest order, $P(t)$ is given by

$$P(t) = \int_{\epsilon_L}^{\epsilon_F} d\epsilon \int_{\epsilon_L}^{\epsilon_F} d\epsilon' \rho(\epsilon) \rho(\epsilon') \langle k_+ k_- | \tilde{T}^{(2)}(t) | I \rangle^2 \quad , \quad (19)$$

where ϵ_F and ϵ_L are the Fermi energy and lower conduction band edge of the metal, respectively, $\rho(\epsilon)$ is the density of the conduction band and is assumed to be constant throughout the band,^{6,9,25} the initial and final states $|I\rangle$ and $|k_+ k_- \rangle$, are explained in Fig. 3, and $\tilde{T}^{(2)}(t)$ is the second-order time-evolution operator $T(t)$ in the interaction picture. Assuming that $t = -\infty$ when the incident ions are infinitely far away from the surface, we have

$$\tilde{T}^{(2)}(t) = (-1)^2 \int_{-\infty}^t dt' \hat{H}_I(t') \int_{-\infty}^{t'} dt'' \hat{H}_I(t'') \quad , \quad (20)$$

where

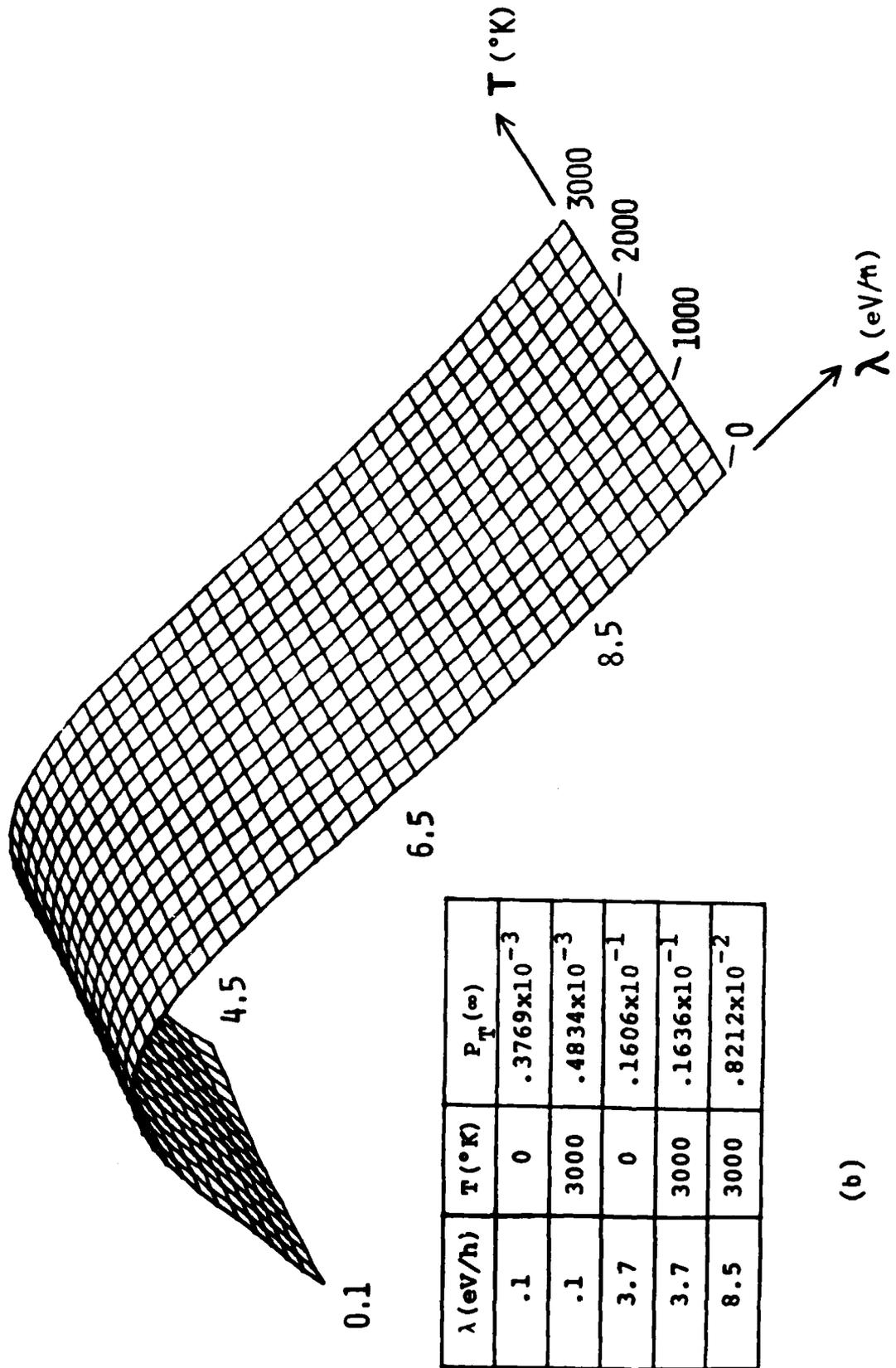
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Fig. 5 (b)

$U = 4.6 \text{ eV}$



(b)

$U=1.5\text{ eV}$

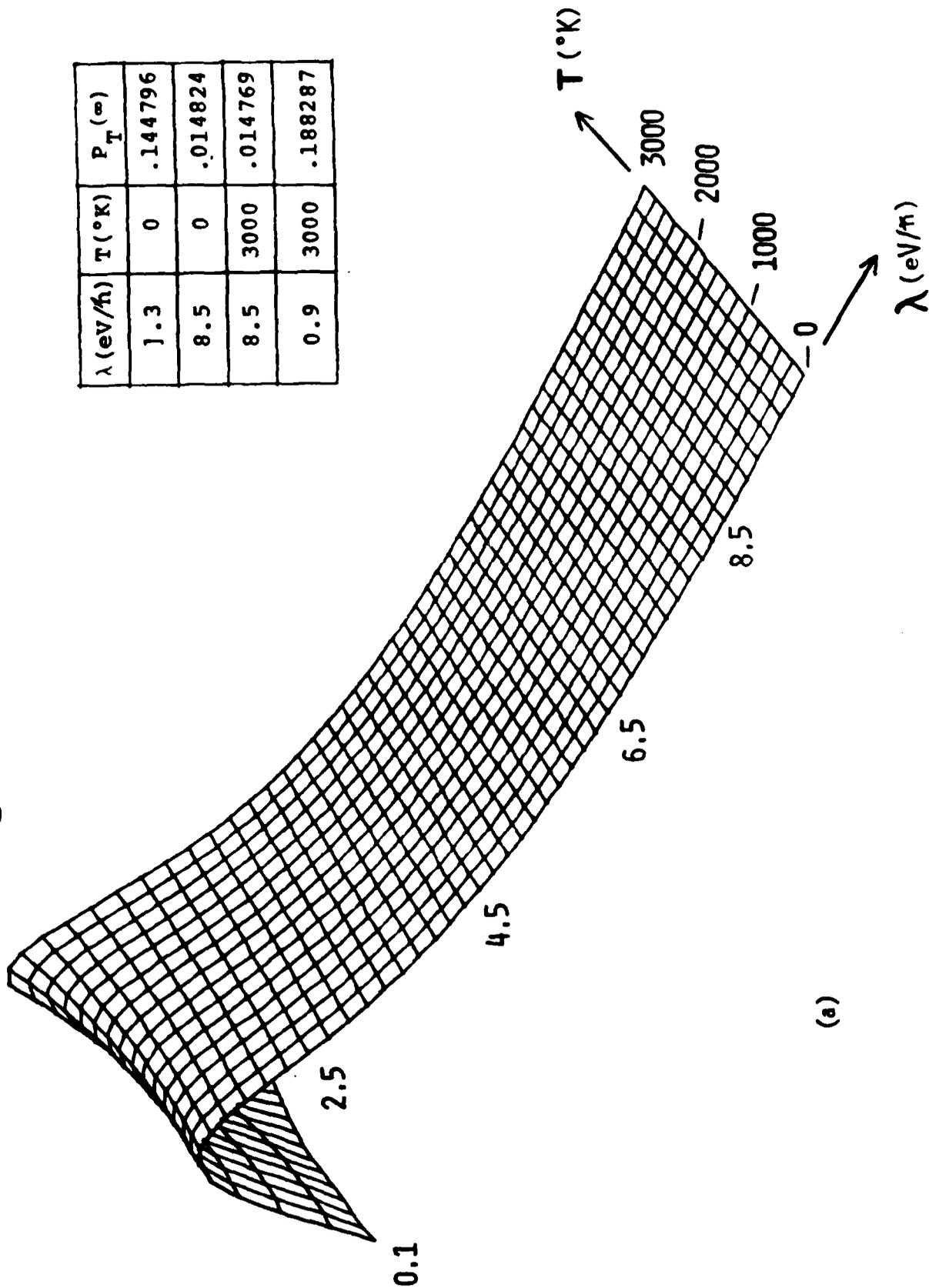


Fig. 5 (a)

(a)

Fig. 4

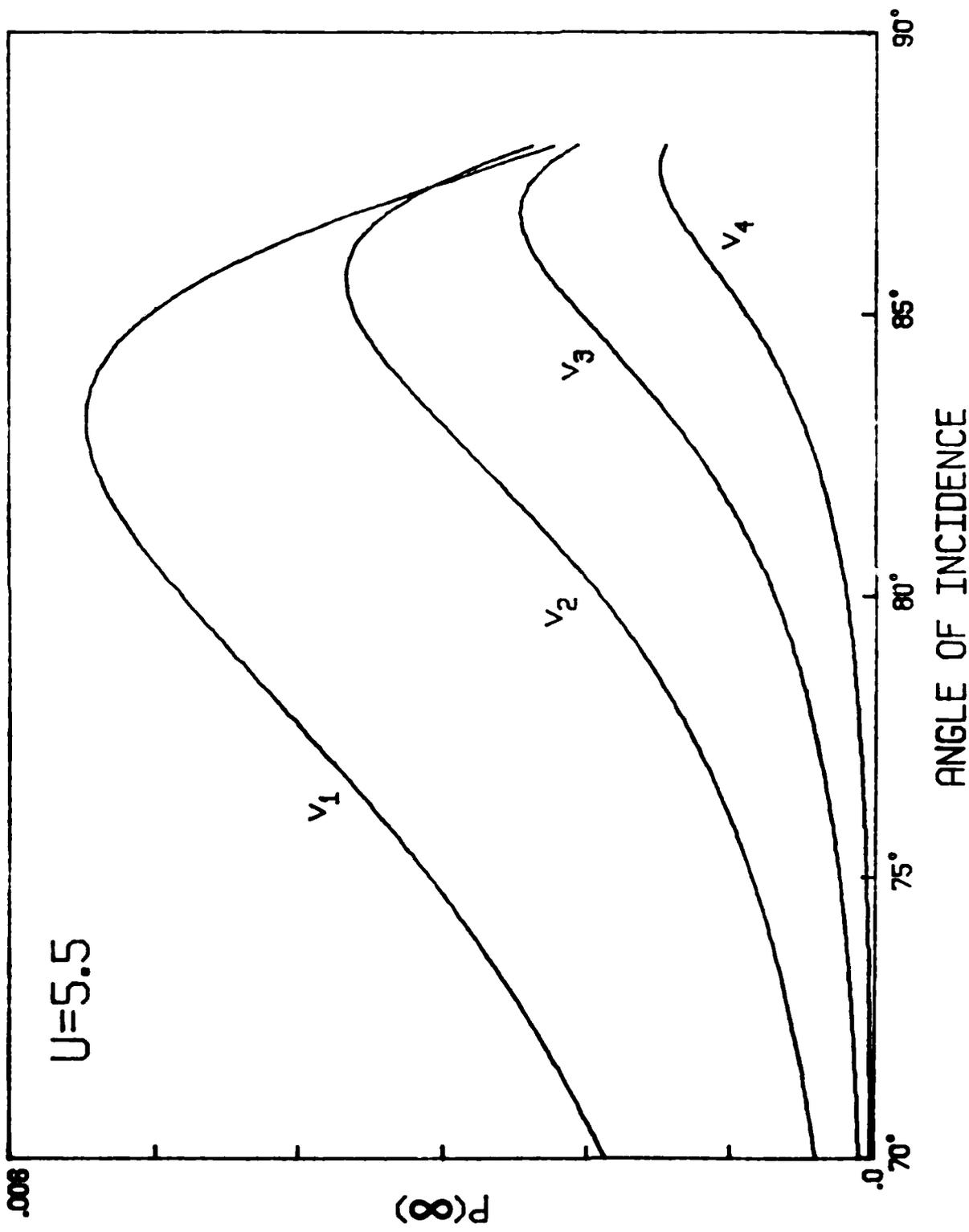
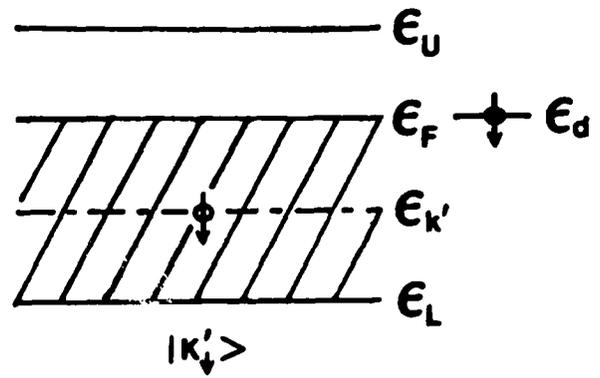
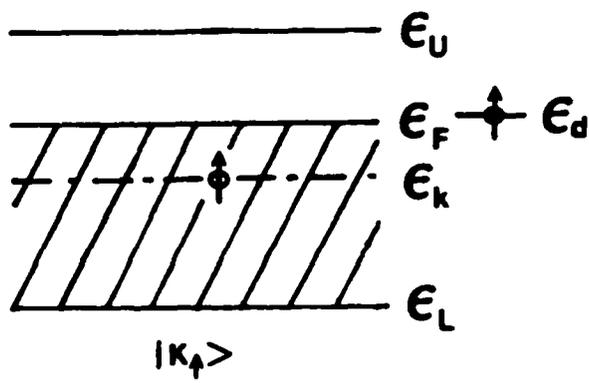
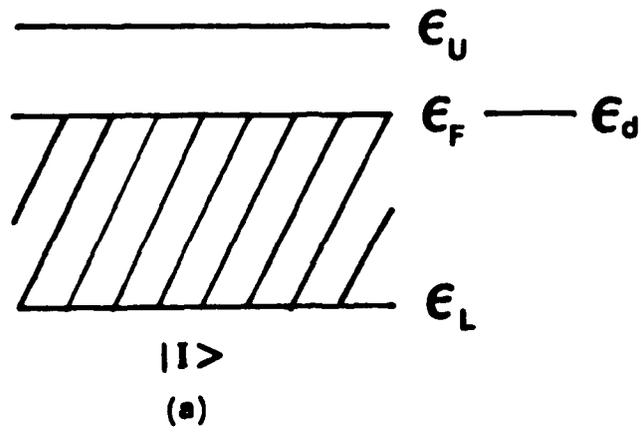
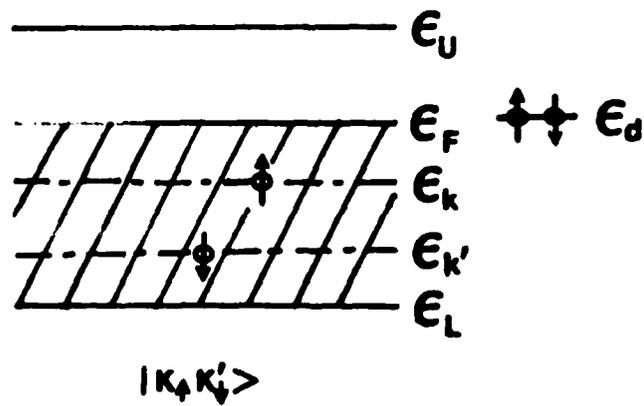


Fig. 3



(b)



(c)

Fig. 2

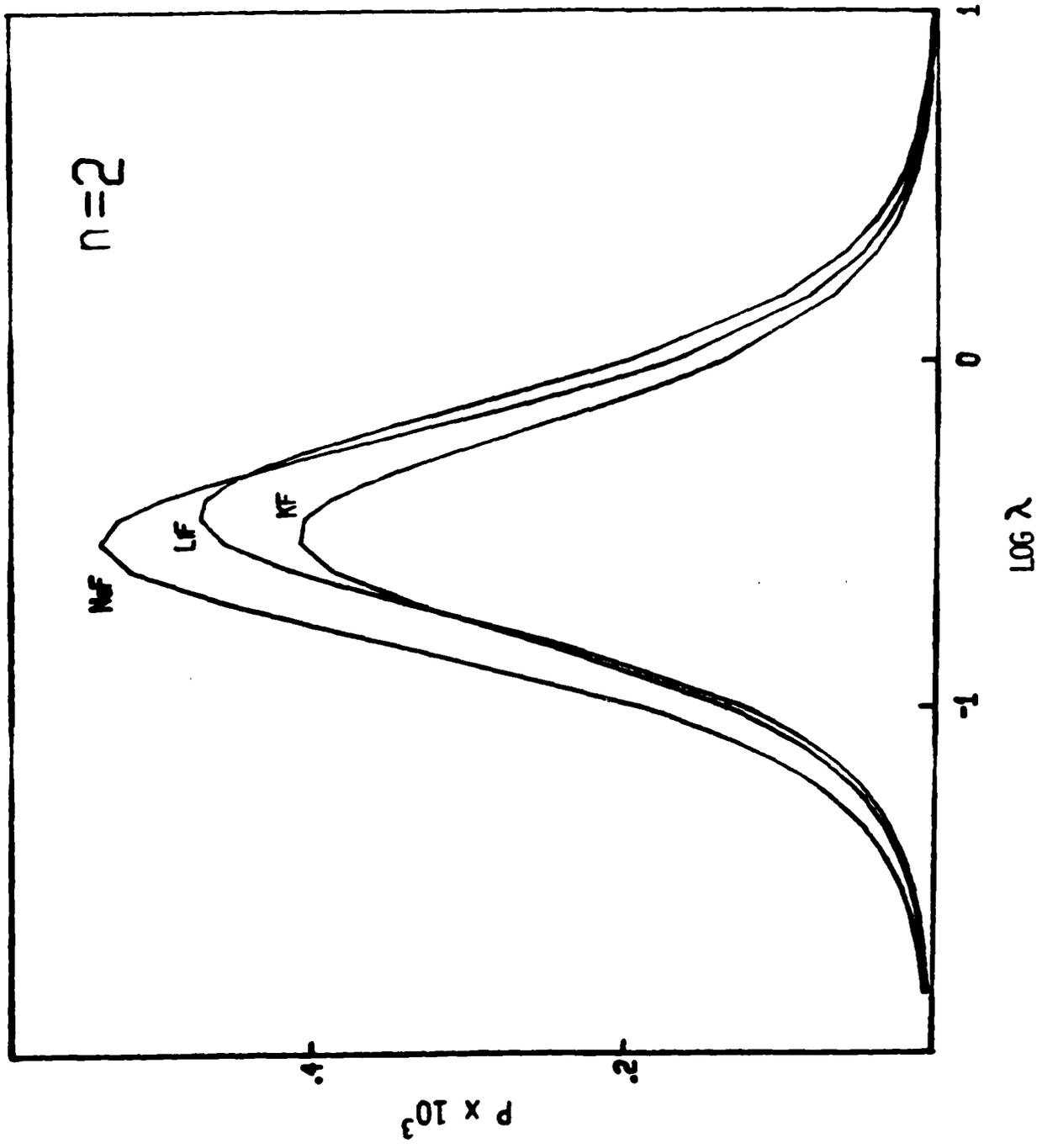


Fig. 1

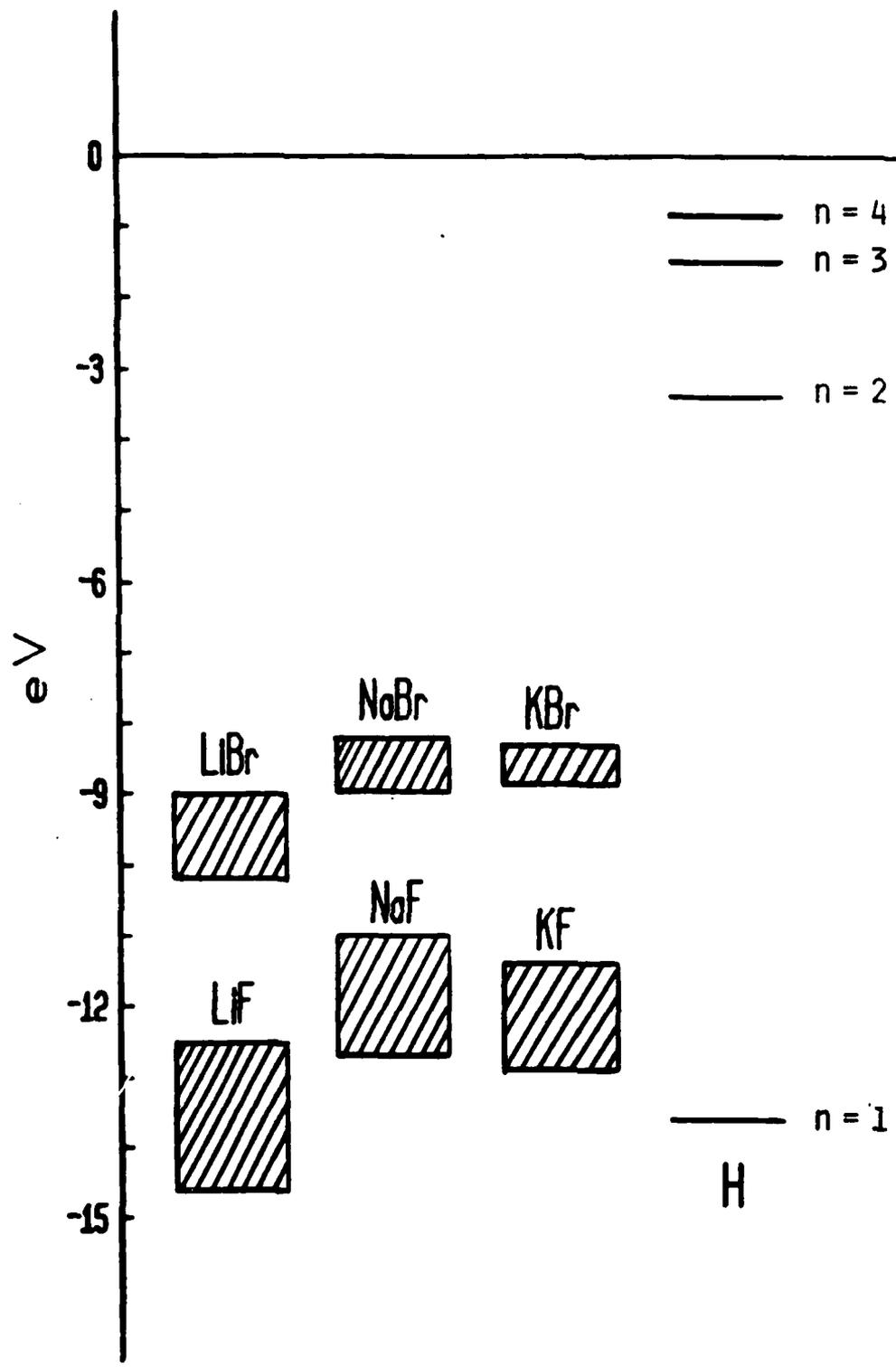


Figure Captions

1. Electronic structure of the first four hydrogenic shells and of the valence band of some alkali-halide solids. Except for charge-transfer from the LiF surface into the hydrogen ground state, the relative qualitative behavior of the neutralization probabilities from various solids into various atomic bound states can be predicted by comparing the relative distance between the atomic levels and the valence bands with the relative width of the latter and by taking into account that the frequency of the n -th shell is proportional to n^2 .

2. Neutralization probability P into the first hydrogenic excited state ($n=2$) from alkali-fluoride surfaces as a function of λ . Comparing with Fig. 1, this behavior is easily understood: both the resonance and bandwidth factors determine that $P(\text{NaF}) > P(\text{KF})$. At low values of λ where the resonance factor is important, $P(\text{KF}) > P(\text{LiF})$; at high values of λ where the bandwidth factor is important, $P(\text{LiF}) > P(\text{NaF})$.

3. Schematic diagram of electron transfer in negative-ion formation at $T = 0\text{K}$. ϵ_U is the upper and ϵ_L the lower edge of the band. (a) Initial state $|I\rangle$: valence state ϵ_d empty, band filled up to the Fermi level ϵ_F . (b) Intermediate states $|k_\uparrow\rangle$ and $|k'_\downarrow\rangle$: states corresponding to the neutralized atom; one electron transferred from the ϵ_k or ϵ'_k level to the ϵ_d level. The arrows denote the spin states of the electrons, and the solid and hollow circles represent electrons and holes, respectively. (c) Final states $|k_\uparrow k'_\downarrow\rangle$: negative-ion states: two electrons transferred to the ϵ_d level.

4. $P(\infty)$ versus θ , the incident angle of impact: $v_1 < v_2 < v_3 < v_4$.

5. $P_T(\infty)$ vs λ for various values of the temperature T : (a) $U = 1.5$ eV and (b) $U = 4.6$ eV. The functional values are given in the inset for several points to illustrate the numerical values.

20. J. R. Hiskes, A. M. Karo, E. Wimmer, A. J. Freeman and S. R. Chubb, *J. Vac. Sci. Technol. A* 2, 670 (1984).
21. P. Massmann, H. J. Hopman and J. Los., *Nucl. Instrum. Methods* 165, 531 (1979).
22. K. H. Berkner, R. V. Pyle and J. W. Stearns, *Nucl. Fusion* 15, 249 (1975).
23. J. R. Hiskes, *J. Phys. (Paris), Colloq.*, 40 (C7), 179 (1979).
24. Y. Muda and T. Hanawa, *Surf. Sci.* 97, 283 (1980).
25. R. Brako and D. M. Newns, *Surf. Sci.* 108, 253 (1981).
26. K. L. Sebastian, V. C. Jyothi Bhasu and T. B. Grimley, *Surf. Sci.* 110, L571 (1981).
27. B. Rasser, J. N. M. van Wunnik and J. Los, *Surf. Sci.* 118, 697 (1982).
28. C. M. Varma, *Rev. Mod. Phys.* 48, 219 (1976).
29. K. S. Lam, K. C. Liu and T. F. George, *Phys. Lett.* 101A, 356 (1984).
30. K. C. Liu, T. F. George and K. S. Lam, *Solid State Commun.* 53, 67 (1985).
31. L. F. Matheiss, *Phys. Rev.* 139, A1853 (1955); I. Petroff and C. R. Viswanatham, *Phys. Rev. B* 4, 799 (1971).
32. R. Gomer and L. W. Swanson, *J. Chem. Phys.* 38, 1613 (1963).
33. D. M. Newns, *J. Chem. Phys.* 50, 4572 (1969).
34. J. W. Gadzuk, *Surf. Sci.* 6, 133 (1967).
35. R. K. Janev and S. B. Vojvodic, *J. Phys. B* 13, 2481 (1980).

References

1. H. H. Brongersma and T. M. Buck, Surf. Sci. 53, 649 (1975).
2. A. Cobas and W. E. Lamb, Phys. Rev. 65, 327 (1944).
3. H. D. Hagstrum, Phys. Rev. 96, 336 (1954).
4. R. Brako and D. M. Newns, Vacuum 32, 39 (1982).
5. N. H. Tolk, J. C. Tully, J. Kraus, C. W. White and S. H. Neff, Phys. Rev. Lett. 36, 747 (1976).
6. W. Bloss and D. Hone, Surf. Sci. 72, 277 (1978).
7. P. W. Anderson, Phys. Rev. 124, 41 (1961).
8. D. M. Newns, Phys. Rev. 197, 1123 (1969).
9. R. Brako, Phys. Rev. B 30, 5629 (1984).
10. A. Blandin, A. Nourtier and D. W. Hone, J. Phys. (Paris) 37, 369 (1976).
11. L. V. Keldish, Soviet Phys. JETP 20, 1018 (1965).
12. F. Battaglia and T. F. George, J. Chem. Phys., in press.
13. F. Battaglia, T. F. George and A. Lanaro, Surf. Sci., submitted.
14. E. G. Overbosch and J. Los, Surf. Sci. 108, 117 (1981).
15. J. N. M. van Wunnik, B. Rasser and J. Los, Phys. Lett. 87A, 288 (1982).
16. J. N. M. van Wunnik, J. J. C. Geerlings and J. Los, Surf. Sci. 131, 1 (1983); J. N. M. van Wunnik, J. J. C. Geerling, E. H. A. Granneman and J. Los, Surf. Sci. 131, 17 (1983).
17. E. G. Overbosch, B. Rasser, A. D. Tenner and J. Los, Surf. Sci. 92, 310 (1980).
18. E. G. Overbosch and J. Los, Surf. Sci. 108, 99 (1981).
19. E. Wimmer, A. J. Freeman, M. Weinert, H. Krakauer, J. R. Hiskes and A. M. Karo, Phys. Rev. Lett. 48, 1128 (1982).

IV. Summary

A perturbative treatment using a Fano-Anderson effective interaction has been presented for one-electron transfer processes in positive-ion scattering from surface, i.e., ion neutralization, and the conditions under which the perturbative series has fast convergence have been discussed. In particular, fast convergence is obtained when the interaction time is short enough and when the ionic level is not in resonance with any states of the valence band. For two-electron transfer leading to negative-ion formation, the Anderson correlation energy U is included in the analysis, and qualitative agreement is obtained with experiments on the conversion of H^+ (D^+) to H^- (D^-) by scattering from a cesiated $W(110)$ surface. Temperature effects are considered, and it is seen that negative-ion formation is significantly enhanced at finite temperature T , provided $k_B T$ is not less than U . Improvements on the calculations are possible by incorporating the image potential into the ionic energy level shift. Finally, a more microscopic approach^{9,34,35} is possible by considering the ion-surface interaction strength V_k (see Eq. (13)). Once this is completed, the ion-surface scattering can be understood from a microscopic point of view.

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where ϵ_0 is the ionic energy when the ion is far away from the surface. The decrease of the ionic energy as it approaches the surface leads to the situation that the ionic level is in resonance with conduction electrons of the metal. As such, electron tunnelling is possible.

To make our arguments more specific, we look at Eq. (20), which can be written, with the help of Eq. (21), as

$$\bar{T}^{(2)}(t) = (-1)^2 \int_{-\infty}^t dt' e^{iH_0' t'} H_I(t') e^{-iH_0' t'} \int_{-\infty}^{t'} dt'' e^{iH_0'' t''} H_I(t'') e^{-iH_0'' t''}. \quad (27)$$

Here we distinguish H_0' and H_0'' , where the former corresponds to the Hamiltonian in which one of the electrons is already transferred to the ion, while the latter corresponds to that of the incident positive ion. They are given, respectively, by

$$H_0''(t) = \sum_{k\sigma} \epsilon_k c_{k\sigma}^\dagger c_{k\sigma} + \sum_d \epsilon_d'(t) c_{d\sigma}^\dagger c_{d\sigma} + U n_{d\sigma} n_{d,-\sigma} \quad (28)$$

and

$$H_0'(t) = \sum_{k\sigma} \epsilon_k c_{k\sigma}^\dagger c_{k\sigma} + \sum_d \epsilon_d''(t) c_{d\sigma}^\dagger c_{d\sigma} + U n_{d\sigma} n_{d-\sigma} \quad (29)$$

where $\epsilon_d'(t)$ and $\epsilon_d''(t)$ are of the form of Eq. (26) but with different image potentials. The one in $\epsilon_d'(t)$ is the atom-surface image potential, and that in $\epsilon_d''(t)$ is the ion-surface image potential. The forms of $H_0''(t)$ and $H_0'(t)$ only differ in the ionic energy level due to the change of state resulting from electron transfer. Since the effect of the image potential is small, $\epsilon_d'(t)$ might be taken as independent of time, i.e., independent of position within the framework of the classical trajectory approximation. We expect this consideration to give rise to better quantitative comparison with experimental measurements.¹⁵

where ϵ_U is the upper edge of the conduction band and is set equal to 5 eV to mimic the usual experimental situation of light atoms impacting on a transition metal surface.³¹ Performing calculations similar to the case of $T=0$, we obtain the dependence of $P_T(\infty)$ on the dynamical variable λ and the temperature T for different values of U as shown in Fig. 5. One can readily see that temperature effects are more prominent for small U [Fig. 5(a)], while there is hardly any effect for large U [Fig. 5(b)]. One can thus conclude that the negative-ion formation is significantly enhanced at finite temperature T , provided $k_B T$ is not less than the Anderson correlation energy U .

In the above calculation, we have assumed that the ionic level ϵ_d is constant in time. However, it is well known that a charge outside the metal surface induces an image of opposite charge inside the metal due to the mobility of conduction electrons of the metal. The induced image in turn interacts with the ion by an effective Coulombic attraction,³²

$$W = - \frac{q^2}{4(z + \lambda_{TF})} , \quad (24)$$

where q is the charge of the ion, z is the distance between the ion and the surface, and λ_{TF} is the Thomas-Fermi screening length which is given by

$$\lambda_{TF}^{-2} = 4\pi e^2 \rho(\epsilon_F) . \quad (25)$$

The expression of Eq. (24) has proved to be a good approximation³³ down to the distance of $\lambda_{TF}/2$ from the surface. Taking the image potential of Eq. (24) into account, the energy level for the incident ion is

$$\begin{aligned} \epsilon_d(t) &= \epsilon_0 + W \\ &= \epsilon_0 - \frac{q^2}{4[z(t) + \lambda_{TF}^2]} , \end{aligned} \quad (26)$$

$$\tilde{H}_I(t) = \exp(iH_0 t) H_I(t) \exp(-iH_0 t) . \quad (21)$$

The experimental observation of outgoing negative ions after the scattering event is complete is represented by $P(\sigma)$. We take $\epsilon_L = -10$ eV, $\epsilon_F = -0.06$ eV, $\lambda = v \cos\theta$ and $\Delta = \rho V_k = 0.43 \exp(-0.01 v)$ (in the unit of eV), where v is the magnitude of the velocity, θ is the angle between the incident particle and the normal direction normal to the surface, and the exponential dependence of Δ on v accounts for the loss of particles due to penetration into the surface. Here we also assume that the ionic energy level is fixed during the scattering event, and therefore we put ϵ_d as the zero energy level in the calculation. The results of the calculation of $P(\sigma)$ versus grazing angle θ for various incident velocities of the ion are shown in Fig. 4. They are in qualitative agreement with experimental measurements¹⁵ on the conversion of H^+ (D^+) to H^- (D^-) by scattering from a cesiated $W(110)$ surface. Further improvement of the theoretical calculations will be discussed later.

We have also extended the above unified point of view to consider the effect of temperature on the negative-ion formation at a surface.³⁰ At finite temperature $T \neq 0$, the distribution of the conduction electrons in the solid is governed by the Fermi-Dirac distribution given as

$$f(\epsilon) = \frac{1}{1 + \exp[(\epsilon - \epsilon_F)/k_B T]} , \quad (22)$$

where k_B is the Boltzmann constant. Taking this into account, the probability of negative-ion formation, $P_T(t)$, at time t for the case of finite temperature is

$$P_T(t) = \int_{\epsilon_L}^{\epsilon_U} d\epsilon \rho(\epsilon) f(\epsilon) \int_{\epsilon_L}^{\epsilon_U} d\epsilon' \rho(\epsilon') f(\epsilon') |\langle k_+ k_- | \tilde{T}^{(2)}(t) | I \rangle|^2 , \quad (23)$$

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