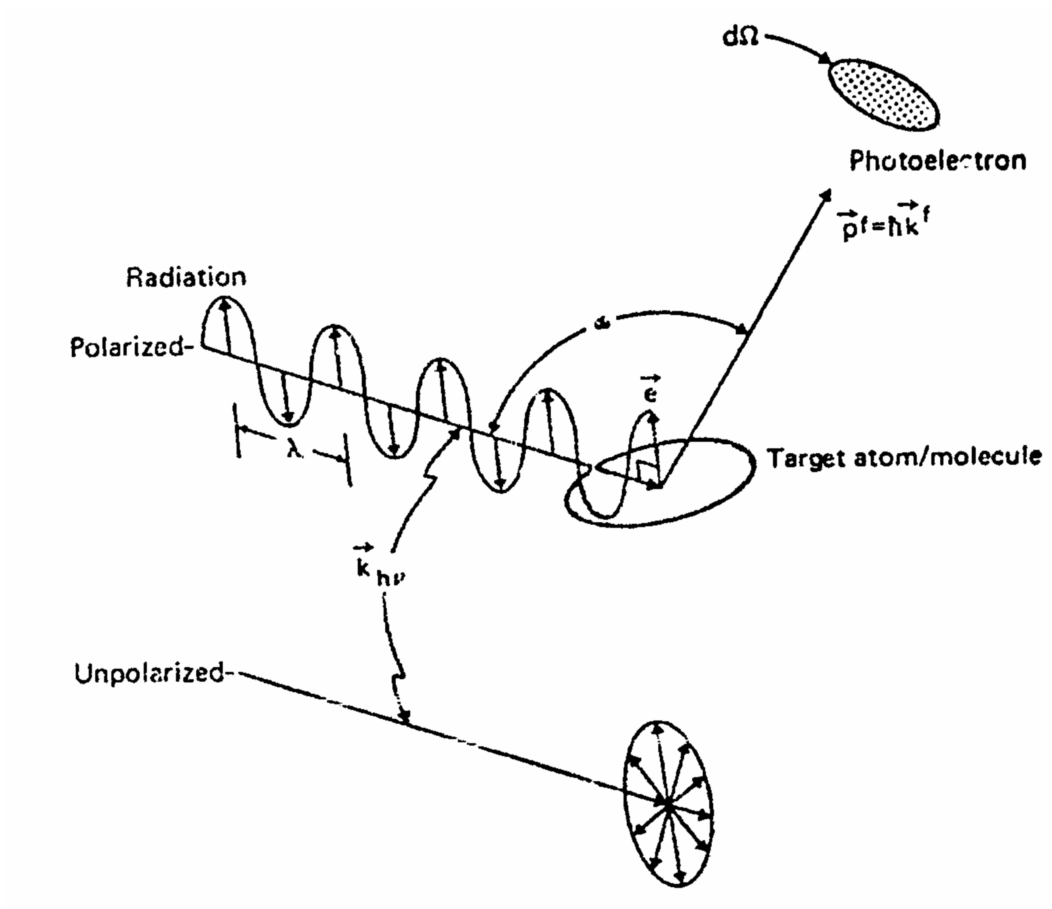
# Transition probabilities and photoelectric cross sections



General geometry for defining the differential cross-section $d\sigma/d\Omega$, Showing both polarized and unpolarized incident radiation. The polarization vector e is parallel to the electric field E of the radiation. In order for the dipole approximation to be valid, the radiation wave length $\lambda$ should be much larger than typical target dimensions.

Cross section = $\sigma$ = 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 $d\sigma/d\Omega$

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

The perturbation of electromagnetic radiation on N electron system

(weak field limit)

$$\hat{H} = -e/(2mc)\ (A.p)$$

$p = -i\hbar$▼, $A = A(r, t)$, vector potential of the field. p is an operator. (as symbol is not there in powerpoint)

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 the square of the matrix element,

$$|M_{if}|^2 = |\langle \Psi^f(N) \mid \Sigma_{i=1}^{N} A(r_i).p_i | \Psi^i(N) \rangle|^2$$

$$= \hbar^2 A_0^2 |\langle \Psi^f(N) \mid \Sigma_{i=1}^{N} \exp(i\, k_{h\nu}.r_i)\, e. \nabla_i | \Psi^i(N) \rangle|^2$$

This is proportional to $d\sigma/d\Omega$

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.

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

In the weak coupling case,

$$\Psi^f(N) = A(\phi^f(1)\ \chi^f(1),\ \Psi^f(N-1))$$

Here the k subscript of the ionic function is suppressed. Primary $k \rightarrow f$ excitation event is rapid. So the other electrons look at the photoemission event without redistribution. This is the “sudden approximation”.

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

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

**t** is the one electron transition operator

Use of this ---“Sudden approximation”

Thus the transition probabilities are proportional to,

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

If the overlap integral has to be non zero, both $\Psi^f$ and $\Psi_R$ must belong to the same irreducible representation. This is the origin of the ‘monopole’ selection rule.

$\Psi_R$ 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 ($E^f(N\text{-}1, k)$ k = 1, 2, … the validity of sudden approximation is that $[E^f(N\text{-}1), k) – E^f(N\text{-}1)\ k')]\ \ t'/\hbar<<1$

t’ is the time required for k → 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 $< \phi^{f}|r| \phi_{A\lambda} > \;\; \alpha \;\; \pm (d\sigma_{A\lambda}^{(AO)} / d\Omega)^{1/2}$

$\phi A\lambda$ correspond to orbital $\lambda$ of element A.

## 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 $\phi_k$ 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, $\lambda$ the symmetry.

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

LCAOs can be made with various approximations. $\phi^f$ 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 l character
4. Multiple scattering $\chi_\alpha$ method, numerically accurate.

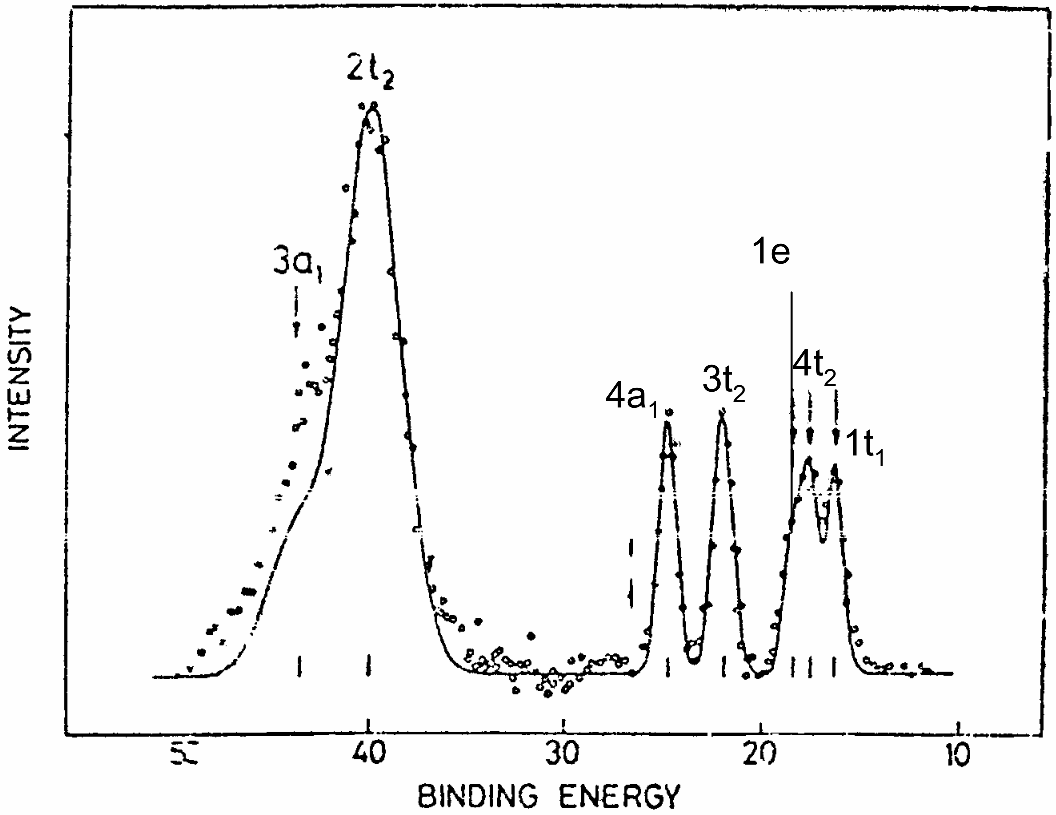
A given photoemission event may lead to several vibrational states, even when a single vibrational level is initially populated.
The electronic cross section can be partitioned for different vibrational states, simply by multiplying by appropriate Franck-condon factors.

So far 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 $\phi_k$ to be assumed as LCAO. Atomic orbitals $\phi_{A\lambda}$ may be assumed to be the representation of $\phi_k$. $\phi_{A\lambda}$ can be Slater or Gaussian. Consider final state $\phi^f$ such that $E^f = h\nu - E_b^v(k)$. Assume that this $\phi^f$ is somehow determined.

Matrix element for photoemission from molecular orbital $\phi_k$ is,

$$<\phi^f|r|\phi_k> = <\phi^f| r |\Sigma_{A\lambda} C_{A\lambda k} \phi_{A\lambda}> = \Sigma_{A\lambda} C_{A\lambda} <\phi^f|r| \phi_{A\lambda}>$$



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.