INTERNATIONAL ATOMIC ENERGY AGENCY
UNITED NATIONS EDUCATIONAL, SCIENTIFIC AND CULTURAL ORGANIZATION
INTERNATIONAL CENTRE FOR THEORETICAL PHYSICS
I.C.T.P., P.O. BOX 586, 34100 TRIESTE, ITALY, CABLE: CENTRATOM TRIESTE

UNITED NATIONS INDUSTRIAL DEVELOPMENT ORGANIZATION

INTERNATIONAL CENTRE FOR SCIENCE AND HIGH TECHNOLOGY
c/o INTERNATIONAL CENTRE FOR THEORETICAL PHYSICS 34100 TRIESTE (ITALY) VIA GRIGNANO, 9 (ADRIATICO PALACE) P.O. BOX 586 TELEPHONE 040-224572 TELEFAX 040-224575 TELEX 460449 APH I

SMR. 628 - 34

Research Workshop in Condensed Matter, Atomic and Molecular Physics (22 June - 11 September 1992)

Working Party on: "Energy Transfer in Interactions with Surfaces and Adsorbates" (31 August - 11 September 1992)

"Theoretical Description Dynamic Charge Transfer Processes at Surfaces"

D. LANGRETH
Rutgers State University
Department of Physics
P.O. Box 849
Piscataway NJ 08855-0849
U.S.A.

These are preliminary lecture notes, intended only for distribution to participants.

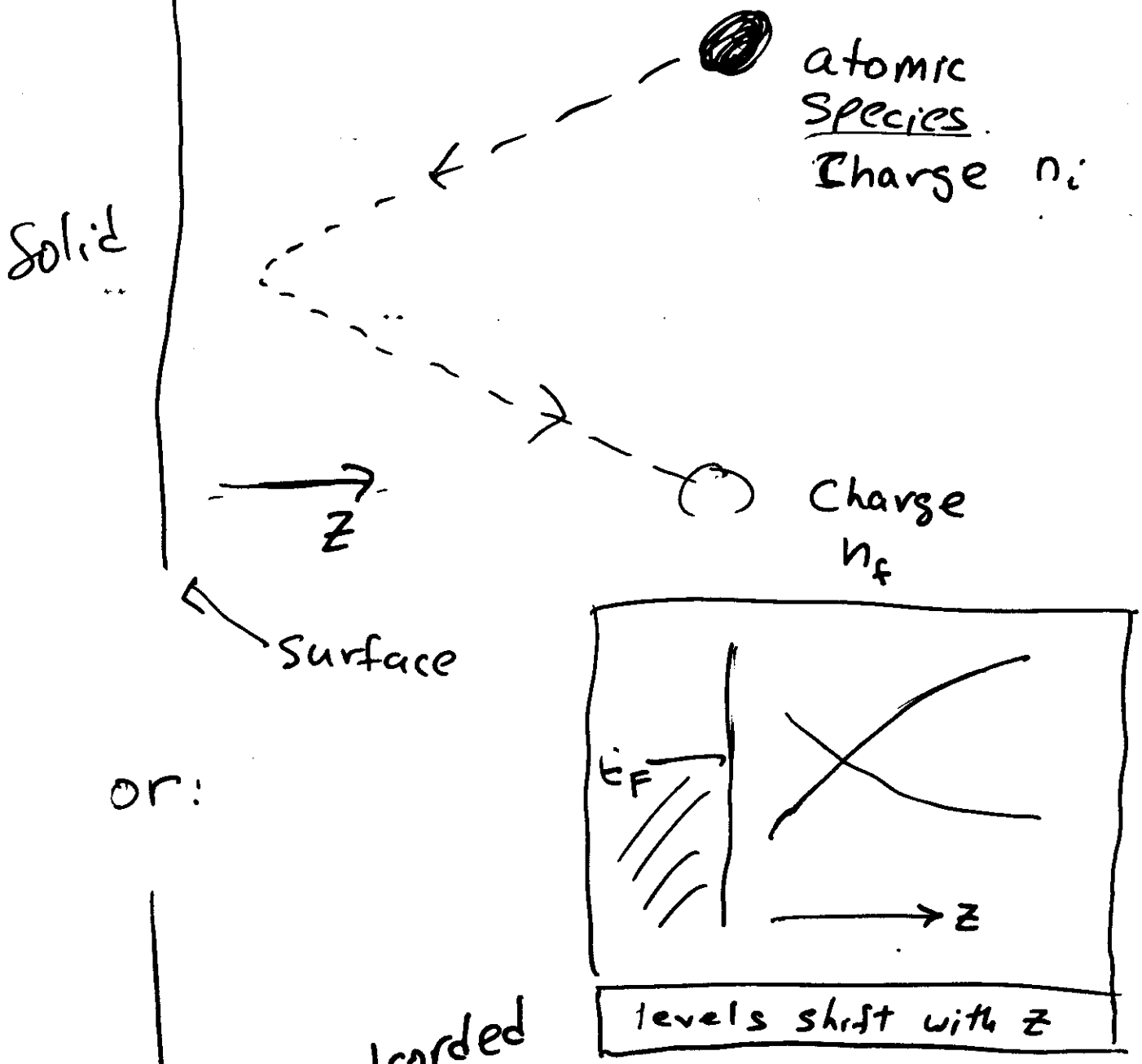
Theoretical Description of Dynamic Charge Transfer Processes at Surfaces

David Langreth

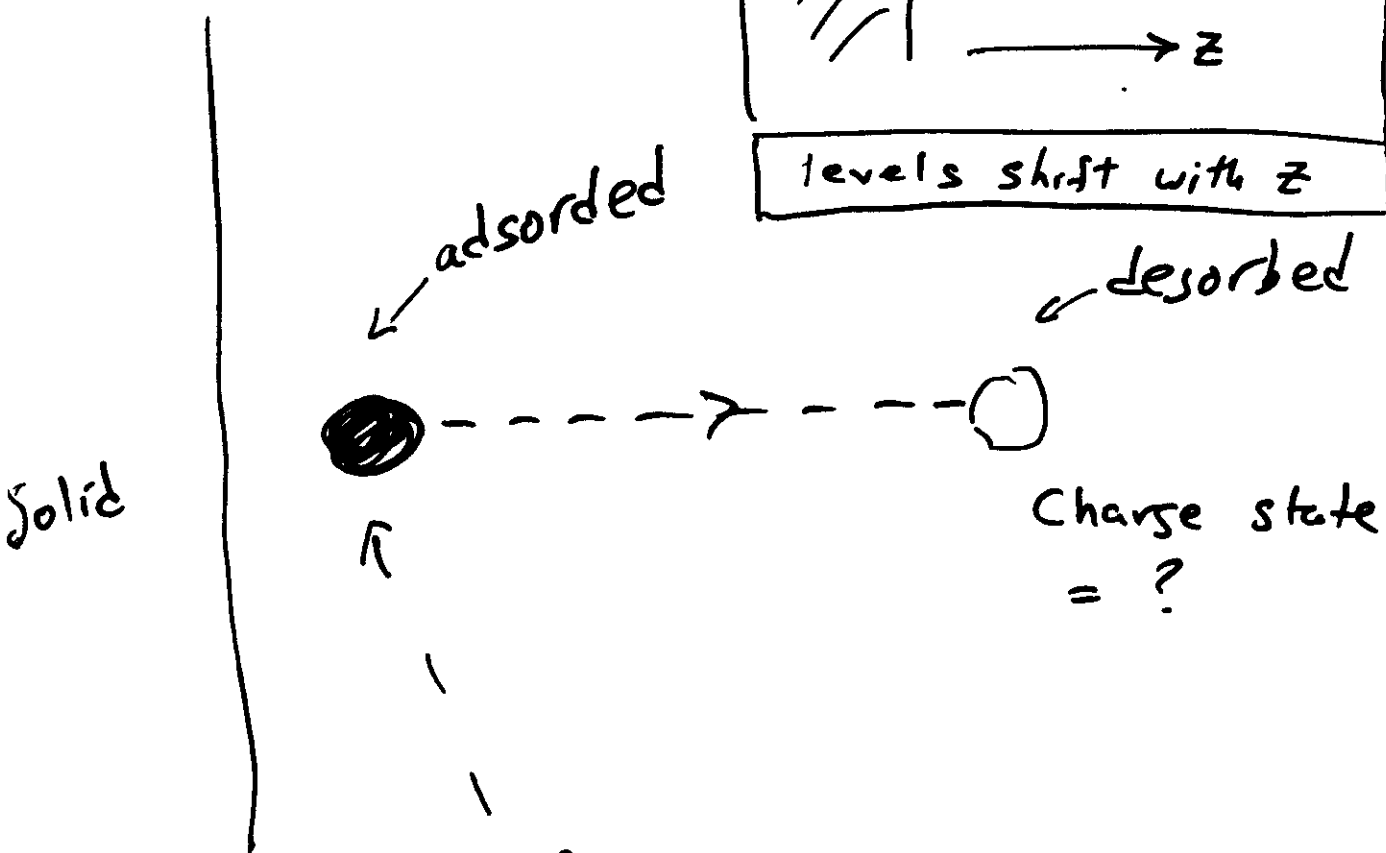
Collaborators: H. Shao

P. Nordlander

Example:


atomic
Species
Charge n_i
Solid
z
Charge
n_f
Surface
ϵ_F
z
levels shift with z

or:


adsorded
desorbed
Solid
Charge state
= ?
e

Charge transfer probability depends on:

✓ 1. Relative position of $\epsilon_a(\vec{R})$ to ϵ_F
Nordlander + J. Tully

✓ 2. Local tunneling rates $\Gamma(\vec{R})$
i.e. instantaneous adiabatic
widths of atomic levels.
Nordlander + Tully

✓ 3. Dynamics of electronic charge states for $R = R(t)$
Shao, Langreth, + Nordlander

? 4. Feedback of 3. on atomic trajectory, velocity, etc.

1+2 can be calculated with frozen nuclei. 3+4 need nonadiabatic dynamical treatment.

Shift + Broadening of atomic levels

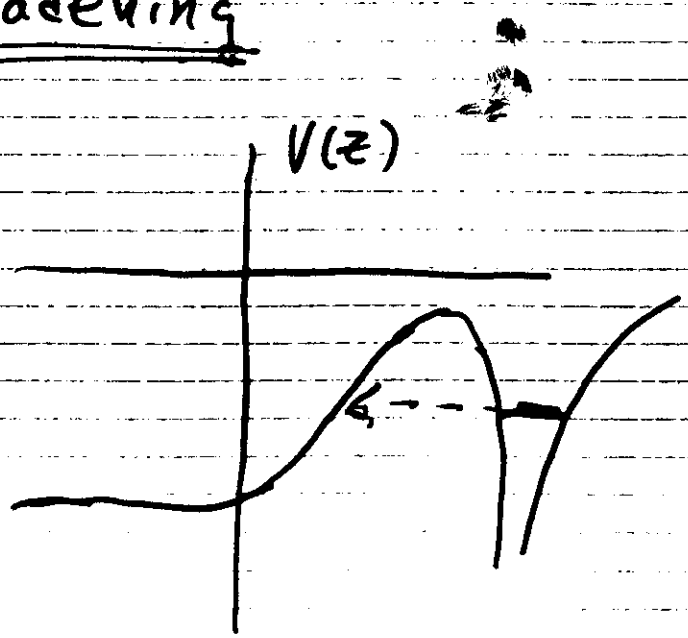
Shift - due to relaxation of electrons near surface - a fast process

Asymptotic forms from image potential arguments:

1. Neutral atom (or) ionization level } take to ∞, bring + ion back, costs $-\frac{1}{4z}$ $\Rightarrow$ $\epsilon_n = \epsilon_n^0 + \frac{1}{4z}$

2. Negative ion (or) affinity level } take extra electron to ∞, costs $\frac{1}{4z}$ $\Rightarrow$ $\epsilon_A = \epsilon_A^0 - \frac{1}{4z}$

Broadening



$$\Gamma(z) \sim \Gamma_0 \, e^{-\alpha z}$$

Ab initio calculations of level shifts + adiabatic widths [P. Nordlander]

H/Al

Image pot. like shifts

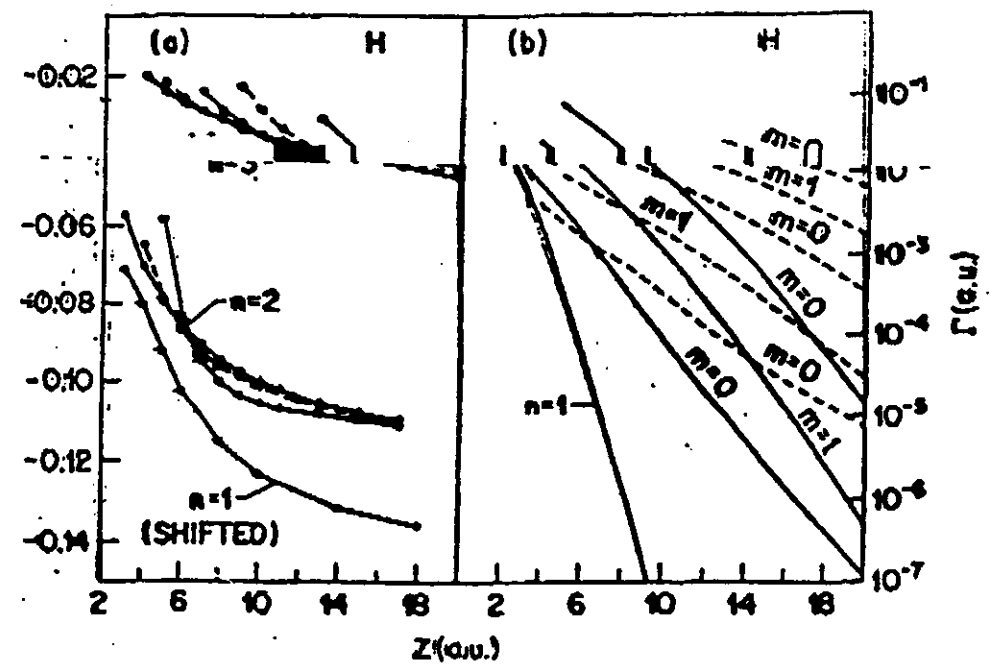


FIG. 3. Calculated energy shifts and widths for hydrogen on Al. In the left part of the figure, the real part of the energy is shown. The $n=1$ state has been shifted 0.35 a.u. upward in energy. The solid curves are the $m=0$ states. The dashed curves are the $m=1$ states. Distances are in a.u. measured from the jellium edge and energies in Hartrees.

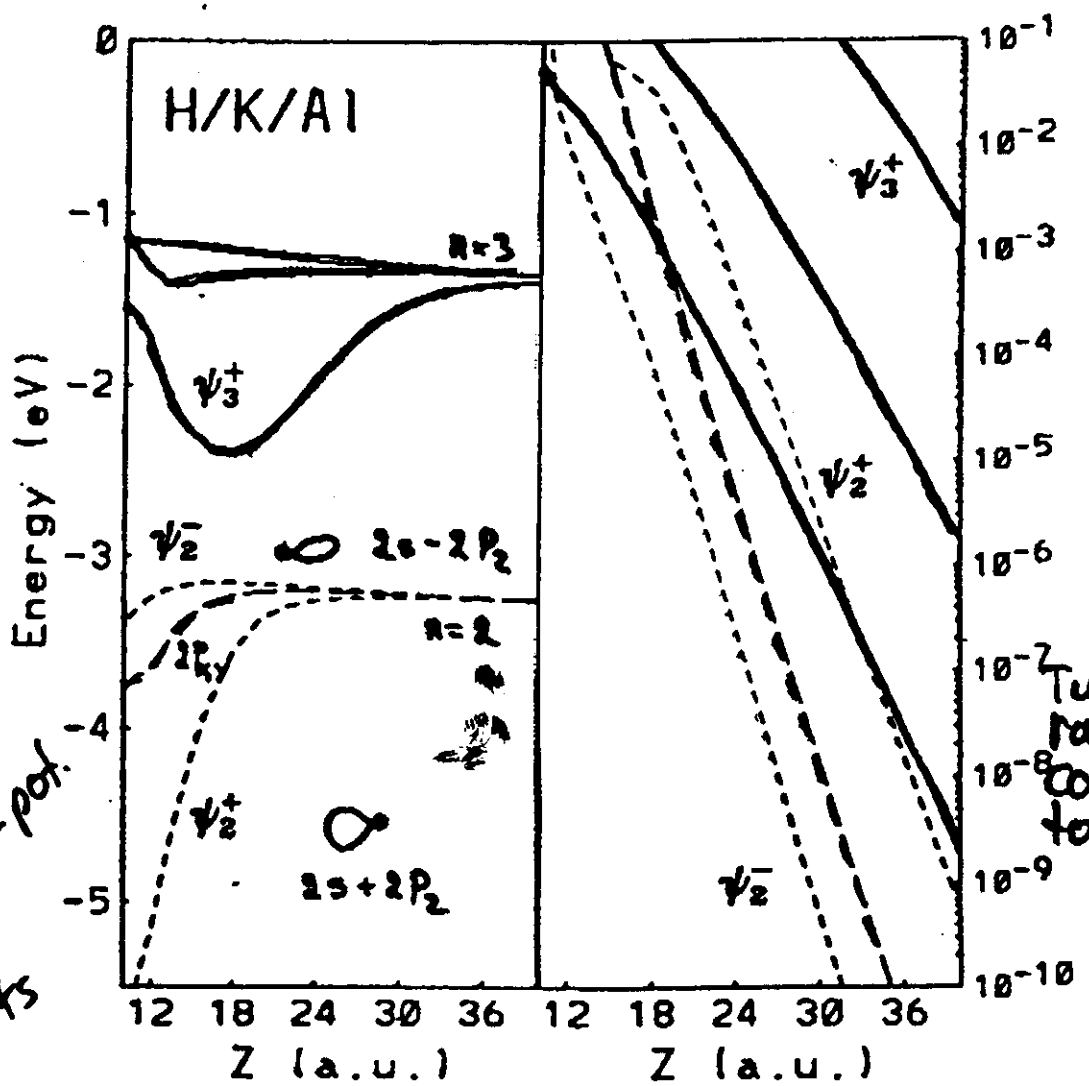
H/Al $n=2,3$ levels hybridize

$\psi_2^+ = \psi_{2s} + \psi_{2p} \sim 0 + \infty =$ 

$\psi_2^- = \psi_{2s} - \psi_{2p} \sim 0 - \infty =$ 

Width depend on orientation

Results for H outside K/Al



non-image-pot. like shifts

Tunneling rates increased compared to H/Al

Impurity induced potential increase hybridization states oriented towards surface shifts downwards non-image-like shifts

Fig. 2

Dynamics of electronic charge states for $R = R(t)$

Most of physics believed to be contained in time-dependent Anderson Model:

$$H(t) = \sum_{\sigma} \epsilon_\sigma(t)\, n_\sigma(t)$$

$$+ \frac{1}{2} \sum_{\sigma \neq \sigma'} V_{\sigma\sigma'}\, n_\sigma(t)\, n_{\sigma'}(t)$$

$$+ \sum_{k} \epsilon_k(t)\, n_k(t) + \sum_{\sigma k} V_{\sigma k}(t)\, C_k^\dagger(t)\, C_\sigma(t) + \text{h.c.}$$

σ = atomic state label - (including spin)

k = substrate state label - (including spin)

$$\Gamma_\sigma(t) = 2\pi \left| V_{\epsilon_\sigma(t)}(t) \right|^2 \rho(\epsilon_\sigma(t))$$

$\Gamma_\sigma(t)$ — $\epsilon_\sigma(t)$ — From one-electron calculations

$V_{\epsilon_\sigma(t)}(t)$ — Value of this implied

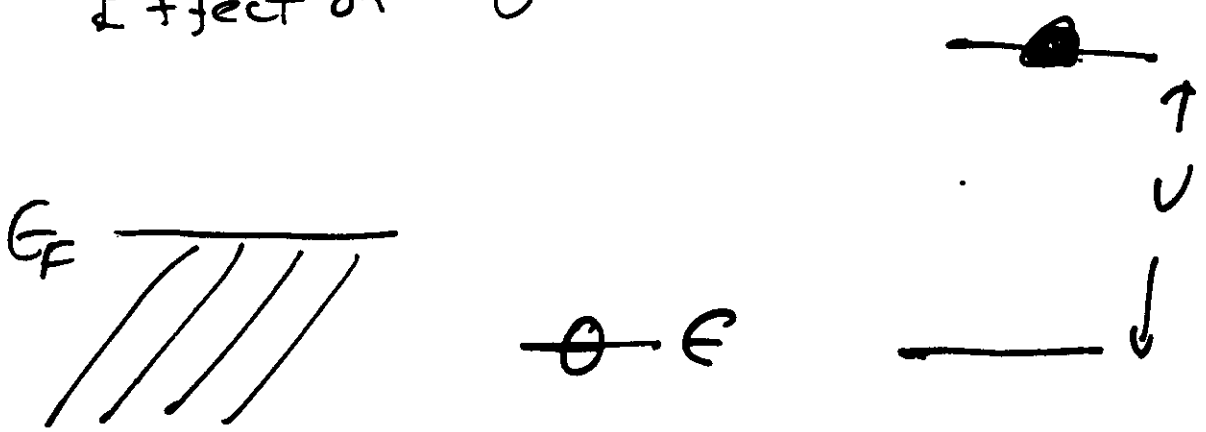
Conventional model for charge transfer:

Take $U = 0$ (i.e. neglect intra-atomic correlation)

Levels fill + depopulate independently.

This can give, as we show, qualitatively wrong results.

Effect of U



shifts level up by U when filled. If $\epsilon + U >> \epsilon_F + \Gamma$ then restricts to single occupancy.

So take $U = \infty$. Solve by
↳ i.e. $U + \epsilon_a \gg \epsilon_F + \Gamma$

Coleman "slave boson" technique.

$$V_{k\sigma}(t)\, c_k^+(t)\, c_\sigma(t) \longrightarrow$$

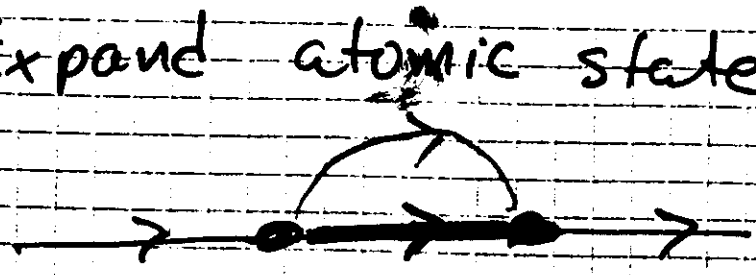
$$V_{k\sigma}(t)\, c_k^+(t)\, c_\sigma(t)\, b^+(t)$$

↑ ↑ ↑ Boson

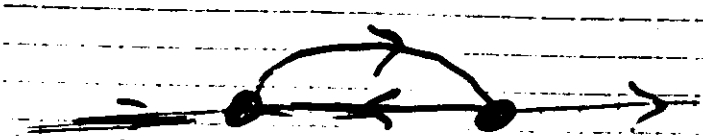
Boson does the bookkeeping so can easily project onto physical subspace.

Approximation:

Expand atomic state self-energy



and boson self-energy



Correct: a) for small broadenings

b) large "n"

Method:

note $n_\sigma(t) = G^<_\sigma(t,t)$

Solve non-equilibrium Dyson equations for $G^<_\sigma(t,t') \equiv \langle f^\dagger_\sigma(t') f_\sigma(t) \rangle$

à la Kadanoff-Baym or Keldysh.

First need advanced + retarded functions:

$$\left(i\frac{\partial}{\partial t} - \epsilon_\sigma(t) \right) G^{A,R}_\sigma(t,t') = \delta(t-t')$$

$$+ \int d\bar{t}\ \Sigma^{A,R}_\sigma(t,\bar{t})\, G^{A,R}_\sigma(\bar{t},t')$$

+ similar equation in t'

Then

$$\left(i\frac{\partial}{\partial t} - \epsilon_a(t) \right) G^<_\sigma(t,t')$$

$$= \int d\bar{t} \left[\Sigma^R(t,\bar{t})\, G^<(\bar{t},t') + \Sigma^<(t,\bar{t})\, G^A(\bar{t},t') \right]$$

+ similar equation in t'

Plus similar set of 4 equations for slave boson

The procedure is to substitute values for Σ (previous transparency) and solve for G. We have done this -in-

1. Special Case (Nordlander PR 43, 2541 (1991))

$$\Gamma^2 \ll \frac{d\epsilon_a}{dt} \quad \text{or} \quad \Gamma \ll |\epsilon_a - \epsilon_F|$$

Reduces to Master Equation:

$$\frac{dn_\sigma}{dt} = \Gamma_\sigma f_\sigma \left(1 - \sum_{\sigma'} n_{\sigma'}\right) - \Gamma_\sigma (1 - f_\sigma) n_\sigma$$

↑ fermi function

Coulomb exclusion factor, which replaces Pauli exclusion factor $(1-n_\sigma)$ of $U=0$ master equation

2. Exact solution:

Shao, Langreth, + Nordlander

(In preparation)

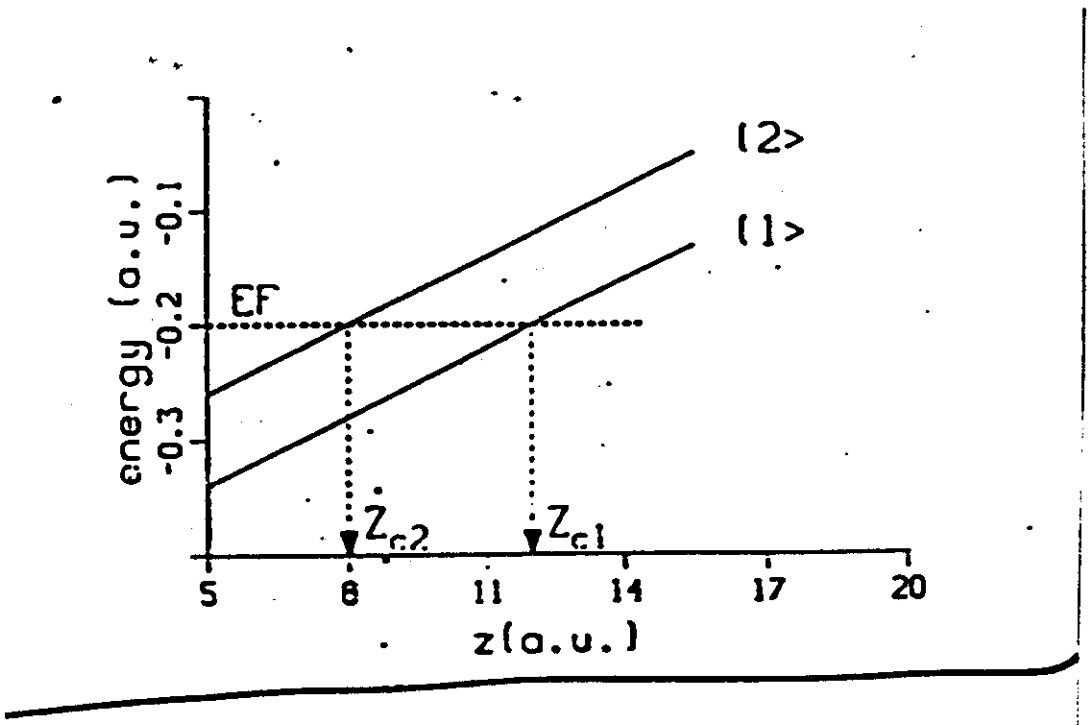


FIG. 4. Schematic plot of the assumed shift of the two atomic energy levels $|1\rangle$ and $|2\rangle$ near a metal surface. The Fermi energy and the crossing distances Z_c^1 and Z_c^2 where the atomic energy level crosses the Fermi energy are indicated.

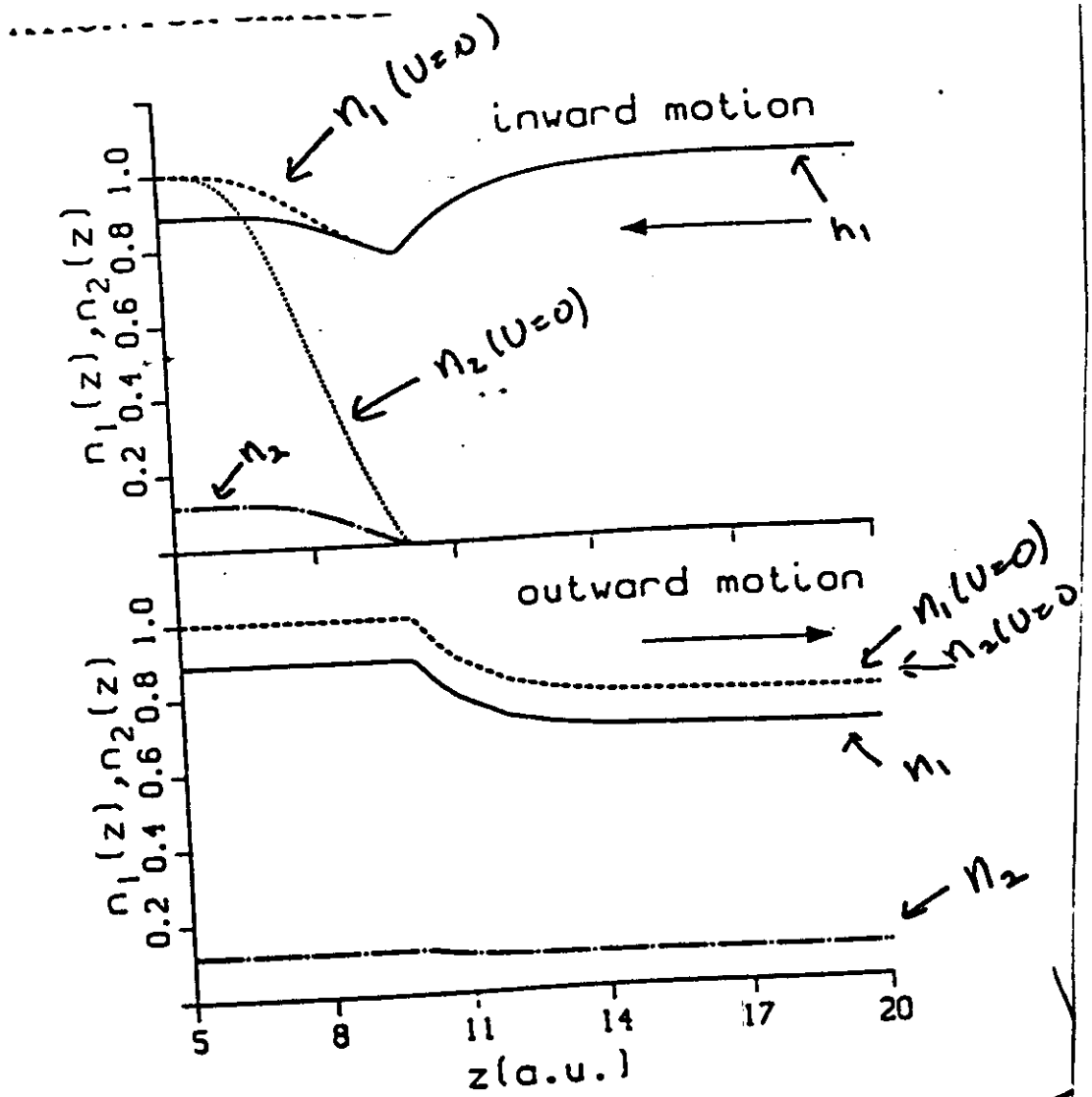
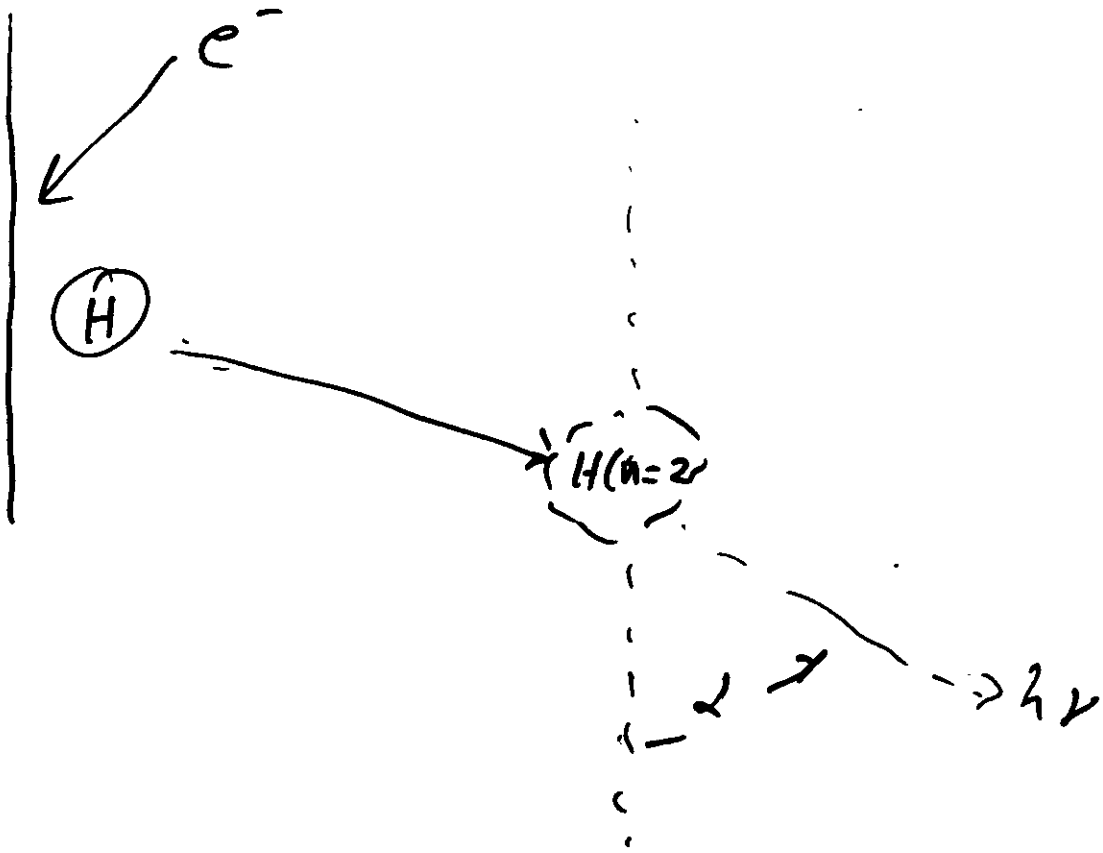


FIG. 7. Comparison of the results from the master equations for infinite U and $U = 0$ for a doubly degenerate atomic level. The trajectory is as defined in Fig. 4. The upper part of the figure shows the population of the different levels as a function of distance from the surface along the ingoing trajectory. The lower figure describes the outgoing trajectory. The parameters of the system are $v = 0.001$, $T = 300$ K, $Z_c^1 = Z_c^2 = 10$ a.u., $b_1 = b_2 = 0.02$, $\Delta_1 = \Delta_2 = 0.2$ a.u., and $\alpha_1 = \alpha_2 = 0.7$ a.u. The metal work function is 0.2 a.u. The solid and dash-dotted lines are $n_1(z)$ and $n_2(z)$ calculated using Eq. (3.18). The dashed and dotted lines are $n_1(z)$ and $n_2(z)$ calculated using Eq. (3.8), i.e., neglecting correlation. During the outgoing trajectory the dotted and dashed lines coalesce, resulting in an apparent dashed line.

Application:

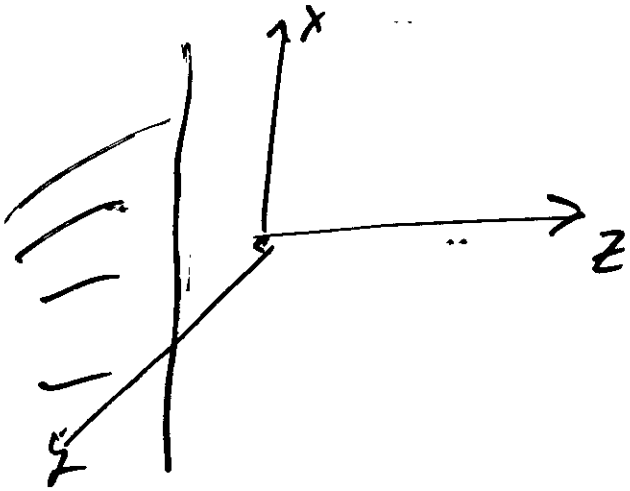
Stimulated desorption of $H(n=2)$ from $Cu(100)_{+Cs}$

P. D. Johnson + C D Tsuei

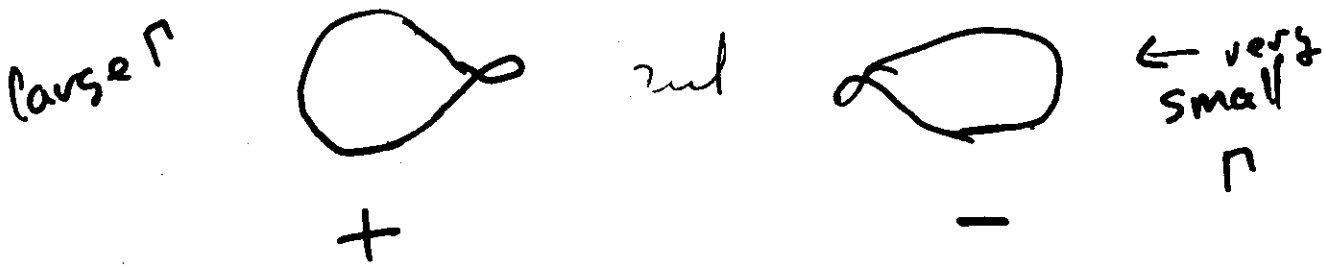


Angular dependence of photon determines relative "final" occupancy of $n=2$ states of H

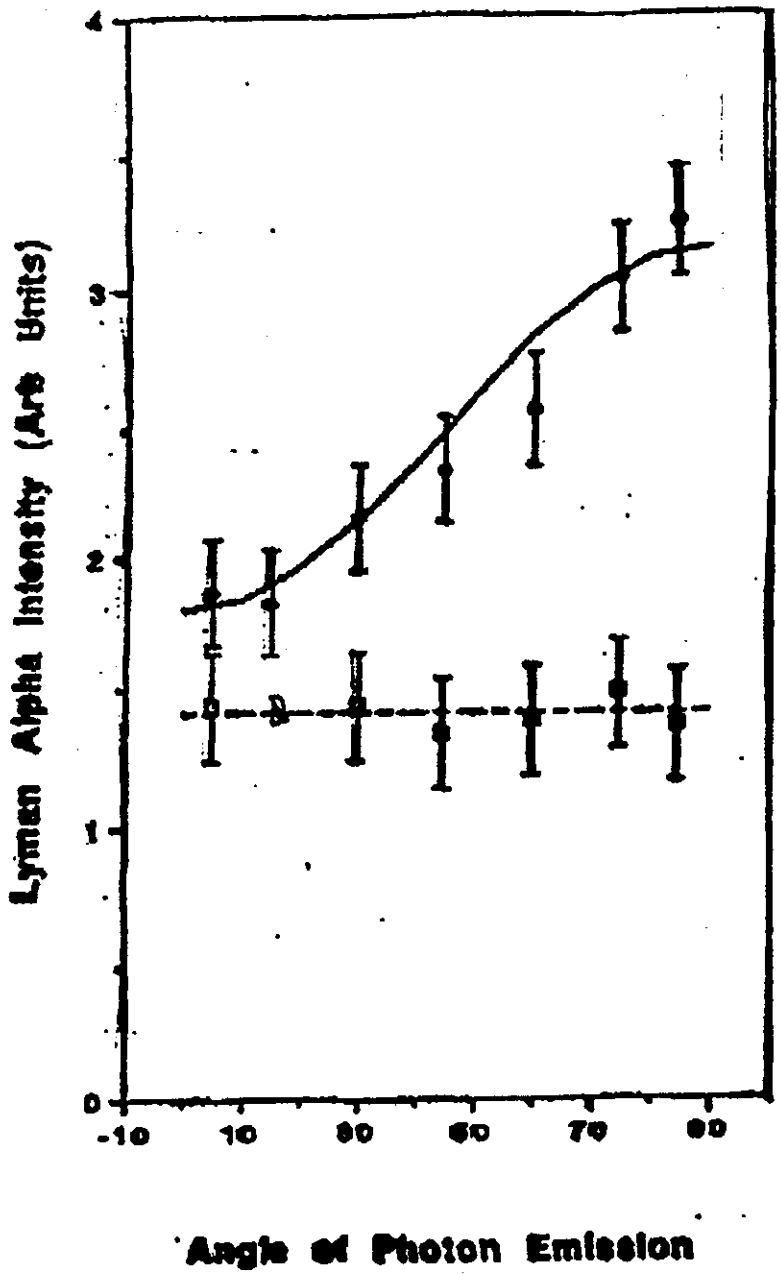
States of $H(n=2)$



$$\psi^{\pm} \propto \psi_{2s} \pm \psi_{2p_z}$$



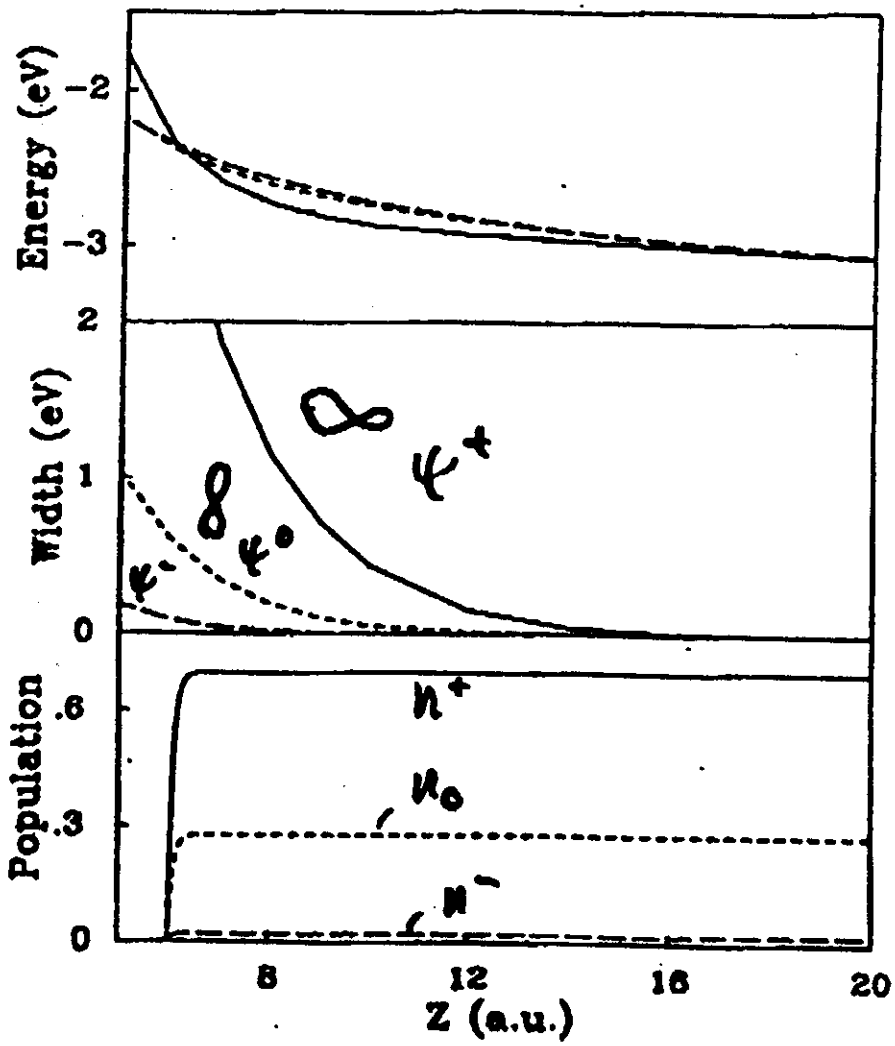
$$\psi_0 \propto \psi_{2p_y}$$
$$\psi_{2p_x}$$


Lyman Alpha Intensity (Arb Units)
0
1
2
3
4
-10
10
30
50
70
90
Angle of Photon Emission

Experiment (Johnson et al.) $n^+/n_0 = 2.5$

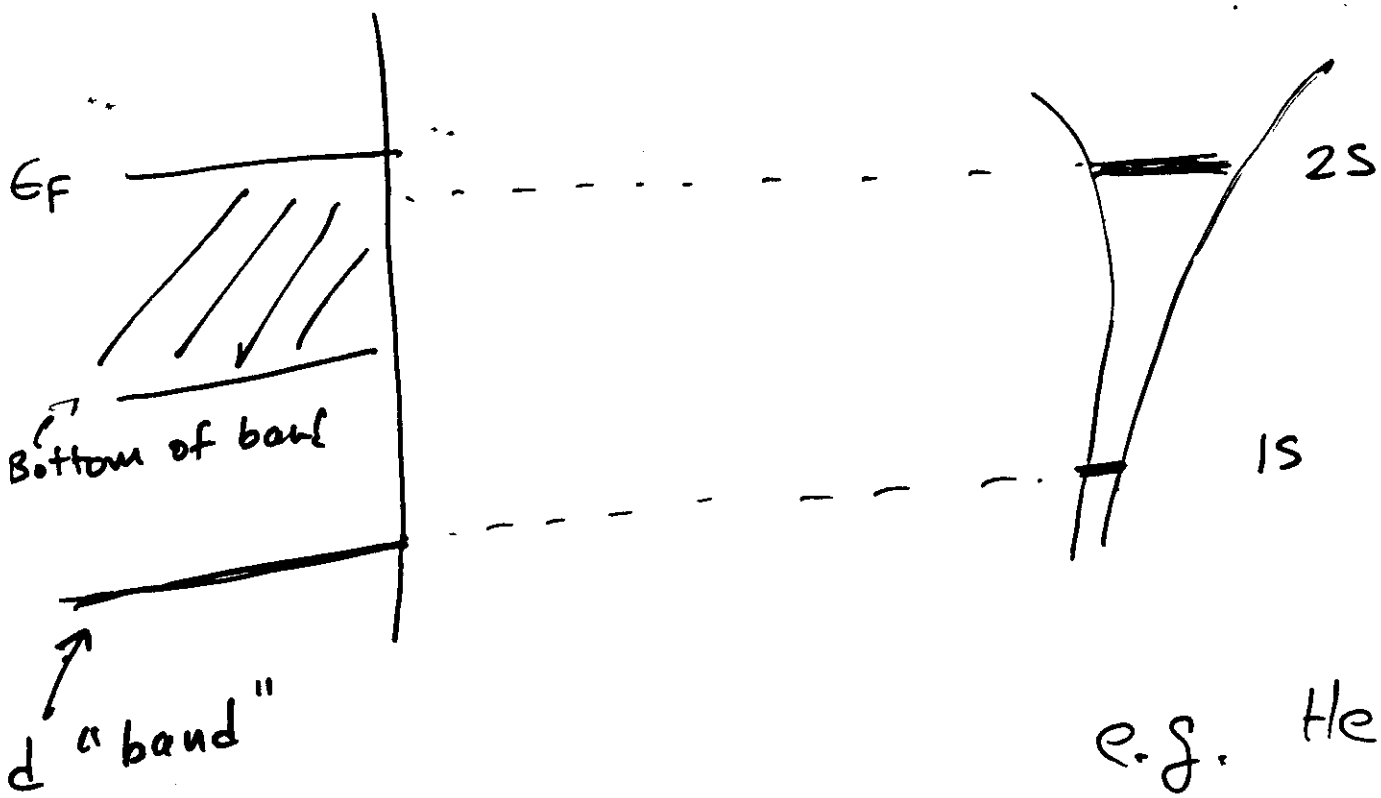
Calculation (Below) $n^+/n_0 = 2.54$

Calculation for $U = 0$ $n^+/n_0 \simeq 1$



Application (In progress)

* Double Resonant tunneling



e.g. Pb

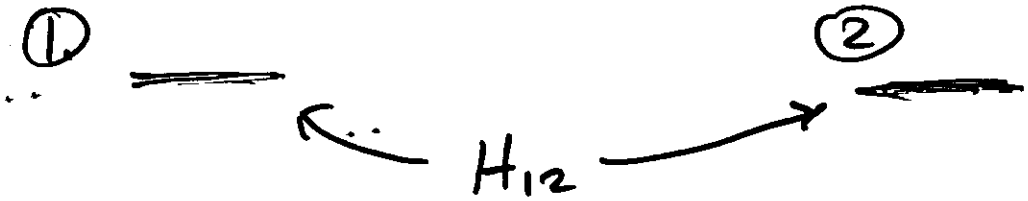
e.g. He^{++}

1. Resonance or near resonance between 1s + d band
   ⟹ Stuckelberg oscillations

2. Tunneling into 2S from conduction band inhibits (thru interatomic U) oscillations + quantum interference with them.

Aside: Stuckelberg oscillations

2 states in resonance



Coupled by H_{12}

$= H_{12}(z(t))$

$z(t)$: distance; a function of time t

Suppose $n_1(0) = 0$, $n_2(0) = 1$

Then $n_1(t) = \sin^2 \alpha$

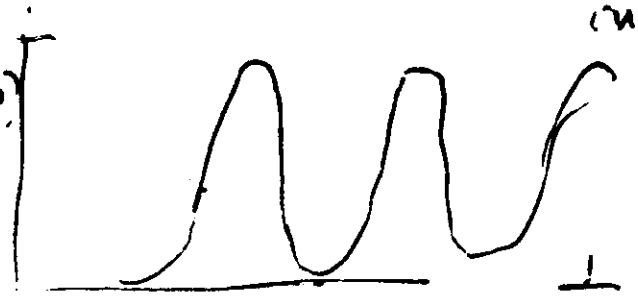
where

$$\alpha = \alpha(t) = \int_0^t H_{12}(z(t))\,dt$$

if $z(t) = \pm v t + z_0$

then $\alpha = \frac{1}{v} \int \underbrace{H_{12}(vt)}_{\text{indep. of } v}\, L(vt)$

Final n_1 periodic in $\frac{1}{v}$



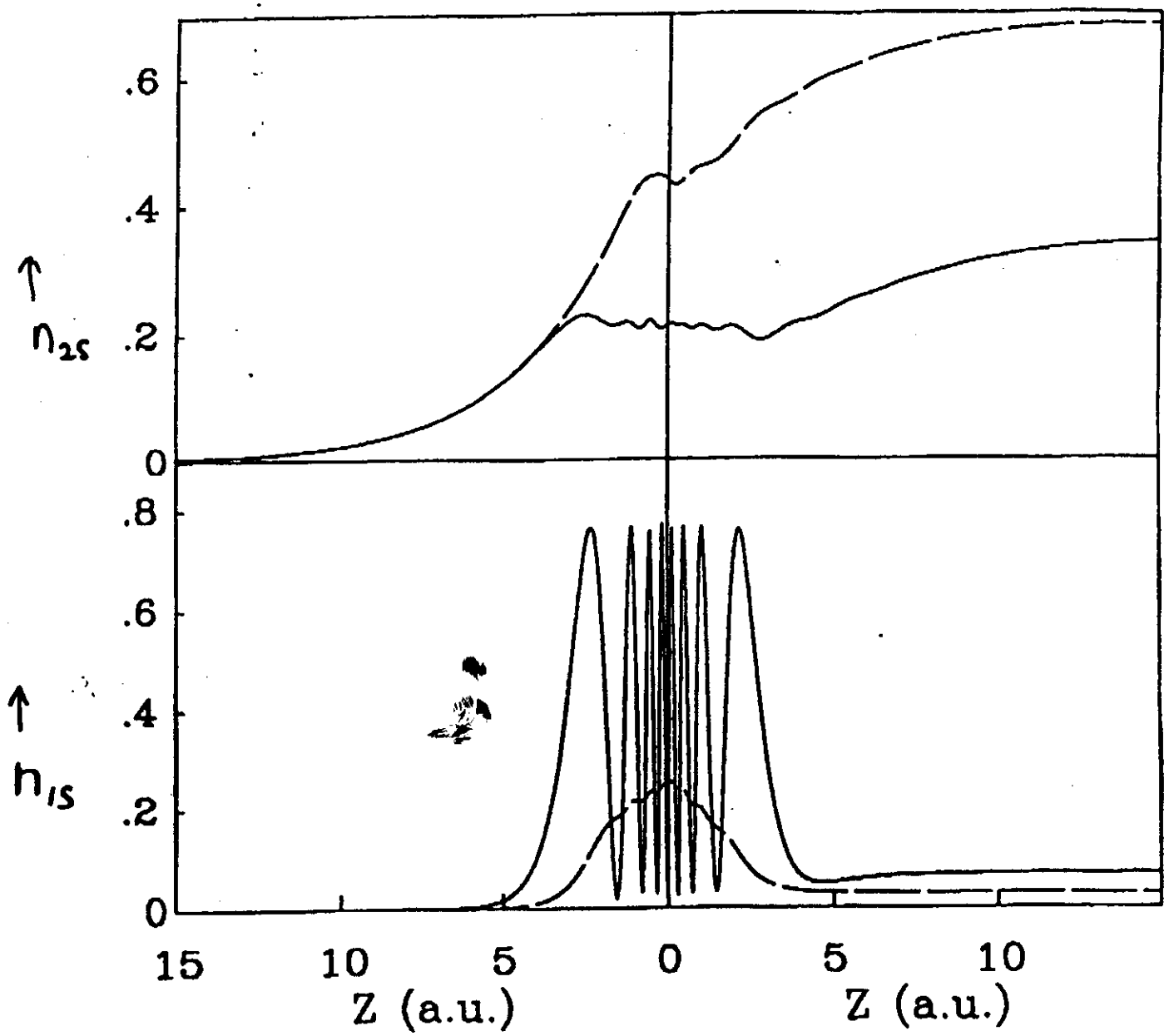


Fig. 8

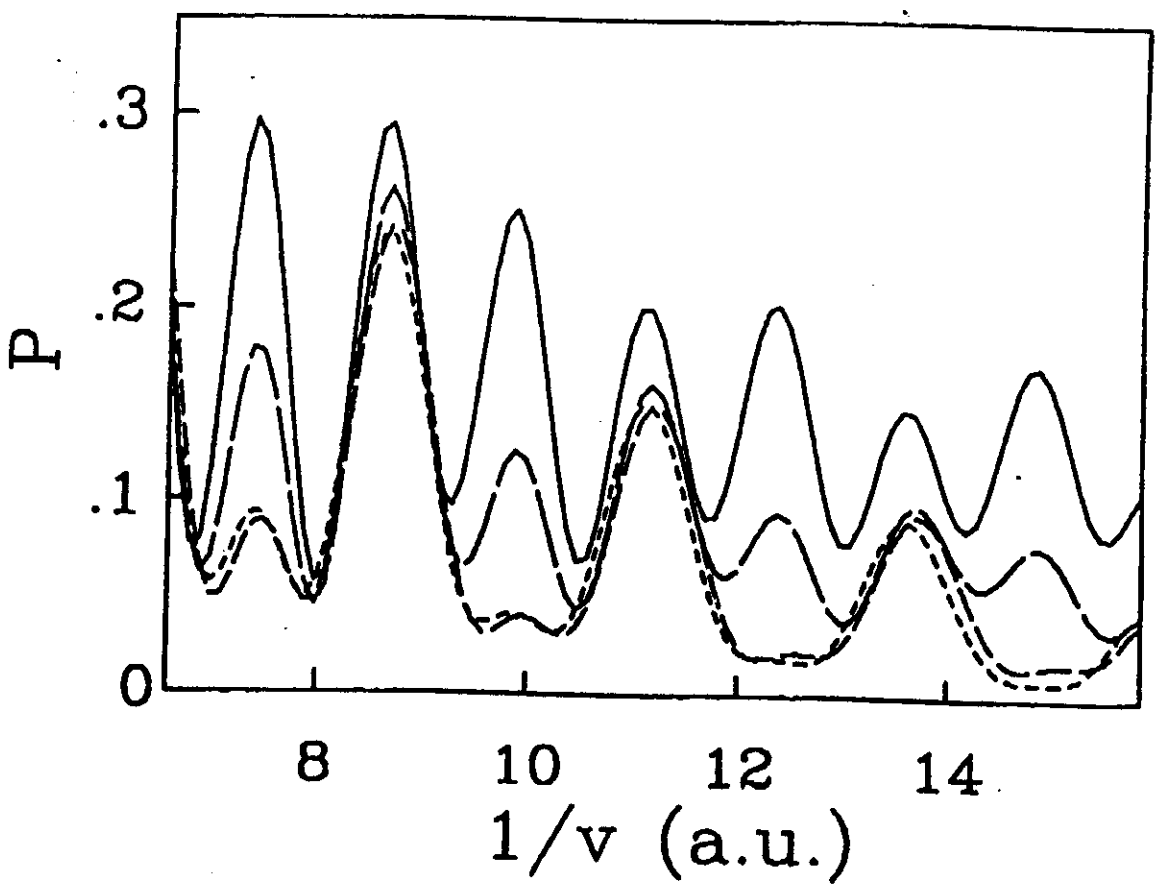
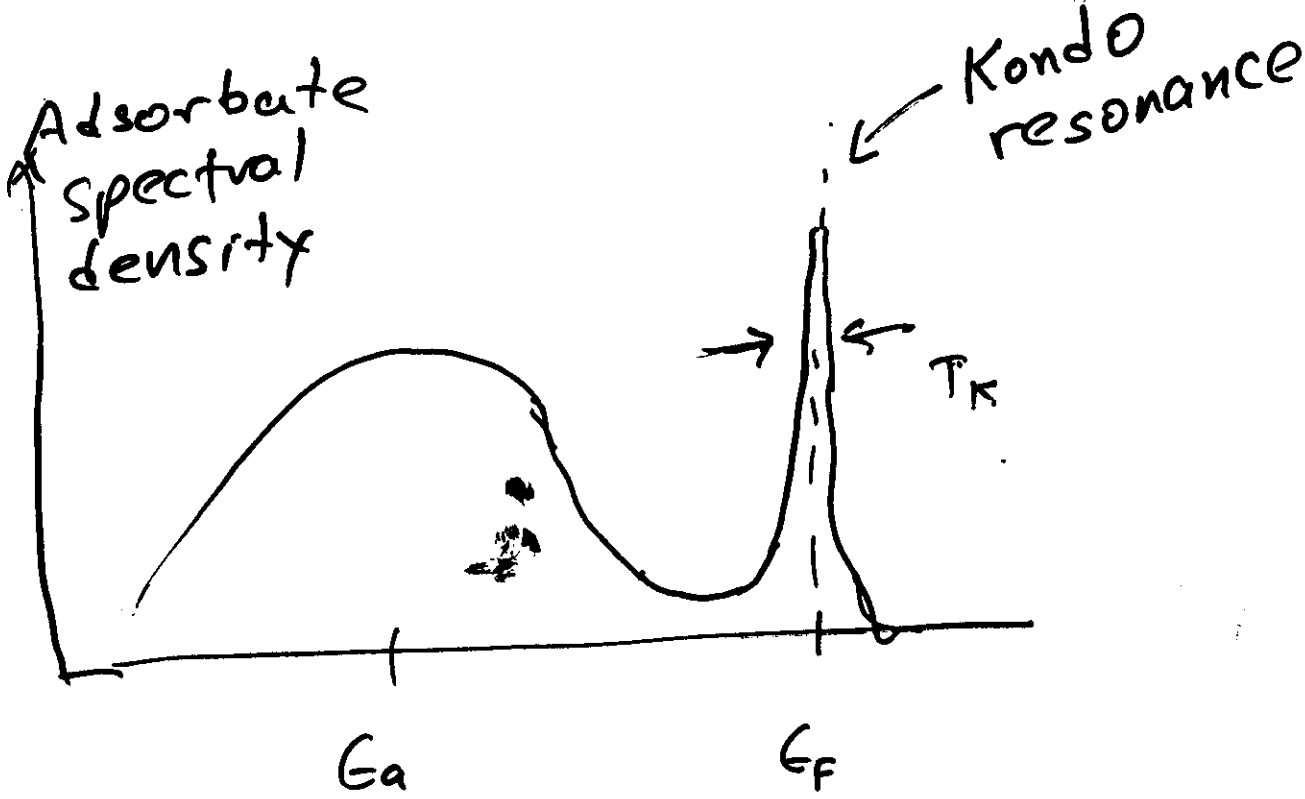


Fig. 9

Application: in Progress

How does the Kondo state and it's appearance & disappearance as $E_a(t)$ shifts affect non-adiabatic phenomena. $E_{na} \propto \left(\frac{d\delta}{dt}\right)^2$



We now have the time-dependent solution, for what Coleman (large n) did statically.

Extension of Time-dependent equations to finite U.

We have made an extension of the multiple auxiliary particle technique to the finite U case

---

So can treat negative ion formation and other phenomena that occur when U becomes small or negative at small Z, if the work function is sufficiently small.

K.E. = 2eV , Li

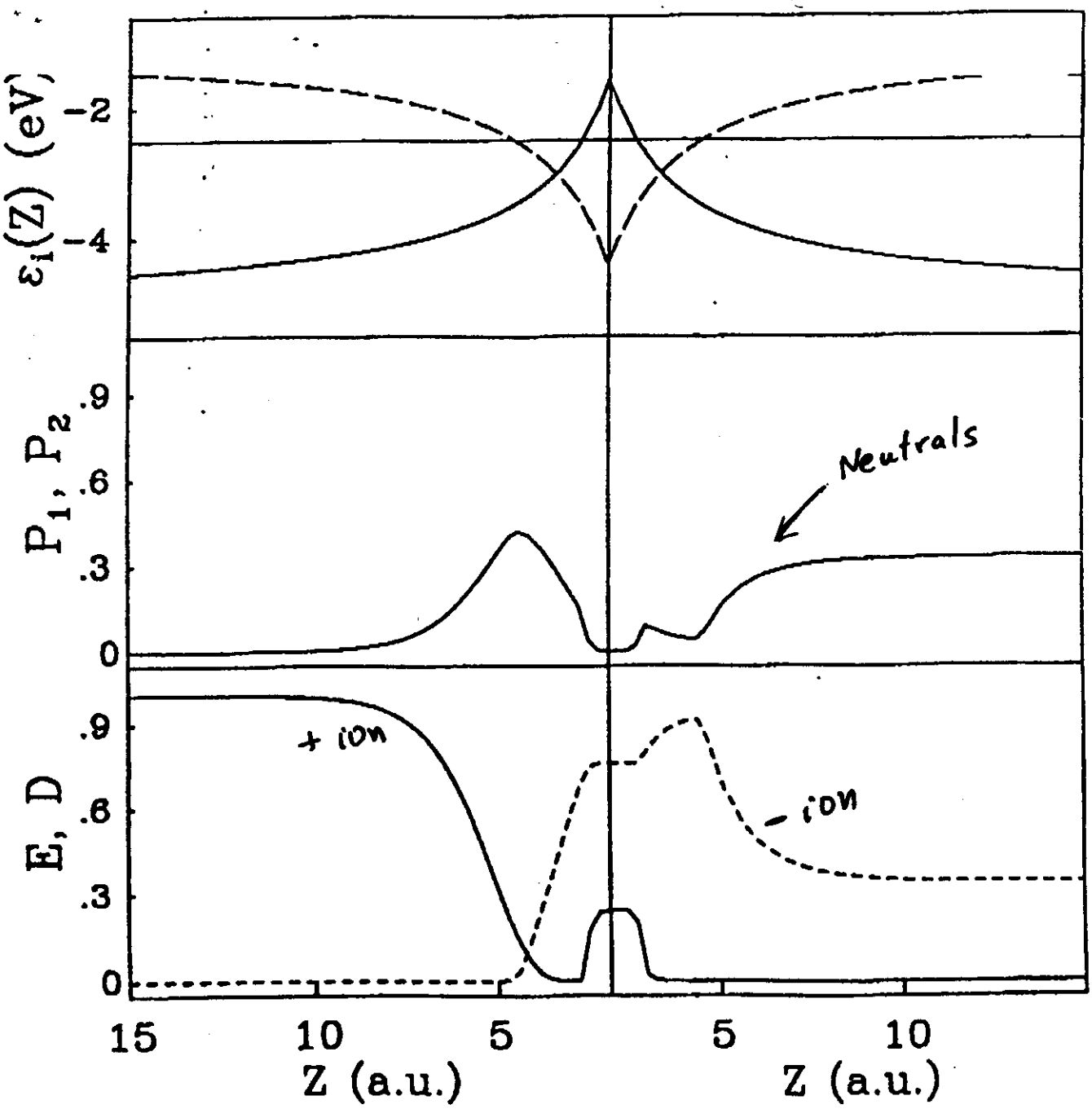


Fig. 14

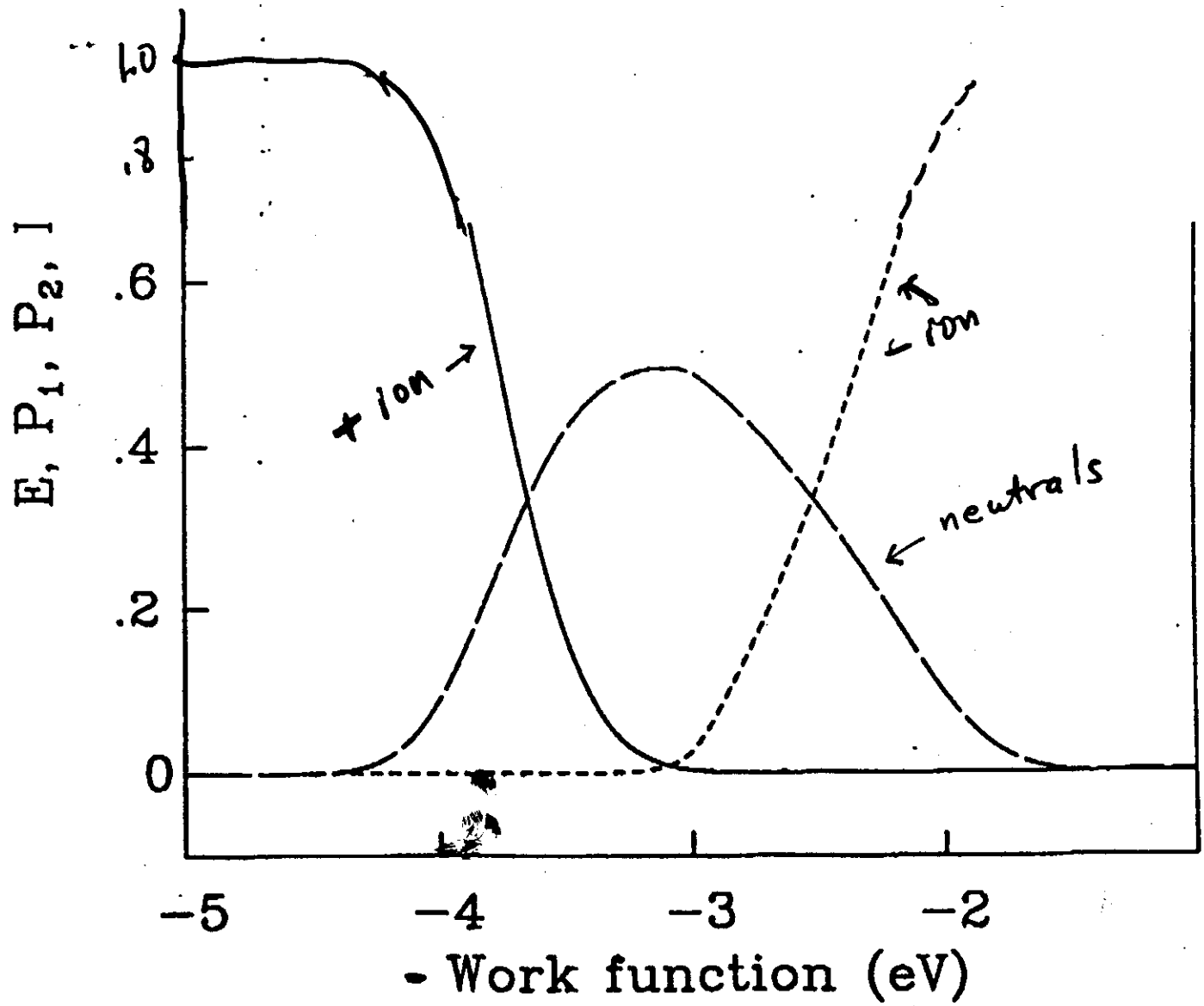
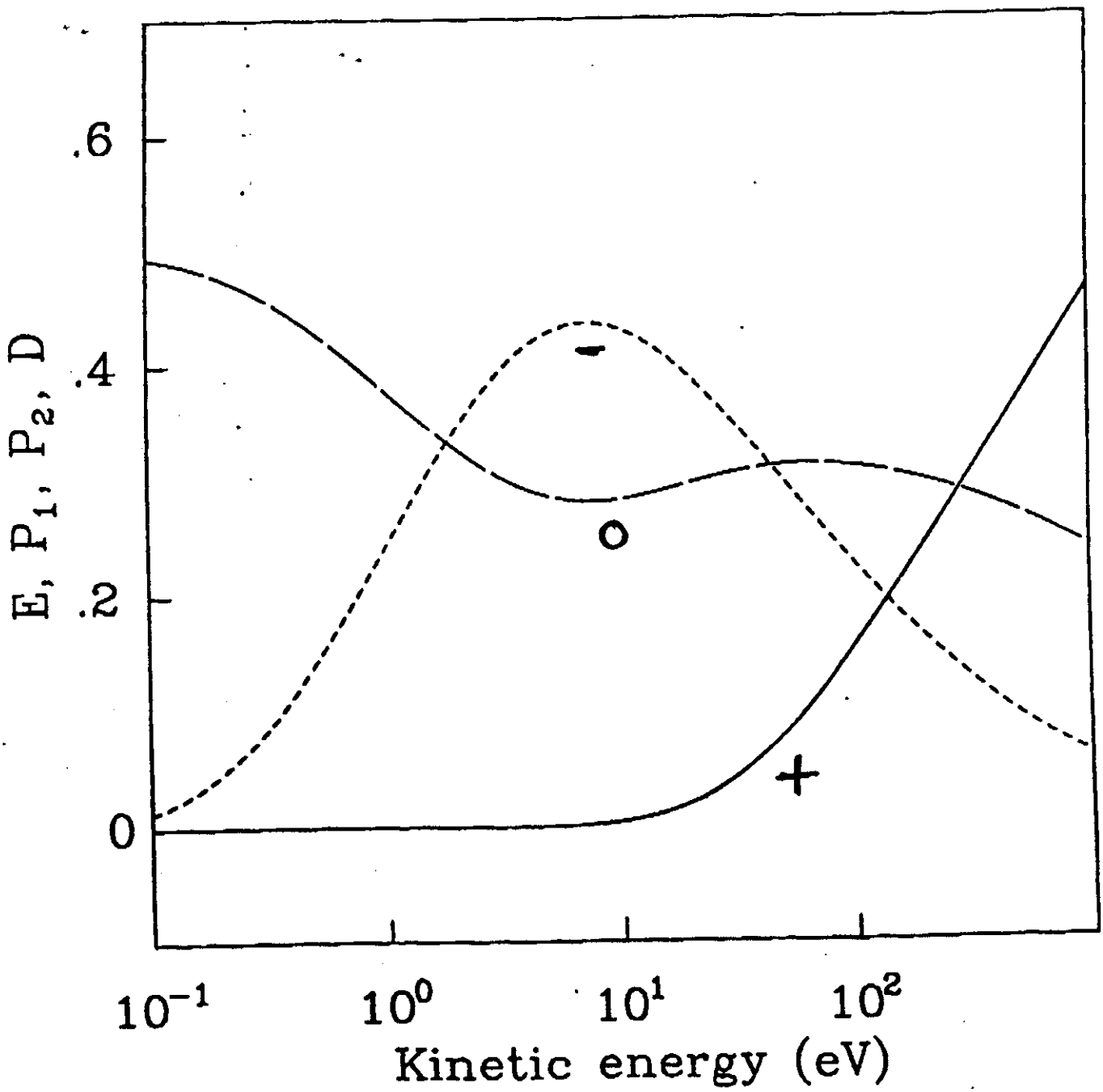


Fig. 15



2.5 wt

Fig. 16

Conclusions

1. Our theory contains information about a wide class of dynamic phenomena involving adsorbates and surfaces including

   a) final charge states in desorption and surface scattering

   b) rate of formation and decay of Kondo and mixed valent states at surfaces

   c) Atomic-like resonance phenomena e.g. Stuckelberg oscillations

   d) $\frac{dS}{dt}$ and hence non-adiabatic energy transfer information.

2. Inclusion of intra-atomic correlations is necessary to get any of the above qualitatively correct.