

**THE
BIG
IDEAS
OF NANOSCALE
SCIENCE & ENGINEERING**

A GUIDEBOOK FOR SECONDARY TEACHERS



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Preface

Nanoscale science and engineering (NSE) is an emerging field. Although defining the nanoscale world is not without debate, *nanoscale* is generally defined as including any material of which at least one dimension is 1 to 100 nanometers. New and refined tools now enable scientists to explore and understand this nanoscale world in ways unforeseeable only a few short years ago. At this scale, materials exhibit novel, often unexpected properties that are not observed at other scales. Based on the discovery of materials' properties and behaviors at this scale, NSE research is rapidly leading to strategies for creating new products and technologies as well as new information likely to have broad societal implications in areas as diverse as healthcare; the environment; and the sustainability of agriculture, food, water, and energy.

The ability to understand the discoveries, technologies, and information resulting from NSE research requires a high degree of science literacy. It is not just today's students but also the adults they will become who will be required to function in a highly technological society. In that society, they will need to make sense of and make decisions about rapid scientific advances. National, state, and local leaders in education must prepare a broad cross section of the U.S. population with the science and engineering knowledge required to meet these demands and to secure an edge in discovery and innovation that will sustain economic prosperity.

While this book sets NSE in the context of larger societal needs for a scientifically informed citizenry, it focuses on the much smaller arena of U.S. schools as a system with a pervasive reliance on traditional means of presenting sci-

ence education. New, emerging, "big ideas" in the field of NSE require a new approach to science education, an approach outlined in this book for ongoing discussion and debate. It is a text primarily for teachers and others interested in 7–12 science education. But because teachers play the most important role in introducing NSE to students in classrooms, it is they who must understand NSE content and be able to integrate it into the disciplines they teach. NSE is not to be thought of as a separate discipline but as the science of all disciplines at the nanoscale. Its interdisciplinary nature thus requires that teachers learn how the critical ideas of NSE connect across disciplines. In addition, NSE content may require new instructional strategies. The task is more complex than simply adding NSE examples into current lessons or inserting an NSE module into the current curriculum.

Yet this book does not prescribe how nanoscale science and engineering should be taught, nor does it provide lesson plans, activities, or specific strategies or prescribe a curriculum sequence for NSE. Instead, we discuss connections among nanoscience ideas and the current curriculum, as well as new ways of considering traditional science content relevant to NSE. The book is designed to support teachers' development of foundational nanoscience content knowledge and skills and to enable teachers to integrate NSE effectively into their classrooms. It provides a reference for secondary teachers who want to help their students understand the exciting new discoveries and applications from NSE research and development—that is, to truly engage their students in 21st-century science education.



Introduction

The Importance of Nanoscale Science and Engineering (NSE) in 7–12 Education

The emerging fields of nanoscience and nanotechnology promise to have extensive implications for all of society as they apply the unique properties of matter at the nanoscale (i.e., 10^9 – 10^7 meters or 1–100 nanometers) to create new products and technologies. Because nanoscale science and engineering (NSE) research involves the study, control, and fabrication of matter across science and engineering disciplines, NSE researchers explore an extremely diverse range of phenomena. Many industries, including electronics, pharmaceuticals, cosmetics, and textiles, employ nanotechnology to improve products. Examples of products currently on the market include transparent zinc-oxide-based sunscreen, scratch-resistant automobile paint, and stain-resistant clothing. The technical advisory group for the President's Council of Advisors on Science and Technology (PCAST) predicts that by 2020 nanotechnology will also contribute to areas such as water purification, medical diagnostics, targeted drug therapies, and better solar cells (PCAST 2005). Clearly, we live in an exciting time with respect to advances in science and technology at the nanoscale.

Society's Individual and Collective Needs

Although little argument exists about the value of nanomedicines to treat, for example, cancer patients, scientists and conservationists caution that some nanoscale materials may

have serious, negative effects on the environment and health of individuals. Nanoscale objects are small enough to cross some biological barriers; thus, familiar materials such as zinc oxide (used in sunscreens) and gold (long used in dental applications) may affect living organisms differently in nanoscale form than in their bulk form. In other words, despite the benefits that result from NSE, legitimate health and environmental concerns also exist.

Understanding these trade-offs is imperative. The need to characterize and to evaluate benefits and risks argues for a scientifically literate citizenry able to consider technological advances in an informed manner. To make wise decisions about the *uses* of science, citizens must be able to consider the consequences and implications of all scientific advances. Most students will not become scientists or engineers, but they will participate in decision making about the work that scientists and engineers do. From privacy concerns related to computerized data storage to stem cell research, citizens are confronting issues related to science and technology in their everyday lives. At the very least, all citizens must be able to read and understand science-based articles in the popular press or on the internet and to make sense of politically charged rhetoric around science-based issues.

Understanding ideas related to NSE is necessary not only for scientific literacy and decision making but also for individual and national

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prosperity. At the time of this writing (2009), the demand for U.S. workers with science and engineering skills is growing five times faster than the rest of the work force (Foley and Hersam 2006). U.S. economic prosperity is increasingly linked with the growth of technology; a large percentage of future jobs will require technology-based skills. By 2020, scientists, engineers, and policy groups predict that technologies and products derived from nanotechnology will contribute more than \$1 trillion each year to the worldwide economy (Roco and Bainbridge 2001). Nearly one million workers knowledgeable in nanoscale science and engineering will be required to support the nanotechnology sector in this country (Roco 2003).

Clearly, future economic prosperity and the ability to make ethical decisions depend on a population with the knowledge required to function in a highly technological society and to produce the knowledge of the future. These conditions are not likely to be met unless preparation begins in schools. The “preparation” aspects are the crux of this book.

As jobs related to science and technology proliferate, education related to these fields is essential. Only if students are educated in growth areas will they have access to predicted career opportunities. This means that NSE education must begin in middle and high school, well before students have chosen a career path in college. This pressing need argues for reviewing the pipeline through which students, particularly those historically underrepresented in science, technology, engineering, and mathematics (STEM) education, come to specialize in STEM-related disciplines. Science education must prepare *all* students to participate not only in the consumption of technological advances but also in the production of these advances. This is especially true in a global economy. The minimal attention

paid to STEM education in the United States has long been recognized as an education problem of great consequence (Foley and Hersam 2006; Schmidt, Wang, and McKnight 2005), a problem that will be exacerbated if traditional methods continue to be the *modus operandi* of U.S. schools and if traditional content continues to be the fare offered in U.S. classrooms.

There is no question that the world in which our students live requires a change in what they learn. As such, this book introduces science educators to the “big ideas” of nanoscale science and engineering.

What Are Big Ideas?

Big ideas are those considered central or fundamental to a discipline. Some big ideas in biology, while fundamental to that discipline, may not be central to chemistry. However, other big ideas are cross-disciplinary, enabling learners to explain a broad range of phenomena both within and across disciplines. In any science discipline, students encounter a number of important ideas, but those considered “big ideas” are core to the discipline. They provide a framework for the long-term development of student understanding, allowing teachers and students to revisit ideas throughout the 7–12 curriculum and to build conceptual understanding during those years. In doing so, understanding becomes progressively more refined, developed, and elaborate. Big ideas in any discipline provide a foundation on which future, more specialized learning can build. This book focuses on the big ideas of NSE while acknowledging the current educational framework into which they must be incorporated.

The Importance of Nanoscale Science and Engineering (NSE) in 7–12 Education

Science Education in U.S. Schools Today

International comparisons reveal that students in the United States do not perform as well as those in other developed countries on tests of scientific knowledge (Schmidt, Wang, and McKnight 2005). The failure of U.S. schools to help learners understand core ideas in STEM education has led to a generation of children ill prepared to enter STEM-related fields and to secure the nation's leadership in science and technology. Without intervention, this gap is likely to increase as technologies become ubiquitous and society becomes more reliant on them. Perhaps most unfortunate is the fact that many children in the nation's rural and large urban areas are not successful in science (Lynch 2000; Grigg, Lauko, and Bockway 2006). The challenge of how to provide quality science instruction to *all* of the nation's young people is a challenge that must be taken on even if it is only improved in some schools. Some of that challenge can be addressed by the curriculum itself.

Researchers from the Third International Mathematics and Science Study (TIMSS) found that curriculum coherence is the dominant predictor of student learning (Schmidt, Wang, and McKnight 2005). When U.S. curricula are compared to those of countries whose students perform better on international benchmarks, the lack of coherence within and across years in U.S. science curricula surfaces as one important factor in this failure. Unfortunately, most of the standards documents used to guide the science curriculum are concerned with coverage of a broad set of ideas rather than with making certain that students develop deep and integrated understanding of key ideas (Wilson and Berenthal 2006). This strategy of broad coverage rather than deep understanding is supported by high-stakes tests that superficially assess science content. The

trouble with covering too many concepts is that students learn neither how ideas are related to one another nor how they can be used to explain or predict phenomena. Instead, they must memorize discrete facts, and of the thousands of facts they might have memorized, they fail if they do not have the "right ones" at their disposal at test time. In addition, standards documents tend to treat all ideas as equally important. They do not identify some ideas (e.g., particle model of matter, classical mechanics, natural selection, plate tectonics) as big ideas that require greater focus in the curriculum and strategic building of understanding across time.

A Strategy for Developing a Coherent Science Curriculum

A coherent curriculum can help students build the kind of deep and meaningful understanding of big ideas that will enable them to explain phenomena within and across disciplines. Coherence refers both to alignment of instruction and assessment and to sequencing of instruction around a small set of ideas, organized to support learners in developing integrated understanding of those ideas (Schmidt, Wang, and McKnight 2005; Swartz et al. 2008). However, in attempting to address a multitude of national, state, and local standards, the U.S. science curriculum hinders the development of coherent curriculum materials and, thus, of students' coherent understanding of science.

To build coherence around a small number of critical big ideas of science, curriculum developers and educators must first know what those critical ideas are. As a first step toward that goal, in 2006 a representative group of scientists, engineers, educators, and learning specialists from across the nation worked together to determine the big ideas of NSE. (See appendixes A and B for a description of the process and a list of participants.) This book presents the group's

Introduction

consensus—not simply the authors’ vision—as to what should be named a “Big Idea of NSE” and which of the big ideas should be introduced in grade 7–12 science classrooms.

NSE represents science and engineering of all disciplines at the nanoscale. The big ideas of NSE described in this book are related not only to nanoscience and nanotechnology but also to science more broadly. That is, the NSE big ideas include many concepts critical for building general science literacy (e.g., structure of matter, size and scale, models and simulations) as defined in national standards documents (AAAS 1993; NRC 1996). In fact, many people consider the big ideas of NSE to be some of the big ideas of all of science. The inherently interdisciplinary nature of NSE creates an opportunity to reorganize the way we think about traditional science content and the way we teach science content. In particular, NSE provides an opportunity to remove demarcations that currently exist between the science disciplines in order to address ideas in a multidisciplinary fashion. As such, we see the big ideas of NSE as the foundation for building coherence in the science curriculum.

Audience for This Book

We intend this book to be used primarily by grade 7–12 science teachers who wish to address NSE in their classrooms or to become more knowledgeable about NSE and its potential for engaging students in science, deepening their understanding of critical science concepts, and developing lifelong learners. This book is not meant to prescribe how NSE should be taught in the classroom or to describe activities and lessons for particular NSE topics, as can be found in other resources (e.g., Jones et al. 2007). The information in this book can help teachers to develop NSE knowledge and skills and to incorporate NSE into the science courses they are now teaching. Science resource persons and

science coordinators may also find the book of value for its potential to shape curriculum decisions at the school or district level.

Organization of This Book

Section 1, “The Nine Big Ideas,” is the foundation of the book. The chapters in this section introduce the reader to and define an NSE big idea, detail the content contained within the big idea, describe how the group of workshop scientists arrived at a consensus for that idea, and provide a justification for defining a concept as an NSE big idea. Each chapter also provides a number of examples that illustrate the content and that describe possible interdisciplinary connections. We also discuss how the NSE content of each big idea relates to the current 7–12 science curriculum.

In Section 2, “Integrating NSE into the 7–12 Science Curriculum,” the chapters are broken down into the nine big ideas (although other big ideas are discussed in each chapter). In each, we give learning goals for that big idea and how these learning goals can be used to develop a coherent curriculum. Teachers may want to refer to the content chapters for each big idea in Section 1 if they are unsure about content information. Section 2 also identifies the prerequisite (both general and specific) knowledge necessary for each big idea, and the prior learning and misconceptions students may bring with them to the science classroom. In addition, Section 2 lists phenomena that could be used to contextualize NSE content in classrooms, as well as questions teachers could ask for discussion or for assessment. Finally, we relate the content in each big idea to the national standards (AAAS 1993; NRC 1996), highlighting both similarities and omissions in the standards with regard to NSE.

In Section 3, “Next Steps,” we discuss the challenges faced by our schools in the development of an NSE-educated citizenry.

The Importance of Nanoscale Science and Engineering (NSE) in 7–12 Education

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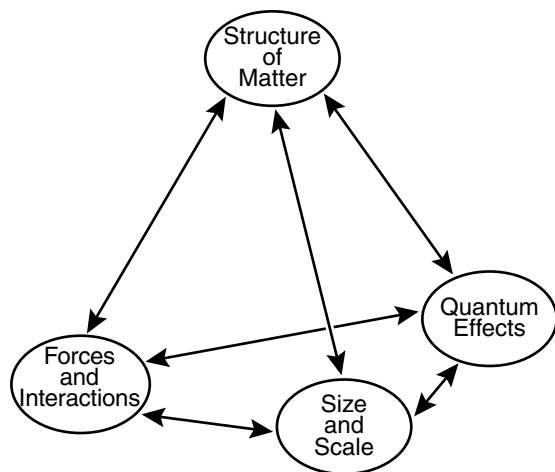


Chapter 1

The Foundational Science Content

Four of the big ideas represent the basic science content, and as Figure 1.1 illustrates, all four are interrelated. Concepts of size and scale connect to the other science content big ideas because size defines the nanoscale, and different physical models (i.e., classical mechanics, quantum mechanics, general relativity) are used to explain the behavior of matter at different scales. Quantum mechanics is required to explain how matter behaves at small scales. For example, a quantum mechanical model of electron behavior (Structure of Matter) is necessary to understand the interactions of matter (Forces and Interactions) at the nanoscale. The structure of matter and the way it interacts are inextricably linked.

Figure 1.1
Representation of the relationships among NSE science content big ideas



None of the science-content big ideas stands alone; each informs and is informed by the others. As authors of this book, we needed to choose how to divide the content among the big ideas. We identified connections among the big ideas, their associated content, illustrative phenomena, and learning goals.

Big Idea 1 Size and Scale

Factors relating to size and geometry (e.g., size, scale, shape, proportionality, dimensionality) help describe matter and predict its behavior.

About Size and Scale

Size is defined as the extent or bulk amount of something. Every object has a size that can be defined in either one, two, or three dimensions. Comparing an object to a reference object or reference standard (e.g., conventionally defined units) defines the size of the object by defining the scale of geometric properties such as length (e.g., meters, feet, miles), area (e.g., square inches, acres), or volume (e.g., cubic feet, liters, gallons). Each of these geometric properties can have values that differ by many orders of magnitude (AAAS 1993).

It is sometimes useful to divide this large range in sizes into scales or “worlds” (e.g., macro-, micro-, nano-, atomic), each characterized not only by the corresponding

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measurement units but also by (1) representative or landmark objects (Tretter et al. 2006), (2) tools that render objects in the world accessible, and (3) models that describe the behavior of matter at that scale. Figure 1.2 illustrates the approximate range of these worlds and some of their characteristics.

Although conceptually dividing the universe into these worlds can be useful as a guide, it is more accurate to consider the worlds on a continuum, in which divisions between them are somewhat blurred rather than explicitly defined. For example, the nanoscale is generally numerically defined as 1–100 nanometers (nm) (Roco 2004). In terms of matter, it is considered to represent the transition between bulk matter and individual atoms and molecules. However, protein and DNA *molecules* are often considered landmark nanoscale objects for the nanoworld. Therefore, the scales and worlds must be used as *guides* to the size landscape rather than as absolute, rigid categories.

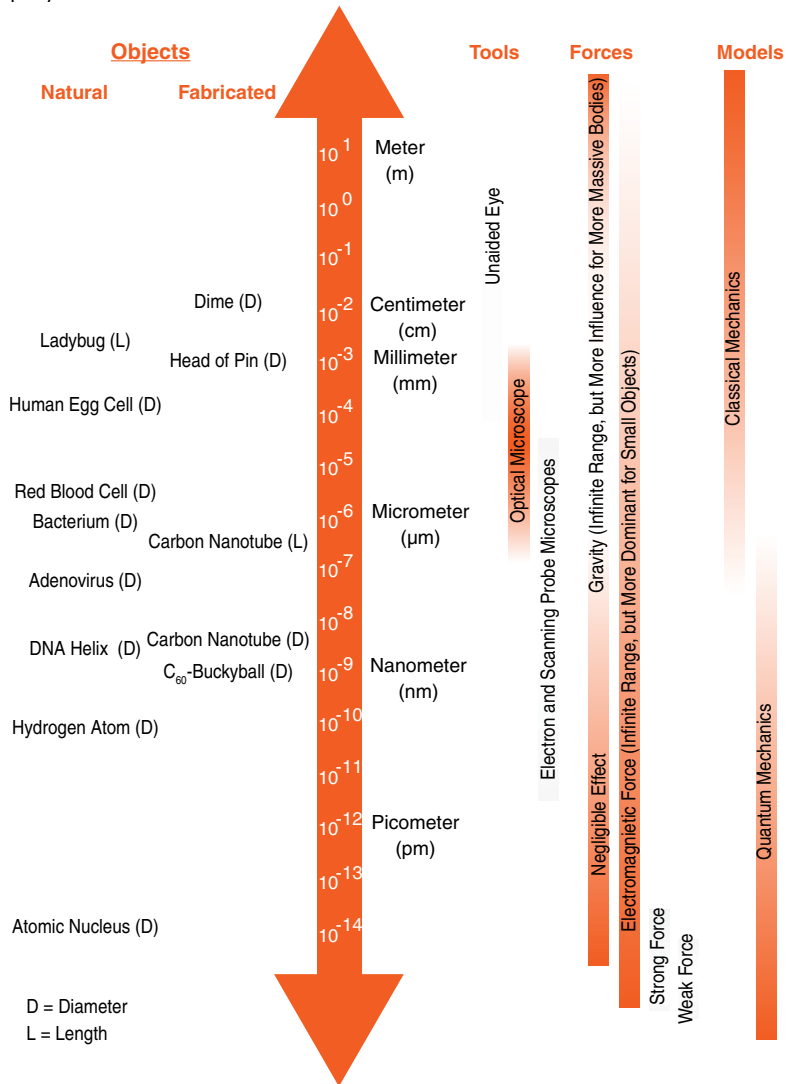
Certain aspects of size and scale are particularly relevant to NSE. The most fundamental aspect is the definition of the nanoscale and how it relates to other scales (e.g., the macroscale, the world of cells, atoms, and molecules). In addition, the effects of changes in scale and shape also play an important role in NSE.

Scaling and Proportionality

Doubling the size of an object affects the surface area and volume disproportionately. For instance, doubling the length of the sides of a cube increases the volume eight-fold, but the surface area of the cube is only increased

Figure 1.2

Illustration of commonly used scales, with representative objects, dominant forces, relevant tools, and most useful physical laws



Source: Adapted from Figure 2-S9 NanoSense Size Matters Unit (<http://nanosense.org/activities/sizematters/index.html>)

The Foundational Science Content

four-fold. Figure 1.3 illustrates this trend. Thus, if a property is dependent on volume (e.g., heat capacity, mass), then that property will change much faster than properties dependent on area (e.g., cooling surface, porosity). People reveal an understanding of this concept when they cut up a hot potato and spread out the pieces so that it will cool more quickly. Because scale does not affect all properties equally, changes in scale usually affect the way in which a system works. For example, if a gazelle grew to the size of an elephant, its legs would break from the weight because while the mass of the gazelle is proportional to its volume, the strength of its legs increases only by the cross-sectional area of its bones (Haldane 1926).

Figure 1.3

Comparison of the surface area (circles) and volume (triangles) of a cube vs. length of side

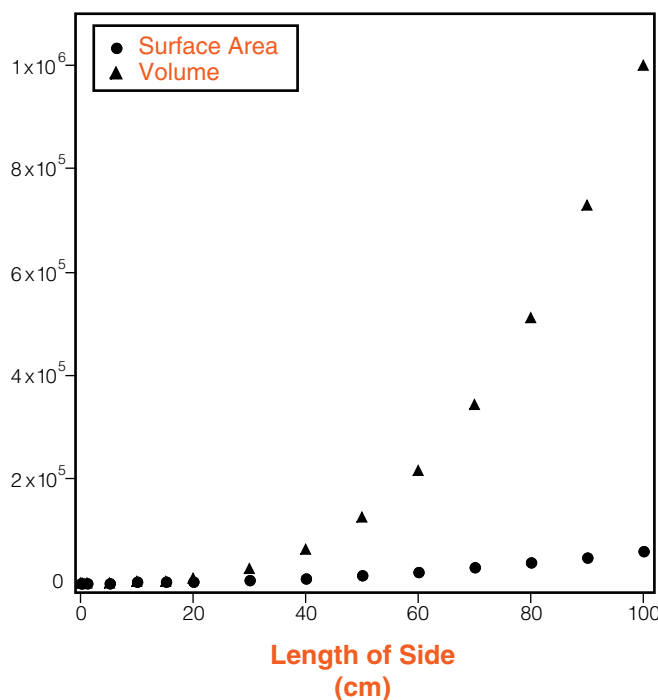


Table 1.1

Effect of shape on the surface-to-volume ratio of a rectangular prism

Dimensions (cm)	Surface Area (cm ²)	Volume (cm ³)	S/V (cm ⁻¹)
10 × 10 × 10	600	1000	0.60
20 × 10 × 5	700	1000	0.70
50 × 10 × 2	1240	1000	1.24
100 × 10 × 1	2220	1000	2.22

Shape

Shape also affects the proportionality between surface area and volume. A 10 × 10 × 10 cm cube may have different properties than a 1 × 10 × 100 cm rectangular prism, even though both have a volume of 1000 cm³. The surface area of the cube is only 27% of the surface area of the extended shape. Table 1.1 illustrates how different arrangements of 100 cubes change the surface area to volume ratio (S/V).^{*} Likewise, for objects with a volume of 100 mm³ (cubic millimeters), the surface area of a cube is ~129 mm², a regular tetrahedron is ~155 mm², and a sphere is ~104 mm². A sphere is *always* the shape with the minimum S/V, which is why objects like bubbles are spherically shaped.

Thus Size and Scale also includes concepts related to the measure of the geometric properties of length, area, volume, and shape, which can be represented using prefixes or scientific notation. In addition, knowledge about defining and measuring the dimensionality of each of these concepts is also important. Length (1-dimensional), area (2-D), and volume (3-D) change disproportionately with changes in size. These differences have implications for the

^{*} This ratio is generally referred to as surface-to-volume ratio. We called it surface area to volume ratio here for clarity. In the rest of the book, we will use the more common terminology, surface-to-volume ratio.

Chapter 1

properties, behavior, and function of matter at all scales but more so at the nanoscale.

Why Is This a Big Idea?

Concepts of size and scale (geometry)* form part of the cognitive framework for making sense of science, and in the context of NSE, they define the nanoscale itself. Scientists tend to work in “worlds” that are defined by scale (e.g., atomic, nano-, micro-). Each world provides guidelines for types of objects that are of similar size and for how the behavior of those objects can be explained and predicted. In addition, worlds are often defined by the instrumentation necessary to observe and measure objects on the scale. For example, the world of cells is generally defined as *microscale*. Optical microscopes, or some other magnifier, are necessary to observe objects on this scale. The resolution limit of optical microscope is approximately $0.2\ \mu\text{m}$ or $200\ \text{nm}$, meaning that they cannot be used to measure objects smaller than $200\ \text{nm}$. This roughly defines the lower limit of the microscale, with the upper limit being what can be seen with the unaided eye (around $0.05\text{--}0.1\ \text{mm}$ or $50\text{--}100\ \mu\text{m}$). The nanoscale is generally defined to include any system or material with at least one dimension falling between 1 and $100\ \text{nm}$. In this range, other tools (e.g., scanning probe microscopes, scanning electron microscopes) are needed to observe and measure phenomena.

Scale is important when explaining phenomena. People make predictions based on macroscale experiences (those visible with the

* Recent literature has used the term *size and scale* to refer to many of the concepts included in this big idea. Like size, shape also characterizes objects and can affect S/V , and thus shape is also included in this chapter. This big idea might better be termed *size and geometry* to encompass all of these factors simultaneously, but we use *size and scale* to be consistent with terminology in the field.

naked eye) that occur in the “world” that can be adequately explained by classical physics. But as the size or mass of an object or material transitions through the nanoscale toward the atomic scale, the ability of classical mechanics to predict the behavior of matter begins to fail. On the atomic and subatomic scales, quantum mechanics must be employed to explain the behavior of matter. As matter transitions between the bulk form and that of individual atoms and molecules, quantum effects become more important.

In addition, the forces that dominate the interactions between matter are also dependent on scale. Although all forces are present in all interactions, gravity generally dominates interactions on the macroscale; electromagnetic forces generally dominate at the nano- and atomic scales; and the strong (or nuclear) force dominates at the subatomic scale. Therefore, knowing the scale of an object helps predict how it will behave. (See “Forces and Interactions,” pp. 18–24, and “Quantum Effects,” pp. 24–34, for more detailed discussion of many of these ideas.)

Even small changes in size can result in large relative changes in area and even larger changes in volume. The surface-to-volume ratio (S/V) is inversely proportional to the size of the object (see Figure 1.4a and b). Changes in S/V can change the way in which objects or systems function or behave. The rate of burning a log is much slower than burning an equal mass of twigs. Inside the human body, nutrient uptake from the small intestine is more efficient due to the millions of projections (i.e., villi) that increase the absorptive surface area. Many of the special properties that matter exhibits on the nanoscale result from the effect of size on S/V . For example, adhesion properties change with increased exposed surface area. An example from everyday life is powdered sugar

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sticking to the sides of a plastic measuring cup whereas larger granulated sugar does not. (This topic is discussed in greater detail in the size-dependent properties section in Chapter 2.)

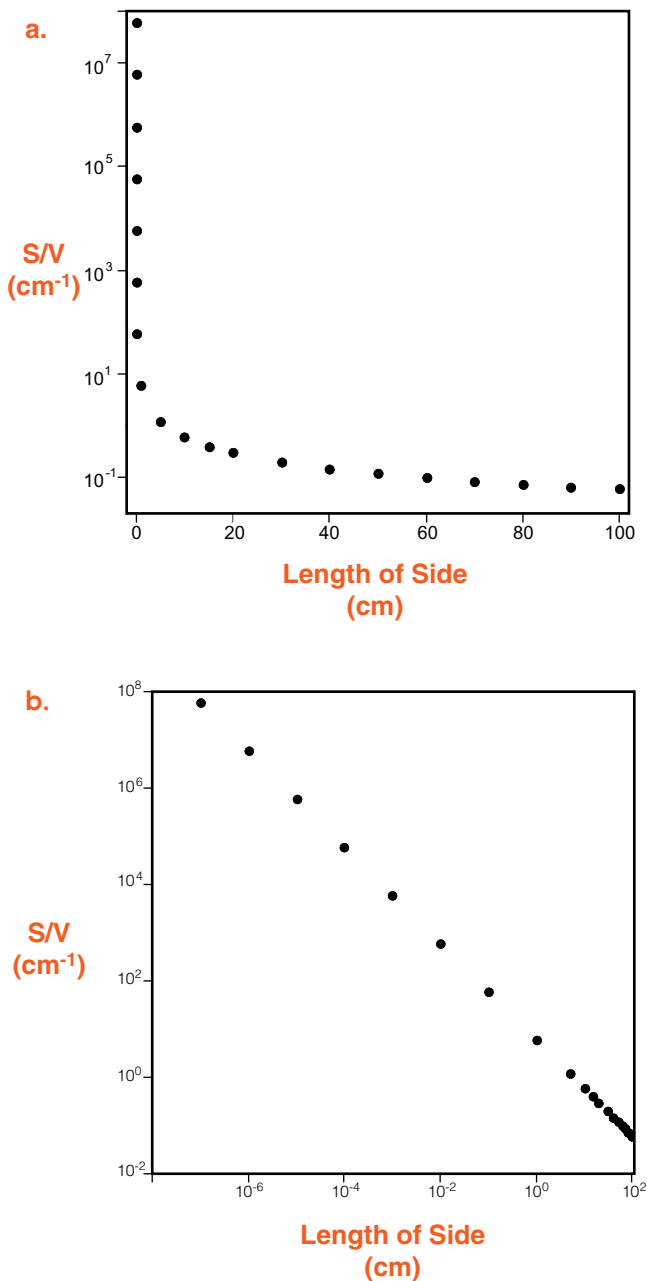
Factors linked to size and scale are tied to progress and the understanding of many aspects of research and development at the nanoscale. Size and scale (and geometry) are critical for developing conceptual understanding of the behavior of matter at the nanoscale as well as the tools used to explore the nanoworld.

Relationship to the 7–12 Curriculum

Mathematics is a large part of size and scale (and geometry). In Program Standard C, the NSES state that “[t]he science program should be coordinated with the mathematics program to enhance student use and understanding of mathematics in the study of science and to improve student understanding of mathematics” (NRC 1996, p. 214). The Benchmarks (AAAS 1993) consider scale to be one of four common themes that have implications throughout all disciplines of science. Indeed, concepts related to size and scale are critical for understanding concepts in astronomy, chemistry, physics, and geology, and they extend beyond the natural sciences to geography and history.

Standard measurement units and numerical values are required to communicate in all of these subject areas. In history, geology, and astronomy, the timeline is much greater than an individual’s life experience. In geography, the scales on maps indicate the size of the representation relative to the thing it represents. Because the relative magnitude of these scales is often large, scientific notation becomes a

Figure 1.4
Surface area-to-volume ratio vs. length of side of cube:
(a) Linear plot (b) Semi-logarithmic plot



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useful means of communicating very large and very small numbers. Implementing scientific notation lends itself to categorizing the size of objects by orders of magnitude. This subject matter tends to fall in the domain of mathematics, but by linking it to science content, student understanding in both disciplines may benefit as one reinforces the other (NRC 1996; Judson and Sawada 2000).

However, size and scale are not simply academic constructs; they also have an impact on students' daily lives. For instance, when cooking for a larger group of people than usual, the person who prepares the food in your house should scale the recipe and increase the ingredients proportionally. It is also necessary for students and their parents to use the scale on a map to estimate the distance and time it will take to arrive at a destination. As students gain experience both in and out of school, they can begin to relate the values and units to the world around them. Doing so helps them develop skills in estimating relative quantities and sizes.

Strong support from mathematics is required in order for students to apply to science the concept of surface-to-volume ratio. Students must learn about ratios and proportions, as well as develop an understanding of what area and volume are and how to calculate them. When teachers link mathematics to scientific phenomena, they contextualize the mathematics so that students consider it in other than an algorithmic manner (NRC 1996). By using real scientific data, students gain experience applying mathematics concepts to nonidealized problems,* which connects well with the

*Nonidealized problems or data are “real” and have imperfections. Idealized math problems, on the other hand, often use data that work perfectly—for example, calculations come out with whole numbers or points fall along a perfect line.

National Council of Teachers of Mathematics standards (NCTM 1989). Linking mathematics skills for organizing and analyzing data prevents a purely descriptive study of science (NRC 1996, pp. 214–218).

Because the nanoscale lies far outside students' everyday experiences, a robust knowledge of concepts related to size and scale can be used by students and by scientists alike as they learn about this intrinsically abstract realm. Developmentally, people first learn about the size of objects in an intuitive way and in reference to their own bodies. Later they use formal and informal learning experiences to understand the meaning, for example, of measurement units, surface area, volume, and scientific notation. Extrapolating from the everyday world to the nanoscale is likely to be impossible without using such conceptual tools. Thus, concepts related to size and scale make up an important part of the cognitive framework for making sense of the nanoworld.

Big Idea 2

Structure of Matter

Materials consist of building blocks that often form a hierarchy of structures. Atoms interact with each other to form molecules. The next higher level of organization involves atoms, molecules, or nanoscale structures interacting with each other to form nanoscale assemblies and structures.

About Structure of Matter

The atomic theory describes a model in which matter is composed of discrete units called atoms. Slightly more than 100 types of atoms make up all substances. The type of atoms and their arrangements determine the identity and affect the properties of a material. For example, hydrocarbons are a class of substances consist-

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ing of combinations of only carbon and hydrogen atoms. Because they all consist of the same type of atoms, materials in this class of compounds share many properties. However, the arrangement of the atoms also plays an important role in the properties of the material. For example, pentane and neopentane both consist of five carbon atoms and twelve hydrogen atoms, but because the atoms are arranged differently, the substances have different properties (see Table 1.2). Similarly, the identity and arrangement of the building blocks of a nanoscale structure or assembly affect its function and properties.

The type and strength of interatomic interactions are determined by the electron configuration of the atoms involved. For example, an increase in the number of electrons affects the strength of London dispersion forces and, in turn, associated properties. Table 1.3 provides an example of the melting and boiling point trends of noble gases as the atomic weight increases. Another example is the electronegativity of an atom—the tendency of an atom to accept an electron, which influences the type of interaction in which it will participate. Atoms with very different electronegativities (e.g., metals with nonmetals) tend to interact through ionic-type electrical forces, whereas atoms of nonmetals with similar electronegativities tend to interact through covalent-type electrical interactions. Likewise, the identity and properties of the building blocks of nanoscale structures and assemblies (i.e., atoms, molecules, nanoscale

Table 1.2

Comparison of some physical properties of pentane and neopentane^a

	Chemical Formula	Boiling Point (°C)	Melting Point (°C)
Pentane	CH ₃ (CH ₂) ₃ CH ₃	36.1	-129.7
Neopentane	C(CH ₃) ₄	9.5	-16.6

^a Weast 1976

Table 1.3

Comparison of boiling and melting points of noble gases^a

Element	Atomic Weight	Melting Point (°C)	Boiling Point (°C)
Helium	He 4.003	< -272.2	-268.9
Neon	Ne 20.179	-248.7	-246.0
Argon	Ar 39.948	-189.2	-185.7
Krypton	Kr 83.80	-156.6	-152.3
Xenon	Xe 131.29	-111.7	-108.1
Radon	Rn ~222	-78	-61.8

^a Weast 1976

assemblies) affect the way that they interact with one another. These ideas will be explored more fully in the Forces and Interactions section, which begins on page 18.

Electrical forces and the motion of the building blocks are essential to the formation and function of assemblies and structures at the nano-, atomic, and molecular scales. All atoms are in constant random motion that is dependent on the heat of the system and is often referred to as thermal motion. The principle that the atoms that compose all substances are in constant random motion has significant implications at the nanoscale. Because thermal motion occurs on the molecular scale, its effects are not apparent at the macroscale. For example,

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Topic: Kinetic Theory

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as a tree log floats down a river, water molecules will be constantly colliding with it. Because the log is so large, the random collisions have no effect on its motion. If the log were a billion times smaller (i.e., nanoscale), then the random collisions with the water molecules would begin to have an effect on its trajectory or its behavior. Thus, for nanoscale phenomena, thermal motion becomes a more important factor. In addition, the number of atoms contained in a nanoscale object may be small enough that the motion of an individual atom affects the properties and behaviors of the whole. These ideas will be explored more specifically in the Forces and Interactions section in this chapter and in the Size-Dependent Properties and Self-Assembly sections in Chapter 2.

Why Is This a Big Idea?

Although scientists' understanding of the structure and behavior of matter at the bulk ($\geq 10^{-7}$ m) and atomic levels is relatively well-developed, limited knowledge exists about how matter behaves as it transitions between these two scales. Recently developed tools have provided researchers unprecedented access to this region of transition—the nanoscale—which is leading to new levels of understanding about the structure and behavior of matter.

The atomic and kinetic theories are the basis for understanding the structure and behavior of matter. In fact, renowned physicist Richard Feynman said:

If, in some cataclysm, all scientific knowledge were to be destroyed, and only one sentence passed on to the next generation of creatures, what statement would contain the most

information in the fewest words? I believe it is the atomic hypothesis (or atomic fact, or whatever you wish to call it) that all things are made of atoms—little particles that move around in perpetual motion, attracting each other when they are a little distance apart, but repelling upon being squeezed into one another. (Feynman 1996, p. 4)

The atomic and kinetic theories explain an enormous number of phenomena, so that without having a thorough understanding of these concepts, it is not possible to comprehend the structure and behavior of matter at any scale, including the nanoscale.

To understand the properties and behavior of matter across scales, it is important to understand the structure and properties of its building blocks. Properties common to all atoms relate to some of the properties of matter observed at the nanoscale. In particular, (a) atoms and molecules are in constant random motion, and (b) the forces that dominate interactions between atoms and molecules are electrical in nature. Both of these properties are essential to the formation and function of assemblies at both the molecular and nanoscales.

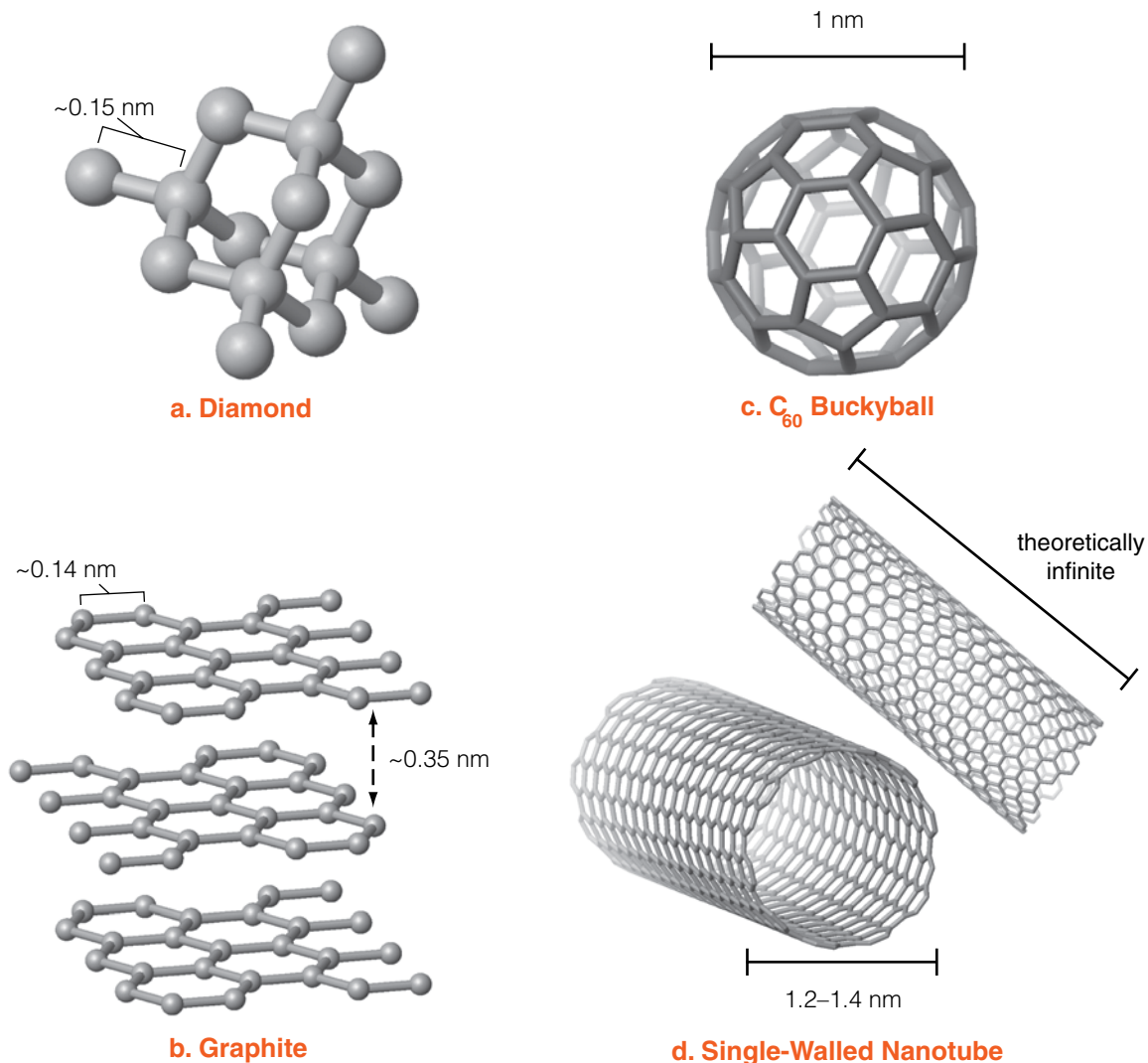
Some of the interesting properties at the nanoscale are related to the specific properties of the constituent atoms. An example is the different forms, or allotropes, of carbon (see Figure 1.5). The forms of pure carbon traditionally taught are diamond, graphite, and charcoal.* In each form, the carbon atoms interact differently with each other, resulting in materials with very different properties (see Table 1.4, p. 14). Diamond is an extended three-

*Each of these forms of carbon has a nanoscale form: Adamants and diamondoids are nanoscale structures that are essentially diamond molecules; polyaromatic hydrocarbons (PAHs) are individual molecules of graphite; and carbon nanofoam is also an amorphous form of carbon.

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Figure 1.5

Representations of some of the allotropes of carbon: (a) Portion of the covalent network of carbon atoms that makes up diamond (b) Portions of three sheets of carbon atoms as they are arranged in graphite (c) C_{60} buckminsterfullerene (d) Single-walled carbon nanotubes



Source: Images were created using MOLMOL (Koradi, Billeter, and Wüthrich 1996). Coordinates for (a) (b), and (c) were obtained from www.nyu.edu/pages/mathmol/library. Coordinates for the carbon nanotube were generated at <http://k.1asphost.com/tubeasp/tubeASP.asp>.

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Table 1.4

Comparison of some physical properties of carbon allotropes

	Diamond	Graphite	C ₆₀ Buckyball	Carbon Nanotube
density (g/cm ³)	3.51 ^a	2.25 ^a	~1.65 ^e	1.33–1.40 ^b (depends on form)
electrical conductivity	insulator	conductor	semiconductor	semiconductor (most)
thermal conductivity (W/cm-K)	23.2 ^a	(Pyrolytic graphite) ^a 19.6 (parallel to sheet) 0.0579 (perpendicular to sheet)	no data	> 2 ^c
hardness (Mohs scale)	10 ^a	~1 ^a	individual ~10 bulk 1–2	no data
bulk modulus (G Pa)	1200 ^e	207 ^e	18 ^e	1000–1300 ^d (depends on form)

^a Weast 1976

^b Gao, Cagin, and Goddard 1997

^c Che, Cagin, and Goddard 2000

^d Dujardin et al. 1998

^e Sussex Fullerene Group n.d.

dimensional network in which every carbon atom interacts with four other carbon atoms (Figure 1.5a, p. 13). It is an insulator and one of the hardest known substances (10 on the Mohs scale). In graphite, each carbon atom bonds to only three other atoms. The atoms form single layers of six-membered carbon atom rings that stack upon one another (Figure 1.5b, p. 13). Graphite is a relatively soft substance (2 on the Mohs scale) and is a conductor. The most recent models of charcoal suggest a structure that is an amorphous combination of these types of interactions.

There are also other allotropes of carbon, which are nanoscale structures. Buckminsterfullerenes, or buckyballs, are hollow, sphere-shaped molecules most commonly represented

as structures consisting of 60 carbon atoms that look much like tiny soccer balls (Figure 1.5c, p. 13). However, structures containing 70, 76, and 84 carbon atoms have also been found in minute quantities in nature. Individual buckyballs are quite hard, perhaps harder than diamond, but as a bulk substance, they are relatively soft. Several potential applications for buckyballs are currently being investigated, including their potential use as lubricants and superconductors. Another allotrope is the carbon nanotube, which is structurally related to buckyballs. Carbon nanotubes are cylindrical fullerenes with an extended structure that looks similar to a tube of chicken-wire fencing (see Figure 1.5d, p. 13). As a material, carbon nanotubes exhibit novel properties such as

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high electrical conductivity and resistance to heat; they are one of the strongest and most rigid materials known. The special properties of carbon atoms allow for many different structures, each with its own unique properties.

Understanding the building blocks of a structure or material is important for understanding its function and properties. For example, proteins are nanoscale objects that carry out critical functions within all living organisms. Twenty different molecules, called amino acids, are the building blocks of proteins. Proteins consist of long chains that can be hundreds of amino acids long. Even if a protein consists of hundreds of amino acids, it is common for a single building block, or amino acid, to affect the structure and function of the whole protein.

Hemoglobin—the component of a red blood cell responsible for carrying oxygen—is a classic example of how changing a single building block of a protein can alter the function. Hemoglobin consists of four amino acid chains, which interact to form a single, functional structure (see Figure 1.6a, p. 16). Two types of amino acid chains are part of hemoglobin, alpha (α) and beta (β). There are two α -chains and two β -chains in every hemoglobin molecule. The α -chains consist of 141 amino acids; the β -chains are 146 amino acids long. Changing a single, positively charged amino acid, glutamic acid, to the neutral amino acid valine (Figure 1.6a, b, p. 16) in the β -chain changes the structure and function of the entire protein. The protein, with the mutation, maintains its structure and solubility when bound to oxygen. However, when oxygen is removed, due to changes in the way the altered amino acid interacts with other parts of the protein, the overall structure of the protein changes. The hemoglobin becomes elongated and rigid and polymerizes into long, structured fibers that give the red blood cells

a sickle shape (Finch et al. 1973). The elongated red blood cells have less flexibility and do not flow through blood vessels well, often clumping and blocking the vessels.

This single change in the amino acid sequence (glutamic acid to valine) within the hemoglobin protein is the cause of sickle cell anemia. As the hemoglobin example illustrates, it is critical to understand the relationship between the building blocks and the structure and function of the whole.

Hierarchical levels of structure, which enable a single material to be multifunctional, are common in natural materials (Viney and Bell 2004). As described, amino acids and amino acid chains make up proteins; nucleic acids are organized groups of atoms that connect together to make strands that combine to form double-helical DNA or RNA structures. Figure 1.7 (p. 17) illustrates the nanoscale building blocks of bone, tooth enamel, and shell (Gao et al. 2003). The needle-like crystals that make up tooth enamel have diameters of approximately 15 to 20 nm with a length of about 1 μm . The plate-like crystals that make up dentin and bone are 2 to 4 nm thick and up to 100 nm in length and are embedded in a collagen matrix. Nacre, the substance that makes up shells, also consists of plate-like crystals that fit together like bricks. These crystals generally range from 200 to 500 nm thick and are up to a few thousand nanometers long. The nanoscale building blocks provide greater tolerance of structural flaws, thus helping maintain optimal strength (Gao et al. 2003). As scientists and engineers develop better means to fabricate and manipulate nanoscale materials, they will be able to exploit this structural advantage by



Topic: Allotropes

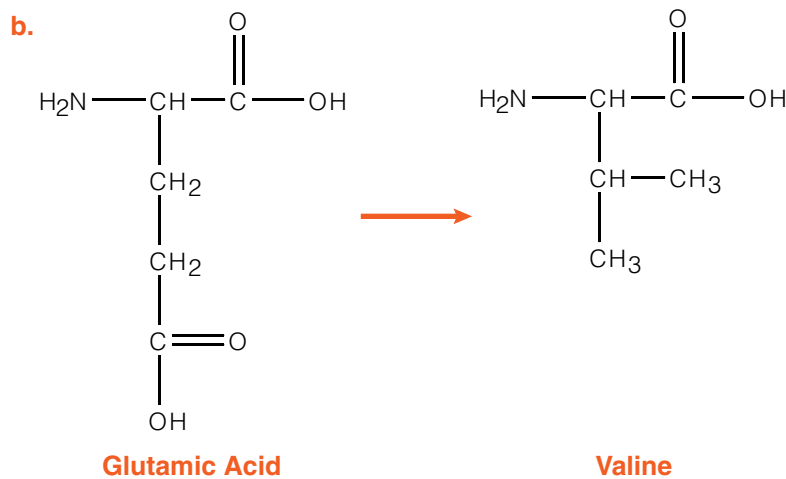
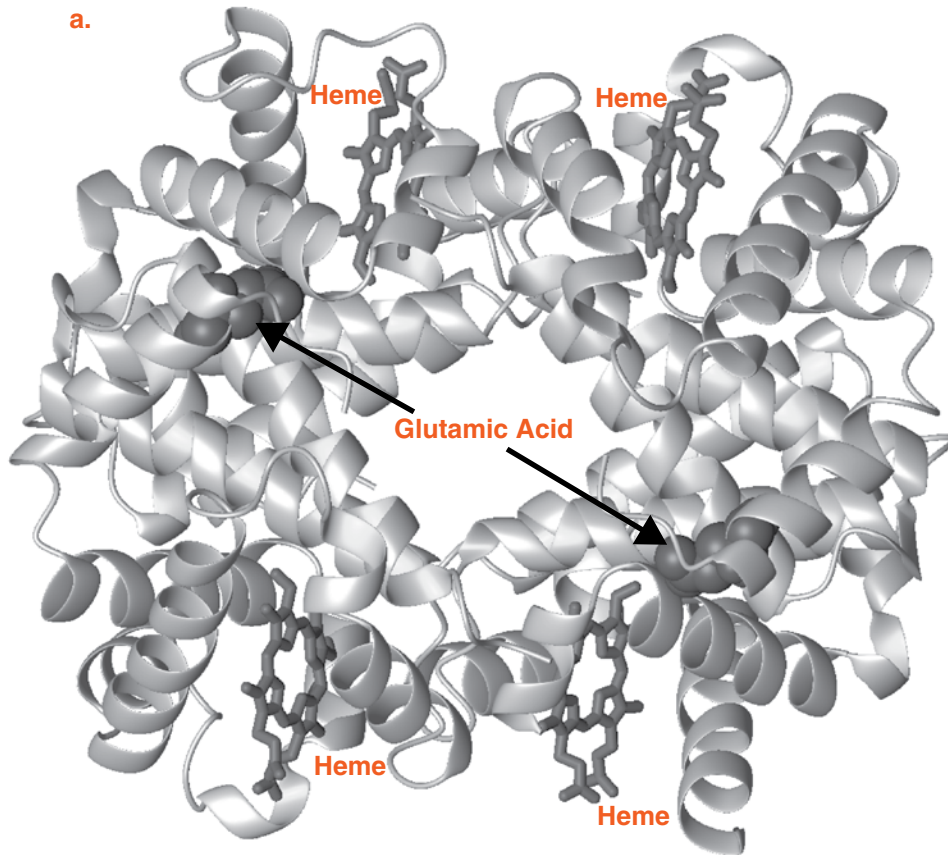
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Figure 1.6

(a) Representation of the peptide backbone of wild-type hemoglobin with four bound heme molecules (b) Illustration of the structure and composition of glutamic acid as compared to valine



Source for (a): 1gzx (the code for the structure of the molecule in the figure) is from RCSB Protein Data Bank; image created using MOLMOL (Koradi, Billeter, and Wüthrich 1996).

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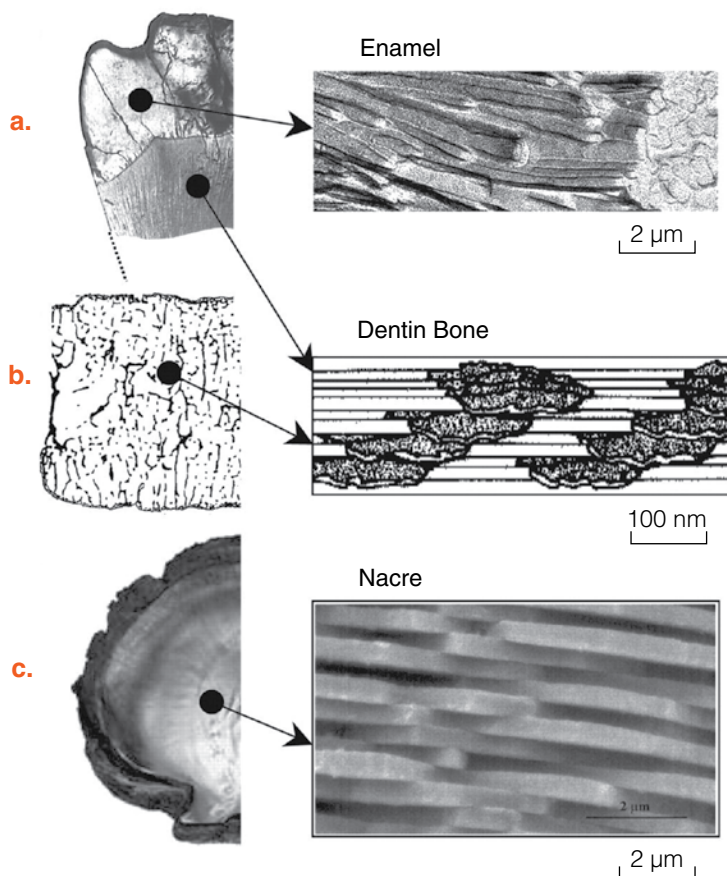
using nanoscale building blocks in designed materials.

Billions of years of naturally occurring “research” have optimized an extremely broad range of natural materials, systems, and processes, often of great complexity, that form and regulate the world around us. One of the major areas of NSE research involves biomimetics, which relates to the design and fabrication of new materials by mimicking the relevant aspects of natural biological materials. Natural materials have several advantages: They are made from renewable resources; they are synthesized in aqueous environments at or near ambient temperatures; and they are biodegradable, so they have an advantage for supporting sustainability (Viney and Bell 2004). Bone (biomineralization), tooth enamel, spiders’ web threads, and muscle fibers are just a few examples of materials on which research currently focuses. For instance, as a better and more permanent alternative to medical procedures such as hip replacement surgery, scientists and engineers are working to regenerate bone or to create a material similar to bone using manufactured materials as scaffolds (Jones and Hench 2003; Li 2003).

For students to understand the interesting properties of matter at the nanoscale, they must first develop a deep understanding of the structure and function of its building blocks: atoms, molecules, and other nanoscale structures or assemblies.

Figure 1.7

Images of the macroscale and nanoscale structure in biological hard tissue: (a) Tooth enamel (b) Dentin or bone (c) Nacre (shell)



Source: Reprinted with permission from Gao, H., B. Ji, I. L. Jäger, E. Arzt, and P. Fratzel. 2003. *Proceedings of the National Academy of Sciences, USA* 100 (10): 5597–5600. Copyright 2003 National Academy of Sciences, U.S.A.

Relationship to the 7–12 Curriculum

Many of the ideas related to the structure of matter are currently in the national science standards. They provide a critical foundation for understanding the properties and behaviors of nanoscale objects and materials.

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Nanoscale materials themselves are made of atoms, molecules, or other nanoscale objects; therefore many of the same principles apply.

The relationship between the building blocks and the structure and function of the final product (e.g., structure, material, assembly) can be expanded beyond chemistry into other disciplines. The hemoglobin example is appropriate for a biology or biochemistry class when students learn about genetics and proteins. Ideas about hierarchical structure can also be addressed in multiple disciplines. Small, defined sets of building blocks make up proteins, RNA, and DNA, which in turn can combine with various components to form more complex structures that carry out and regulate the functions that maintain life. The process of biomineralization, which involves hierarchical structure, is relevant in chemistry, biology, geology, and engineering depending on the phenomena under study. Applying a concept to multiple phenomena can help students make sense of basic principles as they extend their understanding to include new situations.

Big Idea 3

Forces and Interactions

All interactions can be described by multiple types of forces, but the relative impact of each type of force changes with scale. On the nanoscale, a range of electrical forces with varying strengths tends to dominate the interactions between objects.

About Forces and Interactions

Four fundamental forces describe all interactions: gravitational, electromagnetic, nuclear (or strong), and weak forces. At the macroscale, the gravitational force—a force between masses that is always attractive—is usually dominant.

Forces derived from electrical charges, a subset of the electromagnetic force, generally dominate at the nano- and atomic scales.

Examples include chemical bonding and biomolecular recognition. The nuclear (or strong) force is responsible for keeping the nuclei of atoms together; thus it is dominant on the subatomic scale (length scale of $\sim 10^{-15}$ m). The weak force is also involved in subatomic scale phenomena such as beta decay and other nuclear reactions.



Topic: Dipole Interactions

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A Continuum of Electrical Forces

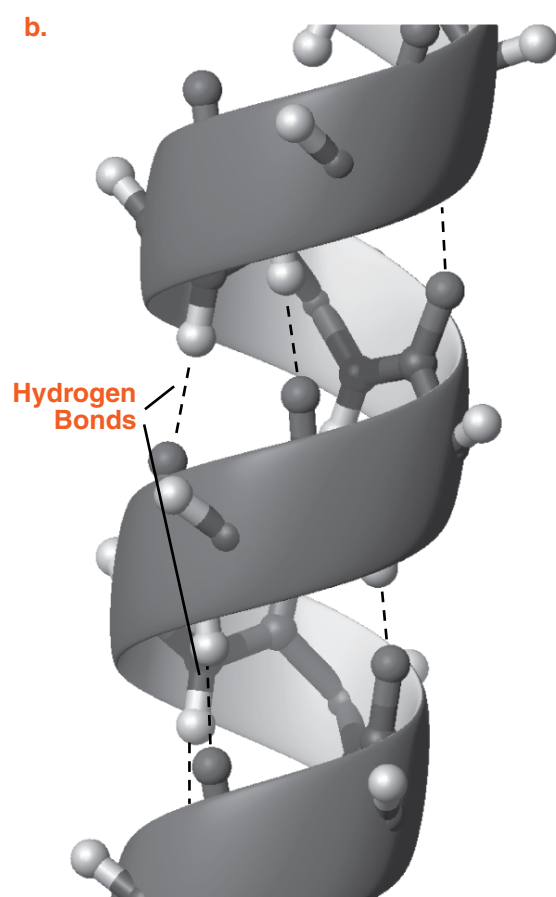
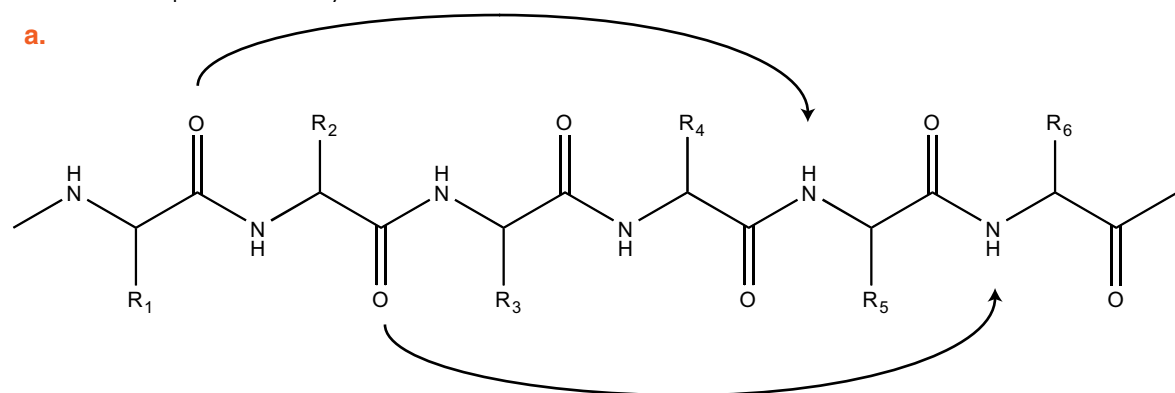
Small objects of nano- and atomic length scales (e.g., atoms, molecules, nanoparticles) interact in a variety of ways, all of which are dominated by forces that are electrical in nature. These electrical forces create a continuum of forces that describe most of the interactions within matter on the nano- and atomic scales, the strength of which depends on the entities involved. Net attractive forces must bring and hold the components together in order to form a stable complex.

Many of these electrical forces occur between permanent (static) charges and are labeled as electrostatic forces, the strength of which is described by Coulomb's law. There are several types of electrostatic interactions. Ionic interactions occur between ions of integer charges. They are most commonly represented as interactions between ions in salts (i.e., ionic bonding). Other examples include interactions between charged amino acids within or between biomolecules, which are commonly referred to as "salt bridges." Dipole-dipole interactions occur between opposite partial charges that result from an uneven distribution (a separation) of positive and negative charge and are weaker

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Figure 1.8

(a) The $i, i+4$ hydrogen bonding pattern stabilizes alpha helical polypeptides. R represents the amino acid side chains. (b) A cartoon representation of an alpha helix. Hydrogen bonds are represented by dotted lines.



than ionic interactions. Hydrogen bonds are a type of dipole-dipole interaction that occurs between a hydrogen atom attached to a highly electronegative atom (most commonly oxygen, nitrogen, or fluorine) and another electronegative atom that has a lone pair of electrons.

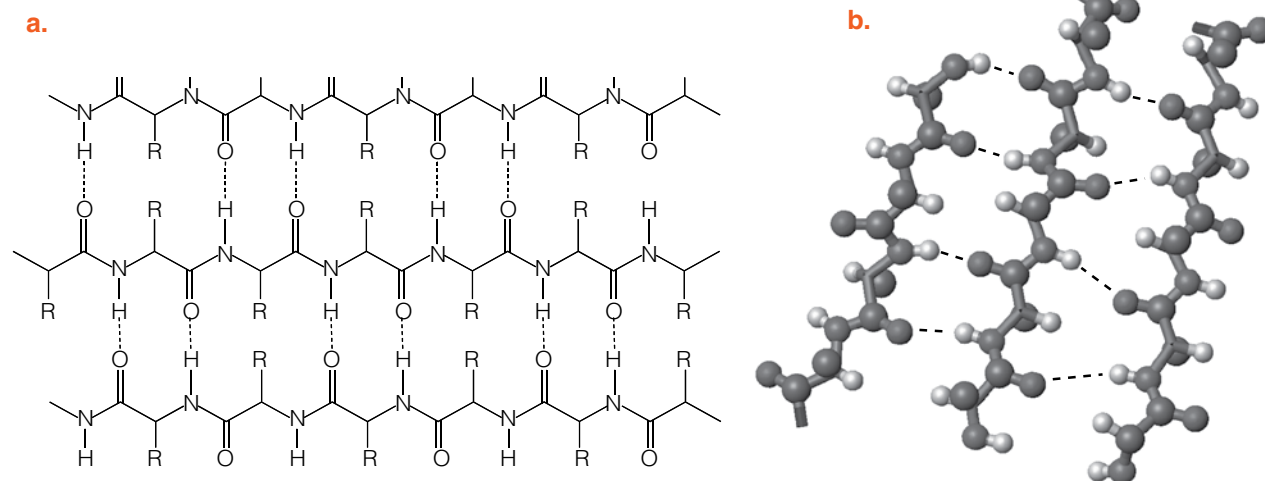
Although often defined as an intermolecular force, hydrogen bonding also plays an important structural role within many large (nanoscale) molecules, such as biomolecules. For example, proteins consist of chains of amino acids that adopt structures known as alpha helices and beta sheets. As the name suggests, alpha helices consist of a spiraling amino acid chain that is stabilized by hydrogen bonds between the carbonyl (C=O) of amino acid i to the amide hydrogen (NH) four amino acids further along the chain ($i+4$) as shown in Figure 1.8. Beta-sheets consist of extended strands of amino acids that are held together with hydrogen bonds as illustrated in Figure 1.9 (p. 20). Hydrogen bonds between base pairs of DNA

Source: This image was created using MOLMOL (Koradi, Billeter, and Wüthrich 1996).

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Figure 1.9

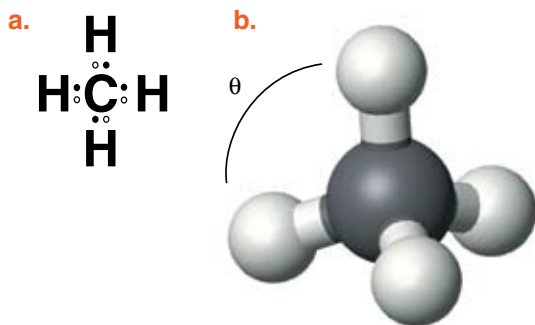
(a) Hydrogen bonds stabilize an anti-parallel beta sheet. Hydrogen bonds are represented by dotted lines. R represents the amino acid side chains. (b) Alternate representation of an anti-parallel beta sheet. Hydrogen bonds are represented by dotted lines.



Source for (b): Created using MOLMOL (Koradi, Billeter, and Wüthrich 1996).

Figure 1.10

(a) Lewis dot representation of methane illustrates the electron sharing between the carbon and hydrogen atoms. The open circles represent the electron contributed by the hydrogen atoms and the solid dots, the electrons contributed by the carbon atom. (b) The distance between the hydrogen atoms of methane is maximized in this tetrahedral arrangement.



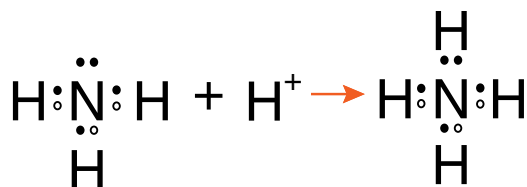
and RNA are an important part of maintaining the familiar double-helical structure.

Covalent bonds are characterized by the sharing of one or more electron pairs between atoms to balance the attraction and repulsion that occur between two atoms. This class of interactions tends to be used to describe interactions between nonmetals that have similar electronegativities. The strength of the covalent bonding depends both on the distance and the angle of the interaction between atoms. For example, methane adopts a tetrahedral structure to maximize the distance between the hydrogen atoms (see Figure 1.10).

A related type of interaction is the coordinate covalent bond in which the shared pair of electrons comes from a single atom as illustrated in Figure 1.11. Coordinate covalent bonds commonly occur between transition metals and nonmetals. A large number of substances, including many minerals, are governed by this type of interaction.

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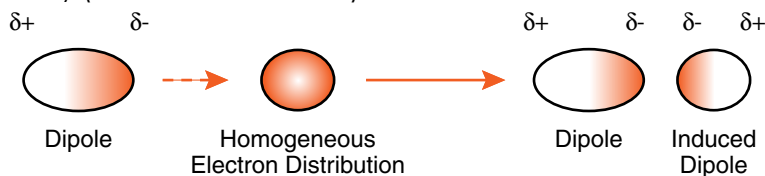
Figure 1.11
An example of coordinate covalent bonding



In contrast to interactions governed by electrostatic forces, some types of interactions involve a dynamic behavior of electrons. The electron distribution within an atom (or molecule) may shift to create a partial charge—an induced dipole. Induced dipoles may be created when a neutral, nonpolar atom is brought into close proximity to a polar entity (see Figure 1.12) or an electric field. London forces involve two or more induced dipoles,* which result from momentary, or instantaneous, shifts in the electron distribution of neutral atoms (or molecules). Like electrostatic interactions, the strength of the interactions depends on distance but falls off more rapidly (r^6) with atomic separation. Although generally considered intermolecular, London forces also play a role in intramolecular structure.

Delocalized electrons, which are electrons that are not associated with a single atom or covalent bond, are another example of dynamic behavior of electrons. For example, in metallic bonding, electrons are delocalized and shared among a lattice of atoms, which is the source of some metallic properties. The atoms of a metal

Figure 1.12
Illustration of a dipole–induced-dipole interaction. δ^+/δ^- represent partial positive and negative charges respectively ($0 < \delta^+ < 1$; $-1 < \delta^- < 0$).



* London dispersion and induced dipoles are often grouped together as van der Waals forces, but by definition, van der Waals forces also include dipole-dipole interactions (and hydrogen bonds). To prevent confusion, when possible, we specify the individual type of interaction.

are held together by the electrostatic attraction between the positively charged metal ions and the delocalized electrons. Aromatic compounds also involve delocalized electrons.

Although categorizing forces helps characterize the range of electron behavior that mediates interactions at the atomic, molecular, and nanoscales, these forces rarely exist in pure form. Instead, they represent benchmarks along a continuum of electrical forces, the strength and character of which are defined by the partners involved in the interaction.

Specificity

Electrical forces not only are important in interactions between atoms and molecules but also dominate the interactions between structures and assemblies at the nanoscale. For example, electrical forces govern the interactions between biomolecules, many of which are nanoscale structures. Various combinations of electrical forces control the strength and specificity of the interactions between these molecules in order to perform and finely regulate the biological processes that maintain life. For example, as part of the replicating process, single-stranded DNA binding protein (SSBP) is responsible for separating the strands of the double helix to

allow the DNA polymerase to create the complementary strand. To perform this function, SSBPs must be able to bind to *any* sequence of DNA. SSBPs accomplish this by binding only

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to the negatively charged phosphate backbone of the DNA through ionic interactions. The strength of the interaction is the same regardless of the point on the DNA strand to which the SSBP binds (Kowalczykowski, Bear, and von Hippel 1981). In contrast, the DNA-binding proteins that regulate gene expression bind to double-stranded DNA through a unique network of ionic interactions to the phosphate backbone and hydrogen bonds (dipole-dipole interactions) to the DNA bases. The interactions between this type of DNA-binding protein and DNA are quite selective. The strength of the interaction between the protein and a specific set of base-pairs along the strand is at least 1,000 times greater than the interaction at any other point along the helix. Thus, the nature of the interaction between proteins and DNA differs depending on the interacting entities (von Hippel and Berg 1986; Stevens and Glick 1997).

Strength of Interactions

Many factors play a role in the interaction between two components. For example, a polar solvent (e.g., water) will weaken electrostatic interactions. Likewise, the presence of ions in the solvent will affect the affinity of two entities interacting through electrostatic forces. For any interacting entities, the relative concentrations and temperature will affect the formation of the complex.

The same electrical forces and principles that are involved in chemical bonding—biomolecular recognition and all interactions at the nano-, molecular, and atomic scales—are important to consider in the design, fabrication, and manipulation of nanoscale materials (see *Self-Assembly*, p. 43, for examples). Therefore, it is necessary to understand them in order to understand and predict the function and behavior of natural and fabricated nanoscale materials.

Why Is This a Big Idea?

Nanotechnology exploits the unique interactions of matter on the nanoscale to create structures and materials with new functionality. To design and build them, it is critical to understand how they are structured, which includes understanding how they are held together. Therefore, it is necessary to have an understanding of the electrical forces that dominate the interactions between the atoms, molecules, and nanoscale structures that create nanoscale assemblies and materials.

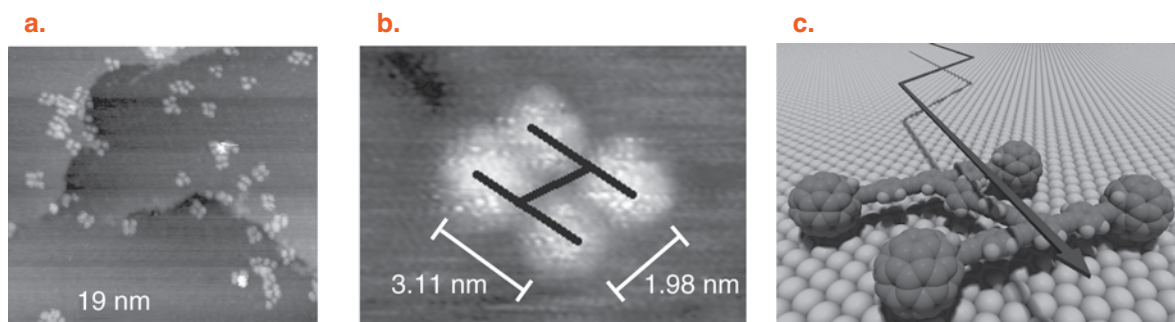
Because the dominant forces that mediate an interaction are largely determined by scale, the same forces govern interactions between a large variety of entities. The electrical forces that bond atoms together to form molecules are also involved in interactions between nanoscale objects, both natural and fabricated. Biological molecules and molecular machines are some of the natural nanoscale objects that fall into this category, including DNA, proteins, and the ribosome. The strength and specificity of the interactions between biological molecules is extremely important as these molecules perform and regulate the biological processes that maintain life (e.g., DNA replication, protein synthesis). Likewise, interactions at the nanoscale play an important role in Earth systems, as the processes that build materials up and break them down often occur at the nanoscale (Hochella 2006). For example, many geological mineralization processes, including mineral dissolution, are mediated by electrical forces between microbes (primarily prokaryotes) and mineral surfaces (Hochella 2002).

Although the interactions dominated by electrical forces occur at a scale too small to see, the effects of those interactions can often be easily detected at the macroscale. One of the most

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Figure 1.13

Nanocar on a surface of gold atoms: (a) Scanning tunneling microscope (STM) image of the nanocars on a gold surface (b) STM image of one nanocar with scale bars (scale bars based on Shirai et al. 2005) (c) Representation of the molecular structure of the nanocars



Source: Figures reproduced with permission from J. M. Tour of Rice University.

familiar examples is rubbing a balloon on carpet and sticking it to the ceiling (electrostatic force). Another example is observing that flour and powdered sugar stick to a plastic measuring cup more than granulated sugar does because the attractive electrical forces between the powdered materials and the cup's surface are stronger than the gravitational forces acting on them (electrodynamic and electrostatic forces). Soap washes off oil and grease (hydrophobic/hydrophilic), but water is enough to wash off something sticky and sugary (hydrogen bonding). Our sense of touch is the result of a variety of electrical forces. Electrical forces are critical for explaining an enormous range of phenomena in the world around us.

Electrical forces also have an impact beyond the fabrication of nanoscale structures and assemblies. Once they have been created, nanoscale products are often difficult to control and manipulate. For example, researchers fabricated a nanoscale "car" with buckyballs (C_{60}) as wheels (see Figure 1.13). At room temperature, the electrical forces between the wheels and surface were so strong that the nanocar stuck to the surface. However,

at 200°C, the car was freed and able to roll across the surface. Therefore, understanding and controlling the electrical forces that can occur between two objects is important not only when building a nanoscale structure but also when determining the usefulness of the final product (Shirai et al. 2005).

Electrical forces play a critical role in nano- and atomic scale interactions crucial to all natural and living systems. As nanotechnology aims to control matter, scientists and engineers must consider electrical forces in all aspects of the process—design, fabrication, characterization, processing, and manipulation.

Relationship to the 7–12 Curriculum

High school chemistry courses typically introduce students to the bonds that keep molecules together. Chemical bonds are mediated through the electrons of the participating atoms but are rarely equated to electrical forces. In addition, curricula often represent bonds as categories of interactions (i.e., ionic, dipole-dipole, induced dipole, covalent), using algorithms (e.g., electronegativity

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differences) and rules (e.g., octet rule) that help students categorize interactions. While these algorithms are useful, over-reliance on them may hinder students' ability to consider electrical forces as a continuum (Taber and Coll 2002). Viewing electrical forces in terms of discrete categories may impede their conceptual understanding of phenomena (Levy Nahum et al. 2007). Students need to be reminded that the octet rule, Lewis dot structures, and other representations are models used to help explain how atoms interact, and as models, they can emphasize only a portion of any given phenomena. Relying solely on simple models and categories will hinder students' abilities to connect the electrical forces involved in chemical bonding to those that govern a range of other interactions, including those that occur at the nanoscale.

Sometimes it seems to me that a bond between two atoms has become so real, so tangible, so friendly, that I can almost see it. Then I awake with a little shock, for a chemical bond is not a real thing. It does not exist. No one has ever seen one. No one ever will. It is a figment of our own imagination.

—Charles A. Coulson, 1955

Connecting chemical bonds to electrical forces may help students understand that the same electrical forces dominate at the nano- and atomic scales, which include not only chemical bonding but also interactions between nanoscale structures both natural (e.g., proteins, DNA) and fabricated (e.g., nanotubes). This approach may also help remove some of the artificial barriers erected between disciplines through the traditional patterns of science instruction. In addition, curricula tend to present shape as the primary determinant of

recognition. Although shape plays an important role, complementary shape acts to align the electrical forces that govern the interaction. Focusing on electrical forces instead of chemical bonding or on shape as the primary determinant of recognition decreases emphasis on discipline-specific explanations of phenomena. In particular, the idea of electrical forces might support students in developing a broader understanding of interactions on the nano- and atomic scales.

Big Idea 4

Quantum Effects

Different models explain and predict the behavior of matter better, depending on the scale and conditions of the system. In particular, as the size or mass of an object becomes smaller and transitions through the nanoscale, quantum effects become more important.

About Quantum Effects

It is not necessary to have a deep understanding of quantum mechanics in order to develop a fundamental understanding of many nanoscale phenomena (e.g., tunneling, quantum dots). A general, qualitative understanding of these fundamental quantum mechanical concepts is adequate for the nonspecialist:

- All matter exhibits both wave-like and particle-like characters. This implies that we cannot simultaneously determine the position and momentum of a particle.
- Only discrete amounts, quanta, of energy may enter or exit certain systems (e.g., atoms, molecules, quantum dots)—energy is quantized. This is true not only for atomic

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and subatomic systems but also for many nanoscale systems.

- Because of the wave-particle duality, we cannot predict exactly what did or will happen to matter at certain scales (i.e., atomic scale, subatomic scale, and often nanoscale). Instead, only the probability of a given outcome can be measured. This has implications for electron behavior within atoms, chemical bonding, and intermolecular interactions.
- An approximation of the Pauli exclusion principle for nonexperts is that two electrons cannot be in the exact same quantum state within the same system (atom). This relates to the arrangement of elements in the periodic table and the associated trends observed.

Many educators question whether ideas about quantum mechanics should be introduced in the secondary science curriculum at all. The national science standards, designed to define science literacy, contain at least some of the ideas listed above (AAAS 1993; NRC 1996). In addition, most, if not all, of these ideas are presented in a typical high school chemistry course. The vote by participants (scientists, engineers, and formal and informal science educators) at a national workshop for K–12 NSE education was nearly unanimous for the inclusion of quantum mechanics at the high school level (for more information on the workshop, see p. 3 in the Introduction and also Appendix A). Therefore, Quantum Effects is included as one of the big ideas of NSE. The challenges and some potential strategies for bringing ideas related to quantum mechanics to the secondary science classroom are discussed in Chapter 8.

Classical mechanics has its foundation in Newton's laws of motion. The model is used to describe the motion of a range of phenomena

that occur over a range of scales—from the behavior of single-celled organisms to the flight of a bullet, from movement of a car to movement of planets. Yet, as matter transitions from the bulk (micro- to macroscale) to the atomic scale, classical mechanics fails in its ability to describe the behavior of matter. At this point and smaller (e.g., subatomic), it becomes necessary to use quantum mechanics to explain phenomena such as the color/spectrum of burning elements or tunneling.

It is difficult to assign an exact point at which the transition occurs. Size is relative, and as such, the point at which quantum mechanics becomes important depends on the object or system being observed as well as the act of observation. This is because any observation of an object requires an interaction between the object and a measuring device. If making a measurement or observing the object causes a negligible disturbance to the object, then the object can be considered to be “big,” and classical mechanics can be used to describe its behavior. However, if the disturbance caused by the measurement or observation is significant, then the size of the object in the absolute sense is “small,” and a different model, quantum mechanics, must be applied.

Werner Heisenberg (1958) used a related thought experiment to develop the idea of uncertainty. His experiment involved using a microscope to measure the path of an electron. The resolution limit of a light microscope is approximately one-half that of the wavelength of the incident light. Therefore, the uncertainty of the position of the observed object is proportional to the wavelength of the incident light. To increase the resolution (or minimize the uncertainty) such that the position of something as small as an electron could be tracked, incident light with a much shorter wavelength (higher

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frequency) must be used as a probe (i.e., gamma rays). However, in order to detect the electron, a gamma-ray photon must hit it. When the photon impacts with the electron, it will impart some momentum. This will change the momentum of the electron, which is the very object that was being measured. In other words, the act of measuring the position changes its momentum.

The smaller the wavelength of the incident photon, the more precisely the position of the electron can be determined. However, the smaller the wavelength of the photon, the larger the momentum it has, which will result in a larger change in the momentum of the electron after impact. Thus, although the position of the electron is known more precisely, the uncertainty of its momentum is greater, so the exact position and momentum of an electron cannot be simultaneously determined. This idea is described by the Heisenberg uncertainty principle, which is illustrated by Equation 1.1, where x denotes position, p is momentum, and h is Planck's constant. Einstein was the first to show this relationship with the photon.

Equation 1.1
Heisenberg uncertainty principle

$$\Delta x \Delta p \geq h$$

Several other uncertainty relationships describe pairs of complementary observables that cannot simultaneously be measured exactly (e.g., energy and time). In these cases, as one observable is measured more precisely, the other necessarily becomes less defined. Thus it is impossible to predict the *exact* behavior of matter; only predictions about the *probability* of what will happen can be calculated. This realization changed the way that we think about science and about nature itself as illustrated by Feynman and Heisenberg:

[P]hilosophers have said before that one of the fundamental requirements of science is that whenever you set up the same conditions, the same thing must happen. This is simply not true, it is not a fundamental condition of science. (Feynman 1996, p. 35)

If we want to describe what happens in an atomic event, we have to realize that the word "happens" can only apply to the observation, not to the state of affairs between two observations. (Heisenberg 1958)

Yes! Physics has given up. We do not know how to predict what would happen in a given circumstance and we believe now that it is impossible, that the only thing that can be predicted is the probability of different events. It must be recognized that this is a retrenchment in our earlier ideal of understanding nature. It may be a backward step, but no one has seen a way to avoid it. (Feynman 1996, p. 135)

The Heisenberg uncertainty principle is a consequence of matter having both a particle- and a wave-like nature. All things will exhibit either wave-like or particle-like properties depending on how they are observed. Since Newton, scientists have debated whether light should be described in terms of waves or particles. Einstein's work on blackbody radiation showed that light exhibits both wave-like and particle-like behavior. A few years earlier, J. J. Thomson's research with cathode rays provided experimental evidence for the particle-nature of electrons. First, he established that cathode rays are beams of negatively charged particles, or electrons. He then determined the mass-to-charge ratio for the negatively charged particles by measuring the amount that a magnetic field deflects the beam. He found that this ratio was independent of the

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cathode material, thus establishing that electrons have a particle nature.

After the realization that light could behave both as a particle and a wave, the question of whether matter would exhibit the same dual behavior became a focus of research. Louis de Broglie predicted that matter also has a wave-like nature with the relation in Equation 1.2. The momentum (p) of a particle is inversely proportional to its wavelength (λ), as described by de Broglie, where h is Planck's constant. In 1927, two independent research groups showed that a beam of electrons could create a diffraction pattern, thus illustrating the wave-like character of electrons. This provided evidence that matter can exhibit both wave-like and particle-like behavior.

Equation 1.2

The de Broglie relation

$$\lambda = h/p$$

Macroscale objects such as baseballs also exhibit wave-like behavior, but the de Broglie wavelength is so much smaller than the baseballs themselves that we only observe the average position. At these scales (e.g., macroscale), the wave-like character is not important for explaining phenomena. At smaller scales (e.g., nano-, atomic, and subatomic scales) the wavelength is on the order of the size of the objects and the wave character becomes more important.

In Latin, the word *quantum* means amount. In quantum physics, only certain discrete amounts of energy can enter or exit a system. These amounts are some multiple of $h\nu$, where h is Planck's constant and ν is the frequency of the radiation. These quanta are so small that the allowed changes in energy for macroscopic objects appear to be continuous. However, at smaller scales quantization

becomes more important. The electrons produced when metals are exposed to ultraviolet light (the photoelectric effect) provide experimental evidence for energy quantization. Electrons are not ejected from the metal unless a certain threshold frequency is met, regardless of the intensity of the incident radiation. Likewise, the kinetic energy of the ejected electrons is directly proportional to the frequency of the incident radiation but is independent of the intensity. Emission spectra of energetically excited hydrogen atoms also provide experimental evidence for energy quantization.

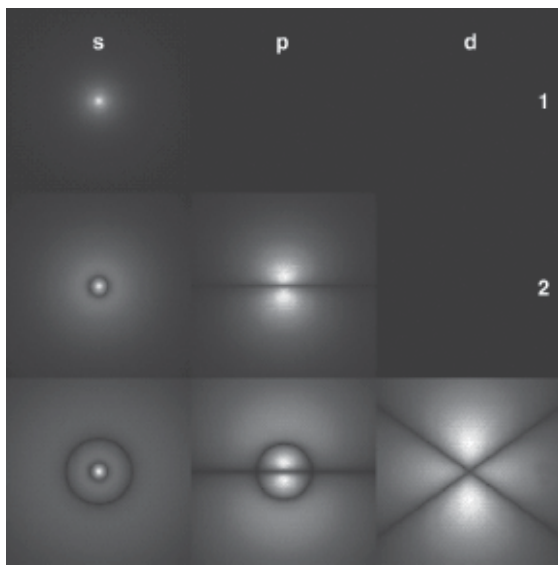
A full characterization, or quantum state, of a particle is defined by four quantum numbers. The particle of interest in this case is the electron. The principle quantum number n designates the state. In the case of the electron, it defines the energy level that the electron occupies within an atom. In other words, it specifies the multiple of $h\nu$, such that $E = nh\nu$.

The second quantum number, orbital angular momentum l , is associated with the orbital, or subshell, designations within each energy level. Within the classical mechanical model, an object can rotate with any angular momentum. However, according to quantum mechanics, angular momentum is quantized so only certain values are allowed. Figure 1.14 (p. 28) illustrates the probability electron densities for the hydrogen atom. For electrons, the s -orbitals are spherically symmetric probability distributions surrounding the nucleus of the atom that are associated with a quantum number $l = 0$. The p -orbitals are two-lobed distributions represented by an angular momentum quantum number of $l = 1$ (see Table 1.5, p. 29).

The magnetic quantum number m designates the energy levels available in each subshell. For example, for s -orbitals, $m = 0$, which

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Figure 1.14
Probability distribution plots for hydrogen



Source: Image downloaded from Wiki Commons courtesy of GNU Free Documentation License, Version 1.2.

indicates there is just one state for an s -orbital at each energy level. For p -orbitals, $m = -1, 0,$ or 1 , so there are three different states (i.e., p_x, p_y, p_z). Table 1.5 illustrates the relationship between the angular momentum and magnetic quantum numbers. The final quantum number s is the spin quantum number. While l defines the orbital angular momentum of the electron, s defines its angular momentum independent of its motion around the nucleus. Spin is the “intrinsic, characteristic and irremovable angular momentum of a particle” (Atkins 1991, p. 223). It is an intrinsic property of electrons in the same way that its rest mass and charge are intrinsic properties of electrons. The value of s for electrons is either $+1/2$ or $-1/2$.

To describe atoms that contain many electrons, an orbital approximation is used. According to the Pauli exclusion principle,* two

electrons in the same system cannot exist in the same state (i.e., have the same set of quantum numbers). Since electrons have either spin $+1/2$ or $-1/2$, then only two electrons can occupy the same orbital—one electron with spin $+1/2$ and one with spin $-1/2$. These electrons are considered to be paired. Additional electrons must occupy higher-energy orbitals. This has a profound impact on atomic structure and molecular bonding. Pauli developed this theory to account for the periodicity of the elements.

Why Is This a Big Idea?

Quantum effects play an important role in all aspects of NSE. Classical mechanics cannot always reliably predict and explain the behavior of matter on the nanoscale, so in those cases, quantum mechanics must be applied to explain the novel properties of materials that are being exploited by nanotechnology. In addition, some of the tools that have been developed to help explore the nanoscale world require quantum mechanics to explain their function.

The quantization of energy states is apparent in many nanoscale materials and is an important factor in determining the chemical and physical properties of a material. Unbound, or unconfined, electrons can move freely and can absorb any amount of energy (see Figure 1.15). In contrast, when an electron becomes bound, or *confined* within a system like an atom or molecule, only certain types of motion are allowed. The motion and energy levels become quantized and are defined by quantum numbers l and n respectively. The more strongly the electron is confined, the larger the separation between allowed energy levels (El-Sayed 2001).

* Although the Pauli principle is often represented as something akin to “two electrons cannot have the same spin,” the principle is actually much broader. The Pauli principle relates to a class of particles called fermions. By definition, within a single system no two fermions can be described by the same quantum state (i.e., same set of quantum numbers). An electron is an example of a fermion and the atom is the system.

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Table 1.5

Relationship between the orbital angular momentum and magnetic quantum numbers

Orbital (subshell)	Orbital Angular Momentum (l)	Magnetic Quantum Number (m)
s	0	0
p	1	-1, 0, +1
d	2	-2, -1, 0, +1, +2
f	3	-3, -2, -1, 0, +1, +2, +3
g	4	-4, -3, -2, -1, 0, +1, +2, +3, +4

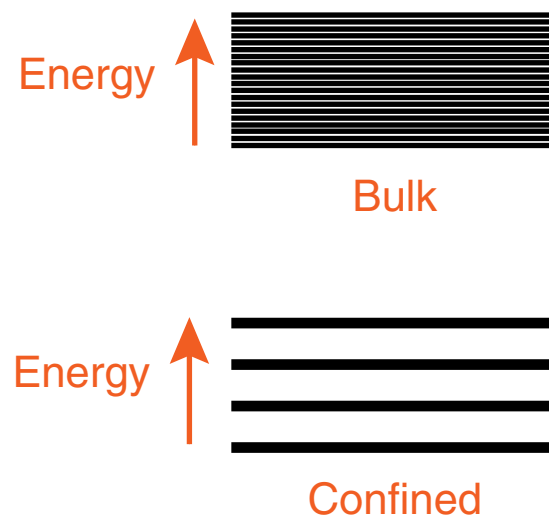
Conductivity of metals is due to delocalized electrons where an electron is shared among a lattice of positively charged nuclei. Band theory is a model used to describe electron behavior in metals. At 0 K, the electrons lie in the valence band, which describes the highest filled orbital, and the higher energy conduction band is empty (see Figure 1.16, p. 30). Electrons in the conduction band move in response to an applied electric field. In metals, there is no gap between the valence and conduction bands, so electrons move freely and current flows through the metal. Because the electrons are free to move within the solid, the allowed energy states are essentially continuous. However, when the size of the metal particle becomes very small, the electrons have less freedom to move and become confined. In this state, the electrons acquire kinetic energy, or confinement energy, and the energy states become discontinuous, which leads to a separation of the valence and conduction bands.

Once the separation, or band gap, approaches or is greater than kT , where k is Boltzmann's constant and T is temperature, the motion of the electrons becomes quantized and the metal becomes a semiconductor. If the separation becomes great enough, the material will transition to an insulator. At the nanoscale, materials that are conductors on the macroscale may lose their conductivity, and vice versa.

Quantum dots, which range in size from 2 nm to greater than 100 nm in diameter, are nanoscale semiconductors in which electrons are confined in all three dimensions. Their small size gives them special electrical and optical properties. Like atoms, quantum dots have quantized energy spectra because the electrons are confined. The intensity and energy of light emitted from a quantum dot is inversely proportional to its size, as summarized in Table 1.6. As the size of the quantum dot gets larger, the energy separation, or band gap, decreases, and

Figure 1.15

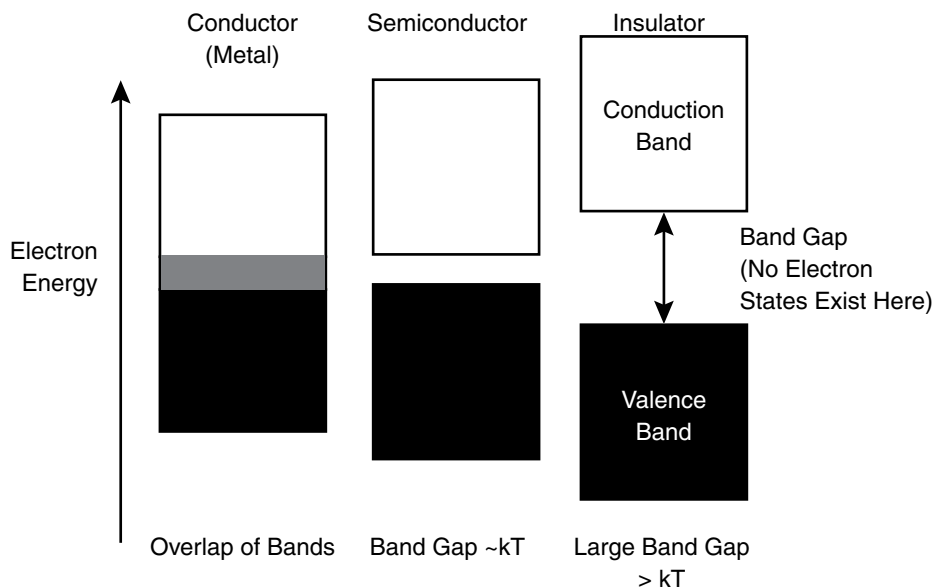
The energy levels in bulk metal are continuous, but become discrete when the electrons become confined.



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Figure 1.16

The band gap between the valence and conduction bands determines the conductive properties of a material.



the light emitted shifts toward the red end of the spectrum (decreasing the size affords a blue shift). The special properties of quantum dots have potential applications as diverse as diode lasers, amplifiers, and biological sensors. They also have an extremely high quantum yield—the efficiency with which absorbed light produces some effect—which makes them potential candidates for more efficient solar cells.

The wave-particle duality is also an important factor in NSE. In particular, tunneling is a quantum mechanical effect that occurs when an object transitions through a classically forbidden energy state. An analogy of this phenomenon might be pushing a ball up a hill. If not provided with enough energy, the ball cannot roll over the hill to the other side. However, according to quantum mechanics, there is some nonzero probability that a particle lies anywhere described by the wave function. If the wave function predicts that the particle may

Table 1.6

Size dependence of quantum dot fluorescence emission after excitation at 365 nm

Approximate Diameter (nm)	Color	Approximate Emission Wavelength (nm)
2	blue	490
3	green	525
4	yellow	570
5	red	620

lie on the other side of the “hill,” it is possible for the particle to “tunnel through” to the other side of the potential energy “hill” because of its wave-like character. This movement is energetically forbidden in classical mechanics. While the probability of this occurring on any scale is never zero, on the nanoscale and smaller, it is observed more frequently because the wave

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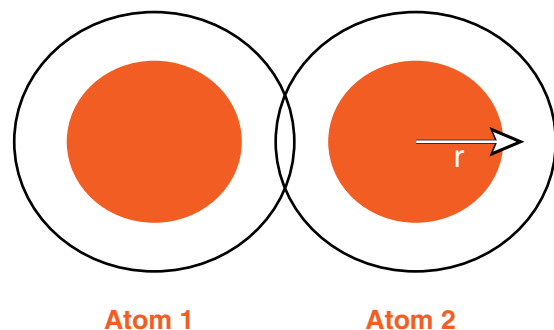
behavior of an object becomes more significant when its size or mass gets very small.

Because of the Heisenberg uncertainty principle, electrons are described not in terms of position but in terms of electron density defined by a probability distribution, which describes the *probability* of finding an electron at a distance r from the atomic nucleus. The probability density is greatest near the nucleus and falls off rapidly (exponentially) with increasing r . Thus, an electron spends a majority of its time near the nucleus. When two atoms are brought into close proximity (< 1 nm) to each other, the electron densities overlap (see Figure 1.17). At this point, an electron from atom 1 may move into the electron cloud of atom 2 without any energy added to the system. The electron has *tunneled* from atom 1 to atom 2. Classical mechanics predicts that this transfer would require an input of energy. The probability of tunneling occurring is exponentially dependent on the distance between the two atoms.

Quantum tunneling is exploited in one of the important tools of NSE, the scanning tunneling microscope (STM). STMs are nonoptical microscopes that work by scanning a sharp electrical tip across a conductive or semiconductive surface. The tip is so sharp that a single atom lies at the end (see Figure 1.18, p. 32). A constant voltage applied to the tip creates a continuous current flowing between the tip and the sample. If the tip is brought close enough to the surface (tenths of nanometers), the electron clouds of the atom on the tip interact with the electron clouds of the surface atoms and electrons may tunnel between the tip and the surface, creating an increase in current. As the tip scans at a constant height from the surface, the overlap of the electron clouds changes, and with it the probability of tunneling changes. A higher surface height affords greater overlap of the electron clouds and greater probability of

Figure 1.17

Two atoms with slightly overlapping electron densities



Source: Adapted from Ellis et al. 1993, p. 18.

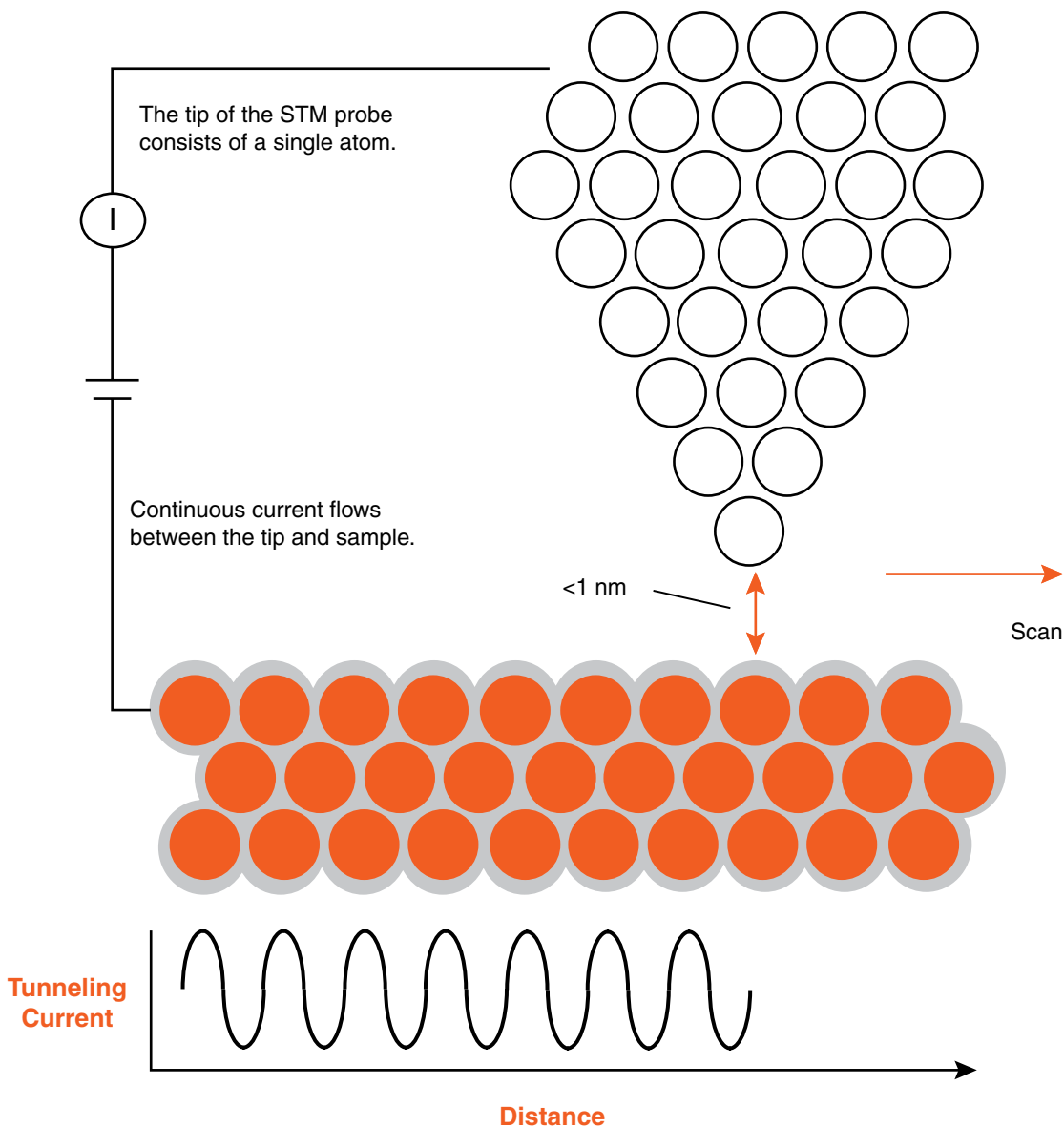
tunneling, which results in an increase in current with height (see Figure 1.18, p. 32; Ellis et al. 1993). Because tunneling is so dependent on the distance between the tip and surface atoms, the STM provides an extremely sensitive measure of interatomic distance and therefore the topography of a surface. The STM can create images of surfaces to a 0.2 nm (2 Å) resolution, which is the size of some types of individual atoms (see Tools and Instrumentation in Chapter 3 for more information).

Quantum tunneling is involved in a range of phenomena. There are many biological systems—such as the porphyrin in the heme/cytochrome system, β -carotene, and the chlorin in chlorophyll—that exploit quantum tunneling as part of their functions (i.e., electron transfer). The tunneling phenomenon is also used in many electronic applications. In particular, it plays a role in flash memory, which is computer memory that can be electrically erased and reprogrammed. It is currently used in digital cameras, cell phones, digital music players, and USB flash drives. Even a simple light switch relies on electrons tunneling through a layer of oxide.

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Figure 1.18

Illustration of a scanning tunneling microscope probe scanning a surface. Below is a representation of the relative tunneling current as the probe moves across the surface.



Source: Adapted from Ellis et al. 1993, p. 17.

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Uncertainty and spin play a crucial role in the structure of matter and the way in which it interacts. Spintronics, or spin electronic research, aims to utilize the electron spin, as well as its charge, to carry information in solid-state devices. Already, this technology is used to increase the sensitivity of read-head sensors in hard disk drives and in magnetic random access memories (MRAMs) (McCray 2009). Ultimately, researchers hope that exploiting both electron charge and spin will decrease the power required for electronic devices.

Interactions at the nanoscale are generally dominated by electrical forces. To develop a conceptual understanding of these forces and relevant phenomena, students must have a probabilistic, or quantum mechanical model, of electron behavior rather than a solar system (classical) model of the atom.

Relationship to the 7–12 Curriculum

Our life experience is with objects and phenomena within the macroscale that can be explained with classical physics. To explain phenomena on scales too small for us to directly experience (i.e., nano-, atomic, subatomic), we must apply quantum mechanics, which is an extremely complex subject that requires extensive experience in both mathematics and science. Its counterintuitive predictions are difficult to grasp even for expert scientists. Thoughts of leading 20th century scientists may be comforting:

I think it is safe to say that no one understands quantum mechanics. (Richard Feynman 1996)

Anyone who is not shocked by quantum theory has not understood a single word. (Niels Bohr, n.d.)

I myself only came to believe in the uncertainty relations after many pangs of conscience.... (Werner Heisenberg 1958)

What I am going to tell you about is what we teach our physics students in the third or fourth year of graduate school.... It is my task to convince you not to turn away because you don't understand it. You see my physics students don't understand it.... That is because I don't understand it. Nobody does. (Richard Feynman, Nobel Lecture, 1966)

However, the difficulty of the subject matter does not preclude a qualitative introduction of quantum effects to grades 7–12 students. It is obviously inappropriate to introduce quantum mechanics in a rigorous manner using mathematical models. Reasoning about the strengths and limitations of models is in accordance with current science education standards (NRC 1996; AAAS 1993), reflecting the fact that understanding the role of models is a fundamental part of the scientific process (see Models and Simulations in Chapter 3 for more detail). As such, it is reasonable for students to begin to understand the limitations of classical mechanics as well as the advantages of some aspects of the quantum mechanical model.

In fact, a typical high school chemistry course contains many if not all of the basic quantum mechanical ideas in this section of the chapter. To understand chemical bonding, intermolecular interactions, and related ideas such as polarizability, students must hold a probabilistic model of electron behavior. They must consider electron distribution as opposed to individual electrons located in a certain place. In addition, students must understand that only certain amounts of energy are allowed in or out of atomic and molecular systems. A deeper, more mathematically rooted description

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of quantum effects can then be introduced in grades 13–16 and above.

However, for students to develop even a basic, qualitative understanding of quantum effects will require time in the curriculum (how *much* time is still unclear). It is not unusual to introduce these complex and nonintuitive ideas over a few days; unfortunately, there is no reason to believe that such cursory treatment of these complex ideas will lead to student learning. If this level of knowledge is desired for students, we must prioritize these ideas in the curriculum and work to develop effective instructional strategies to help students develop a useful, applicable understanding of quantum mechanical ideas.

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