Lecture 10

Transition probabilities and photoelectric cross sections

TRANSITION PROBABILITIES AND PHOTOELECTRIC CROSS SECTIONS

Cross section = σ = Transition probability per unit time of exciting a single atom or molecule or solid specimen from $\Psi^i(N)$ to $\Psi^f(N)$ with unit incident photon flux of 1 cm^{-2} sec^{-1}. If the direction of PE is defined with respect to photon polarization and propagation. It is called dσ/dΩ

$$\sigma = \int d\sigma/d\Omega \ d\Omega$$

The perturbation of electromagnetic radiation on N electron system (weak field limit)

$$\hat{H} = -e/(2mc) \ (P \cdot A + A \cdot P)$$

$P = -i\hbar \nabla$, A = A(r, t), vector potential of the field.

If the electromagnetic wave is traveling in uniform medium, it is possible to choose A such that ∇. A = 0 thus P. A = 0, in XPS we consider only A. P.

There are exceptions, UPS "Surface photo effect"

Electromagnetic wave is assumed to be a plane wave.
$A(r,t) = e A_0 \exp [i(k_{h\nu}.r - 2\pi\nu t)]$

e is a unit vector parallel to E, electric field
A_0 – amplitude factor
$k_{h\nu}$ is wave vector of propagation $| k_{h\nu}| = 2\pi/\lambda$

Transition probability from $\Psi^i(N)$ to $\Psi^f(N)$ can be given by matrix element,
$|M_{if}|^2 = |\langle \Psi^f(N) | \Sigma_{i=1}^N A(r_i).p_i|\Psi^i(N)\rangle |^2$
$= \hbar^2 A_0^2 |\langle \Psi^f(N) | \Sigma_{i=1}^N \exp(i k_{h\nu}.r_i) e. \nabla_i|\Psi^i(N)\rangle|^2$

Integration is over the space and spin coordinates of all the electrons. Intensity of photon flux is proportional to A_0^2. Find state $\Psi^f(N)$ corresponds to electron emission through wave vector k^f (momentum $p^f = \hbar k^f$) oriented within solid angle $d\Omega$.

There are many ways by which this expression can be evaluated. The initial state is represented as an antisymmetrised product of active k orbital from which photoemission occurs and the N-1 electron remainder $\Psi_R(N-1)$, representing passive electrons.

$\Psi^i(N) = \mathring{A}(\phi_k(1)\ \chi_k(1),\ \Psi_R(N-1))$

In the weak coupling case,
$\Psi^f(N) = \mathring{A}(\phi^f(1)\ \chi^f(1),\ \Psi^f(N-1))$

Here the k subscript of the ionic function is suppressed primary k$\rightarrow$f excitation event is rapid. This is the "Sudden approximation".

The operation of one electron transition operator on the N electron function is assumed to be like,

$$\langle \psi^f(1) | \Sigma_{i=1}^N t_i | \psi^i(1) \rangle = \langle \phi^f(1) | t | \phi_k(1) \rangle \langle \psi^f(n-1) | \psi_R(n-1) \rangle$$

Thus the transition probabilities are proportional to,

$$\langle \phi^f(1) | t | \phi_k(1) \rangle |^2 | \langle \Psi^f(N-1) | \Psi_R(N-1) \rangle |^2$$

If the overlap integral has to be non zero, both Ψ^f and Ψ_R must belong to the same irreducible representation. This is the origin of the 'monopole' electron rule. (Ψ_R is not a valid ionic state wave function. It is only a non-unique representation of N-1 passive electrons.

Let us see whether sudden approximation is valid.
If the excitation from k sub shell yields a number of final state energies ($E^f(N-1, k)$) k = 1, 2, … the validity of sudden approximation is that $[E^f(N-1), k) – E^f(N-1) k')]$ t'/$\hbar$<<1

t' is the time required for k $\rightarrow$ f photoelectron to leave the system, K and k' are a set of final states of significant intensity.

$|< \phi^f |r| \phi_{A\lambda} >|^2 \; \alpha \; d\sigma_{A\lambda}^{(AO)} / d\Omega$

or $< \phi^f |r| \phi_{A\lambda} > \; \alpha \; \pm (d\sigma_{A\lambda}^{(AO)} / d\Omega)^{1/2}$

This will give,
$d\sigma_k^{(MO)} / d\Omega \; \alpha \; \Sigma_{A\lambda} \; |C_{A\lambda k}|^2 \; (d\sigma_{A\lambda}^{(AO)}/d\Omega)$

$|C_{A\lambda k}|^2$ is the not population of atomic orbital A_λ in the molecular orbital k. The model discussed has been applied with high accuracy to molecular systems.

Solids and Valence bands

Three step model involving
a)   Excitation from orbital ϕ_k to ϕ^f
b)   Electron transport via ϕ^f to surface during which elastic or inelastic process may occur.
c) Passage of e^- through the surface, reflection and refraction may occur as a result of surface potential. A zeroth step involving the penetration of radiation to the depth were excitation occurs may be included.

For non overlapping, localised orbitals atomic cross sections may be used for slightly overlapping quasi-molecular orbitals the previous method may be used. For highly overlapping valence levels the following procedure is used

For a crystalline solid, the orbitals ϕ_k and ϕ^f will be Bloch functions

$\phi_k(r) = \phi_k(r) = n_k(r) \exp(ik.r)$ and
$\phi^f(r) = \phi_k^f(r) = n_k^f(r) \exp(ik^f.r)$

The electron makes a transition from $\phi_k(r)$ to $\phi^f(r)$. The kinetic energy inside the surface $E'_{kin,i}$ gets reduced to E_{kin}, outside the surface by a factor V_0.
V_0 corresponds to the barrier height.

$d\sigma/d\Omega = C(1/h\nu) |<\Psi^f(N)| \Sigma_{l=1}^{N} \exp ik_{h\nu}$

For E_{kin} = 1000 eV, $v/c \approx$ 0.06 or v = 2x10^9 cm/s

For an atomic diameter of 2A the escape time,
t' = 2 x 10^{-8}/2 x 10^9 = (10^{-17})s.
t/h = 1/65 eV^{-1}. For a final state separation of 10eV, the condition is
Violated

The initial and final States can also be represented in terms of single
determinant Hartree Fock wave function.

$$\Psi^i(N) = \hat{A}(\phi_1\chi_1, \phi_2\chi_2, \ldots, \phi_k\chi_k, \ldots, \phi_N\chi_N)$$
$$\Psi^f(N) = \hat{A}(\phi_1^{'}\chi_1, \phi_2^{'}\chi_2, \ldots, \phi^f\chi^f, \ldots, \phi_N^{'}\chi_N)$$

The transition element,
$$< \Psi^f(N)|\Sigma_{l=1}^N t_i| \Psi^i(N) = \Sigma_m \Sigma_n <\phi_m^{'}(1)| t | \phi_n(1)> D^{fi}(m/n)$$
m and n over all occupied orbitals. D^{fi} is the (N-1) x (N-1) passive
electron overlap determinant.

This expression assumes relaxed orbitals. If the wave function is un relaxed, the matrix element can be approximated as,

$$\langle \Psi^f(N) | \Sigma_{l=1}^N t_i | \Psi^l(N) \rangle = \langle \phi^f(1) | t | \phi_k(1) \rangle D^{fi} (f/k)$$

In evaluating the cross section, two sum rules have been pointed out

1) The weighted average B.E over all final states $\Psi^f(N-1,k)$ associated with $k \rightarrow f$ transition equals Koopmans' theorem BE - $\in_k$.

If I_k is the intensity of a transition $\Psi^f(N-1, k)$ corresponding to BE $E_b(k)$,

$$-\varepsilon_k = \Sigma_k I_k E_b(k) / \Sigma_k I_k = \Sigma_k |\langle \Psi^f(N-1)k \rangle | \Psi_R(N-1) \rangle|^2 E(b)$$

2) The sum of all intensities associated with the states $\Psi^f(n-1,k)$ is
Given by,

$$I_{tot} = \Sigma_k I_k = c \, \Sigma_k |<\phi^f(1) \mid t \mid \phi_k(1)>|^2 \, |<\Psi^f(N-1, k) \mid \Psi_R(N-1)>|^2$$
$$= c|< \phi^f(1)| t \mid \phi_k(1)>|^2$$

A more accurate method is to describe the functions in terms of many configurations such CI methods are necessary to explain many final state effects.

Atoms

Neglecting relaxation and assuming non relativistic Hamiltonian each PE transition is from spin orbital $\phi_k \chi_k = \phi_{n,l,ml} \, \chi_{ms}$ to spin orbital $\phi^f \chi^f = \phi(E^f, l^f, m_1^{f)} \chi_{ms}{}^f$ where E^f is the PE kinetic energy $h\nu - E_b{}^v(n,l)$

The selection rules are,

$\Delta l = l^f - l - \pm 1$

$\Delta_{m1} = m_1{}^f - m_1 = 0, \pm 1$

$\Delta_{ms} = m_s{}^f - m_s = 0$

L^f can be $l + 1$ or $l-1$, $l+1$ is more important in XPS.
In an atom the situation generally encountered is as follows. Atom takes all orientations and the PE makes an angle α with the radiation.
The total cross section for a given sub shell n,l is,

$\sigma_{nl}(E^f) = (4\pi\alpha_a a_0{}^2/3)\ (h\nu)[l\ R_{1-1}{}^2(E^f) +\ (l+1)\ R_{l+1}{}^2(E^f)]$

α_0 – fine structure constant a_0 – Bohr radius $R_{l\pm1}(E^f)$ are radial matrix
Elements between
$\phi_{n,l,ml}$ and $\phi(E^f, l^f, m_l{}^f)$.

$R_{l\pm1}(E^f) = \int_0^\infty R_{nl}(r)\ r\ R_E{}^f,_{l\pm1}(r)r^2\ dr = \int_0^\infty P_{nl}(r)\ r\ P_E{}^f,_{l\pm1}(r)\ dr$

$P_{nl}(r) / r \equiv R_{nl}(r)$, radial part of $\phi_{n,l.ml}$

$P^f_{E, l\pm1}(r)/r \equiv R^f_{E, l\pm1}(r)$, radial part of $\phi(E^f l^f m^f_l)$

differential cross section,

$$d\sigma_{nl}/d\Omega \ (E^f) = \sigma_{nl}/4\pi[1-(1/2)\beta_{nl}(E^f) \ P_2(\cos\alpha)]$$
$$= \sigma_{nl}/4\pi[1+(1/2) \ \beta_{nl}(E^f)(3/2 \ \sin^2\alpha-1)]$$

$\beta_{nl}(E^f)$ – asymmetry parameter
$P_2(\cos \alpha) = \frac{1}{2} (3 \cos^2 \alpha-1)$

Allowed values of β_{nl} is $-1 \leq \beta \leq +2$
+ve β corresponds to photoelectron emission at 90^0.
-ve β corresponds to photoelectron emission either parallel or anti-parallel.
$\beta = 0 \rightarrow$ isotope distribution.

For S electron $l = 0$ $l^f = 1$, $\beta = +2$

$d\sigma_{ns}(E^f)/d\Omega = (\sigma_{ns}(E^f)/4\pi) \sin^2\alpha$

Max. intensity at $\alpha = 90^0$ zero intensity at $\alpha = 0^0$ and 180^0.

For a $\beta = -1$,
$d\sigma_{nl}(E^f)/d\Omega = d\sigma_{nl}(E^f)/4\pi$

Zero intensity at $\alpha = 90^0$. Max value at $\alpha = 0^0$ and 180^0.

The equation for $d\sigma/d\Omega$ can be written as,

$d\sigma_{nl}(E^f)/d\Omega = A + B \sin^2 \alpha$
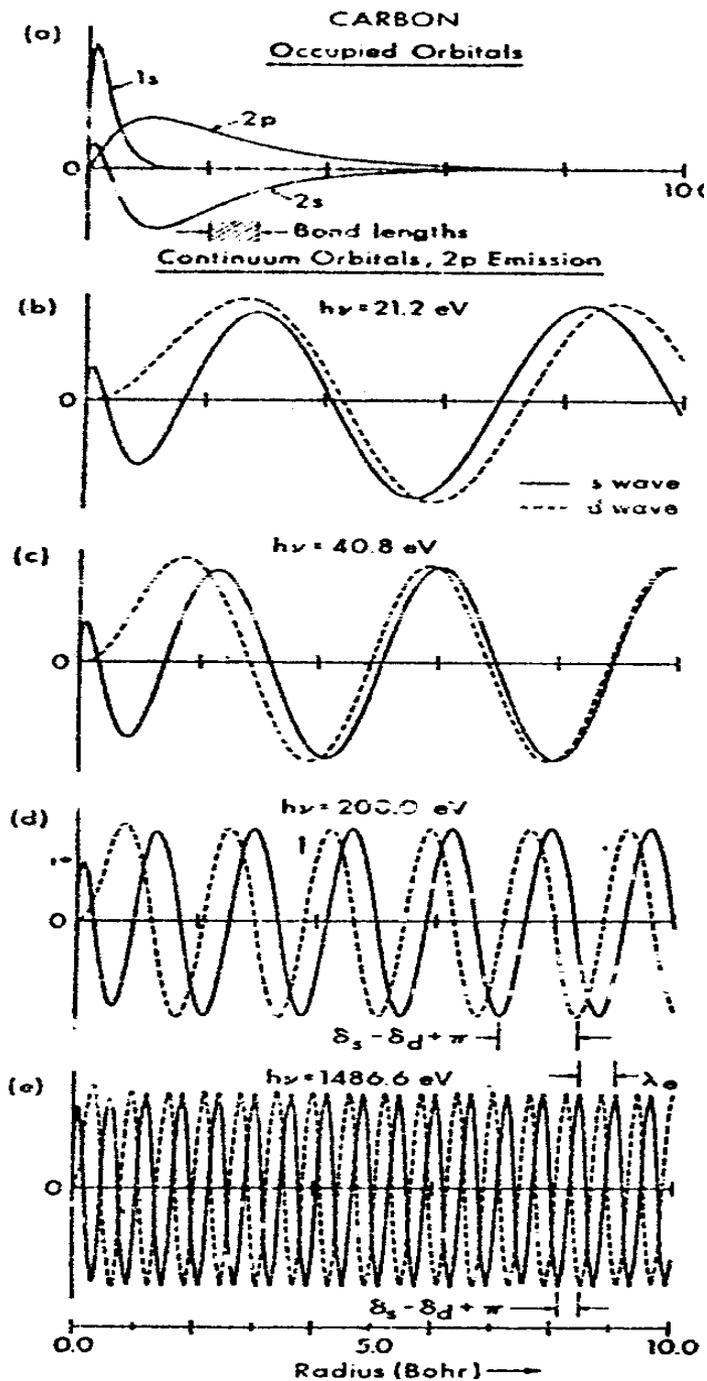
A and B are constants.

$A = (\sigma_{nl}/4\pi) \, (1-\beta_{nl}/2)$

$B = (\sigma_{nl}/4\pi). \, 3\beta_{nl}/4.$

From an empirical evaluation of A and B,
β_{nl} can be calculated

$\beta_{nl} = 4B/(3A+2B)$

Due to dipole approximation, the results may not be an complete agreement the expression.

CARBON
Occupied Orbitals

(a)

1s
2p
2s
Bond lengths
Continuum Orbitals, 2p Emission

(b) hν = 21.2 eV

s wave
d wave

(c) hν = 40.8 eV

(d) hν = 200.0 eV

$\delta_s - \delta_d + \pi$

(e) hν = 1486.6 eV

λ_e

$\delta_s - \delta_d + \pi$

0.0   5.0   10.0
Radius (Bohr) →

Radial functions P(r) = r · R(r) for (a) the occupied orbitals of atomic carbon and (b)-(c) the continuum photoelectron orbitals resulting from C2p excitation at different photon energies as indicated. Continuum wave functions for both allowed emission channels are shown (l+1→d wave, l-1→s wave). Note the non-sinusoidal character near the nucleus, and the decrease in the electron deBrogile wavelength λ_e with increasing kinetic energy.
The definition of The phase shift ($\delta_s \rightarrow \delta_d + \pi$ is also indicated for hν = 200.0 eV and 1486.6 eV.
In (a), the range of typical bond lengths between carbon and low-to-medium Z atoms is also shown for comparison.

Molecules

Generally more difficult due to difficulty in accurately representing the states

       At typical XPS energies atomic cross sections are good approximations. Core orbitals are atomic and bonding effects are negligible. Hole is localised and continuous orbital has very nearly atomic properties. At very low energies of excitation cross section resonances due to molecular geometry is observed

Valence level cross section is more complex. Initial orbital ϕ_k can be written using LCAO

$\phi_k = \Sigma_{A\lambda} \, C_{A \, \lambda k} \, \phi_{A\lambda}$

K is a symmetry label $2\sigma_g$, $1\pi_n$ etc $\phi_{A\lambda}$ is an atomic orbital, A designates atom, λ the symmetry.

(A for O_2, λ = 1s) $C_{A\lambda K}$ is expansion co efficient

LCAO s can be made with various approximations. ϕ^f can represented as one of the following
1. Simple plane wave of the form exp (ik.r) Not accurate, does not represent the atomic potentials not properly orthogonalised
2. OPWs. Not accurate at high energies.
3. Expansion in terms of partial waves of different I character
4. Multiple scattering χ_α method numerically accurate.

A given photoemission event may lead to several vibrational states,
Even when a single vibrational level is initially populated.
The electronic cross section can be partitioned for different vibrational
states. Simply by multiplying by appropriate Franck-condon factors.

So for we assumed random orientation on an atomically ordered substrate
adsorbed molecules can be well ordered most of these calculations are
done for ups.

we can take the initial orbital ϕ_k may be assumed to be LCAO. Atomic
orbitals $\phi_{A\lambda}$ may be assumed to be the representation of ϕ_k. $\phi_{A\lambda}$ can be
Slater or Gaussian. Consider final state ϕ^f such that $E^f = h\nu - E_b^\nu(k)$.
Assume that this ϕ^f is somehow determined.

Matrix element for photoemission from molecular orbital ϕ_k is,
$\langle\phi^f|r\,|0\phi_k\rangle = \langle\phi^f|\,r\,|\Sigma_{A\lambda}\,C_{A\lambda k}\,\phi_{A\lambda}\rangle = \Sigma_{A\lambda}C_{A\lambda}\langle\phi^f|r|\,\phi_{A\lambda}\rangle$

Photoelectric cross section is proportional to square of this matrix element. Thus σ is related to atomic orbitals $\phi_{A\lambda}$. In the near nuclear region, ϕ^f will look like final state orbital from atom. In the region of XPS energies valence orbitals will give similar kinetic energies and the continuous orbitals will have similar oscillatory behaviour. It can be argued that it is the region near the nucleus that most of the non-zero contributions to the matrix element occurs. As the distance is increased ϕ^f rapidly becomes an oscillatory functions with period ~0.35Å, the de Brogile
 wavelength for the photoelectron.

This is shown for C2p emission from atomic carbon. Near the nucleus, the initial AO has large spatial variation so that a non-canceling contribution to the matrix element occurs. In the slowly varying tail of the AO, the oscillations in ϕ^f will make an approximate canceling variation in the matrix element integration.

The square of the matrix element can then be written as,

$$d\sigma/d\Omega = c(1/h\nu) \, |< \Psi^f(N)| \, \Sigma_{i=1}^N \exp(ik_{h\nu}\, r_i) \, e.\wp_I \, |\Psi^I(N)>|^2$$

C is a constant, A_0 eliminated in the normalisation to unit photon flux. For atoms and molecules the cross section has to be averaged over all initial and final states. If all initial g_i states are equally populated,

$$d\sigma/d\Omega = (c/gi) \, (1/h\nu) \, \Sigma_{i,f} |< \Psi^f(N)| \, \Sigma_{i=1}^N (ik_{h\nu}\, r_i) \, e.\wp_i| \, \Psi^i(N)>|^2$$

If unpolarised radiation is used the summation has to be over all the electric field orientations. The final summation will be over $\Sigma_{i,f,e}$. These are all orientations for the target molecule or atom. That has to be included in the summation.

Vibrational excitation has to be included. Taking B.O approximation and assuming effect of perturbing radiation on nuclear coordinates negligible,
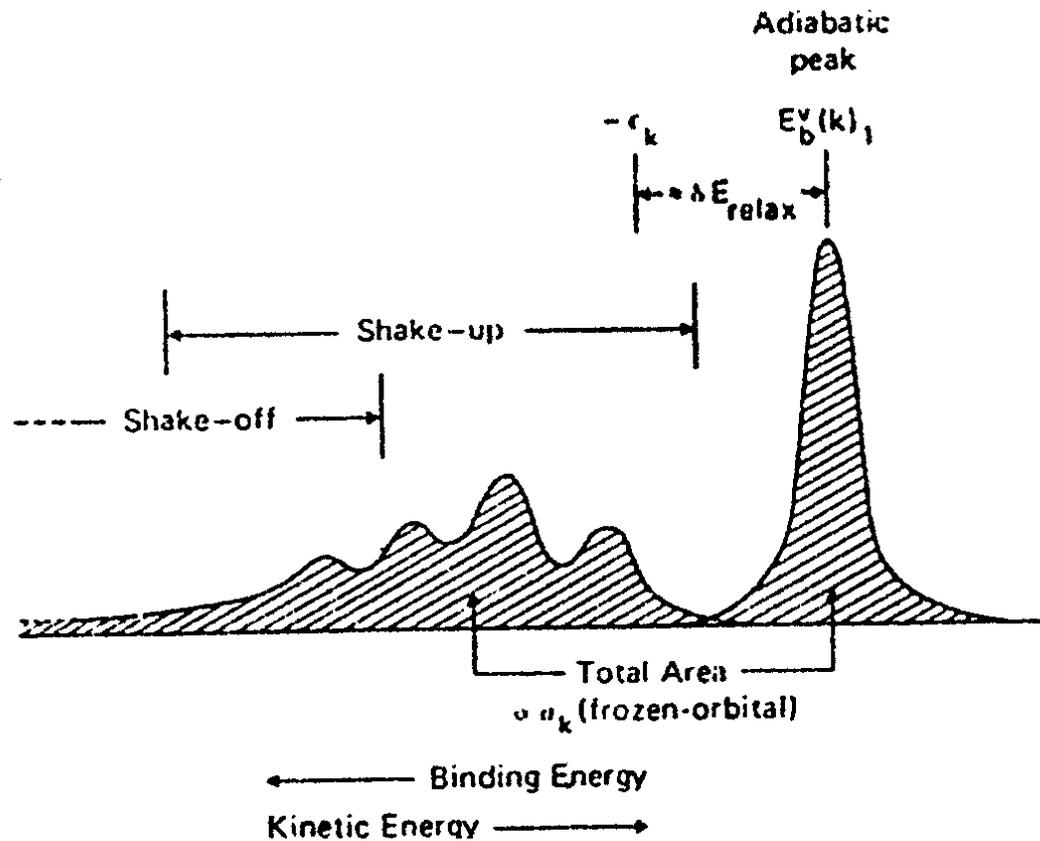
$$d\sigma/d\Omega = (c/g_i)\,(1/h\nu)\,\Sigma_{i,f}\,|<\Psi^f(N)|\,\Sigma_{i=1}^{N}(i\,k_{h\nu}\,r_i)\,e.\&_i|\,\Psi^I(N)>|^2$$

$$|<\Psi_{vib}{}^f(P)|\,\Psi_{vib}{}^i(P)>|^2$$

We will consider the electronic aspects of the matrix element.

We can assume that the photon wavelength is much larger than the dimension of the system, then $Exp(i\,k_{h\nu}\,r_i)$ is unity.

$$d\sigma/d\Omega = c/g_i(1/h\nu)\,\Sigma_{i,f}|e<\Psi^f(N)|\,\Sigma_{i=1}^{N}\,\&_i|\,\Psi^I(N)>|^2$$

This assumption is called neglect of retardation or the dipole approximation

Schematic illustration of a photoelectron spectrum involving shake-up and shake-off satellites. The weighted average of all binding energies yields the Koopmans' Theorem binding energy $-\in_k$ and the sum of all intensities is proportional to a frozen-orbital cross section σ_k. The adiabatic peak corresponds to formation of the ground state of the ion $[E_b(k)_1 \equiv E_b(K=1)]$.
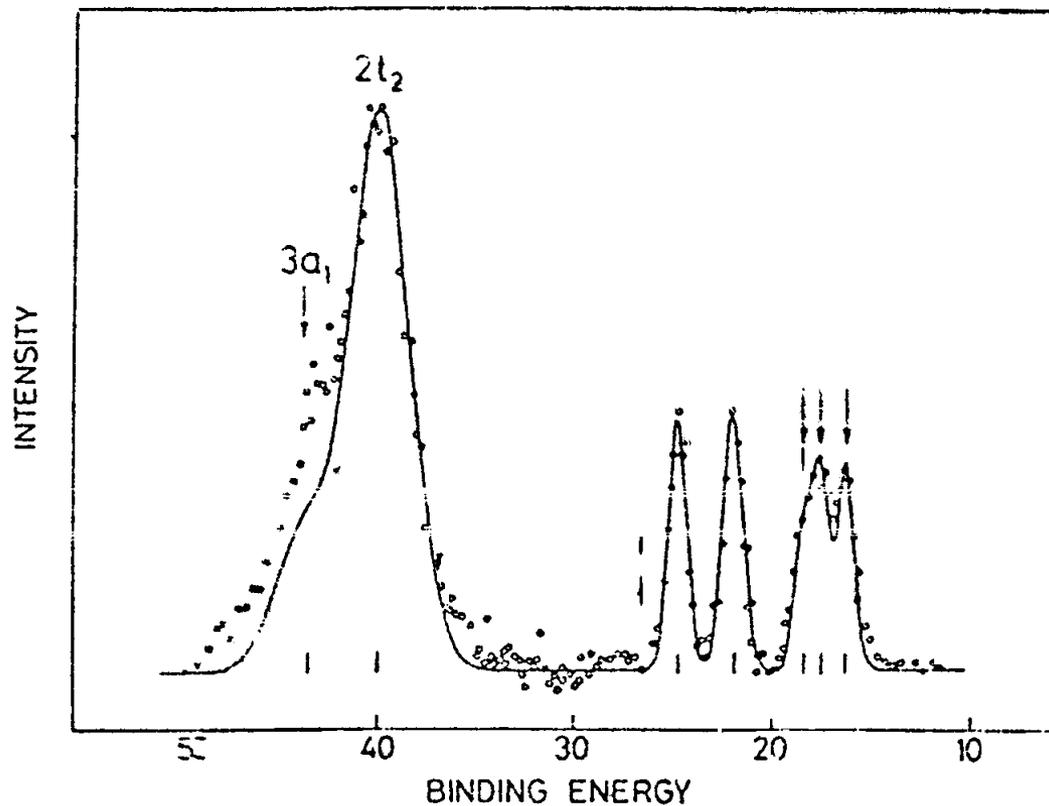
Experimental XPS spectrum for the valence levels of gaseous CF_4 in comparison with theoretical curve. Relative atomic subshell cross-sections were determined experimentally. $MgK\alpha$ radiation was used for excitation.

Electron propagation outside the surface implies a free-electron orbitals, $\phi_k^f(r) = C \exp(i\, K^f.r)$ with momentum $P^f = \hbar\, k^f$. K^f need not be k_f. The major source of difference could be refraction. Refraction conserves only the wave vector parallel to the surface ($k_{||}^f = K_{||}^f$). These effects are small except in grazing angle emission.

The one electron matrix element associated with the matrix element B is $<\phi_k^{f|}A\nabla|\phi_E>$. The symmetry properties of Bloch functions mean that this would be non-zero only if k and k^f are related by reciprocal lattice vector g.

$$k^f = k + g$$

Transitions satisfying this selection rule is called direct. At high excitation energies, wave vector of the photon also has to be included in the conservation equation

$$k^f = k + g + k_{h\nu}$$

For e.g. for $h\nu$ = 1486.6 eV, $|k^f| \approx 2\pi/\lambda_e \approx 19.7$ $(A^o)^{-1}$ for valence emission. $|k_{h\nu}| = 2\pi/\lambda = 0.7$Å.

Typical magnitude of reduced wave vector $|k| \approx 2.0$Å.
Transitions violating this selection rule are called non-direct.
They are possible $\rightarrow$ phonons, imperfections or emission from localised orbitals such as 4f.

Inelastic Scattering in Solids

If a mono energetic flux N_0 at energy E_{kin} is generated at a point, the no loss flux N_0 at length I can be given as,

$N = N_0 \exp[-l/\Lambda_e(E_{kin})] \Lambda_e$

Λ_e is the electron attenuation length. This means that inelastic scattering occurs after photoemission, extrinsic. Photoelectron energy loss can also be intrinsic, occurring during excitation. The Attenuation lengths are measured by XPS or Auger. The results fall in a universal curve.

minimum Λ_e occurs around 30-100 eV and below which it increases. Maximum surface sensitivity at 30-100eV. The high energy data can be fitted to,

$$\Lambda_e(E_{kin}) \, \alpha \, (E_{kin})^{0.52}$$

Λ_e may not be a constant for a material. It may vary from bulk to surface as the dominant mode of extrinsic inelastic scattering may vary depending on whether it is bulk or surface. For a free electron metal, it may not deviate much.

Models and attenuation length measurements.
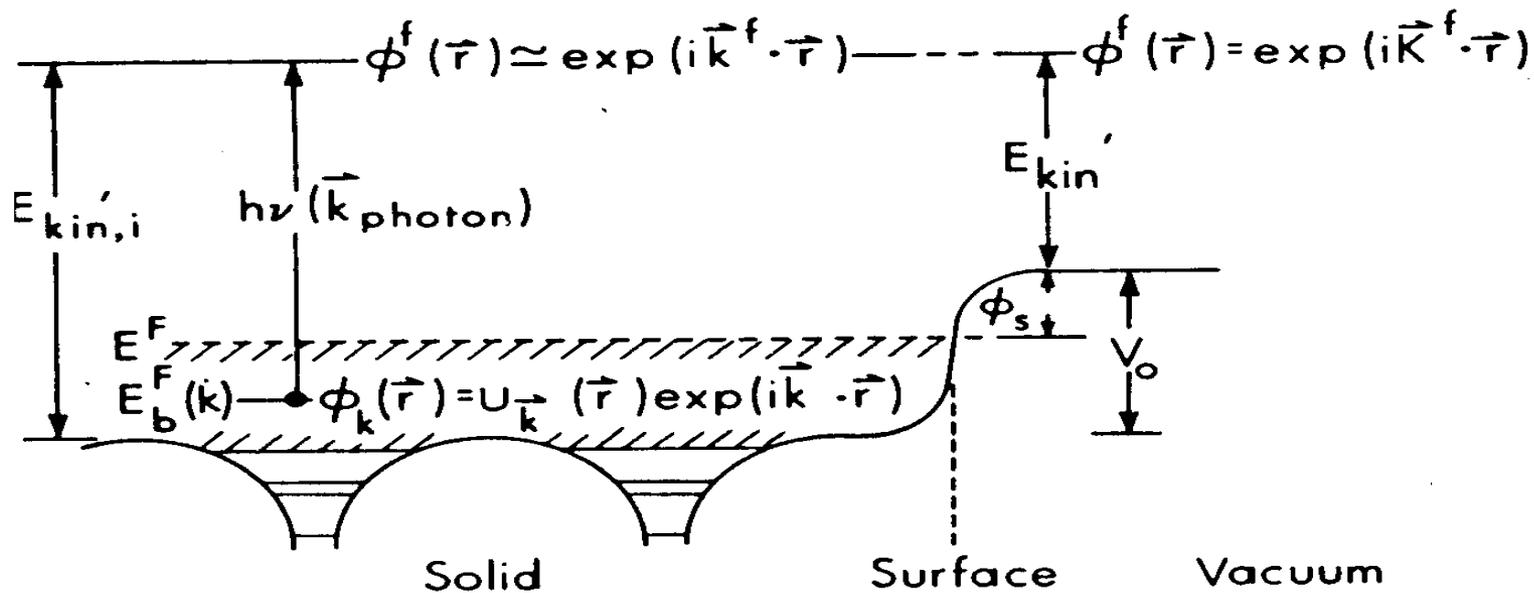
Fig. 12. One-electron model of photoemission in a metallic solid, shown as an energy-level diagram superimposed on the one-electron potential energy curve near the surface. The initial and final states inside the solid are assumed to have Bloch-wave character. Applicable conservation relations on energy and wave vector are also shown.
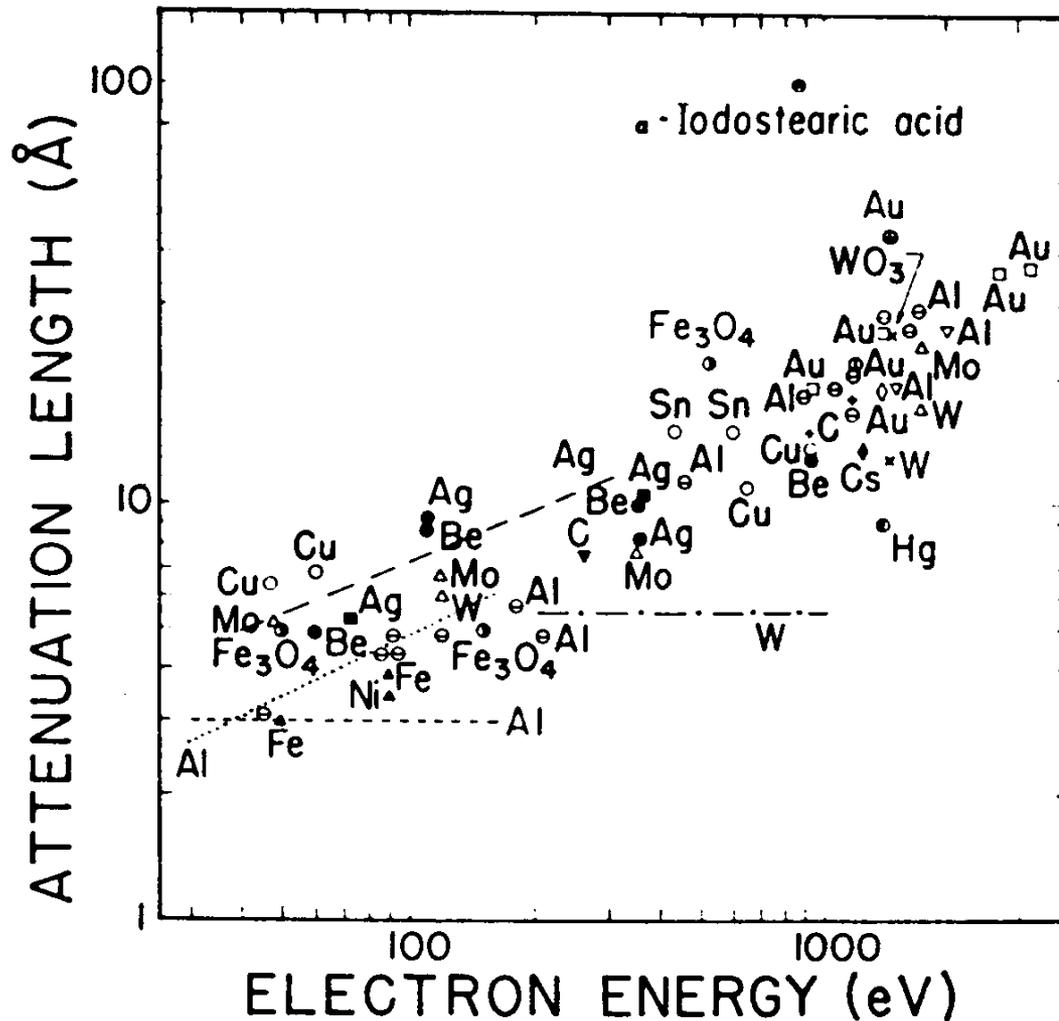
Fig. 16. Summary of experimental values for the electron inelastic attenuation length λ_e for various solids. (From Powell, ref. 20.)