Synchrotron radiation
and
applications of synchrotron radiation

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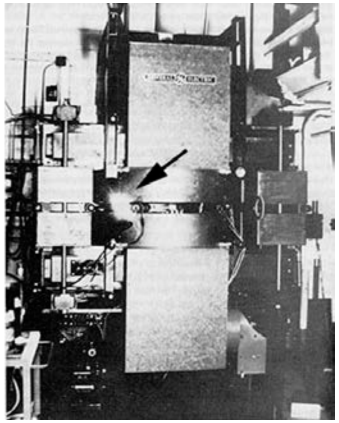
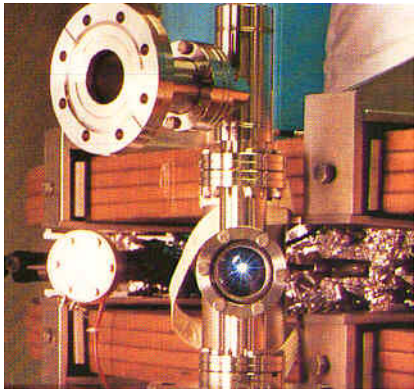
Synchrotron radiation
and
synchrotron radiation facilities

What is synchrotron radiation?

Synchrotron radiation was first observed at a synchrotron (at the General Electric Synchrotron Accelerator in 1946).
Today synchrotron radiation for use in materials experiments is normally produced in *electron storage rings*.



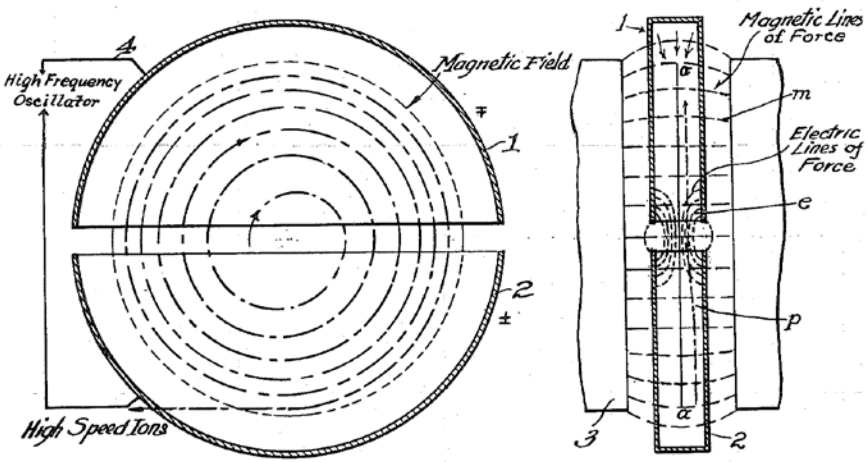


Cyclotron: accelerator with constant magnetic field in electric field-free space and alternating electric field for acceleration, spiral electron trajectory, increasing electron energy

Synchrotron: accelerator with varying magnetic and electric fields, fixed electron trajectory, increasing electron energy

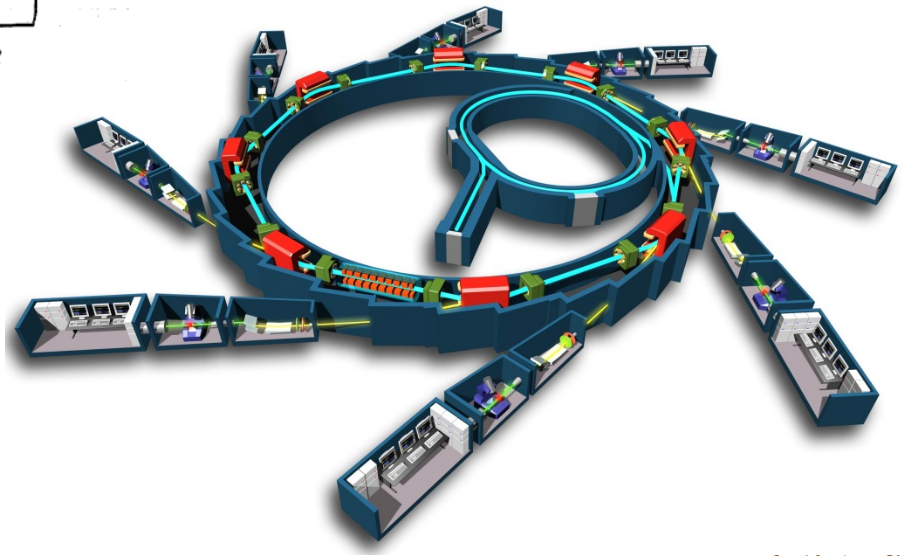
Storage ring: accelerator with fixed electron trajector and fixed electron energy, electron speed close to speed of light, fields of bending magnets fixed, alternating electric field for compensating energy loss

Cyclotron, synchrotron, storage ring

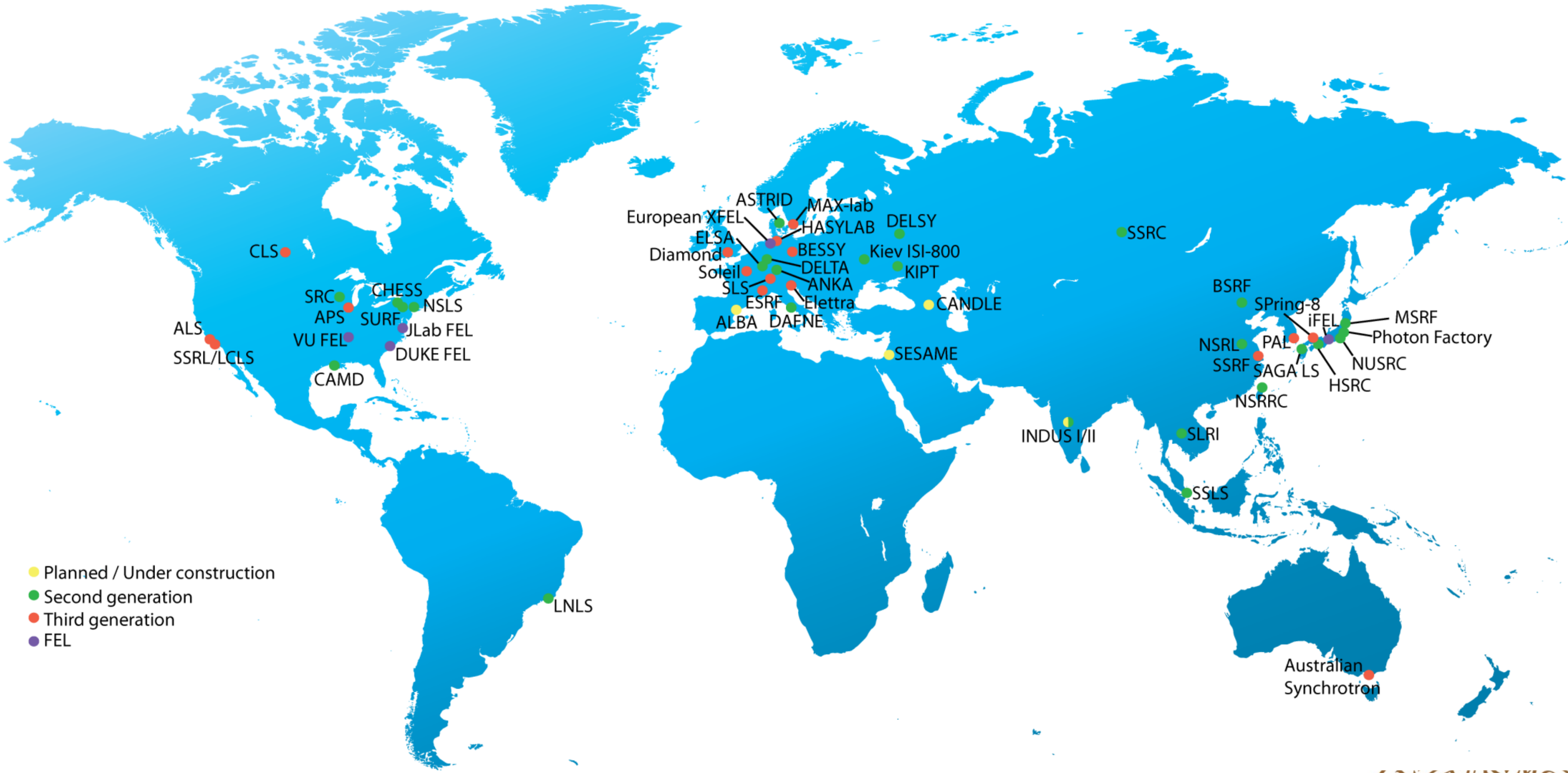


Cyclotron

Synchrotron / storage ring



Synchrotron radiation facilities around the world



www.diamond.ac.uk

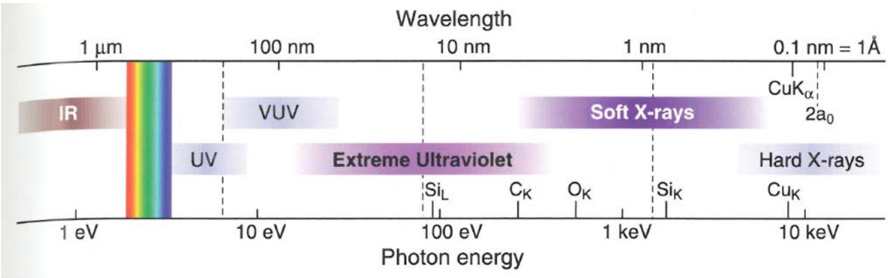
Action of a synchrotron radiation source

www.isa.au.dk – ASTRID, Aarhus University, Denmark

Properties of synchrotron radiation

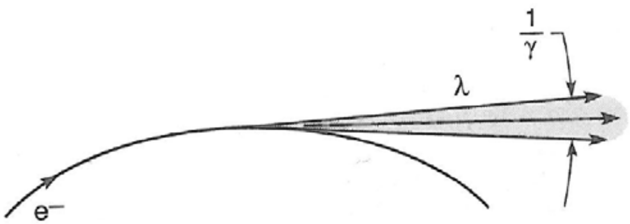
Adapted from Terasawa and Kihara *in:* H. Saisho and Y. Gohshi (Eds.), *Applications of Synchrotron Radiation to Materials Analysis*, Elsevier, Amsterdam, 1996

(1) A continuous spectrum from the infrared to the X-ray region.



(2) High intensity, owing to the high current electrons accumulated in the storage ring.

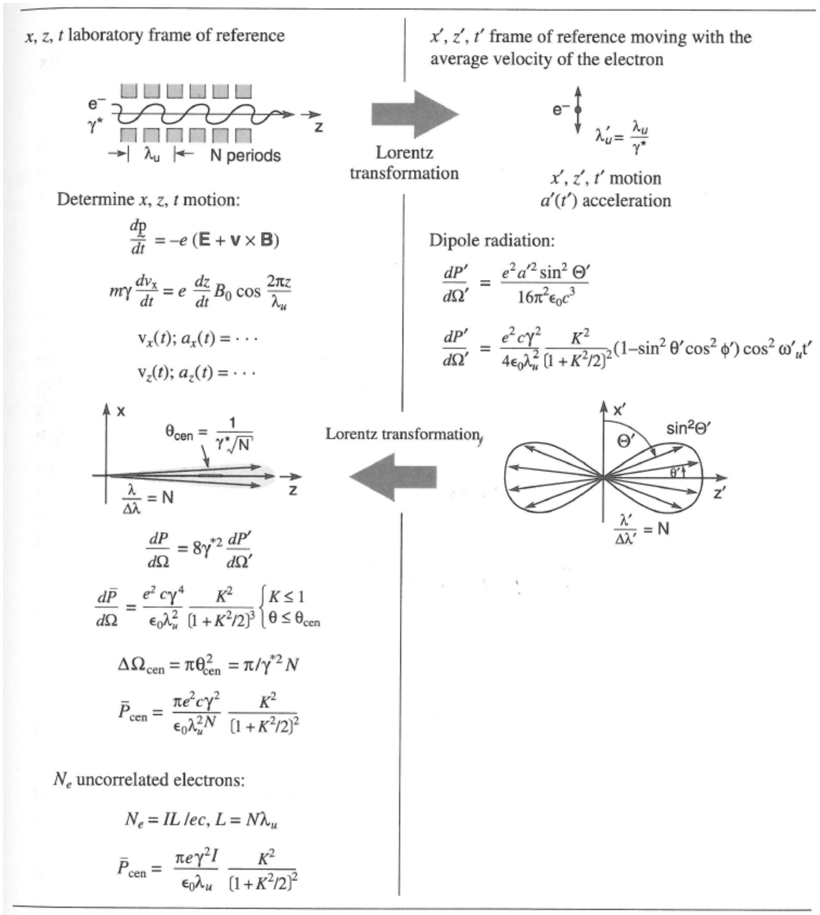
(3) Collimation of the emitted radiation in the instantaneous direction of flight of the emitting particles (the angular spread is of the order of 1 mrad).



A relativistic speeds (Lorentz contraction factor $\gamma = 1/(1-v^2/c^2)^{1/2}$) electrons emit into the forward direction.

Images: D. Attwood, Soft X-rays and Extreme Ultraviolet Radiation, Cambridge University Press, Cambridge, 1999.

Light emission of relativistic electrons



D. Attwood, Soft X-rays and Extreme Ultraviolet Radiation, Cambridge University Press, Cambridge, 1999.

Properties of synchrotron radiation

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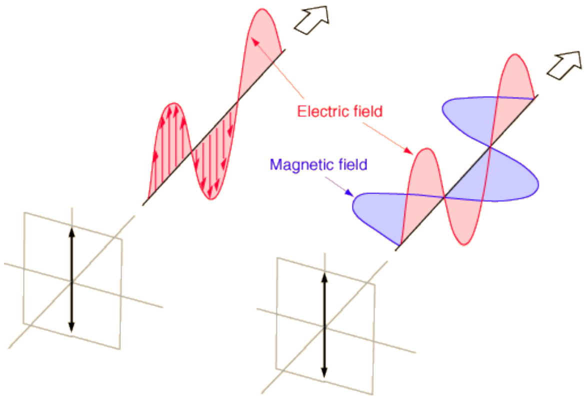
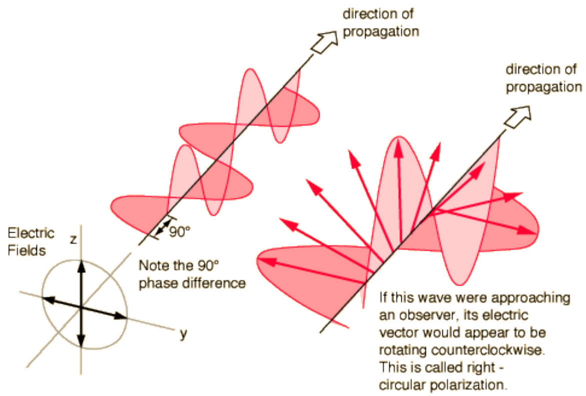
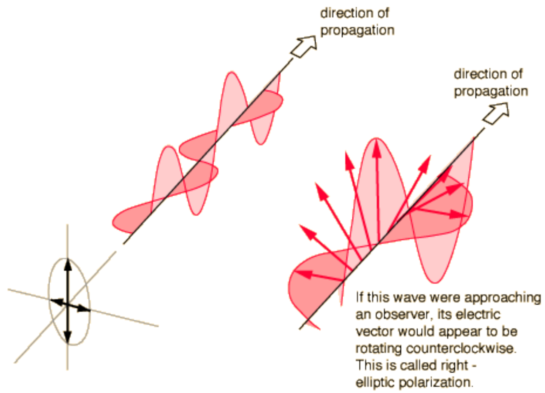
(4) Polarisation control



Linear polarisation



Circular polarisation



Elliptical polarisation

Images: hyperphysics.phy-astr.gsu.edu.

Properties of synchrotron radiation

Adapted from Terasawa and Kihara *in:* H. Saisho and Y. Gohshi (Eds.), *Applications of Synchrotron Radiation to Materials Analysis*, Elsevier, Amsterdam, 1996

(5) High brilliance of the source, because of the small cross section of the electron beam and the high degree of collimation of the radiation.

Flux = number of photons/(s mm^2)

Brilliance = flux/(mrad^2 0.1% BW)

0.1% BW denotes a bandwidth of $10^{-3}\nu$ centered around the frequency ν.

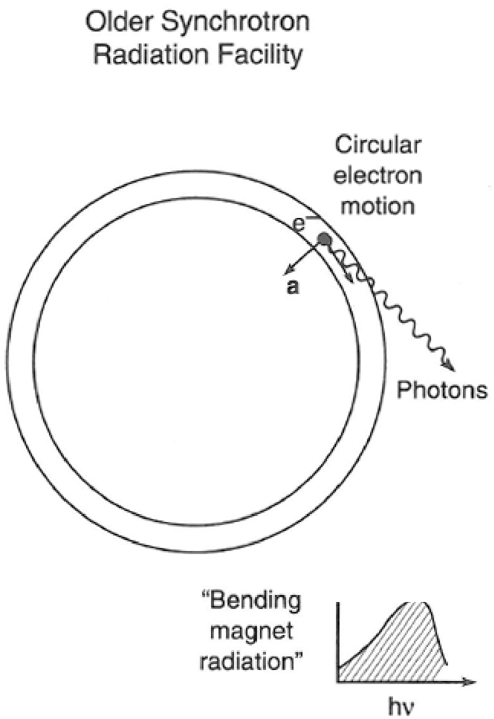
(6) A time structure with pulse lengths down to 100 ps.

(7) Absolute calculability of all the properties of the source.

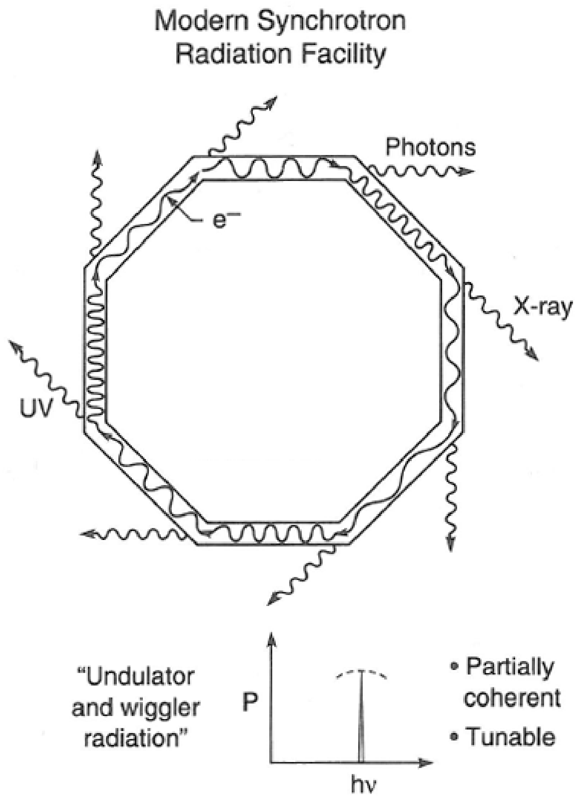
(8) Cleanliness of the source, since the light emission takes place in an ultra-high vacuum, in contrast to the situation in gas discharge or spark lamps.

Ways of producing synchrotron radiation

Images: D. Attwood, Soft X-rays and Extreme Ultraviolet Radiation, Cambridge University Press, Cambridge, 1999.



Radiation from bending magnets

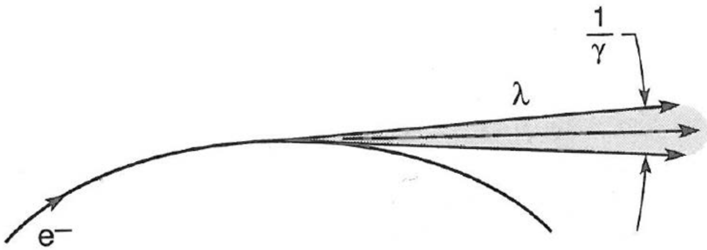


Radiation from insertion devices (undulators and wigglers) and partly from bending magnets

Bending magnet radiation

Photon flux per unit angle and 0.1% BW:

$$\left.\frac{d^3F_B}{d\theta\, d\psi\, d\omega/\omega}\right|_{\psi=0} = 1.33\times 10^{13} E_e^2(\text{GeV}) I(\text{A}) H_2(E/E_c) \frac{\text{photons/s}}{\text{mrad}^2\cdot(0.1\%\ \text{BW})}$$



H_2: modified Bessel function (tabulated)

Critical energy: $$E_c = \hbar\omega_c = \frac{3e\hbar B\gamma^2}{2m}$$

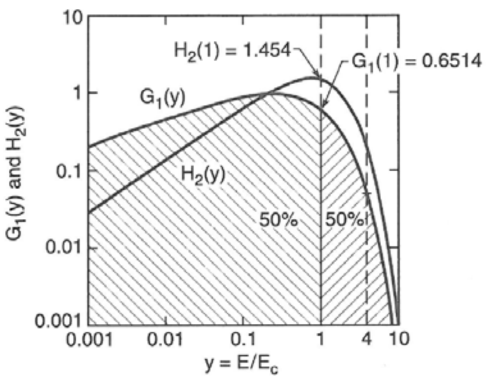
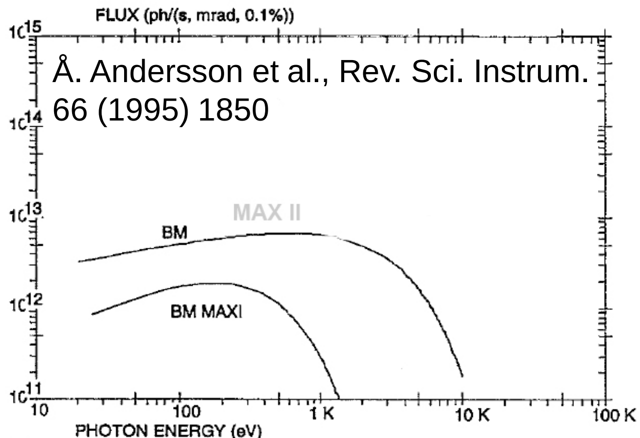


FIGURE 5.7. The functions $H_2(y)$, representing on-axis photon flux from a bending magnet, and $G_1(y)$, representing the vertically integrated photon flux, as functions of photon energy normalized to the critical photon energy. Half the radiated power is in photons of energy greater than E_c, and half in photons of energy less than E_c (following Kim[3]). Note that for a photon energy of $4E_c$ the photon flux is reduced a factor of about 10 from its value at E_c.



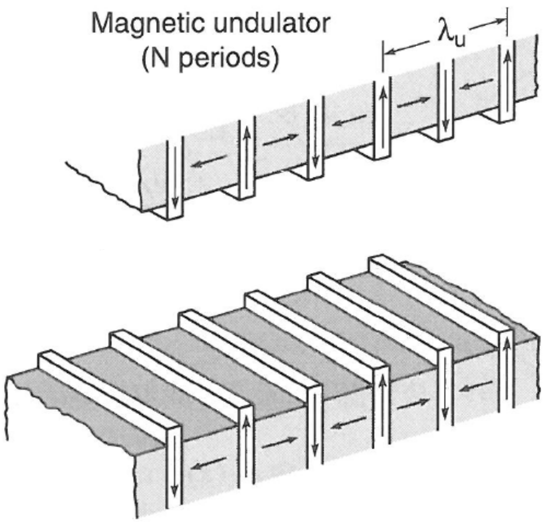
Å. Andersson et al., Rev. Sci. Instrum. 66 (1995) 1850

Images: D. Attwood, Soft X-rays and Extreme Ultraviolet Radiation, Cambridge University Press, Cambridge, 1999.

Undulators and wigglers

Undulator equation:

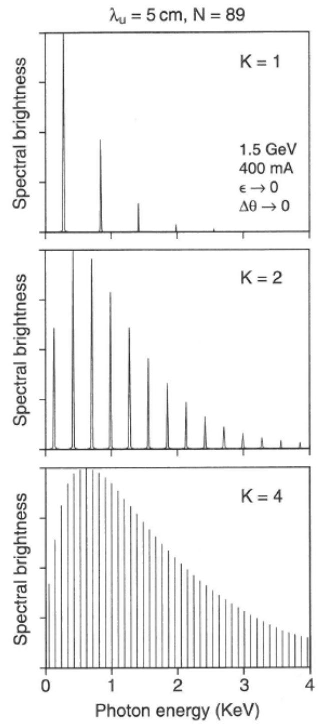
$$\lambda = \frac{\lambda_u}{2\gamma^2}\left(1 + \frac{K^2}{2} + \gamma^2\theta^2\right) \qquad K \equiv \frac{eB_0\lambda_u}{2\pi mc}$$



$$\lambda \simeq \frac{\lambda_u}{2\gamma^2}$$

$$\theta_{cen} \simeq \frac{1}{\gamma^* \sqrt{N}}$$

$$\left[\frac{\Delta\lambda}{\lambda}\right]_{cen} = \frac{1}{N}$$



Undulator radiation ($K \lesssim 1$)

- Narrow spectral lines
- High spectral brightness
- Partial coherence

$$\lambda = \frac{\lambda_u}{2\gamma^2}\left(1 + \frac{K^2}{2} + \gamma^2\theta^2\right)$$

$$K = \frac{eB_o\lambda_u}{2\pi mc}$$

Wiggler radiation ($K >> 1$)

- Higher photon energies
- Spectral continuum
- Higher photon flux (2N)

$$\hbar\omega_c = \frac{3}{2}\frac{\hbar\gamma^2 eB_o}{m}$$

$$n_c = \frac{3K}{4}\left(1 + \frac{K^2}{2}\right)$$

Images: D. Attwood, Soft X-rays and Extreme Ultraviolet Radiation, Cambridge University Press, Cambridge, 1999.

Why undulators and wigglers?

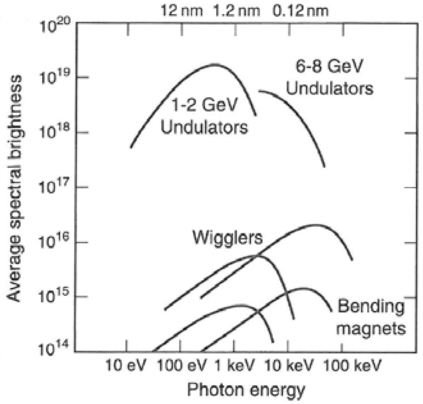
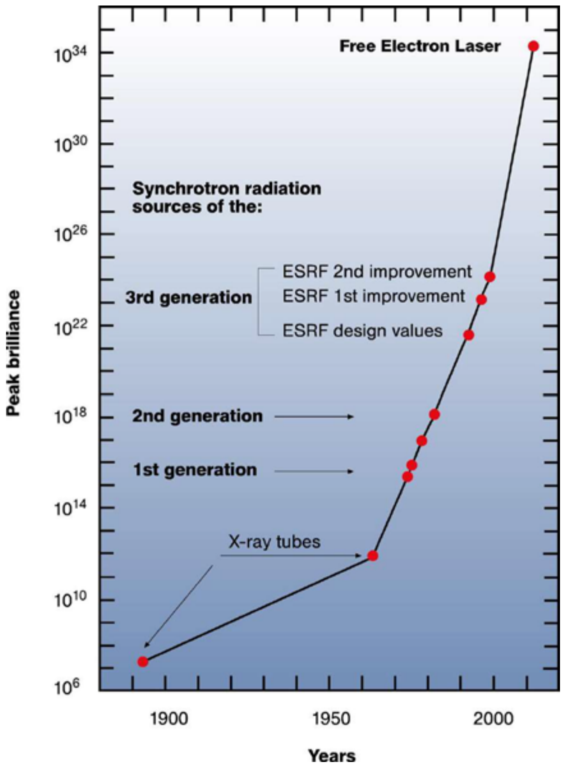


FIGURE 5.24. General trends of spectral brightness for undulator radiation, wiggler radiation, and bending magnet radiation, showing the complementary nature of soft x-ray (1–2 GeV) and hard x-ray (6–8 GeV) storage ring facilities. High spectral brightness is particularly useful for experiments involving scanning microscopy and partial coherence, diffraction from small crystalline samples, and other studies which generally benefit from radiation of minimal divergence emanating from a small source size. Units as in Eq. (5.65).

D. Attwood, Soft X-rays and Extreme Ultraviolet Radiation, Cambridge University Press, Cambridge, 1999.

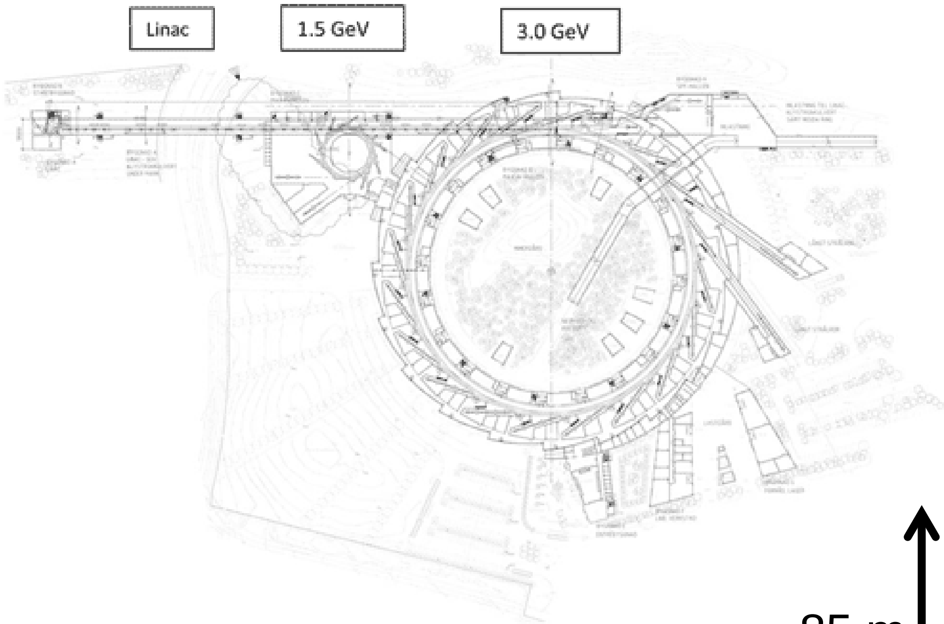


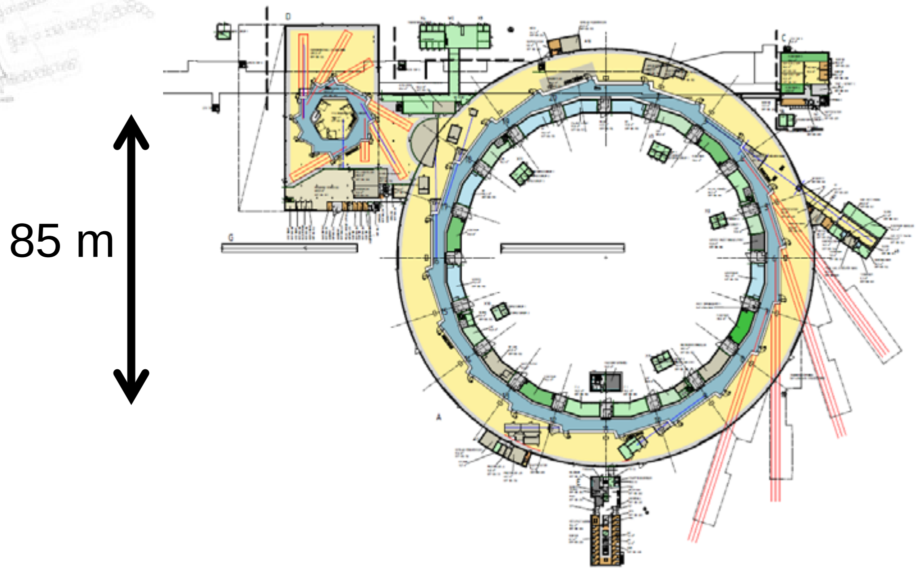
Improved flux / brilliance
as compared to bending magnet sources!

www.hasylab.de

MAX IV – the world's brightest synchrotron radiation source

MAX IV Laboratory – the national synchrotron radiation facility in Lund





Circumference 3 GeV ring: 528 m
Circumference 1.5 GeV ring: 96 m

Why will MAX IV be world-best?

Circumference (m)	528
Nr of straight sections	20
Injection	full energy, top-up
Stored current (mA)	500
Horizontal emittance (nm rad)	0.2 - 0.3
Vertical emittance (nm rad)	< 0.008
Horizontal beam size (σ μm)	42- - 52
Vertical beam size (σ μm)	< 6

Circumference (m)	96
Nr of straight sections	12
Injection	full energy, top-up
Stored current (mA)	500
Horizontal emittance (nm rad)	6.0
Vertical emittance (nm rad)	0.06
Horizontal beam size (σ μm)	184
Vertical beam size (σ μm)	13

Characteristics will allow:
nanofocusing, use of coherence, extremely high resolution, use of very small biological samples, …

MAX IV LABORATORY

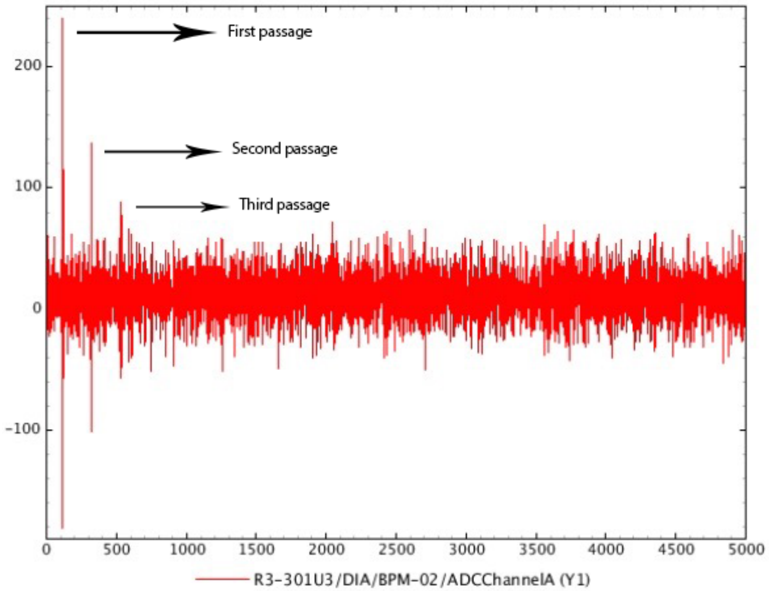
3 GeV ring

1.5 GeV ring

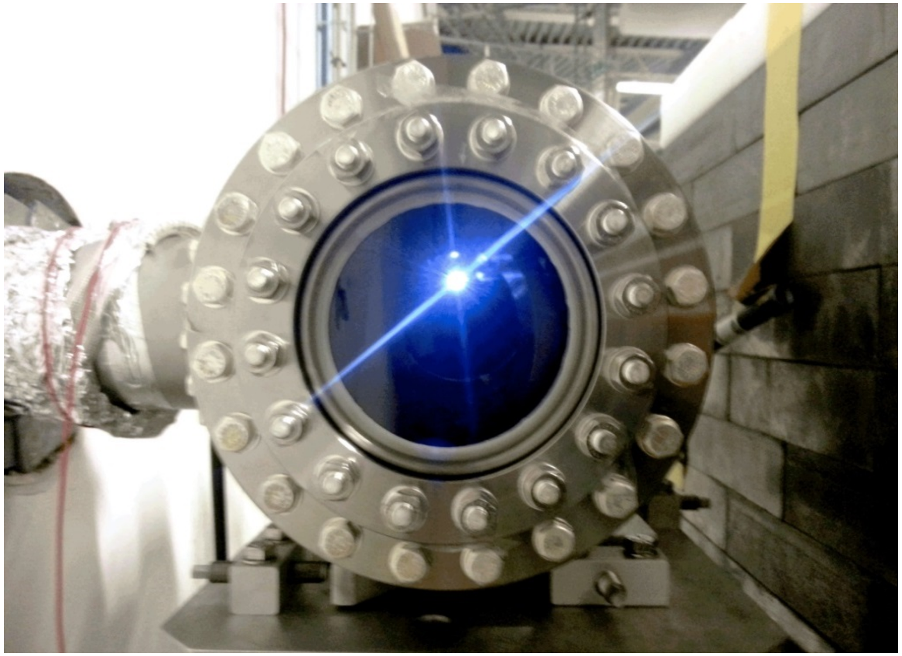
Linac (1.5 and 3 GeV)

Inauguration: 21 June 2016

Sweden is not dark!

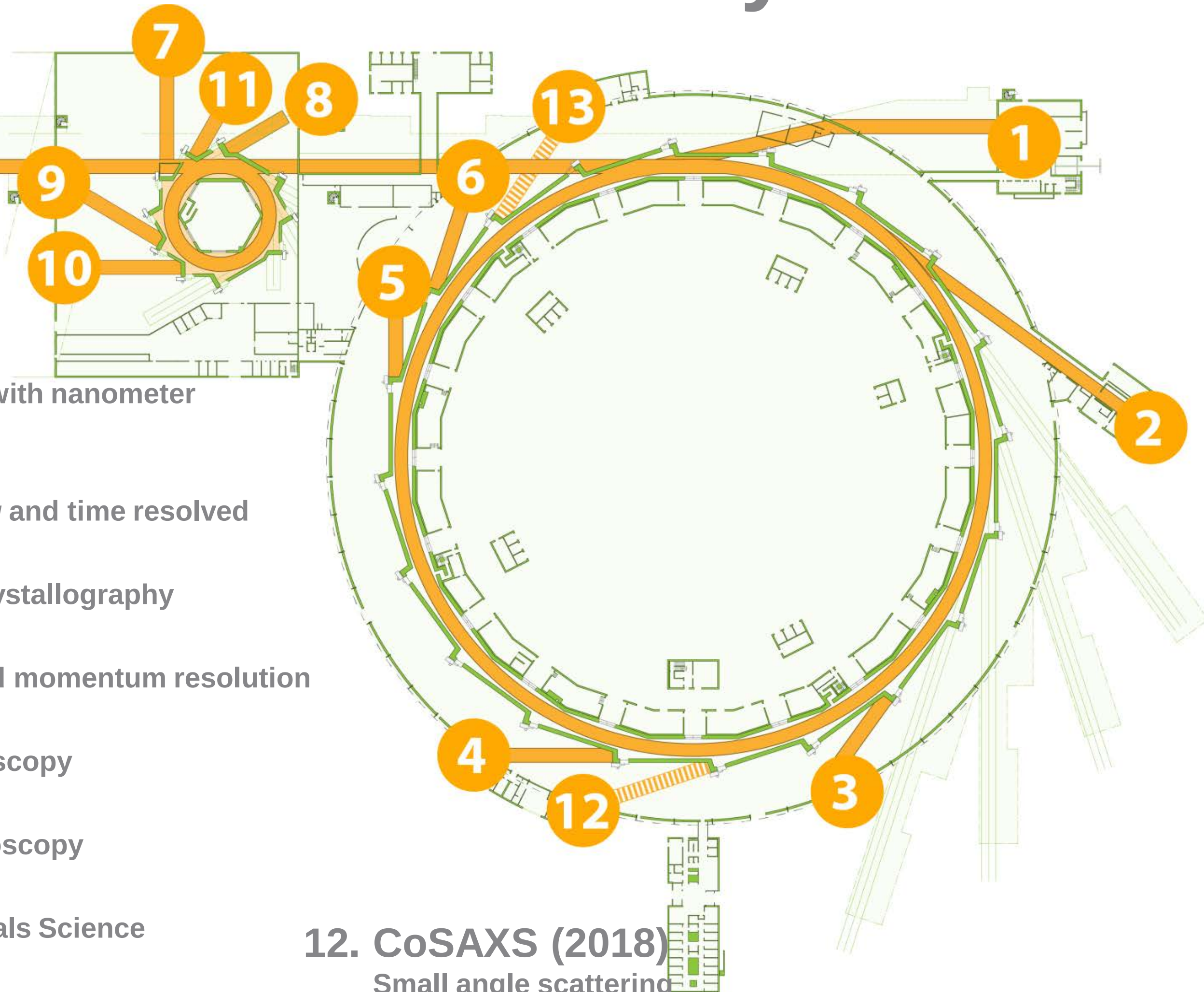


26 August 2015: circulating electron beam in the 3 GeV ring of MAX IV



2 November 2015: synchrotron radiation recorded

The MAX IV Laboratory



1. **FemtoMAX (2015)**
   Ultra-fast processes in materials
2. **NanoMAX (2016)**
   Imaging, spectroscopic & scattering with nanometer resolution
3. **BALDER (2016)**
   X-ray absorption spectroscopy *in-situ* and time resolved
4. **BioMAX (2016)**
   Highly automated macromolecular crystallography
5. **VERITAS (2016)**
   RIXS with unique resolving power and momentum resolution
6. **HIPPIE (2016)**
   High-pressure photoelectron spectroscopy
7. **ARPES (2017)**
   Angle resolved photoelectron spectroscopy
8. **FinEstBeaMS (2017)**
   Estonian-Finnish Beamline for Materials Science
9. **SPECIES (Transfer) (2017)**
   VUV High-pressure photoelectron spectroscopy and RIXS
10. **FlexPES (Transfer) (2017)**
    Photoelectron Spectroscopy and NEXAFS
11. **MAXPeem (Transfer) (2017)**
    Photoelectron microscopy
12. **CoSAXS (2018)**
    Small angle scattering
13. **SoftiMAX (2018)**
    Coherent Soft X-Ray Scattering, Holography…
14. **DanMAX (2019)**

Initial beamline programme

- **BioMAX (3 GeV ring):** A multipurpose high throughput beamline for macromolecular crystallography.
- **VERITAS (3 GeV ring):** A beamline for soft X-ray Resonant inelastic X-ray scattering (RIXS) in the energy range of 275-1500 eV.
- **HIPPIE (3 GeV ring):** A state-of-the-art beamline for high pressure X-ray photoelectron spectroscopy (HP-XPS), high pressure X-ray absorption spectroscopy (HP-XAS) as well as XPS and XAS in ultrahigh vacuum.
- **NanoMAX (3 GeV ring):** A hard X-ray beamline for micro- and nanobeams.
- **FemtoMAX (Linac):** A beamline situated on the extension of the linac to facilitate studies of the structure and dynamics of materials with X-ray pulses of 100 fs.
- **ARPES (1.5 GeV ring):** A beamline for angle resolved photo electron spectroscopy (ARPES)c overing photon energies between 10-1000 eV but with emphasis on the lower energy range.
- **Balder (3 GeV ring):** A beamline for in-situ hard X-ray spectroscopy.
- **SPECIES (1.5 GeV ring):** A VUV beamline for high pressure X-ray photoelectron spectroscopy (HP-XPS) and Resonant inelastic X-ray scattering (RIXS)
- **FinEstBeaMS (1.5 GeV ring):** A beamline for soft x-ray spectroscopy on vapours and materials
- **SoftiMAX (3 GeV ring):** A beamline for coherent x-ray imaging and for scanning transmission x-ray microscopy (STXM).
- **CoSAXS (3 Ge V ring):** A beamline for small angle x-ray scattering (SAXS).
- **FlexPES/PEEM (1.5 GeV ring):** Transfer of the Photoemission electron microscopy and of a soft x-ray spectroscopy beamline from present MAX-lab.

Applications of synchrotron radiation

Applications of synchrotron radiation

Spectroscopy

X-ray absorption spectroscopy, including
X-ray magnetic circular dichroism
X-ray emission spectroscopy
Photoelectron spectroscopy, including
Angle-resolved photoemission spectroscopy
Vibrational spectroscopy
…

Imaging

X-ray tomography
Synchrotron infrared microspectroscopy
Photoemission electron microscopy
Scanning x-ray microscopy
Phase contrast microscopy
…

Scattering

Powder diffraction, crystallography
Small angle x-ray scattering
Inelastic x-ray scattering
Magnetic scattering
Time resolved x-ray scattering
…

Microfabrication

X-ray lithography

List by no means complete!

Applications of synchrotron radiation

Spectroscopy

X-ray absorption spectroscopy, including
X-ray magnetic circular dichroism
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Photoelectron spectroscopy, including
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X-ray tomography
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…

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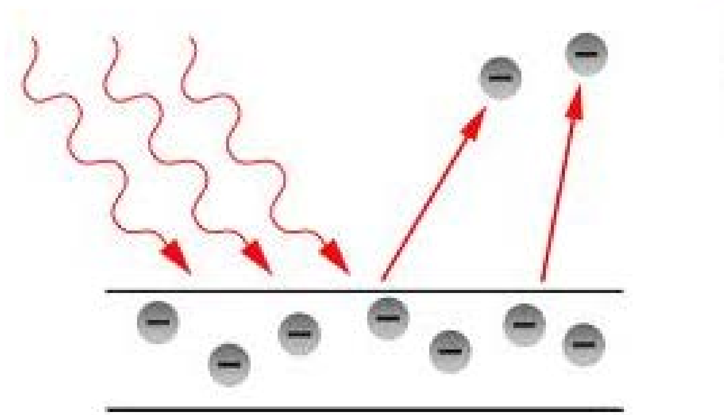
List by no means complete!

X-ray photoelectron spectroscopy

(X-ray) Photoelectron spectroscopy

Photon in – electron out, i.e. PES is an *electron spectroscopy*

Photoelectric effect (observed by Heinrich Herz 1887, explained by Albert Einstein in 1905)

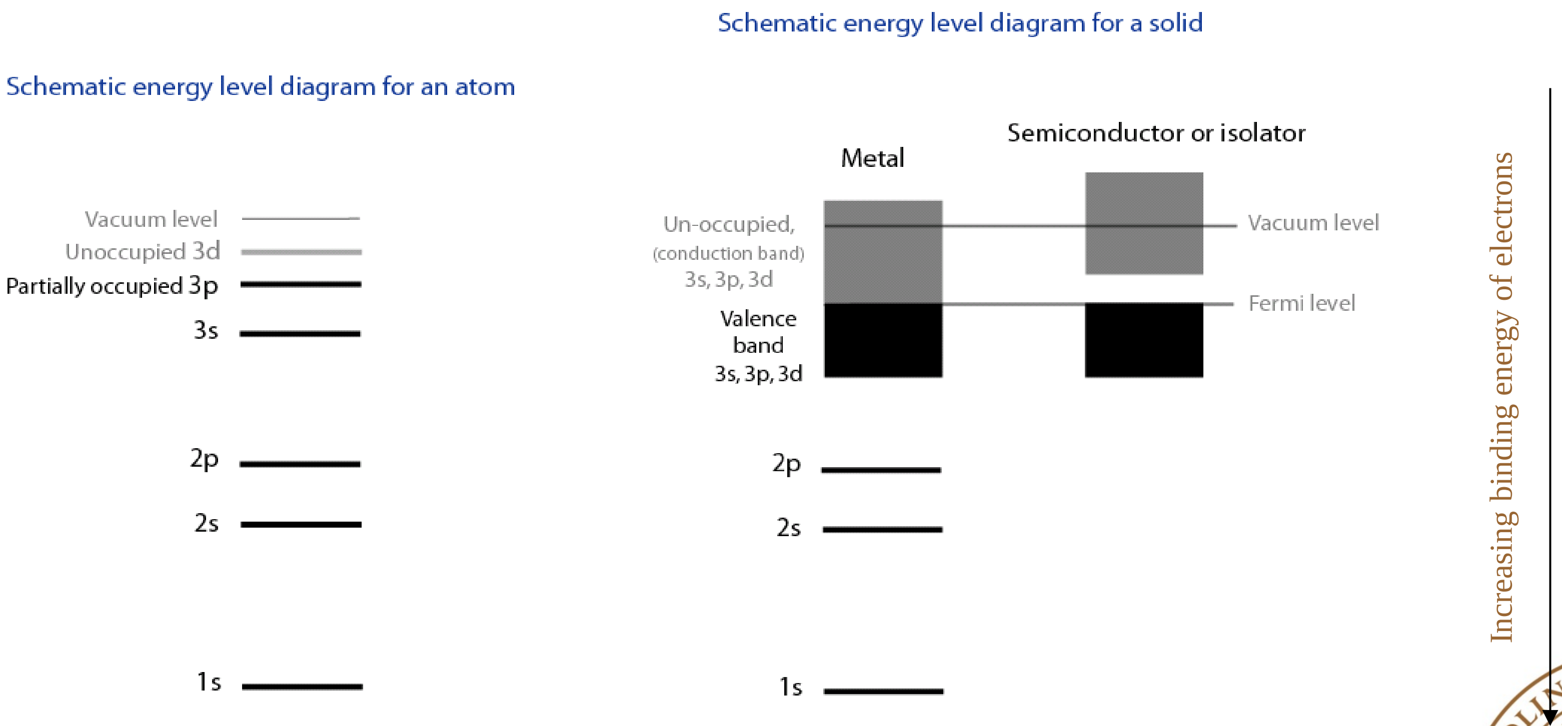


www.physicsforum.com

Works (of course) on atoms, molecules, and solids

Energy levels of atoms and solids

All electron spectrocopy methods rely on the electronic structure of atoms, molecules, and solids



Note: Energies not to scale

X-ray photoelectron spectroscopy

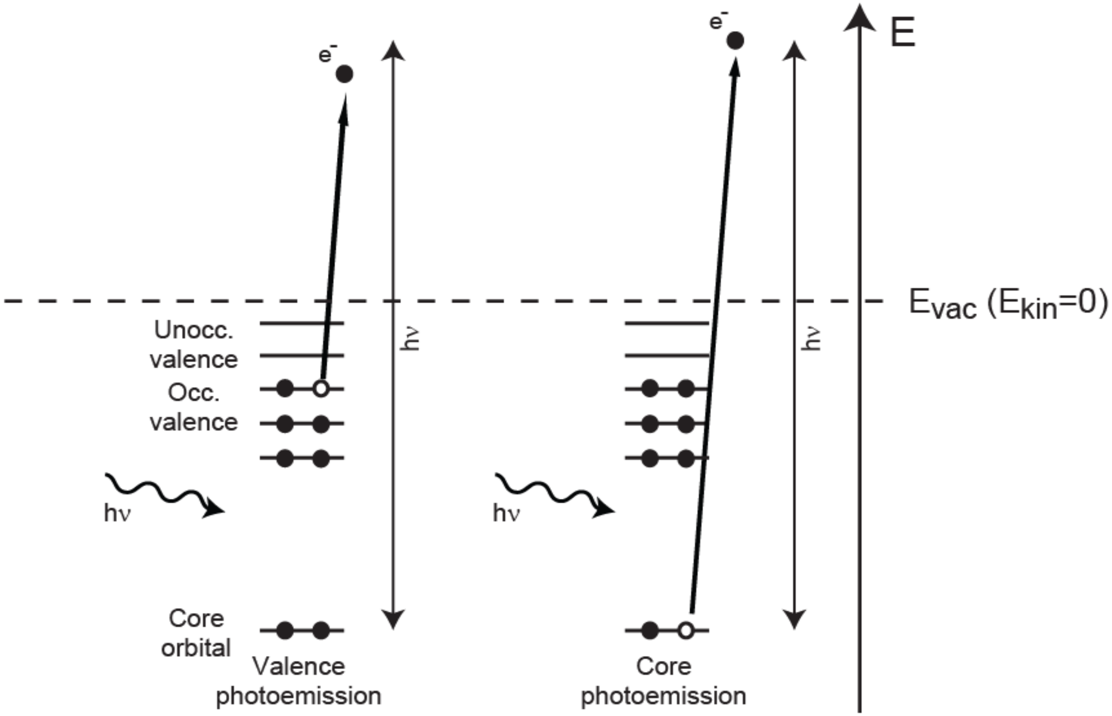
Photoelectron spectroscopy = Photoemission spectroscopy
XPS = X-ray photoelectron spectroscopy
UPS = Ultraviolet photoelectron spectroscopy

Hard x-ray:
approx. 1200 – 250,000 eV

Soft x-rays:
approx. 20 – 1200 eV

Vacuum ultraviolet:
approx. 6 – 20 eV

Ultraviolet:
approx. 3 – 6 eV



X-ray photoelectron spectroscopy

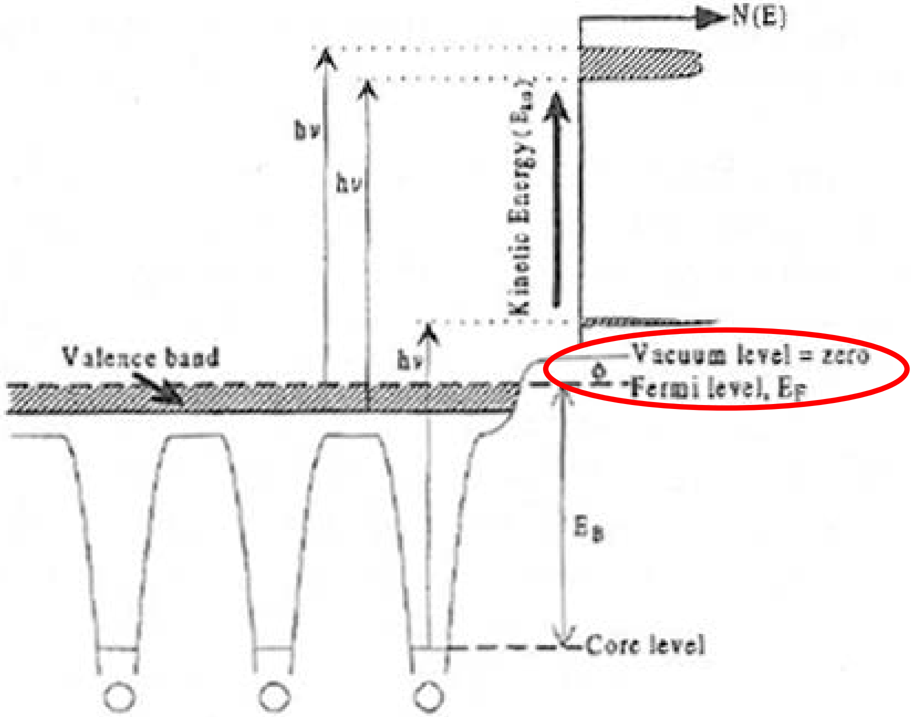
is given by experiment settings (tunable at synchrotron radiation facility!)

can be determined

$$h\nu = E_B + E_{kin} + \phi$$

quantity of interest!

can be measured



φ = work function
N(E) = number of electrons with a particular kinetic energy
E_B = binding energy

Fig. 2.2 The energetics of an X-ray photoemission experiment.

Core level binding energies:

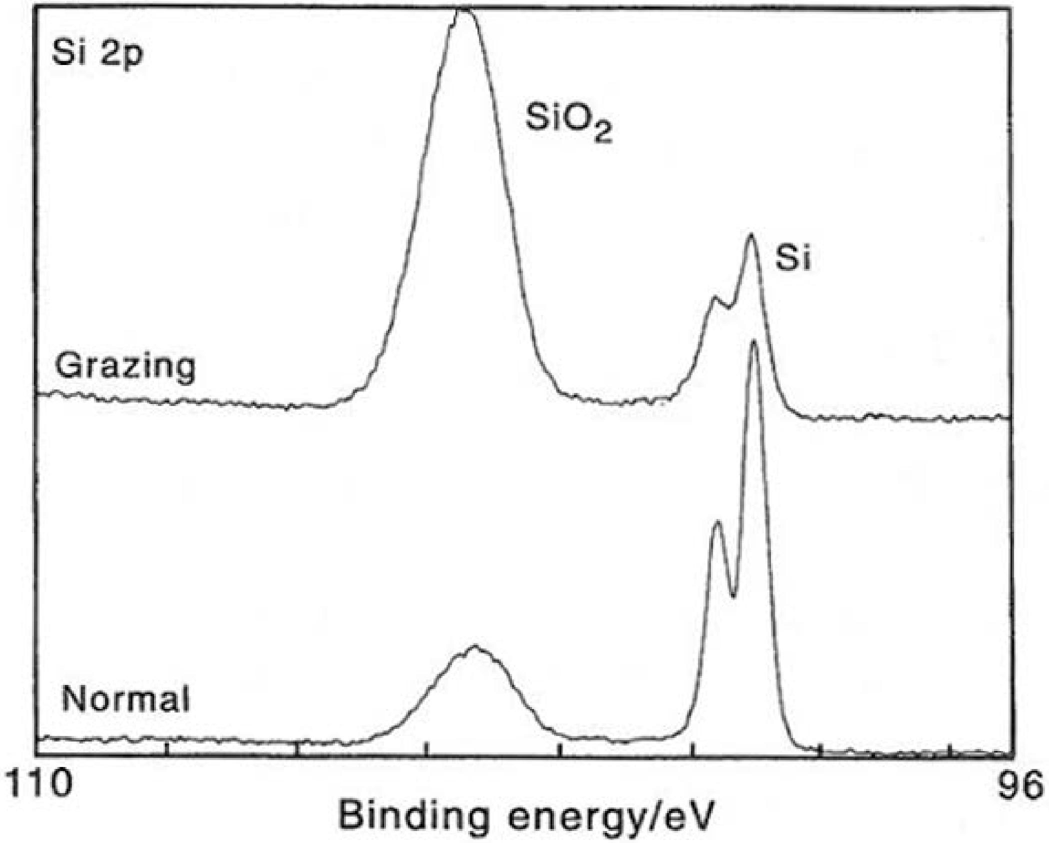
characteristic for the elements

| Binding energies

		1s	2s	2p1	2p3	3s	3p1	3p3	3d3	3d5	4s	4p1	4p3	4d3	4d5	4f5	4f7	5s	5p1	5p3	
1	H	14																			H
2	He	25																			He
3	Li	55																			Li
4	Be	112																			Be
5	B	188																			B
6	C	284																			C
7	N	410	2s	2p1	2p3	3s	3p1	3p3	3d3	3d5	4s	4p1	4p3	4d3	4d5	4f5	4f7	5s	5p1	5p3	N
8	O	543	23																		O
9	F	686	30																		F
10	Ne	863	41	14	14																Ne
11	Na	1072	64	31	31																Na
12	Mg		90	51	51																Mg
13	Al		119	74	74																Al
14	Si		153	103	102																Si
15	P		191	134	133	14															P
16	S		229	166	165	17															S
17	Cl		270	201	199	17															Cl
18	Ar		319	243	241	22	3p1	3p3	3d3	3d5	4s	4p1	4p3	4d3	4d5	4f5	4f7	5s	5p1	5p3	Ar
19	K		378	296	293	33	17	17													K
20	Ca		439	350	347	44	25	25													Ca
21	Sc		501	407	402	53	31	31													Sc
22	Ti		565	464	458	62	37	37													Ti
23	V		630	523	515	69	40	40													V
24	Cr		698	586	577	77	46	45													Cr
25	Mn		770	652	641	83	49	48													Mn
26	Fe		847	723	710	93	56	55													Fe
27	Co		927	796	781	103	63	61													Co
28	Ni		1009	873	855	112	69	67													Ni
29	Cu		1098	954	934	124	79	77													Cu
30	Zn		1196	1045	1022	140	92	89	10	10											Zn
31	Ga			1144	1117	160	108	105	20	20											Ga
32	Ge					184	128	124	32	31											Ge
33	As					207	148	143	45	44											As
34	Se					232	169	163	58	57											Se
35	Br					256	189	182	70	69	4s	4p1	4p3	4d3	4d5	4f5	4f7	5s	5p1	5p3	Br
36	Kr					287	216	208	89	88	22										Kr
37	Rb					322	247	238	111	110	29	14	14								Rb
38	Sf					358	280	269	135	133	37	20	20								Sf
39	Y					395	313	301	160	158	45	25	25								Y
40	Zr					431	345	331	183	181	51	29	29								Zr
41	Nb					470	379	364	209	206	59	35	35								Nb
42	Mo					508	413	396	233	230	65	38	38								Mo
43	Tc					544	445	425	257	253	68	39	39								Tc
44	Ru					587	485	463	286	282	77	45	45								Ru
45	Rh					629	522	498	314	309	83	49	49								Rh
46	Pd					673	561	534	342	337	88	54	54								Pd
47	Ag					718	604	573	374	368	97	58	58	4d3	4d5	4f5	4f7	5s	5p1	5p3	Ag
48	Cd					772	652	618	412	405	109	68	68	11	11						Cd
49	In					828	704	666	453	445	123	79	79	19	19						In
50	Sn					884	757	715	494	486	137	91	91	26	25						Sn
51	Sb					946	814	768	539	530	155	105	105	35	34						Sb
52	Te					1009	873	822	585	575	171	114	114	44	43			14			Te
53	I					1071	930	874	630	619	186	123	123	52	50			16			I
54	Xe					1144	997	936	685	672	209	141	141	65	63			19			Xe

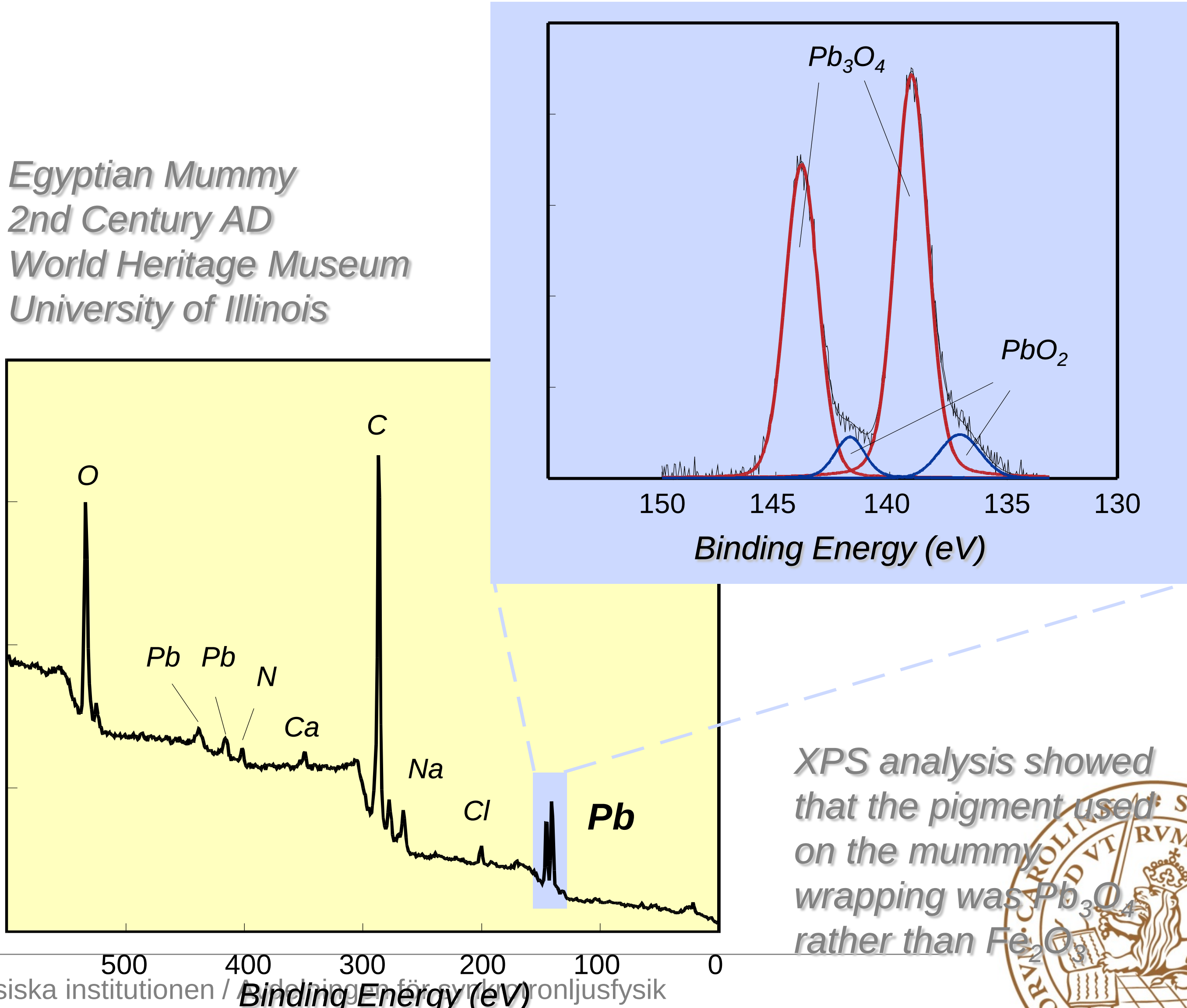
55	Cs	1064	997	738	724	230	170	158	77	75			24			Cs
56	Ba	1137	1062	795	780	254	192	179	92	90			23			Ba
57	La		1126	851	834	274	210	195	104	101			34	17	17	La
58	Ce		1184	900	882	290	222	207	112	108			37	18	18	Ce
59	Pr			950	930	305	237	218	114	114			38	20	20	Pr
60	Nd			1001	980	318	248	227	120	120			38	23	23	Nd
61	Pm			1060	1034	337	264	242	129	129			38	22	22	Pm
62	Sm			1110	1083	349	283	250	132	132			41	20	20	Sm
63	Eu			1166	1136	366	289	261	136	136			34	24	24	Eu
64	Gd				1186	380	301	270	141	141			36	21	21	Gd
65	Tb					398	317	284	150	150			42	28	28	Tb
66	Dy					412	329	293	154	154			63	26	26	Dy
67	Ho					431	345	306	161	161			51	20	20	Ho
68	Er					451	362	320	169	169			61	25	25	Er
69	Tm					470	378	333	180	180			54	32	26	Tm
70	Yb					483	392	342	194	185			55	33	26	Yb
71	Lu					507	412	359	207	197			58	34	27	Lu
72	Hf					537	437	382	224	213	19	17	64	37	30	Hf
73	Ta					566	464	403	241	229	27	25	71	45	37	Ta
74	W					594	491	425	257	245	36	34	77	47	37	W
75	Re					628	521	449	277	263	45	43	81	44	33	Re
76	Os					657	549	475	294	279	55	52	86	60	48	Os
77	Ir					692	579	497	313	297	65	62	98	65	53	Ir
78	Pt					726	610	521	333	316	76	73	105	69	54	Pt
79	Au					763	643	547	354	336	89	85	110	75	57	Au
80	Hg					803	681	577	379	359	104	100	127	84	65	Hg
81	Tl					845	721	608	406	385	122	118	137	100	76	Tl
82	Pb					893	762	645	435	413	143	138	148	107	84	Pb
83	Bi					942	807	681	467	443	164	159	161	120	94	Bi
84	Po											184				Po
85	At											210				At
86	Rn											238				Rn
87	Fr											268				Fr
88	Ra											299				Ra
89	Ac											319				Ac
90	Th											333				Th
91	Pa						1168	968	714	677	344	335	290	226	179	Pa
92	U							1046	781	739	391	380	325	262	197	U
93	Np							1086	816	771	414	402			206	Np
94	Pu							1121	850	802	439	427			216	Pu
95	Am								883	832	463	449			216	Am
96	Cm								919	865	487	473			232	Cm

Chemical shifts in x-ray photoelectron spectroscopy



XPS Analysis of Pigment from Mummy Artwork

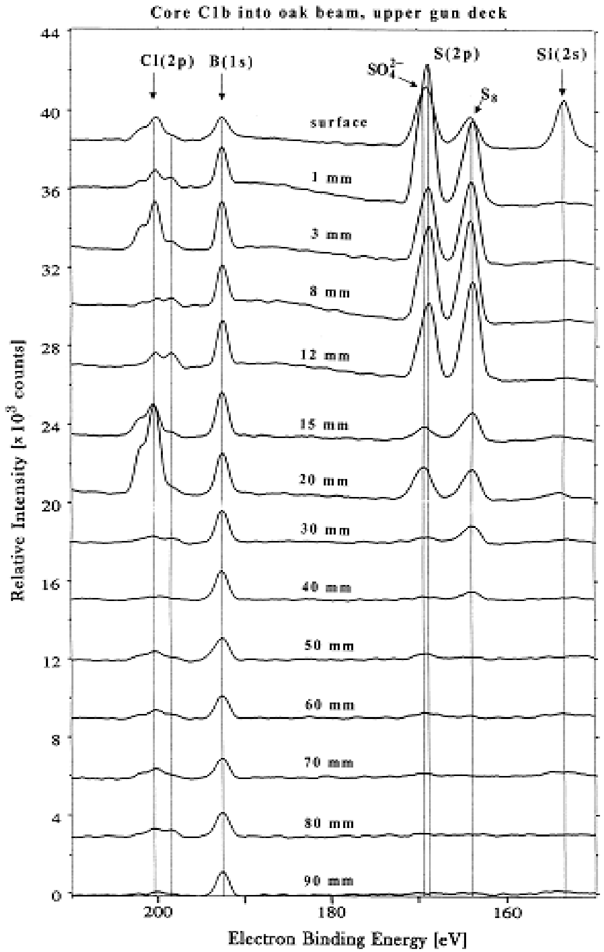
Egyptian Mummy
2nd Century AD
World Heritage Museum
University of Illinois



XPS analysis showed that the pigment used on the mummy wrapping was Pb_3O_4 rather than Fe_2O_3

Saving the Vasa with XPS?

http://www-ssrl.slac.stanford.edu/research/highlights_archive/vasa.html

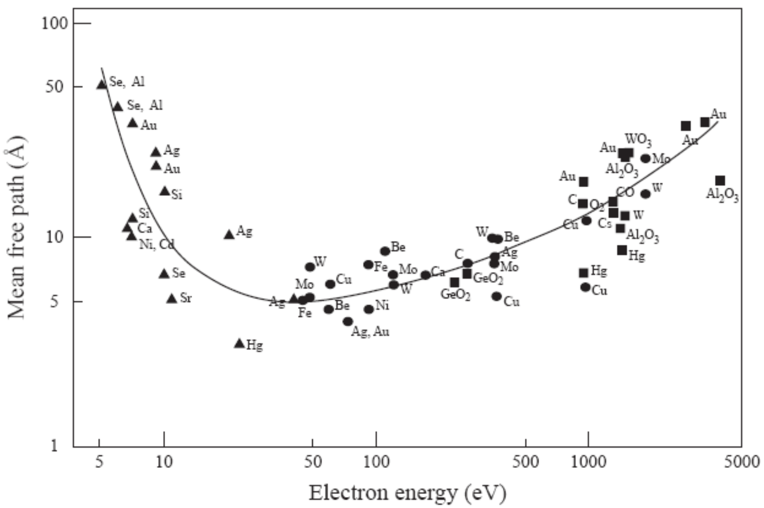


The study shows that in humid museum atmospheres a stepwise sulfur oxidation produces sulfuric acid:

$$S(s) + {}^{3}/_{2}O_2 + H_2O \rightarrow 2H^{+}(aq) + SO_4^{2-}$$

Mean free path I

XPS and AES rely on the **short mean free path** of **low energy electrons** in solids for achieving **surface sensitivity.**



The intensity removed (-dI) per length travelled (dx)

$-dI = \sigma N' I \, dx$ (σ: cross section for inelastic processes)

(N': Scattering centers per cm^3)

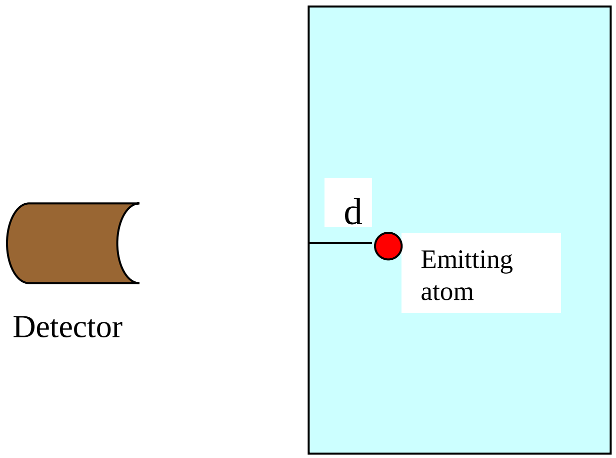
$$I(x) = I_0 \, e^{-\sigma N' x} = I_0 \, e^{-x/\lambda}$$

where $\lambda = (\sigma N')^{-1}$ is the mean free path

I(x) is the intensity of electrons that have not lost any energy after they have travelled the distance x in the solid.

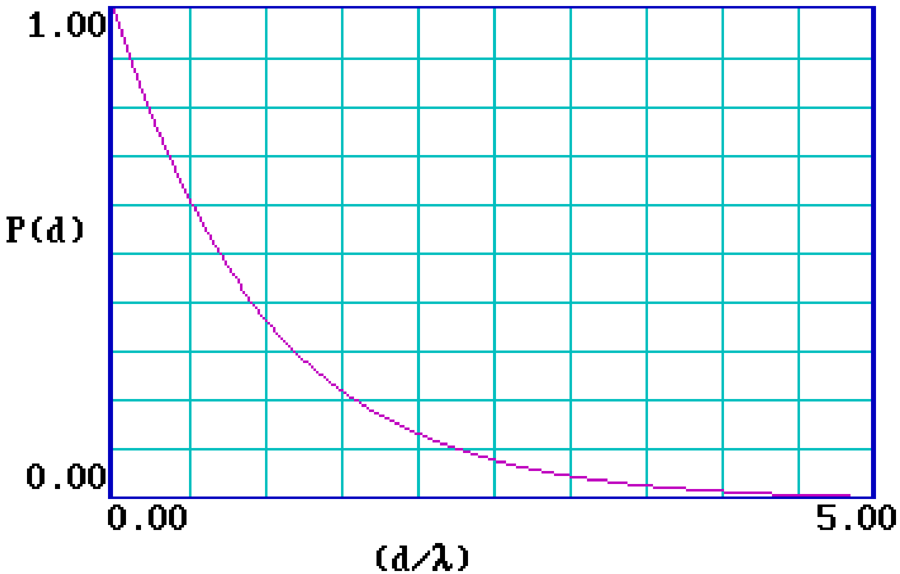
So, if you made all atoms in a solid emit electrons at a given energy of around say 70 eV and detected all electrons coming out of the sample with that energy, the majority of the electrons would come from the first few atomic layers.

Mean free path I



Probability of an electron travelling the distance d through a material <u>without</u> losing energy (λ : mean free path)

$P(d) = e^{-d/\lambda}$ (remember $\lambda=\lambda(E)$)

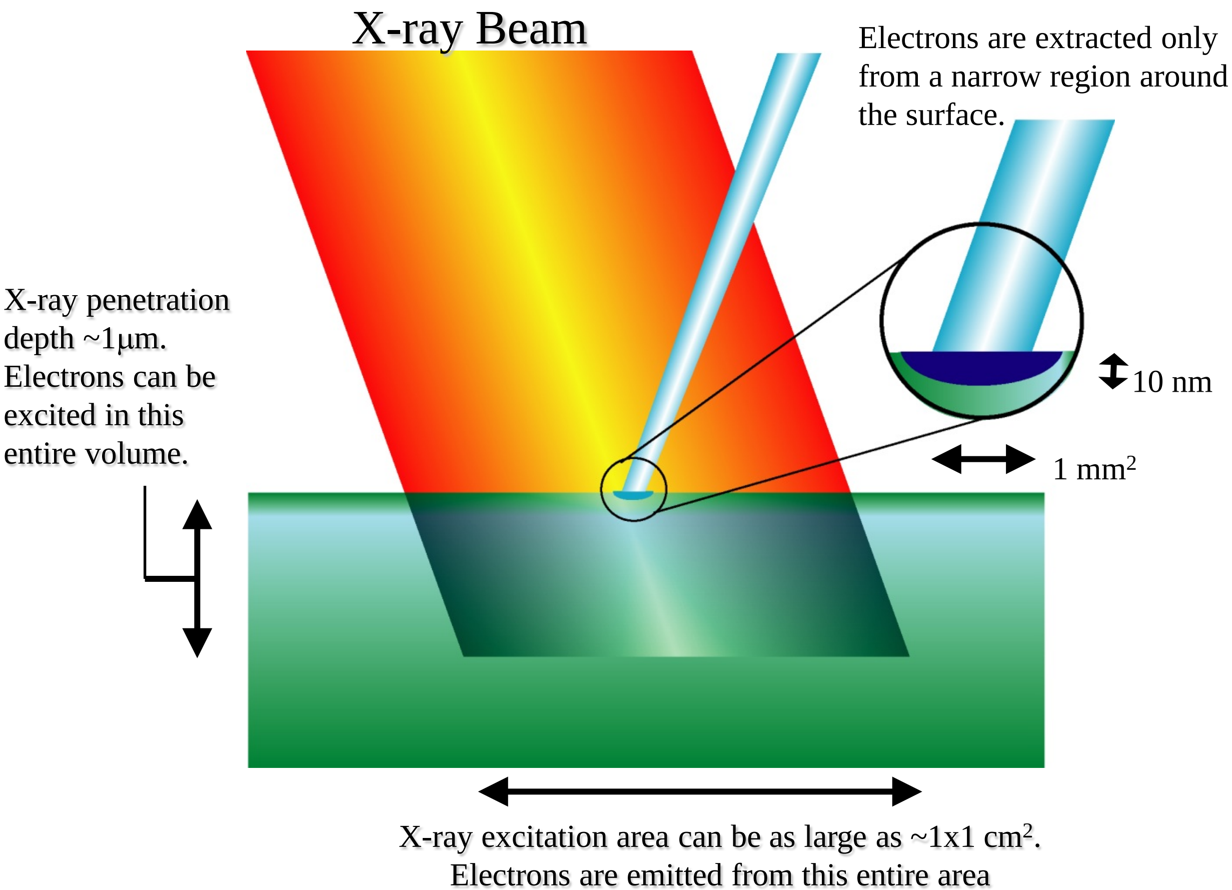


As you see virtually no electrons make it for more than 5λ without loosing energy.

Actually most of the electrons which escape from a surface without loosing energy have originated from within 1-2 * λ below the surface. Remember the minimum λ is about 5 Å.

X-ray photoelectron spectroscopy

Photon energies: 100-2000eV, Electron energies: 0-1000eV

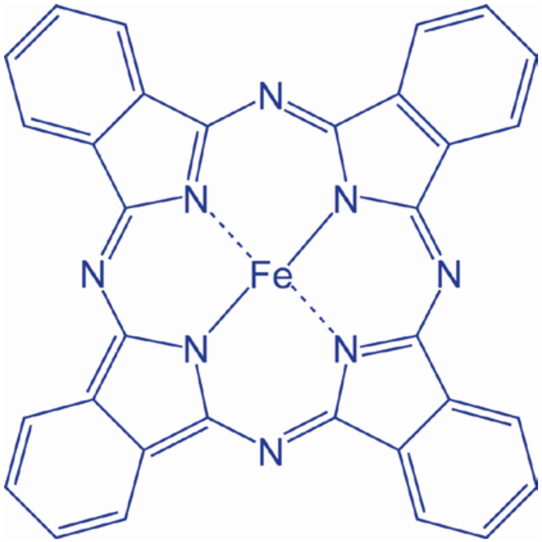


X-ray photoelectron spectroscopy

- **delivers elemental information**
- **delivers chemical information**
- **on solids: very surface sensitive**

Iron phthalocyanine

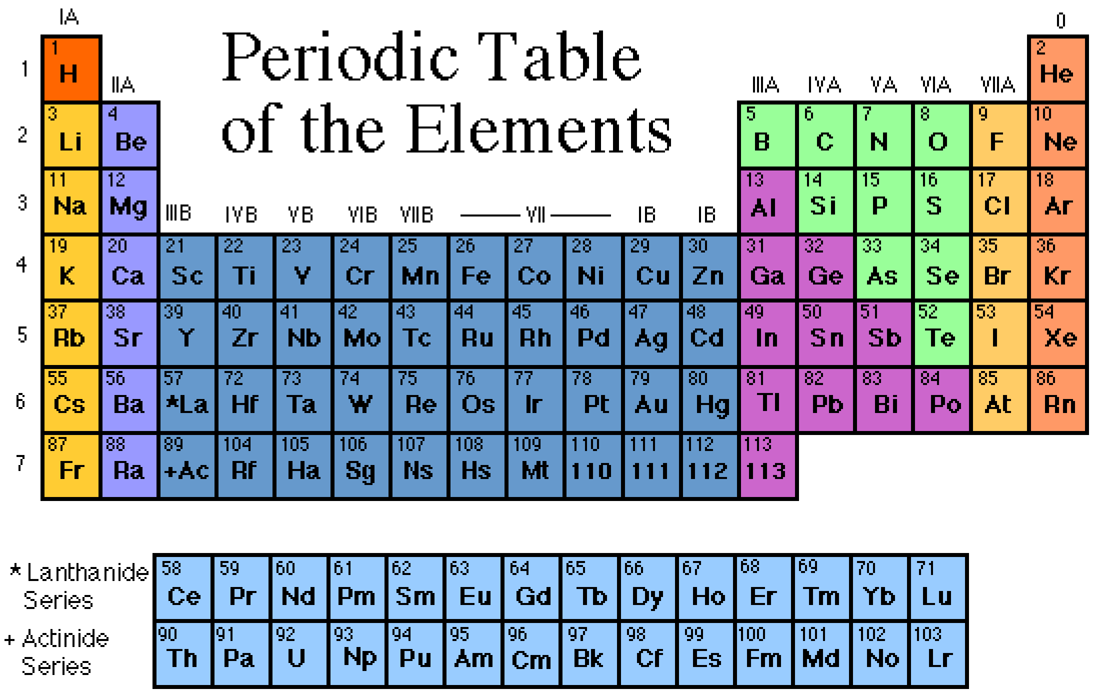
Iron phthalocyanine
(FePc)



- Similar to haem (responsible for oxygen storage and transport in mammals)
- Iron in ionic state (+2)
- Iron behaves very much as a single atom, but is modified due to presence of ”macrocycle”

What are the electron configurations of Fe and Fe(II)? What are the spin quantum numbers of Fe and Fe(II)?

Do not confuse with notation from atomic spectroscopy!
Atomic spectroscopy: Fe I = neutral helium, Fe II = Fe^{+}, etc.
Chemical notation: Fe(I) = Fe^{+}, Fe(II) = Fe^{2+}, etc.



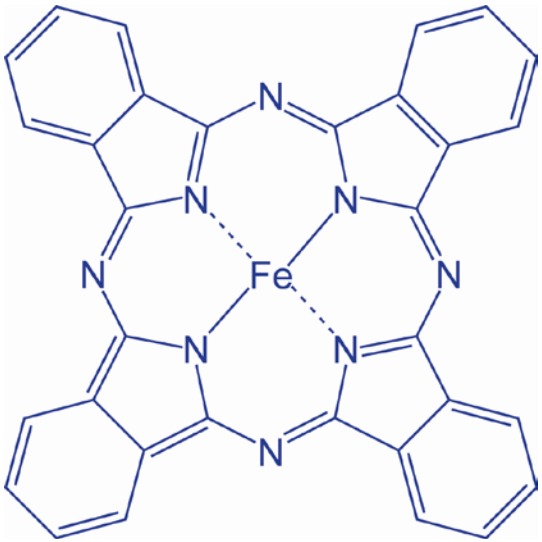
What are the electron configurations of Fe and Fe(II)? What are the spin quantum numbers of Fe and Fe(II)?

Hund's rules for ground state configurations:

(a) Highest possible S
(b) Highest possible L for the S from (a)
(c) Highest possible J for more than half-filled shell, smallest possible J for less than half-filled shell

What are the electron configurations of Fe and Fe(II)? What are the spin quantum numbers of Fe and Fe(II)?

What are the electron configurations of Fe and Fe(II)? What are the spin quantum numbers of Fe and Fe(II)?

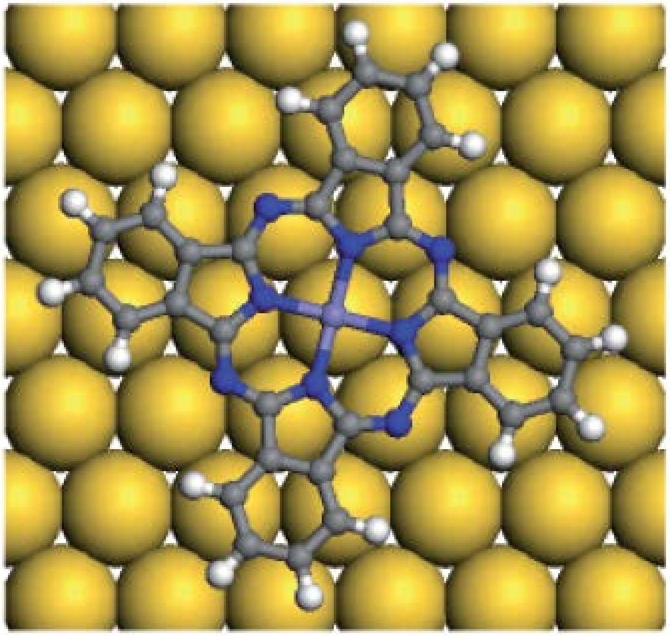


In general, in transition metal complexes the electron configurations are hydrogen-like!

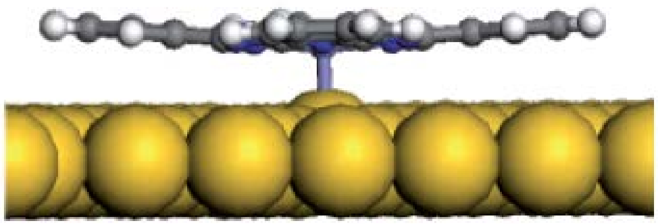
Furthermore the d levels split up due to the ”ligand field”.

Iron phthalocyanines on a Au(111) surface

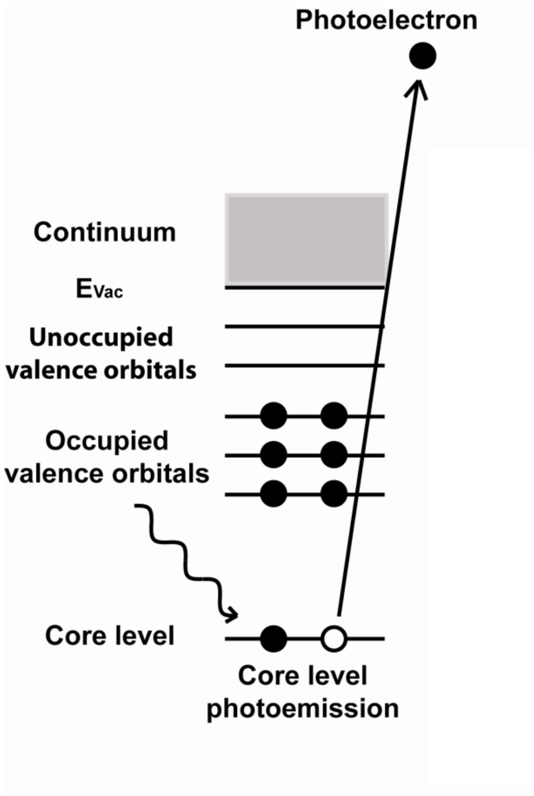
b) Configuration 2

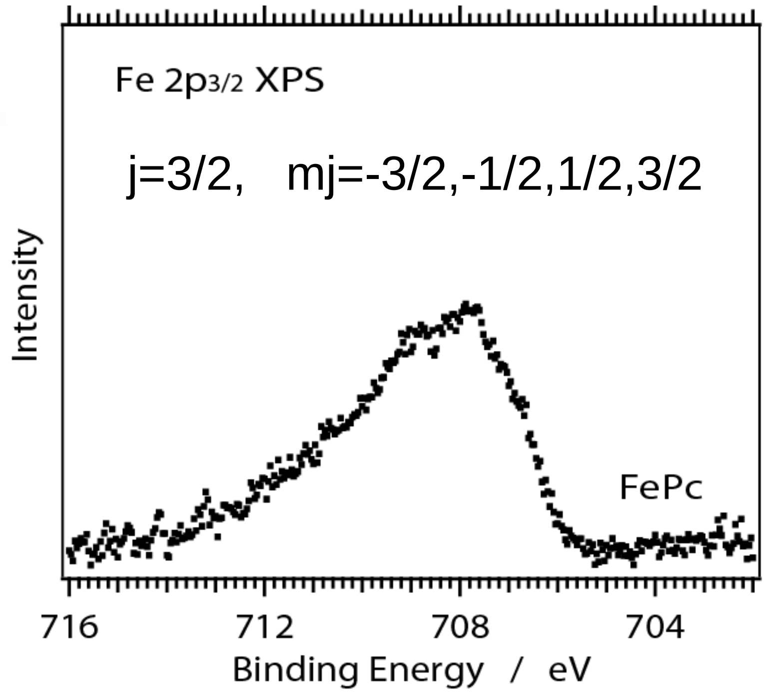


f) Configuration 2



X-ray photoelectron spectroscopy



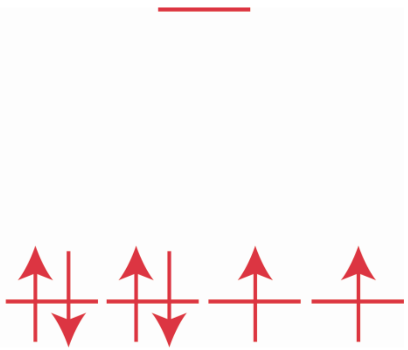


We just said that S=1 and further L needs to be an integer number. How can J be a half-integer?

”$2p_{3/2}$” is about the angular momentum of the core (hole) level only!

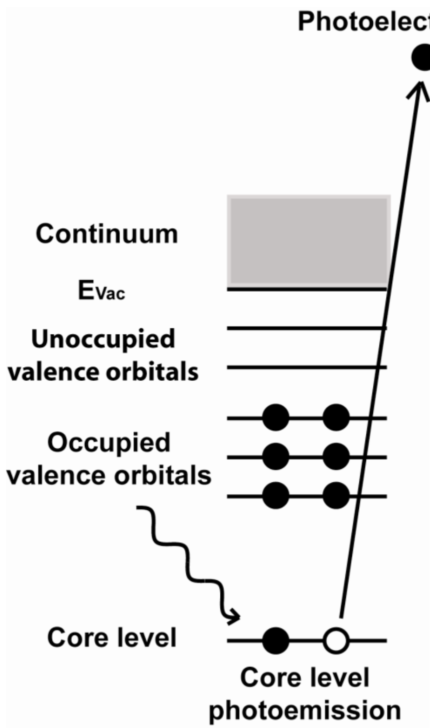
X-ray photoelectron spectroscopy

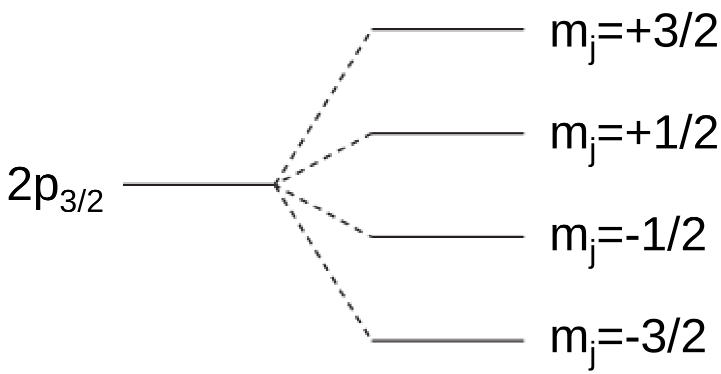
Metal valence levels of iron phthalocyanine



S=1

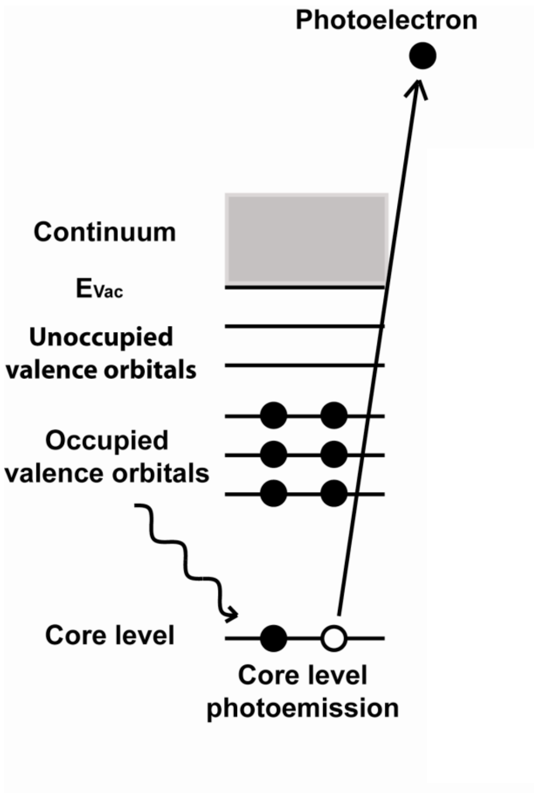
FePc

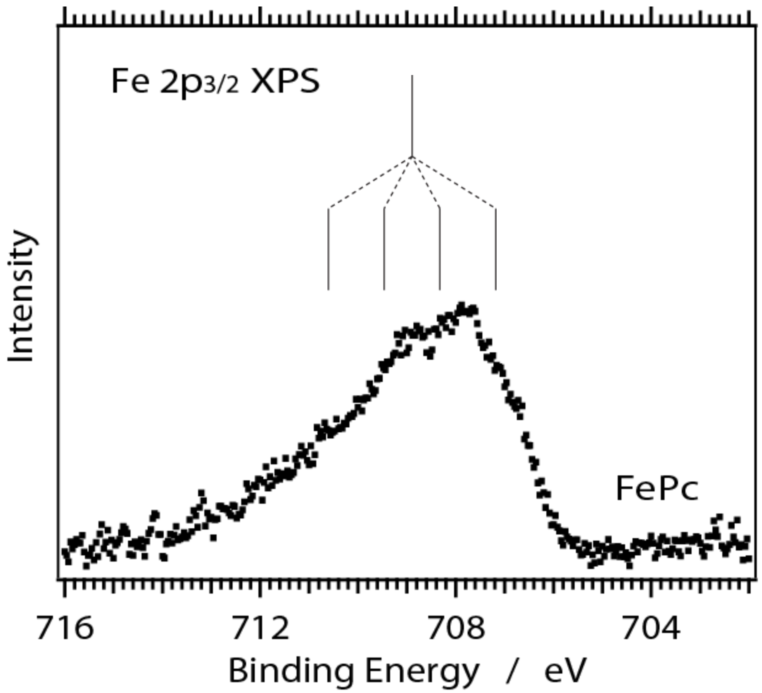




Coupling of valence spin angular momentum
with angular momentum of the core hole!

X-ray photoelectron spectroscopy

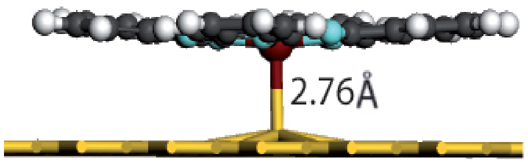




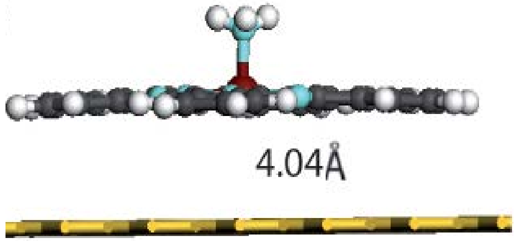
j=3/2, mj=-3/2,-1/2,1/2,3/2

Pyridine, carbon monoxide, nitric oxide on iron phthalocyanine

FePc/Au(111)



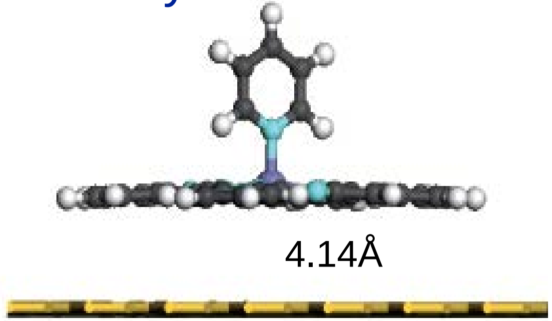
NH_3/FePc



Binding enery: 0.55 eV

$\mu_s = 0.27\ \mu_B$

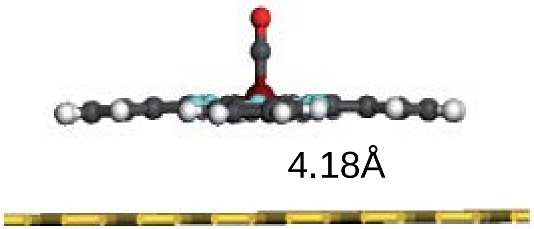
Pyridine/FePc



Binding enery: 0.6 eV

$\mu_s = 0.25\ \mu_B$

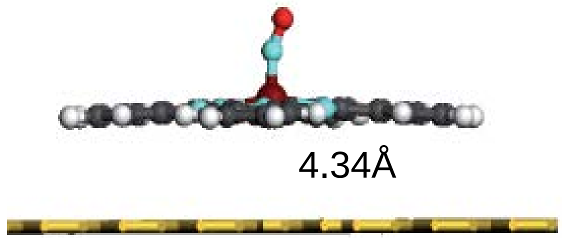
CO/FePc



Binding enery: 1.4 eV

$\mu_s = 0.09\ \mu_B$

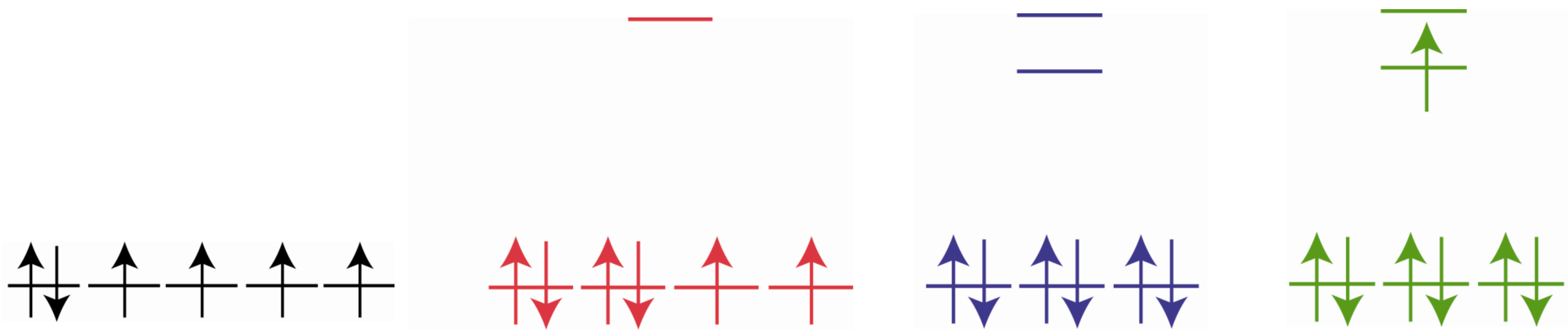
NO/FePc



Binding enery: 1.6 eV

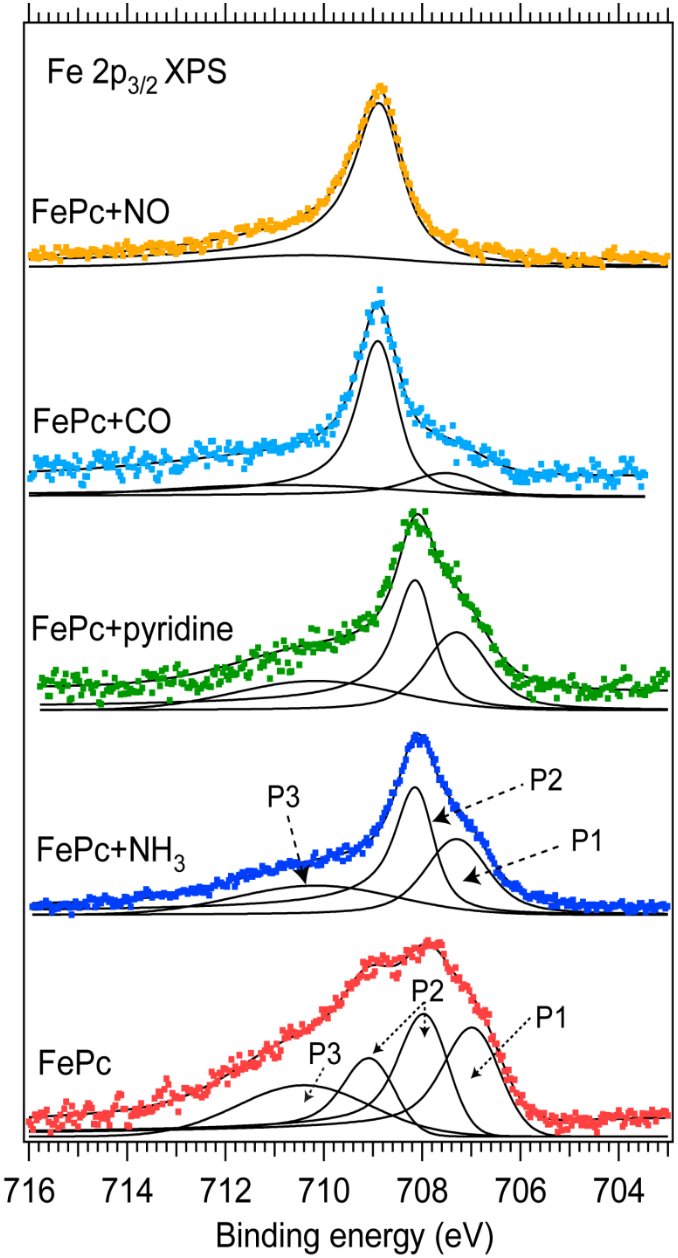
$\mu_s = 0.84\ \mu_B$

d-levels of iron phthaloycanine



S=2	S=1	S=0	S=1/2
atomic Fe	FePc	FePc-NH_3 FePc-pyridine FePc-CO	FePc-NO

Ligand field splitting



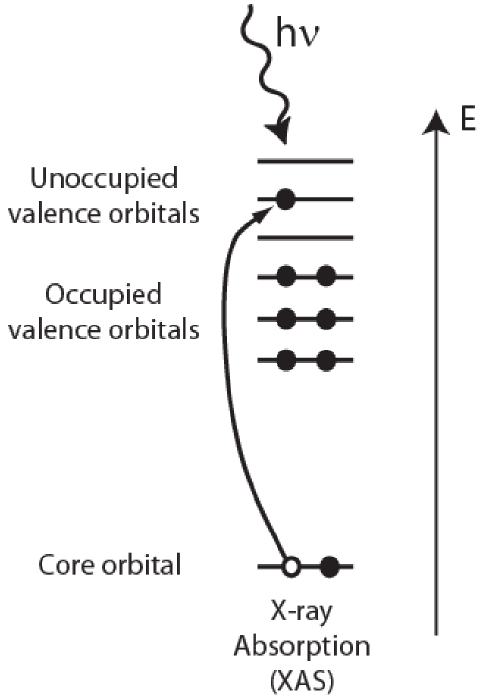
	Width (eV)	S
FePc/Au(111)	**2.29**	**1**
NH_3/FePc/Au(111)	**1.02**	**0**
Py/FePc/Au(111)	**1.02**	**0**
CO/FePc/Au(111)	**1.01**	**0**
NO/FePc/Au(111)	**1.26**	**1/2**

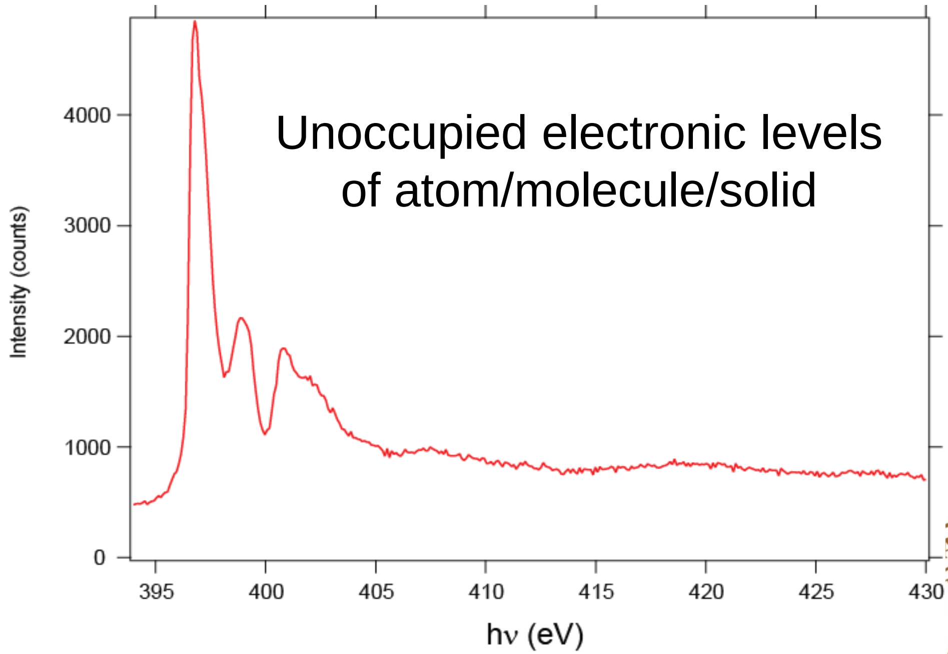
NH_3, pyridine, CO quench the spin; NO reduces the spin

X-ray absorption spectroscopy

X-ray absorption spectroscopy

XANES = X-ray Absorption Near Edge Structure
NEXAFS = Near Edge X-ray Absorption Fine Structure
XAS = X-ray Absorption Spectroscopy

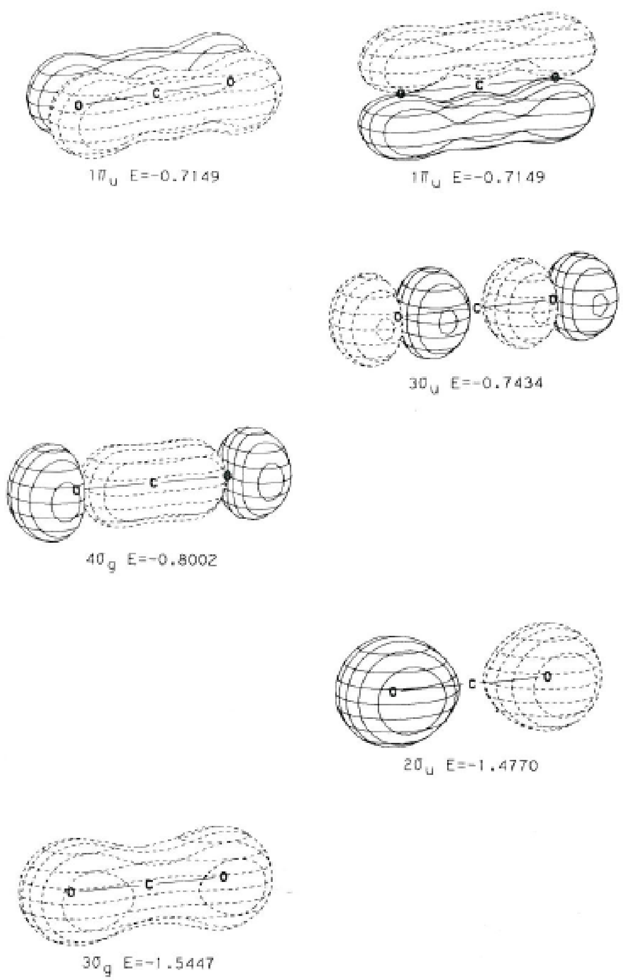




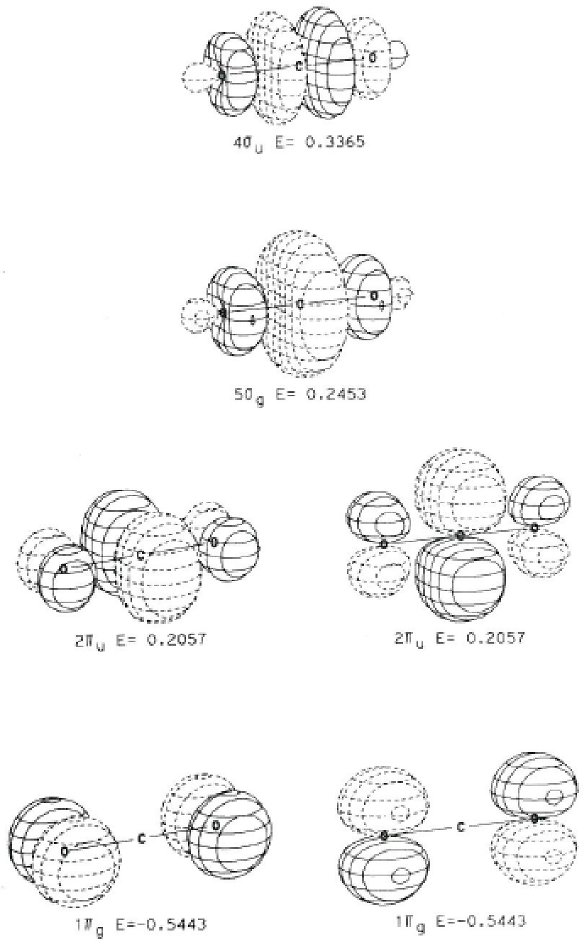
Linear combination of atomic orbitals

σ* and π* orbitals

45. Carbon Dioxide Symmetry: $D_{\infty h}$



Carbon Dioxide (Continued)



Excitations in x-ray absorption

Electron removed typically from 1s orbital

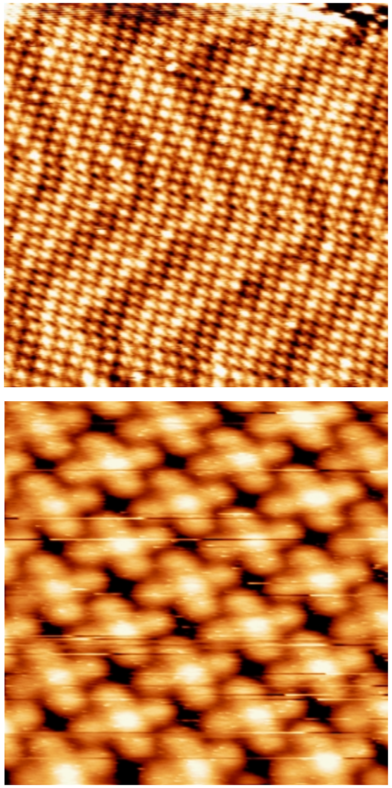
Dipole selection rule: $\Delta l=1$

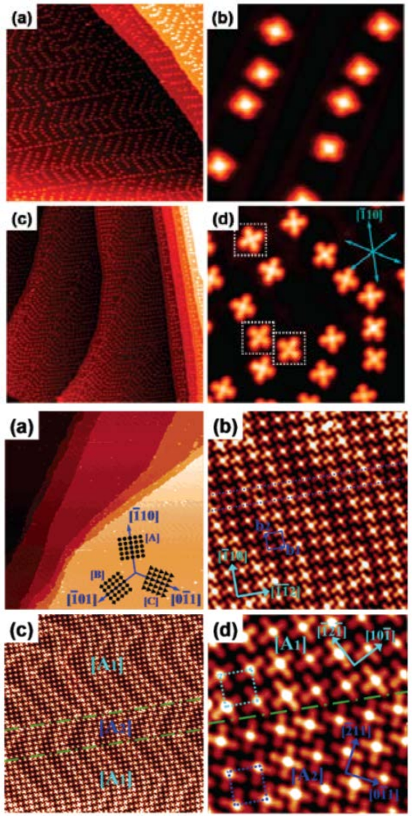
Implies that electron only can be put into *atomic* orbital with l=1 (p) only

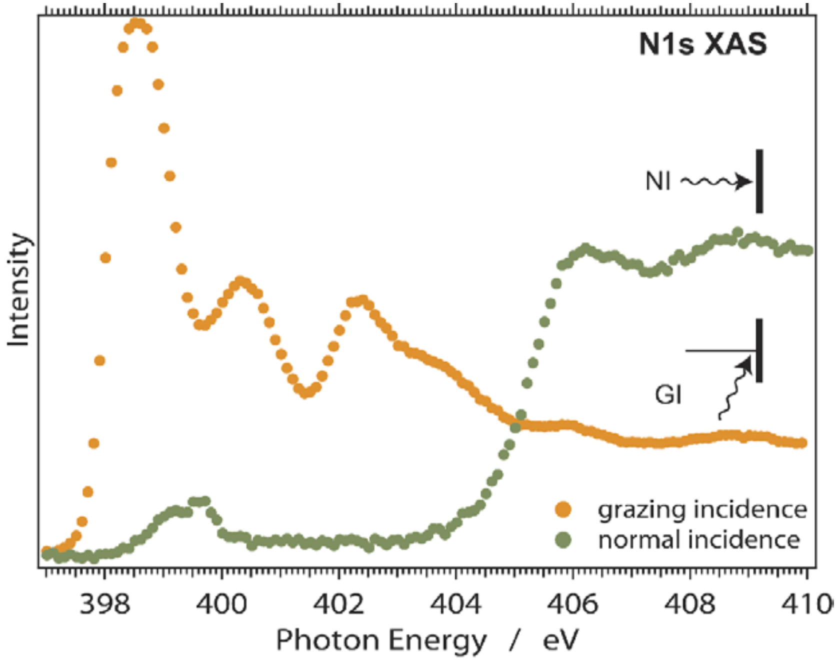
Both σ^* and π^* orbitals have p atomic orbital character –
σ^* along bond axis
π^* perpendicular to bond axis

→ makes possible determination of molecular geometry at surface

Geometry determination for iron phthalocyanine on a Au(111) surface







Z. H. Cheng et al.,
J. Phys. Chem. C 111 (2007) 9240
J. Phys. Chem. C 111 (2007) 2656

Take-home messages

Synchrotron radiation:

• Extremely powerful tool for investigation of matter (atoms, molecules, solids)
• Extremely high ”brilliance” (photon flux into solid angle)
• Lunds hosts a world-leading synchrotron radiation facility – MAX IV

X-ray photoelectron spectroscopy:

• Photon in – electron out
• Probes occupied states
• Elemental analysis
• Chemical analysis (down to spin)
• when applied to solids: very surface sensitive

X-ray absorption spectroscopy:

• Probes unoccupied states
• Chemical analysis
• Geometry determination