Introduction to electron spectroscopy: fundamental interactions, analyzers, electron optics

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Rm. CCR 208
## COURSE OUTLINE

### Surface and Interface Science - Spring 2013

#### Syllabus

<table>
<thead>
<tr>
<th>Lecture #</th>
<th>Date</th>
<th>Instructor</th>
<th>Lecture Topic</th>
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<tr>
<td>1</td>
<td>Fri. 25-Jan.</td>
<td>RAB</td>
<td>Introduction to course: why are surfaces interesting, begin surface thermodynamics and surface structure</td>
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<tr>
<td>2</td>
<td>Mon. 6-Sept.</td>
<td>RAB</td>
<td>Surface Thermodynamics</td>
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<td>3</td>
<td>Fri. 1 Feb.</td>
<td>RAB</td>
<td>RESCHEDULED: Tues. 29 Jan. 5:00-6:20PM Room: ARC 108</td>
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<tr>
<td></td>
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<td>RAB</td>
<td>Surface Structure, Two-dimensional Lattices</td>
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<td>4</td>
<td>Mon. 4-Feb.</td>
<td>PB</td>
<td>Electron diffraction methods, LEED, RHEED, Scanning probe</td>
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<td>6</td>
<td>Fri. 8-Feb.</td>
<td>LF</td>
<td>Microscopy: Principles of SEM, TEM, LEEM</td>
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<td>6</td>
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<td>LF</td>
<td>Intro to electron spectroscopy: Analyzers, electron optics</td>
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<td>7</td>
<td>Fri. 15-Feb.</td>
<td>RAB</td>
<td>Surface/Film Composition: XPS</td>
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<td>Ion Scattering Methods: RBS (channeling, NRA, ERD)</td>
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<td>9</td>
<td>Fri. 22-Feb.</td>
<td>TG</td>
<td>Ion Scattering II - MFIS (Channeling, Blooming, HighRes RBS)</td>
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<td>Mon. 25-Feb.</td>
<td>LW</td>
<td>Lab session: Ion Scattering [Meet in NPL]</td>
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<td>11</td>
<td>Mon. 1-Mar.</td>
<td>RAB</td>
<td>Intro to Electronic Properties [Term Paper Topic Due]</td>
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<td>12</td>
<td>Mon. 4-Mar.</td>
<td>DHV</td>
<td>Band Structure, Bulk, Film, Surface</td>
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<td>13</td>
<td>Fri. 8-Mar.</td>
<td>EG</td>
<td>Chemist’s approach to electronic structure: From bonds and bands</td>
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<td>14</td>
<td>Mon. 11-Mar.</td>
<td>RAB</td>
<td>Measuring electronic structure: UPS, ARUPS, IPS</td>
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<td>Fri. 15-Mar.</td>
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<td>Lab session: X-ray Photoelectron Spectroscopy [Meet in NPL]</td>
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<td>Spring Break [No Classes]</td>
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<td>Spring Break [No Classes]</td>
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<td>RAB</td>
<td>3 Hour Mid-term Exam LOCATION TBA</td>
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<td>RAB</td>
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<td>Adsorption, desorption, diffusion, energy transfer, sticking, atom scattering, etc.</td>
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<td>22</td>
<td>Mon. 15-Apr.</td>
<td>SO</td>
<td>Nucleation and growth of nanostructures and films</td>
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<td>23</td>
<td>Fri. 19-Apr.</td>
<td>WW</td>
<td>Surface Magnetism</td>
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<td>Mon. 22-Apr.</td>
<td>FMZ</td>
<td>Photovoltaics</td>
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<td>Fri. 26-Apr.</td>
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<td>RAB</td>
<td>Student papers due; oral presentations</td>
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RAB = Bartynski  PB = Batson  LF = Feldman  EG = Garfunkel  TG = Gustafsson  JH = Hinch
DV = Vanderbilt  FZ = Zimmerman  MC = Chhowalia  SO = Oh  VP = Podzorov  WW = Wu
SR = Rangan  FC = Cosandey  LW = Wielunski
## SURFACE ANALYSIS TECHNIQUES

<table>
<thead>
<tr>
<th>Method</th>
<th>Particle Measured</th>
<th>Process</th>
<th>Information</th>
<th>Monolayer Sensitivity</th>
<th>Effective Probing Depth</th>
<th>Depth Profiling</th>
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<tr>
<td>Auger Emission Spectroscopy (AES)</td>
<td>Auger Electrons</td>
<td></td>
<td>Elements Li-U</td>
<td>$10^{-1}$</td>
<td>20 Å</td>
<td>In Combination with Sputtering</td>
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<tr>
<td>Scanning Electron Microscopy</td>
<td>X-Rays</td>
<td></td>
<td>Elements Na-U</td>
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<td>10000 Å</td>
<td>None</td>
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<td>Transmission Electron Microscopy</td>
<td>Diffracted Electrons</td>
<td>None</td>
<td>Compound Identification</td>
<td>None</td>
<td>500 Å</td>
<td>None</td>
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<td>Elements Li-U, Chemical Bonding</td>
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<td>30 Å</td>
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<td>Secondary Ion Mass Spectrometry</td>
<td>Sputtered Ions</td>
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<td>Elements H-U</td>
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<td>Via Sputtering</td>
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<td>Rutherford Backscattering Spectroscopy</td>
<td>Scattered Mils (H⁺, He⁺)</td>
<td></td>
<td>Elements Be-U</td>
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<td>100 Å</td>
<td>Via Energy Loss</td>
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<td>Particle Induced X-Ray Emission</td>
<td>X-Rays</td>
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<td>1000 Å, 10000 Å</td>
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<td>Nuclear Reaction Analysis (NRA)</td>
<td>Light Ion Reaction Product</td>
<td></td>
<td>Light Elements (Li, Be, B, C, O, F...)</td>
<td>$10^{-1}$</td>
<td>100 Å, 10000 Å</td>
<td>Via Energy Loss</td>
</tr>
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Figure 9.1 Electromagnetic spectrum indicating the region used for photoelectron spectroscopy. Ultraviolet photoelectron spectroscopy corresponds to incident photons in the UV region; X-ray electron spectroscopy corresponds to incident photons in the X-ray region.
Figure 6.2 Schematic of energetic photons incident on a surface and creating characteristic electrons relatively deeply in the solid. Only those electrons created near the surface escape with no loss of energy.
Figure 6.13 Monte Carlo electron trajectory simulation of a 20 keV beam at normal incidence on Fe. The density of trajectories gives a visual impression of the interaction volume. [From Goldstein et al. (1981).]
Figure 8.3 The relative importance of the three major types of photon interactions. The lines show the values of $Z$ and $h\nu$ for which the neighboring effects are equal.
Figure 8.6 Mass absorption coefficient (a) for elements from \(Z = 2-40\) for \(K_a\) radiation from a variety of sources and (b) as a function of energy for different absorbers.
Figure 8.4 The mass absorption coefficient $\mu/\rho$ (cm$^2$/g) of Ni versus $\lambda$. 
Figure 8.2 Schematic of the photo effect from an electron bound in a square well. The full curve shows the approximate wave function used in the calculation while the dashed line shows the true wave function in the region $x = \pm a$. 
Figure 9.14 Calculations of the photoelectric cross section for different subshells throughout the periodic chart. The incident radiation is 1.5 keV. (a) The dominant shells most used in XPS; (b) the complete set of subshells. [From J. H. Scofield, J. Electron Spectrosc. 8, 129 (1976).]
Figure 6.6 Ionization cross section versus reduced energy $U$ for interactions within a solid. [From Chang, in Kane and Larrabee, Eds., Characterization of Solid Surfaces (Plenum Press, New York, 1974).]
Figure 6.8 Electron gas with $\frac{4}{3} \pi r^3 n$ electrons around a positive core and undergoing a radical contraction $\delta r$. 

ELECTRON GAS

$n = \text{electrons/cm}^{-3}$
Figure 6.9 Energy loss spectrum for electrons reflected from Al for incident primary electron energy of 2 keV. The loss peaks are made up of a combination of surface and bulk plasmon losses.
Figure 6.4 Universal curve for electron mean free path. [From G. Somerjai, Chemistry in Two Dimensions: Surfaces (Cornell University Press, Ithaca, N.Y., 1981), by permission.]
Figure 6.1 Schematic diagram of a cylindrical mirror analyzer used for electron energy detection in various electron spectroscopies.
Figure 9.2  Schematic of the basic apparatus used in X-ray photoelectron spectroscopy. X-rays are produced at the Al anode by bombardment of electrons created at the filament. The X-rays impinge on a sample producing photoelectrons which are detected after analysis in the electron energy analyzer.
Figure 9.4 Schematic of an X-ray monochromation system.
Figure 9.3 The two components of the $K_\alpha$ spectrum ($K_{\alpha_1} + K_{\alpha_2}$) which comprise the $K_\alpha$ spectrum of Al. [Spectrum from Siegbahn et al., 1967.]
Figure 9.10 Binding energies of the elements.
Figure 9.8 Electron lines from the L₁ subshells of the third period elements (sodium to chlorine) excited with magnesium Kα radiation (1.25 keV). [From Siegbahn et al., 1967.]
Figure 9.7 The energy spectrum of electrons from the 1.25 keV photon irradiation—Mg (Kα)—of nickel. The energy axis is in terms of binding energy, i.e., \( hv - E_{\text{kin}} \). The vertical axis is denoted as \( N(E)/E \) to denote that the admittance of the spectrometer decreases as \( 1/E \). [From Phi Handbook, Eden Prairie, MN.]
Figure 9.9 Electron spectra from a large variety of elements in the electron binding energy range of $\sim 600$ eV to $\sim 20$ eV. The incident photon radiations are Mg and Al Kα. [From Siegbahn et al., 1967.]
Figure 9.11 The chemical shift in binding energy of the Si 2p line for elemental Si and SiO$_2$. The spectra are taken with Al K$_\alpha$ radiation. [From Phi Handbook, Eden Prairie, MN.]
Figure 9.12 Carbon 1s chemical shifts in ethyl trifluoroacetate. The four carbon lines correspond to the four carbon atoms within the molecule. [Adapted from Ghosh, 1983.]
Figure 9.6 Schematic of the relevant energy levels for binding energy measurements. Note that the conducting specimen and spectrometer housing are in electrical contact and thus have common Fermi levels. The incoming photons, energy $h\nu$, create an electron of kinetic energy $E_{\text{kin}}$ relative to the vacuum level of the sample. The electron is detected by a spectrometer with a work function $\phi_{\text{spec}}$ so that the measured energy $E_{\text{kin}} = E_{\text{kin}}^1 - (\phi_{\text{spec}} - \phi_{s})$. 
Figure 6.13 Monte Carlo electron trajectory simulation of a 20 keV beam at normal incidence on Fe. The density of trajectories gives a visual impression of the interaction volume. [From Goldstein et al. (1981).]
Figure 6.5 Schematic of an electron of momentum $mv$ interacting with a free electron at an impact parameter $b$. 
Figure 6.14 The electron range $R \, (\mu m)$ versus incident electron energy for different density, $\rho$, materials. The lines are calculated from Eq. (6.24) with $K = 0.064$ and $\gamma = 1.68$. 
Figure 9.5 Schematic of a double pass cylindrical mirror analyzer (CMA) used in photoelectron spectroscopy.
generate a $dN(E)/dE$ function (insert on Figure 11.9). Differential analysis of a hypothetical spectrum is shown in Figure 11.10. The contribution from the slowly varying background is minimized by the derivative technique. The total backscattered background current with energy greater than 50 eV is typically 30% of the primary beam current. The noise level due to this current and the ratio of the analyzer $\Delta E$ to Auger line width generally establishes the signal-to-noise ratio and hence the detection limit for impurities in the sample. A typical value for the detection limit is 1000 ppm, ≈ 0.1 atomic %.

Figure 11.9 Spectrum of 2 keV electrons scattered from a solid. The inset shows the regime for Auger spectroscopy. The energy scale is nonlinear. [From Ilbach, 1977.]
Figure 11.5 Auger electron and X-ray yields per K vacancy as a function of atomic number. The curves are from Eq. (11.12). [From Siegbahn et al., 1967.]
cess. Further, Auger linewidths are broader than XPS lines. Consequently, the latter technique is typically used to explore changes in chemical binding.

11.2.4 Estimate of the Auger Transition Probability in a Hydrogenlike Atom: KLL Transition

In the usual manner the transition probability for the Auger effect, \( W_A \), can be written as

\[
W_A = \frac{2\pi}{\hbar} \rho(k) |\phi_f(r_1)\psi_f(r_2)|^2 \frac{e^{2}}{|r_1 - r_2|}\phi_i(r_1)\psi_i(r_2) \, dr_1 \, dr_2 .
\]

(11.2)

where \( \rho(k) = m (V/\pi^{3/2} \hbar^2) k \sin \theta \, d\theta \, d\phi \) is the density of states associated with normalization in a box of volume \( V \) and for a KLL Auger transition from a hydrogenlike atom:

\[
\phi_i(r_1) = \frac{1}{\sqrt{6a^3}} \frac{r_1}{a} e^{-r_1/2a} Y_{1}^{0}(\theta_1, \phi_1),
\]

(11.3)

\[
\phi_f(r_1) = \frac{2}{\sqrt{a^3}} e^{-r_1/a},
\]

(11.4)

\[
\psi_i(r_2) = \frac{1}{\sqrt{6a^3}} \frac{r_2}{a} e^{-r_2/2a} Y_{1}^{0}(\theta_2, \phi_2),
\]

(11.5)

\[
\psi_f(r_2) = \frac{1}{\sqrt{V}} e^{i k \cdot r_2}.
\]

(11.6)

These wave functions represent electrons in the 2p state, the 1s state, the 2p state, and a free electron, respectively, with \( a = a_0 / Z \) and \( a_0 \) is the Bohr radius. For convenience it is useful to write these equations as functions of \( r/a \):

\[
\phi_i(r_1) = \frac{1}{\sqrt{6a^3}} \phi_i \left( \frac{r_1}{a} \right),
\]

(11.3')

\[
\phi_f(r_1) = \frac{2}{\sqrt{a^3}} \phi_f \left( \frac{r_1}{a} \right),
\]

(11.4')
Figure 6.7 The maximum electron impact ionization cross section per electron (near $U = 4$) versus binding energy for various electron shells. [From Kirschner, in Ibach, 1977.]
much higher than the normal Auger transitions and influence the relative intensities of the Auger lines. For example in Figure 11.1, if an L₃ shell has a vacancy, the L₂ to L₃ transition will be rapid (Coster-Kronig), therefore reducing M electron to L₈ vacancy transitions.

### 11.2 Auger Transitions

#### 11.2.1 Nomenclature

The nomenclature used to describe the Auger processes is shown in Figure 11.1. For vacancies in the K shell, the Auger process is initiated when an outer electron such as an L₃ electron (dipole selection rules are not followed) fills the hole. The energy released can be given to another electron such as another L₃ or an L₂ electron which is then ejected from the atom. The energy of the outgoing electron is $E_K - E_{L₃} - E_{L₃}$. The process described is called a KL Auger transition general terms and, more specifically denoted as KL₃L₃ or KL₃L₂. If there are vacancies in the L shell, one can have Auger processes in which an L₉ electron is excited to another M electron from the M shell. Another Auger process which is the strongest of the M₉L₉M₁ transition involves the same 2s and 3p orbits orbitals, the transitions of maximum of the valence LVV Auger transitions of m
Figure 6.11 Extinction curves for characteristic substrate electrons as a function of average coverage of an overlayer. In these examples the mean free path, $\lambda$, is taken as two monolayers, close to the minimum mean free path achievable. In the case of the uniform overlayer the growth is assumed to be layer-by-layer and the extinction curve is a series of straight lines with the envelope of points at integral coverage corresponding to an exponential decay. The other curves correspond to a “single layer plus islanding” growth mode and a case of pure islanding. For the cases involving islanding it is assumed that 50% of the surface is covered.
Figure 8.3 (a) Attenuation of the Si LVV (92 eV) as a function of Ge coverage. The mean free path corresponds to ~3 Å of Ge. In this example the Ge deposition is at 300° K. (b) Attenuation of the Ge LMM (1147 eV) and Ge MVV (52 eV) Auger lines as a function of Si coverage. [From H. J. Gossman, Ph.D. thesis, State University of New York, Albany, 1984.]
Figure 6.12 Auger yield curve for the deposition of Pb on Cu(100) at room temperature. The solid circles represent the attenuation of the Cu substrate signal and the open squares the growth of the Pb signal. This type of growth corresponds to the "one layer plus islanding" mode. In this example the (average) Pb coverage is measured by RBS. [From R. J. Culbertson, unpublished data.]
where \( x \) contains all non-time-dependent terms. In this calculation we assumed \( k \ll V \) so that terms of order \( k^3 \) and higher can be neglected in practice. Using a lock-in amplifier, for phase sensitive detection, we select the component of the signal associated with the frequency \( \omega \), which is simply the desired quantity \( I' \) or \( dN/dE \) for a cylindrical mirror Auger analyzer. To satisfy this criteria, we require that \( k \) be less than the Auger width of \( \sim 5 \) eV.

An example of the use of derivative techniques is shown in Figure 11.11 for 2 keV electrons incident on a Co sample. In the direct spectrum, \( n(E) \), the main features are the peak of elastically scattered electrons and a nearly flat background. The arrows in Figure 11.11a indicate the energies of oxygen and Co Auger transitions. The derivative spectrum (Figure 11.11b) reveals the LMM Co and KLL carbon and oxygen signals.

**Figure 11.11** Comparison of (a) the spectrum \( N(E) \) and (b) the derivative \( dN(E)/dE \) for 2 keV electrons incident on a Co sample. [From Tousset, in Thomas and Cachard, 1976.]
Figure 6.10 (a) Electron energy loss spectrum for 80 keV electrons transmitted through a 500 Å NiAl film. The dominant peak in the loss spectrum is the single plasmon loss at $\hbar \omega_p \sim 17.8$. The surface plasmon ($\hbar \omega_s = 7.1$ eV) and core excitation (Ni M$_{23}$ and Al L$_{23}$) are indicated. (b) The calculated density of states (DOS) for NiAl (solid line) and Al L$_{23}$ core excitation (data points) from EELS spectra similar to that shown in (a). Core level threshold transitions are shown by arrows. [From Grunes, Barbour, Hung, Mayer and Ritsko, J. Appl. Phys. 56, 168 (1984).]
Figure 6.15 The effective electron ranges in Cu and Al for X-ray production. The ranges denote the end point of penetration of electrons for generation of characteristic \( K_\alpha \) and \( L_\alpha \) X-rays. [From Goldstein et al., 1981.]
Figure 11.5 Auger electron and X-ray yields per K vacancy as a function of atomic number. The curves are from Eq. (11.12). [From Siegbahn et al., 1967.]

Figure 11.5 Auger electron and X-ray yields per K vacancy as a function of atomic number. The curves are from Eq. (11.12). [From Siegbahn et al., 1967.]
Figure 6.16 Electron energy loss spectra for 80 keV electrons incident on thin (about 400 Å) self-supporting films of Si, NiSi₂, Ni₂Si and Ni films. The positions of the bulk plasmon peaks, $\hbar \omega_p$, are shown for the two nickel silicides. [From Barbour et al., in Thin Films and Interfaces II, Baglin, Campbell and Chu, Eds., North-Holland, Amsterdam, 1984].]
Figure 8.5 Comparison of X-ray absorption and X-ray photoelectron spectroscopy. [From Siegbahn et al., in ESCA (Almqvist and Wiksell, Uppsala, Sweden, 1967).]
Figure 8.9 Schematic of the EXAFS process illustrating an emitted $e^-$ scattering from a nearby atom at a distance $R_j$. 
Figure 8.8 Schematic of the transmission experiment and the resulting X-ray absorption $\mu x$ versus $E$ for an atom in a solid.
Figure 8.10 (a) X-ray absorption spectrum of crystalline Ge at a temperature of 100°K. The sharp rise near 11 keV is the K edge and the modulation in $\mu x$ above the edge is the EXAFS. (b) Fourier transform of (a) showing the nearest neighbor and second nearest neighbor distances. [From Lee et al., 1981.]
Figure 6.17 (a) Electron energy loss spectrum of NiSi₂ showing the bulk plasmon peak and the characteristic Ni M₂₃ and Si L₂₃ core level excitations. (b) A comparison of EELS spectra in the energy region of the characteristic Ni and Si core level excitations. [From Barbour et al., Ultramicroscopy 14, 79 (1984).]
Figure 9.13 Three-dimensional plot of the Ni 2p XPS spectra with the Z axis representing time during heat treatment. The spectra illustrate the planar growth of different forms of nickel silicide as shown in the inset. Here chemical shifts are relatively small but the change in intensity indicates a change in composition. [From P. J. Grunthaner, Ph.D. thesis, Caltech, 1980.]
Figure 6.18 Radiation cross section (energy · area/unit frequency) for nonrelativistic Coulomb collisions as a function of $\frac{\hbar \omega}{E}$, Eq. (6.45).
Figure 8.1 (a) Probability density for the hydrogenic wave function for different values of the quantum numbers $n$ and $l$. (b) Energy levels in the hydrogen atom; the vertical lines represent transitions that satisfy the selection rule $\Delta l = \pm 1$. 
Figure 8.7 Comparison of the Cu radiation before and after passage through a Ni filter. The dashed line represents the mass absorption coefficient of nickel. [Adapted from Cullity, 1978.]