Biological and Medical Physics, Biomedical Engineering

Stephen P. Cramer

X-Ray Spectroscopy with Synchrotron Radiation

Fundamentals and Applications

Springer

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Fundamentals and Applications

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To my father, who always asked about the "book" and
To my wife, Sybil, who put up with me writing it

Preface

When I first visited the Stanford Synchrotron Radiation Project as a naïve graduate student in 1974, I had no idea that I was joining a revolution that would continue for the next ~45 years—and that is still under way. At the time, I was a "parasite," grudgingly allowed to use the synchrotron radiation that was a nuisance by-product of storing relativistic charged particles in circular storage rings. Back then, the important science was high energy physics with colliding electron and positron beams. It was exciting to visit the SPEAR control room and watch the gradually and then sharply rising cross sections as they discovered new particles. The ring operators received "palm frond awards" for their efforts, while a Nobel prize was soon awarded to Stanford's Burt Richter and Brookhaven's Samuel Ting for discovery of the J/Ψ particle [1].

Over time, the parasites devoured the host, first taking over the SPEAR storage ring and eventually the entire linear accelerator, which is now the LCLS free electron laser. A similar scenario played out in Germany, where the PETRA ring originally built for positron-electron collisions evolved into the PETRA-III synchrotron radiation lab, and the technology that was to be used in the planned linear collider helped lead to the FLASH and European XFEL free electron lasers. Biology has a word for parasites that consume their hosts: "parasitoids."

Since then (and even earlier), the progress in synchrotron radiation technology and research has been rapid and unrelenting. A Web of Science search yields nearly 50,000 papers under the "synchrotron radiation" topic, and no doubt many more papers based on synchrotron work are buried under other headings. Several Nobel prizes have been based in part on data gathered at synchrotron sources, for structural studies of ATP synthase, the green fluorescent protein, G-protein-coupled receptors, and ribosomes. Ironically, the prizes have all been for structural biology—hardly a consideration when the first storage rings were being designed.

Synchrotron radiation has certainly gone mainstream, not just on the covers of *Physics Today* and *C&En News*. The storage ring SESAME in Jordan is one small step towards peace in the Middle East. The Advanced Light Source in Berkeley appeared in a bad movie—*The Hulk*, and synchrotron radiation even showed up as special advice in a good TV series—*Breaking Bad.*

This text has evolved out of a course given in the Applied Science Department at UC Davis. I have tried to achieve a balance between the synchrotron radiation production side and the spectroscopy that is enabled with these photons. For those who care about the production, transport, and detection of synchrotron radiation, start at the beginning. For those who only care about the spectroscopic applications, you can dive in half way at Chap. 6.

Some comments about style (and substance). In many cases, the derivation of equations from first principles to describe synchrotron radiation or its applications is complex and lengthy. Without apology, I usually present the equations and reference other sources where such derivations have already been done. For the equations themselves, I have adopted the approach used in the ALS Manual, where for practical equations the appropriate units are listed in brackets []. However, the powers of those units are considered obvious and are not listed in the brackets. In general, I have tried as much as possible to refrain from links to websites because it would just be a matter of time before all of the links would be obsolete. But, of course, there are a few exceptions. Another moving target has been facility specifications. Several examples of storage ring properties have changed because of upgrades, but rewriting the text to keep up with changes would be a fool's errand.

I hope you enjoy this first edition, and I hope that it occasionally stimulates what Emerson called "creative reading."

"There is then creative reading as well as creative writing. When the mind is braced by labor and invention, the page of whatever book we read becomes luminous with manifold allusion."

Los Altos, CA Stephen P. Cramer
October, 2020

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As far as learning about X-rays, I thank Keith Hodgson, Seb Doniach, Brian Kincaid, George Brown, Peter Eisenberger, and Herman Winick for advice during my early days with EXAFS. Later, Jerry Hastings and Peter Siddons showed me how to do proper X-ray fluorescence and inelastic scattering experiments, while my introduction to soft X-rays and XMCD came from C. T. Chen, George Sawatzky, Francesco Sette, and John Fuggle. When I embarked on nuclear adventures, Ercan Alp, Yoshitaka Yoda, and Uwe Bergman were there to help. I have also depended on Helmut Wiedemann for his expertise about machine physics and Orren Tench for many years of advice about X-ray detectors. And of course, none of this would have been possible without many years of support from DOE, NSF, and NIH and beam time from SSRP/SSRL, NSLS, ALS, APS, ESRF, PETRA-III, UVSOR, KEK-AR, and SPring-8. I thank all of the students and postdocs who spent long hours at the beamlines while I went home to bed. They were a joy to work with and helped make this journey possible. Finally, I thank my wife, Sybil, for editing numerous papers and proposals over the years and for proofing the galleys of this book with exquisite attention to detail.

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Chapter 1
Introduction and Historical Background

1.1 X-rays and the Electromagnetic Spectrum

This is a book about X-rays—how they are created with synchrotron radiation and how they are used in X-ray spectroscopy. For many of us, our first encounter with X-rays is as a child in a dentist's chair, or with a broken bone in the doctor's office, or perhaps at an airport baggage inspection. Compared to other forms of electromagnetic radiation, such as visible light that we see with, infrared radiation that we feel as warmth on our skin, or microwaves that cook our food, X-rays have always seemed somewhat mysterious—perhaps vaguely associated with Superman in our unconscious mind. However, as illustrated in Fig. 1.1, X-rays are just another part of the continuous spectrum of electromagnetic radiation.

There are many different definitions of the X-ray region. From a chemist's point of view, X-ray radiation is involved in excitation of the core electrons of atoms. This ranges from the 55 eV required to dislodge a 1s electron in lithium to the 116 keV required to do the same for uranium. On the low-energy side, the extreme ultraviolet (EUV) community has laid claim to photons from 30 to 250 eV, while on the high-energy side there are γ-rays, often produced during nuclear reactions and typically involving hundreds of keV or more. Even with a conservative definition of 100 eV to 100 keV, X-rays vary in energy or wavelength by three orders of magnitude, compared to the ~two-fold variation for all of visible light (Fig. 1.1).

Another fuzzy boundary is between "soft X-rays" and "hard X-rays." X-rays are called "soft" when they do not penetrate deeply. For our purposes, soft X-rays are those with energies below ~2 keV, a range normally served by vacuum beamlines and grating monochromators, while hard X-rays are above ~2 keV and generally use crystal monochromators. Some have tried to define a middle region as "tender" X-rays; this seems more cute than useful.

S. P. Cramer, *X-Ray Spectroscopy with Synchrotron Radiation*, Biological and Medical Physics, Biomedical Engineering, https://doi.org/10.1007/978-3-030-28551-7_1

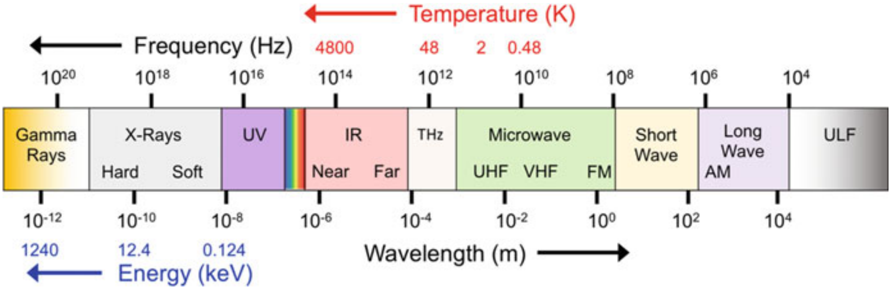

Fig. 1.1 The position of X-rays in the electromagnetic spectrum. The Kelvin scale refers to the temperature of a blackbody that would have maximum radiation at that wavelength

1.2 Sources of X-rays

From Maxwell's equations, we know that all electromagnetic radiation comes from accelerating charges. The most common X-ray sources, so-called X-ray tubes, involve a high-voltage electron current passing through a vacuum from the cathode to anode. In these sources, the broadband radiation results from a deceleration of electrons as they pass by atomic nuclei, hence the German name *bremsstrahlung* or "braking radiation" (Fig. 1.2). These tubes also produce narrow lines of X-ray fluorescence, the result of electronic transitions between different atomic core levels. Respectively, these are examples of *rapid (negative) acceleration* and *bound-state transitions* on a microscopic scale. For many applications, these sources have one major drawback—the radiation is emitted essentially in all directions and from a relatively large volume.

1.2.1 Synchrotron Radiation

As shown in Fig. 1.2, synchrotron radiation results from the *transverse acceleration* of a *relativistic charged particle*. In contrast with conventional X-ray tubes, which radiate from a large source in all directions, in a synchrotron radiation source, the X-rays are emitted from a small bunch of electrons in a narrow cone along the direction of the moving particles. As we will see later, the fact that the particles are relativistic—traveling very close to the speed of light—gives rise to these special radiation properties. Collimation and small source size make synchrotron radiation much more useful than the other sources in Fig. 1.2. To be more quantitative about these benefits, we need to define some figures of merit.

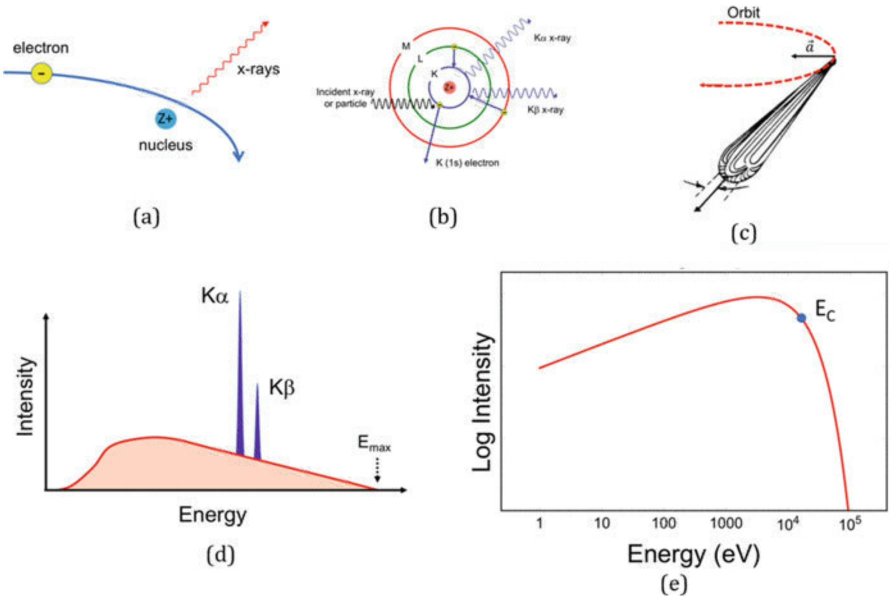

Fig. 1.2 Production of synchrotron radiation vs. other X-ray sources. (**a**) Bremsstrahlung; (**b**) an oversimplified view of Kα and Kβ X-ray atomic transitions; (**c**) synchrotron radiation; (**d**) a generic spectrum from an X-ray tube, exhibiting both bremsstrahlung and characteristic Kα and Kβ emission, the maximum energy $E_{\max}$ is that of the incident electron beam; (**e**) a generic synchrotron radiation source spectrum. Half of the source power is above or below the critical energy E_C

1.3 Brightness: A Figure of Merit

Just like people, some light sources are dim, and some are bright. We all have an intuitive sense of *brightness*. A computer projector emits more photons than an argon laser, yet while lasers require special eye protection and safety classes, we don't have to be certified to show powerpoint presentations (at least not yet). An electrical space heater emits more power than many beamlines, but a space heater cannot drill though metal as can happen with a focused synchrotron beam.

Brightness is associated with the effectiveness and usability of the radiation and it is a figure of merit commonly used to compare X-ray sources. In X-ray optics, it has a formal definition—the brightness $\mathscr{B}$ is the flux $\mathscr{F}$ in photons per unit time per unit solid angle per unit area of source (Fig. 1.3):

$$\mathscr{B} = \frac{d^4\mathscr{F}}{d\theta\, d\psi\, dx\, dy} \cong \frac{\mathscr{F}\left[\text{photons}\,\text{s}^{-1}\right]}{\Delta\Omega\left[\text{mrad}^2\right]\Delta A\left[\text{mm}^2\right]} \tag{1.1}$$

For most applications, one cares about the number of photons in a particular energy range, so an even more important quantity is the "spectral brightness" $\mathscr{B}_s$

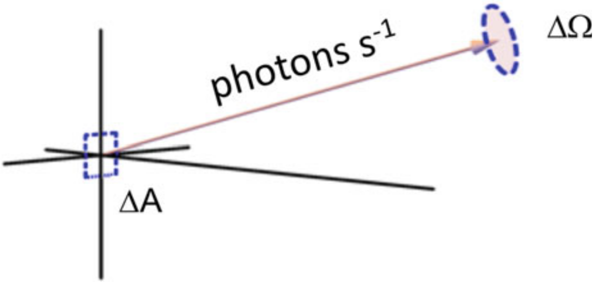

Fig. 1.3 Schematic of quantities involved in definition of X-ray brightness. The spectral brightness is the brightness in a 0.1% $\Delta E/E$ bandwidth

(Eq. 1.2). It is usually clear from the context whether the quantity referred to is brightness or spectral brightness, so we will drop the subscript unless it is needed for clarity. In practical units, X-ray spectral brightness is usually reported as:

$$\mathscr{B}_\mathrm{s} = \frac{\mathrm{photons\,s}^{-1}}{(\mathrm{mm}^2)\left(\mathrm{mrad}^2\right)(0.1\%\Delta E/E)} \tag{1.2}$$

1.3.1 Spectral Brightness of a Blackbody Source

Why not just use a very hot lamp as our X-ray source? To make such a comparison, we use a formula derived by Attwood for the brightness of a blackbody:

$$\mathscr{B}_\mathrm{s} = 3.146 \times 10^{11} \times \left(\frac{kT}{eV}\right)^3 \times \frac{(\hbar\omega/kT)^3}{\exp(\hbar\omega/kT) - 1} \times \frac{\mathrm{photons/s}}{\mathrm{mm}^2 \times \mathrm{mrad}^2 \times (0.1\%\Delta E/E)} \tag{1.3}$$

If we plug in the temperature for the surface of our sun, 5778 K, this corresponds to ~0.498 eV (see Appendix A for conversion factors), and we find that the maximum brightness is at 1.4 eV (or 8860 Å) with a value of ~4 × 10^{10} photons s^{-1} mrad^{-2} mm^{-2}/(0.1%$\Delta E/E$). In the X-ray range, a synchrotron will have a spectral brightness more than ten orders of magnitude higher! Despite the fact that the sun puts out a prodigious amount of energy, it is not a very “bright” source.

Brightness and spectral brightness are useful terms for comparing sources because they are not changed by ideal optical elements such as lenses and mirrors. (The inevitable losses in real optical elements can only diminish brightness.) Once the brightness of a source is set, there are no clever optical tricks for making a source brighter. In contrast, other quantities such as power density depend on your distance from the source or on how the beam is focused. Brightness and spectral brightness are thus intrinsic properties or *source invariants*, and we can use them to objectively compare different X-ray facilities.

1.3.2 Why Is Spectral Brightness Important?

For an X-ray experiment, photons are only of value if you can put them on the sample. If the photons are from a large source and are diverging in all directions, it is difficult to focus them back to a small point. Brighter beams are more useful because they are easier to (a) collect, (b) monochromate, and (c) focus. As we will see in Chap. 4 on X-ray optics, brightness is especially important for X-rays, because of severe limitations on X-ray mirrors, lenses, and monochromators. For X-ray spectroscopy, spectral brightness is even more important, because most X-ray spectroscopy is done using one photon energy at a time, so it helps when the source is tuned to the energy that is desired.

Finally, a couple of warnings about word usage. In some X-ray literature (particularly European sources), the word *brilliance* is used for what we have defined as brightness. In some UV-visible optics literature, what we call brightness is referred to as *radiance*. However, if Born and Wolf were happy to call it brightness [2], then so are we.

1.4 The Synchrotron Radiation Revolution

In the second half of the twentieth century, something very special happened to our ability to produce X-rays—synchrotron radiation sources became available. The existence of synchrotron radiation ("SR") had been predicted since the turn of the century. It was finally seen as visible radiation from a glass synchrotron chamber at General Electric research (GE) in 1947 (Fig. 1.4) [3]! Thanks to the technological development of synchrotron radiation sources, the brightness of available X-ray sources began to double on average approximately every year—a trend noted in the mid-1980s by Munro and Marr [4]. This exponential rate of increase allowed enormous improvements in the quality and quantity of X-ray experiments. The rate of improvement has been faster than Moore's law—the ~18-month doubling time for computer chip density and speed that held for ~40 years from 1975. If airplanes had made the same exponential progress over the last 30 years, we would now be flying faster than the speed of light! (Fig. 1.5).

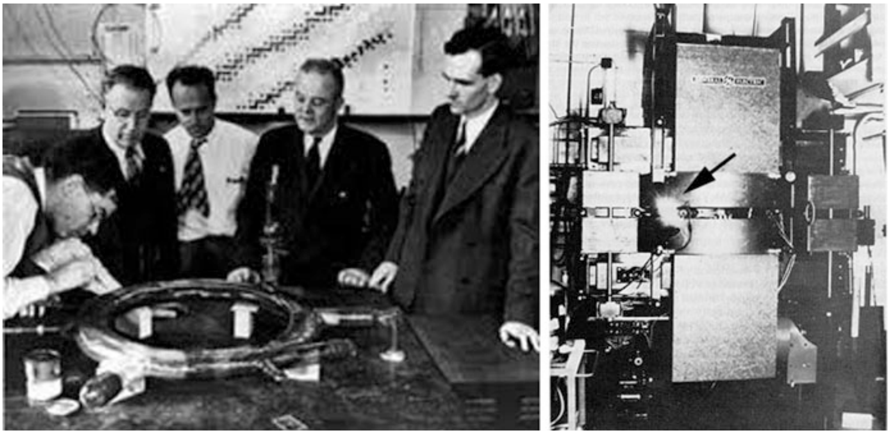

Fig. 1.4 Left: the GE synchrotron design team, left to right: Robert Langmuir, Frank Elder, Anatole Gurewitsch, Ernest Charlton, and Herb Pollock. Right: Synchrotron light from the 70-MeV electron synchrotron at GE

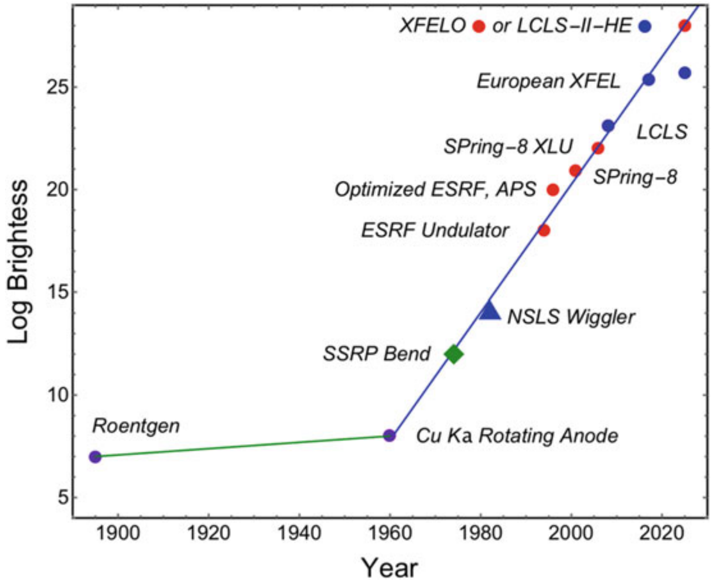

Fig. 1.5 Evolution of average X-ray spectral brightness over time. Symbol code: first generation (◆), second generation (▲), third generation (●), and fourth generation (●). Synchrotron source generations are explained in Chap. 2. Dates and brightnesses are approximate

A Selective X-ray and Synchrotron Radiation History
1895—Röntgen discovers X-rays [5]
1944—Ivanenko and Pomeranchuk predict energy loss in synchrotrons [6]
1947—Blewett observes visible SR at GE synchrotron in Schenectady [3]
1949—Schwinger publishes complete theory [7]
1956—Tomboulian and Hartman use SR for spectroscopy at Cornell [8]
1968—SRC –Tantalus—First fully dedicated SR facility
1976—INS-SOR: First storage ring built solely for SR
1981—SRS at Daresbury: First high-energy storage ring built for SR
1982—NSLS: First storage ring with high brightness (Chasman-Green) lattice
1994—ESRF: First third-generation SR source optimized for undulators
1996—APS: 7 GeV third-generation SR source
1997—SPring-8: 8 GeV third-generation SR source
2001—Tesla test facility (FLASH)—Soft X-ray free-electron laser
2009—LCLS hard X-ray free-electron laser
2017—European XFEL—High repetition rate hard X-ray free-electron laser
2018—MAX-IV MBA lattice approaches diffraction limit

The dramatic change in X-ray brightness from synchrotron radiation drew a new community of scientists into the X-ray field [9]. However, these sources are large and expensive (Fig. 1.6); they have inevitably been “user facilities” no longer under the control of individual scientists. Although working around the clock at a distant lab not under their complete control was a common experience for high-energy physicists, it was less familiar to many chemists and biologists. What has emerged is a new species of scientist—the synchrotron radiation user. There are now many thousands of SR users around the world, ranging from casual visitors to those whose entire careers are based at these facilities.

1.5 Synchrotron Radiation Laboratories

The worldwide inventory of synchrotron radiation sources is a moving target, with new projects constantly coming on line and with some older facilities eventually being retired. As of 2020, there were scores of active or proposed storage ring-based synchrotron facilities around the world (Appendix B). There were also more than a dozen free electron laser facilities based on linear accelerators (Chap. 12).

1.6 Synchrotron Radiation from Outer Space

Humans do not have a monopoly on synchrotron radiation. Nature bends the trajectories of relativistic charged particles in a variety of settings, and the resulting emission has the characteristic spectrum and polarization properties of synchrotron radiation. One example is the Crab Nebula (Fig. 1.7). This is thought to be the

Fig. 1.6 The four largest storage ring dedicated synchrotron radiation sources in the world. Top left: the Advanced Photon Source (APS) at Argonne National Lab near Chicago. Top right: European Synchrotron Radiation Facility (ESRF) in Grenoble, France. Lower left: PETRA-III in Hamburg, Germany. Lower right: SPring-8 near Osaka in Japan

remnants of a Type I supernova that exploded in 1054 CE. At that time it was so bright it could be seen in the daytime, and Chinese astronomers recorded it as a "guest star." Nowadays, at the heart of the nebula is a pulsar or "neutron star," which emits high-energy electrons into the surrounding magnetic field of ~10^{-4} Gauss. The electrons have extraordinarily high energies (up to ~1000 TeV), resulting in synchrotron X-rays up to ~100 keV.

Jupiter is also a source of synchrotron radiation, although at much lower energies (Fig. 1.7). Here, the magnetic field is stronger (~1 Gauss), but the electron energies are lower (~10 MeV) so that the bulk of the radiation is in the microwave region: 0.1–15 GHz. On a vastly different scale, extragalactic "accretion disks" produce synchrotron radiation when jets of relativistic particles spiral around magnetic field lines.

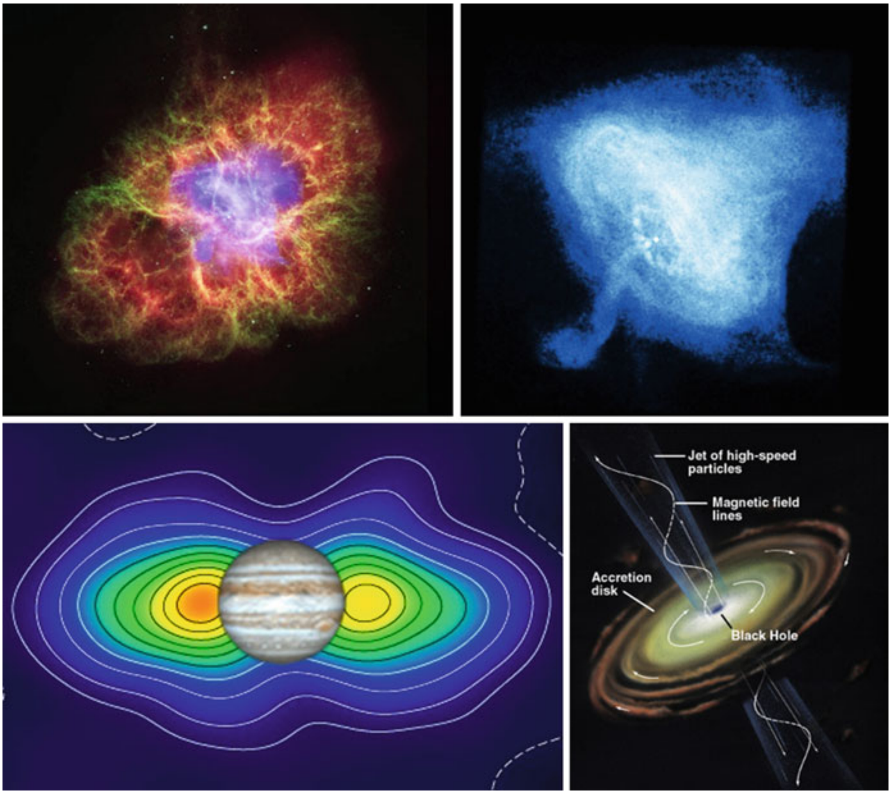

Fig. 1.7 Top left: Crab nebula in visible light. Top right: X-ray emission from the Crab nebula, imaged by the Chandra satellite. Bottom left: Microwave synchrotron radiation from Jupiter. Bottom right: synchrotron radiation from an accretion disk near a black hole

1.7 Suggested Exercises

1. Rigel A is a blue-white star in the constellation Orion with surface gases around ~12,000 K. The way astronomers use the word, Rigel is the 7th "brightest" star in the night sky. Stellar "apparent brightness" is based on the apparent visual magnitude as perceived by the human eye, so it does not separately take into account the distance or size of the star. Assuming a blackbody spectrum, calculate the peak spectral brightness of Rigel A.

   An additional metric used by astronomers is "luminosity." By some estimates, the luminosity of Rigel is >100,000 suns (https://en.wikipedia.org/wiki/Rigel). Compare the astronomical apparent brightness, peak spectral brightness, and luminosity of Rigel and our sun. Another star in Orion, Bellatrix, has a temperature of 21,500 K. Among stars in the sky, it ranks about 22nd on an astronomy apparent stellar brightness scale. How does it compare with Rigel on an intrinsic brightness scale? For more fun, consider Eta Carinae, which is ~180 times the radius of the sun, and has a surface temperature is 36,000–40,000 K.

2. A common value for the average spectral brightness of a synchrotron source is ~10^{20} photon s^{-1} mm^{-2} $mrad^{-2}$/0.1% bandwidth. What temperature is required for a blackbody source to have the same spectral brightness at 10 keV? How does that temperature compare with that of a hydrogen bomb?
3. Apart from brightness and spectral brightness, a third metric for synchrotron sources is peak spectral brightness. This is the spectral brightness over the time interval when the maximum flux occurs. If the average spectral brightness of a synchrotron source is 10^{20} photon s^{-1} mm^{-2} $mrad^{-2}$/0.1% bandwidth, what is the peak spectral brightness if the bunch length is 50 ps and the repetition rate is 1 MHz?

1.8 Reference Books and Review Articles

1. "Synchrotron Radiation—A Powerful Tool in Science" in *Handbook on Synchrotron Radiation*, E.-E. Koch, D. E. Eastman, and Y. Farge, North-Holland, Amsterdam, 1–63 (1983)—overview of early synchrotron radiation sources and references to more detailed accounts. ISBN 978-0444864253.
2. *Particle Accelerator Physics—Basic Principles and Linear Beam Dynamics*, H. Wiedemann, Springer-Verlag, New York, 4th edition (2015)—chapters 2 and 3 contain histories of linear and circular particle accelerators, with extensive references. ISBN 978-3-319-18316-9.
3. *Introduction to Synchrotron Radiation*, G. Margaritondo, Oxford University Press, New York (1988)—chapter 1 has a brief history of X-ray science. ISBN 0-19-504524-6.
4. *An Introduction to Synchrotron Radiation*, P. Willmott, John Wiley and Sons (2011)—chapter 1 has a brief history of X-ray science. ISBN 978-0-470-74579-3.
5. *Synchrotron Radiation News*, Vol. 28, 2015—a special issue devoted to personal reminiscences.
6. "Fifty years of synchrotron science: achievements and opportunities", *Phil. Trans. Royal Soc.* **2019**, *377, A*, S. S. Hasnain and C. R. Catlow, eds.—a special issue based on a 2018 conference
7. *A Skeleton in the Darkroom—Stories of Serendipity in Science*, G. Shapiro, Harper & Row, San Francisco (1986). Ch. 1 recreates Röntgen's discovery of X-rays. ISBN 0-06-250778-8.

Chapter 2
The Storage Ring Complex

Synchrotron radiation sources are among the largest and most expensive scientific instruments ever built. At first glance, the scale and complexity of these facilities, as shown in Figs. 1.6 and 2.1, can be daunting. However, when we look “under the hood,” we find that they all have the same essential components, and furthermore, many of these components are repeated over and over again. The key pieces can be divided into two main categories: *radio frequency systems* to accelerate the particles and also to replenish their energy and *magnets* to bend and focus the charged particle beams. Of course, there needs to be a charged particle source, a massive vacuum system to contain the charged particles, and a safety infrastructure to contain and control the high-energy particles and X-radiation.

Why do we care? In our case of synchrotron spectroscopy:

- The storage ring determines the properties of the particle beam.
- The particle beam sets limits on the properties of the photon beam.
- The photon beam determines how well we can do our experiments.

Most synchrotron radiation sources around the world are based on electron storage rings. These facilities include not only the storage ring itself but the initial source of high-energy electrons, invariably a linear accelerator, and often an intermediate device to raise the particle energy, a “booster synchrotron.” A diagram for a typical storage ring complex is shown in Fig. 2.1.

Although a view of the interior (Fig. 2.1) of a storage ring complex can at first be bewildering, it becomes understandable if you break it up into smaller components, many of which are repeated over and over again. We begin the description of a storage ring at the electron source and then follow the charged particles as they flow through the complex.

S. P. Cramer, *X-Ray Spectroscopy with Synchrotron Radiation*, Biological and Medical Physics, Biomedical Engineering, https://doi.org/10.1007/978-3-030-28551-7_2