... "to see a world in a grain of sand
and Heaven in a wildflower
hold infinity in the palm of your hand
and eternity in an hour ... "

William Blake *"Auguries of Innocence"*

INTRODUCTION

Our wonderful world

Colours! The most beautiful of buds – an apple bud in my garden changes colour from red to rosy after a few days. Why? It then explodes into a beautiful pale rosy flower. After a few months what was once a flower looks completely different: it has become a big, round and red apple. Look at the apple skin. It is pale green, but moving along its surface the colour changes quite abruptly to an extraordinary vibrant red. The apple looks quite different when lit by full sunlight, or when placed in the shade.

Touch the apple, you will feel it smooth as silk.

How it *smells*! An exotic mixture of subtle scents.

What a *taste*: a fantastic juicy pulp!

Sounds ... the amazing melody of a finch is repeated with remarkable regularity. My friend Jean-Marie André says it is the same here as it is in Belgium. The same? Is there any program that forces finches to make the same sound in Belgium as in Poland? A woodpecker hits a tree with the regularity of a machine gun, my Kampinos forest echoes that sound. Has the woodpecker also been programmed? What kind of program is used by a blackbird couple that forces it to prepare, with enormous effort and ingenuity, a nest necessary for *future* events?

What we do know

Our senses connect us to what we call the Universe. Using them we feel its presence, while at the same time we are a part of it. Sensory operations are the direct result of interactions, both between molecules and between light and matter. *All* of these phenomena deal with chemistry, physics, biology and even psychology. In these complex events it is impossible to discern precisely where the disciplines of chemistry, physics, biology, and psychology begin and end. Any separation of these domains is artificial. The only reason for making such separations is to focus our attention on *some* aspects of one indivisible phenomenon. Touch, taste, smell, sight, hearing, are these our only links and information channels to the Universe? How little we know about it! To feel that, just look up at the sky. A myriad of stars around us points to new worlds, which will remain unknown forever. On the other hand, imagine how incredibly complicated the chemistry of friendship is.

We try to understand what is around us by constructing in our minds pictures representing a "reality", which we call models. Any model relies on our perception of reality (on the appropriate scale of masses and time) emanating from our experience, and on the other hand, on our ability to abstract by creating ideal beings. Many such models will be described in this book.

It is fascinating that man is able to magnify the realm of his senses by using sophisticated tools, e.g., to see quarks sitting in a proton,[1] to discover an amazingly simple equation of motion[2] that describes both cosmic catastrophes, with an intensity beyond our imagination, as well as the flight of a butterfly. A water molecule has exactly the same properties in the Pacific as on Mars, or in another galaxy. The conditions over there may sometimes be quite different from those we have here in our laboratory, but we *assume* that if these conditions could be imposed on the lab, the molecule would behave in exactly the same way. We hold out hope that a set of universal physical laws applies to the entire Universe.

The set of these basic laws is not yet complete or unified. Given the progress and important generalizations of physics in the twentieth century, much is currently understood. For example, forces with seemingly disparate sources have been reduced to only three kinds:

- those attributed to *strong interactions* (acting in nuclear matter),
- those attributed to *electroweak interactions* (the domain of chemistry, biology, as well as β-decay),
- those attributed to *gravitational interaction* (showing up mainly in astrophysics).

Many scientists believe other reductions are possible, perhaps up to a single fundamental interaction, one that explains Everything (quoting Feynman: the frogs as well as the composers). This assertion is based on the conviction, supported by developments in modern physics, that the laws of nature are not only universal, but simple.

Which of the three basic interactions is the most important? This is an ill conceived question. The answer depends on the external conditions imposed (pressure, temperature) and the magnitude of the energy exchanged amongst the interacting objects. A measure of the energy exchanged[3] may be taken to be the percentage of the accompanying mass deficiency according to Einstein's relation $\Delta E = \Delta mc^2$. At a given magnitude of exchanged energies some particles are stable.

[1] A proton is 10^{15} times smaller than a human being.

[2] Acceleration is directly *proportional* to force. Higher derivatives of the trajectory with respect to time do not enter this equation, neither does the nature or cause of the force. The equation is also invariant with respect to any possible starting point (position, velocity, and mass). What remarkable simplicity and generality (within limits, see Chapter 3)!

[3] This is also related to the areas of operation of particular branches of science.

Strong interactions produce the huge pressures that accompany the gravitational collapse of a star and lead to the formation of neutron stars, where the mass deficiency approaches 40%. At smaller pressures, where individual nuclei may exist and undergo nuclear reactions (strong interactions[4]), the mass deficiency is of the order of 1%. At much smaller pressures the electroweak forces dominate, nuclei are stable, atomic and molecular structures emerge. Life (as we know it) becomes possible. The energies exchanged are much smaller and correspond to a mass deficiency of the order of only about 10^{-7}%. The weakest of the basic forces is gravitation. Paradoxically, this force is the most important on the macro scale (galaxies, stars, planets, etc.). There are two reasons for this. Gravitational interactions share with electric interactions the longest range known (both decay as $1/r$). However, unlike electric interactions[5] those due to gravitation are not shielded. For this reason the Earth and Moon attract each other by a huge gravitational force[6] while their electric interaction is negligible. This is how David conquers Goliath, since at any distance electrons and protons attract each other by electrostatic forces, about 40 orders of magnitude stronger than their gravitational attraction.

Gravitation does not have any measurable influence on the collisions of molecules leading to chemical reactions, since reactions are due to much stronger electric interactions.[7]

A narrow margin

Due to strong interactions, protons overcome mutual electrostatic repulsion and form (together with neutrons) stable nuclei leading to the variety of chemical elements. Therefore, strong interactions are the prerequisite of any chemistry (except hydrogen chemistry). However, chemists deal with already prepared stable nuclei[8] and these strong interactions have a very small range (of about 10^{-13} cm) as compared to interatomic distances (of the order of 10^{-8} cm). *This is why a chemist may treat nuclei as stable point charges that create an electrostatic field.* Test tube conditions allow for the presence of electrons and photons, thus completing the set of particles that one might expect to see (some exceptions are covered in this book). This has to do with the order of magnitude of energies exchanged (under the conditions where we carry out chemical reactions, the energies exchanged exclude practically all nuclear reactions).

[4]With a corresponding large energy output; the energy coming from the fusion $D + D \rightarrow He$ taking place on the Sun makes our existence possible.

[5]In electrostatic interactions charges of opposite sign attract each other while charges of the same sign repel each other (Coulomb's law). This results in the fact that large bodies (built of a huge number of charged particles) are nearly electrically *neutral* and interact electrically only very weakly. This dramatically reduces the range of their electrical interactions.

[6]Huge tides and deformations of the whole Earth are witness to that.

[7]It does not mean that gravitation has no influence on reagent concentration. Gravitation controls the convection flow in liquids and gases (and even solids) and therefore a chemical reaction or even crystallization may proceed in a different manner on the Earth's surface, in the stratosphere, in a centrifuge or in space.

[8]At least in the time scale of a chemical experiment. Instability of some nuclei is used in nuclear chemistry and radiation chemistry.

On the vast scale of attainable temperatures[9] chemical structures may exist in the narrow temperature range of 0 K to thousands of K. Above this range one has plasma, which represents a soup made of electrons and nuclei. Nature, in its vibrant living form, requires a temperature range of about 200–320 K, a margin of only 120 K. One does not require a chemist for chemical structures to exist. However, to develop a chemical science one has to have a chemist. This chemist can survive a temperature range of 273 K $\pm$ 50 K, i.e. a range of only 100 K. The reader has to admit that a chemist may think of the job only in the narrow range[10] of 290–300 K, only 10 K.

A fascinating mission

Suppose our dream comes true and the grand unification of the three remaining basic forces is accomplished one day. We would then know the first principles of constructing everything. One of the consequences of such a feat would be a catalogue of all the elementary particles. Maybe the catalogue would be finite, perhaps it would be simple.[11] We might have a catalogue of the conserved symmetries (which seem to be more elementary than the particles). Of course, knowing such first principles would have an enormous impact on all the physical sciences. It could, however, create the impression that everything is clear and that physics is complete. Even though structures and processes are governed by first principles, it would still be very difficult to predict their existence by such principles alone. The resulting structures would depend not only on the principles, but also on the initial conditions, complexity, self-organization, etc.[12] *Therefore, if it does happen, the Grand Unification will not change the goals of chemistry.*

Chemistry currently faces the enormous challenge of information processing, quite different to this posed by our computers. This question is discussed in the last chapter of this book.

BOOK GUIDELINES

TREE

Any book has a linear appearance, i.e. the text goes from page to page and the page numbers remind us of that. However, the *logic* of virtually any book is *non*-linear, and in many cases can be visualized by a diagram connecting the chapters that

[9]Millions of degrees.

[10]The chemist may enlarge this range by isolation from the specimen.

[11]None of this is certain. Much of elementary particle research relies on large particle accelerators. This process resembles discerning the components of a car by dropping it from increasing heights from a large building. Dropping it from the first floor yields five tires and a jack. Dropping from the second floor reveals an engine and 11 screws of similar appearance. Eventually a problem emerges: after landing from a very high floor new components appear (having nothing to do with the car) and reveal that some of the collision energy has been converted to the new particles!

[12]The fact that Uncle John likes to drink coffee with cream at 5 p.m. possibly follows from first principles, but it would be very difficult to trace that dependence.

(logically) follow from one another. Such a diagram allows for multiple branches emanating from a given chapter, particularly if the branches are placed logically on an equal footing. Such logical connections are illustrated in this book as a TREE diagram (inside front cover). This TREE diagram plays a very important role in our book and is intended to be a study guide. An author leads the reader in a certain direction and the reader expects to know what this direction is, why he needs this direction, what will follow, and what benefits he will gain after such study. If studying were easy and did not require time, a TREE diagram might be of little importance. However, the opposite is usually true. In addition, knowledge represents much more than a registry of facts. Any understanding gained from seeing relationships among those facts and methods plays a key role.[13] The primary function of the TREE diagram is to make these relationships clear.

The use of hypertext in information science is superior to a traditional linear presentation. It relies on a tree structure. However, it has a serious drawback. Sitting on a branch, we have no idea what that branch represents in the whole diagram, whether it is an important branch or a remote tiny one; does it lead further to important parts of the book or it is just a dead end, and so on. At the same time, a glimpse of the TREE shows us that the thick trunk is the most important structure. What do we mean by important? At least two criteria may be used. Important for the majority of *readers*, or important because the material is fundamental for an understanding of the *laws of nature*. I have chosen the first. For example, relativity theory plays a pivotal role as the foundation of physical sciences, but for the vast majority of chemists its practical importance and impact are much smaller. Should relativity be represented therefore as the base of the trunk, or as a minor branch? I have decided to make the second choice *not* to create the impression that this topic is absolutely necessary for the student. Thus, the trunk of the TREE corresponds to the pragmatic way to study this book.

The trunk is the backbone of this book:

- it begins by presenting Postulates, which play a vital role in formulating the foundation of quantum mechanics. Next, it goes through
- the Schrödinger equation for stationary states, so far the most important equation in quantum chemical applications,
- the separation of nuclear and electronic motion,
- it then develops the mean-field theory of electronic structure and
- finally, develops and describes methods that take into account electronic correlation.

The trunk thus corresponds to a traditional course in quantum chemistry for undergraduates. This material represents the necessary basis for further extensions into other parts of the TREE (appropriate for graduate students). In particular, it makes it possible to reach the crown of the TREE, where the reader may find tasty fruit. Examples include the theory of molecule-electric/magnetic field inter-

[13]This advice comes from Antiquity: ...“*knowledge is more precious than facts, understanding is more precious than knowledge, wisdom is more precious than understanding*”.

actions, as well as the theory of intermolecular interactions (including chemical reactions), which form the very essence of chemistry. We also see that our TREE has an important branch concerned with nuclear motion, including molecular mechanics and several variants of molecular dynamics. At its base, the trunk has two thin branches: one pertains to relativity mechanics and the other to the time-dependent Schrödinger equation. The motivation for this presentation is different in each case. I do not highlight relativity theory: its role in chemistry is significant,[14] but not crucial. The time-dependent Schrödinger equation is not highlighted, because, for the time being, quantum chemistry accentuates stationary states. I am confident, however, that the 21st century will see significant developments in the methods designed for time-dependent phenomena.

Traversing the TREE

The TREE serves not only as a diagram of logical chapter connections, but also enables the reader to make important decisions:

- the choice of a logical path of study ("itinerary") leading to topics of interest,
- elimination of chapters that are irrelevant to the goal of study.[15]

Of course, all readers are welcome to find their own itineraries when traversing the TREE. Some readers might wish to take into account the author's suggestions as to how the book can be shaped..

First of all we can follow two basic paths:

- *minimum minimorum* for those who want to proceed as quickly as possible to get an idea what quantum chemistry is all about[16] following the chapters designated by (▲).
- *minimum* for those who seek basic information about quantum chemistry, e.g., in order to use popular computer packages for the study of molecular electronic structure,[17] they may follow the chapters designated by the symbols ▲ *and* △.

Other paths proposed consist of a *minimum itinerary* (i.e. ▲ *and* △) plus special excursions: which we term **additional**.

- Those who want to use computer packages with molecular mechanics and molecular dynamics in a knowledgeable fashion, may follow the chapters designated by this symbol (♠).
- Those interested in spectroscopy may follow chapters designated by this symbol (Ⓢ).

[14] Contemporary inorganic chemistry and metallo-organic chemistry concentrate currently on heavy elements, where relativity effects are important.

[15] It is, therefore, possible to prune some of the branches.

[16] I imagine someone studying material science, biology, biochemistry, or a similar subject. They have heard that quantum chemistry explains chemistry, and want to get the flavour and grasp the most important information. They should read only 47 pages.

[17] I imagine here a student of chemistry, specializing in, say, analytical or organic chemistry (not quantum chemistry). This path involves reading something like 300 pages + the appropriate Appendices (if necessary).

- Those interested in chemical reactions may follow chapters designated by this symbol (℧).
- People interested in large molecules may follow chapters designated by this symbol (□).
- People interested in exact calculations on atoms or small molecules[18] may follow chapters designated by this symbol (♦).
- People interested in solid state physics and chemistry may follow chapters designated by this symbol (■).

For readers interested in particular aspects of this book rather than any systematic study, the following itineraries are proposed.

- Just before an exam read in each chapter these sections. "*Where are we*", "*An example*", "*What is it all about*", "*Why is this important*", "*Summary*", "*Questions*" and "*Answers*".
- For those interested in recent progress in quantum chemistry, we suggest sections "*From the research front*" in each chapter.
- For those interested in the future of quantum chemistry we propose the sections labelled, "**Ad futurum**" in each chapter, and the chapters designated by (⫤).
- For people interested in the "magical" aspects of quantum chemistry we suggest sections with the label (✠).
  - Is the world real? We suggest looking at p. 38 and subsequent material.
  - For those interested in teleportation please look at p. 47 and subsequent material.
  - For those interested in the creation of matter, we suggest p. 134 and subsequent material.
  - For those interested in tunnelling through barriers, please look at p. 153 and subsequent material.

The target audience

I hope that the TREE structure presented above will be useful for those with varying levels of knowledge in quantum chemistry as well as for those whose goals and interests differ from those of traditional quantum chemistry.

This book is a direct result of my lectures at the Department of Chemistry, University of Warsaw, for students specializing in theoretical rather than experimental chemistry. Are such students the target audience of this book? Yes, but not exclusively. At the beginning I assumed that the reader would have completed a basic quantum chemistry course[19] and, therefore, in the first version I omitted the basic material. However, that version became inconsistent, devoid of several

[18] Suppose the reader is interested in an accurate theoretical description of small molecules. I imagine such a Ph.D. student working in quantum chemistry. Following their itinerary, they have, in addition to the minimum program (300 pages), an additional 230 pages, which gives about 530 pages plus the appropriate Appendices, in total about 700 pages.

[19] Say at the level of P.W. Atkins, "*Physical Chemistry*", sixth edition, Oxford University Press, Oxford, 1998, chapters 11–14.

fundamental problems. This is why I have decided to explain, mainly very briefly,[20] these problems too. Therefore, a student who chooses the *minimum* path along the TREE diagram (mainly along the TREE trunk) will obtain an introductory course in quantum chemistry. On the other hand, the complete collection of chapters provides the student with a set of advanced topics in quantum chemistry, appropriate for graduate students. For example, a number of chapters such as relativity mechanics, global molecular mechanics, solid state physics and chemistry, electron correlation, density functional theory, intermolecular interactions and theory of chemical reactions, present material that is usually accessible in monographs or review articles.

In writing this book I imagined students sitting in front of me. In discussions with students I often saw their enthusiasm, their eyes showed me a glimpse of curiosity. First of all, this book is an acknowledgement of my young friends, my students, and an expression of the joy of being with them. Working with them formulated and influenced the way I decided to write this book. When reading textbooks one often has the impression that all the outstanding problems in a particular field have been solved, that everything is complete and clear, and that the student is just supposed to learn and absorb the material at hand. In science the opposite is true. All areas can benefit from careful probing and investigation. Your insight, your different perspective or point of view, even on a fundamental question, may open new doors for others.

Fostering this kind of new insight is one of my main goals. I have tried, whenever possible, to present the reasoning behind a particular method and to avoid rote citation of discoveries. I have tried to avoid writing too much about details, because I know how difficult it is for a new student to see the forest through the trees. I wanted to focus on the main ideas of quantum chemistry.

I have tried to stress this integral point of view, and this is why the book sometimes deviates from what is normally considered as quantum chemistry. I sacrificed, not only in full consciousness, but also voluntarily "quantum cleanness" in favour of exposing the inter-relationships of problems. In this respect, any division between physics and chemistry, organic chemistry and quantum chemistry, quantum chemistry for chemists and quantum chemistry for biologists, intermolecular interactions for chemists, for physicists or for biologists is completely artificial, and sometimes even absurd. I tried to cross these borders[21] by supplying examples and comparisons from the various disciplines, as well as from everyday life, by incorporating into intermolecular interactions not only supramolecular chemistry, but also molecular computers, and particularly by writing a "holistic" (last) chapter about the mission of chemistry.

My experience tells me that the new talented student who loves mathematics courts danger. They like complex derivations of formulae so much that it seems that the more complex the formalism, the happier the student. However, all these formulae represent no more than an approximation, and sometimes it would be

[20] Except where I wanted to stress some particular topics.

[21] The above described itineraries cross these borders.

better to have a simple formula. The simple formula, even if less accurate, may tell us more and bring more understanding than a very complicated one. Behind complex formulae are usually hidden some very simple concepts, e.g., that two molecules are unhappy when occupying the same space, or that in a tedious iteration process we approach the final ideal wave function in a way similar to a sculptor shaping his masterpiece. All the time, in everyday life, we unconsciously use these variational and perturbational methods – the most important tools in quantum chemistry. This book may be considered by some students as "too easy". However, I prize easy explanations very highly. In later years the student will not remember long derivations, but will know exactly why something *must* happen. Also, when deriving formulae, I try to avoid presenting the final result right away, but instead proceed with the derivation step by step.[22] The reason is psychological. Students have much stronger motivation knowing they *control* everything, even by simply *accepting* every step of a derivation. It gives them a kind of psychological integrity, very important in any study. Some formulae may be judged as right just by inspection. This is especially valuable for students and I always try to stress this.

In the course of study, students should master material that is both simple and complex. Much of this involves familiarity with the set of mathematical tools repeatedly used throughout this book. The Appendices provide ample reference to such a toolbox. These include matrix algebra, determinants, vector spaces, vector orthogonalization, secular equations, matrix diagonalization, point group theory, delta functions, finding conditional extrema (Lagrange multipliers, penalty function methods), Slater–Condon rules, as well as secondary quantization.

The tone of this book should bring to mind a lecture in an interactive mode. To some, this is not the way books are supposed to be written. I apologize to any readers who may not feel comfortable with this approach.

I invite cordially all readers to share with me their comments on my book: **piela@chem.uw.edu.pl**

My goals

- To arouse the reader's interest in the field of quantum chemistry.
- To show the reader the structure of this field, through the use of the TREE diagram. Boxed text is also used to highlight and summarize important concepts in each chapter.
- To provide the reader with fundamental theoretical concepts and tools, and the knowledge of how to use them.
- To highlight the simple philosophy behind these tools.
- To indicate theoretical problems that are unsolved and worthy of further theoretical consideration.
- To indicate the anticipated and most important directions of research in chemistry (including quantum chemistry).

[22] Sometimes this is not possible. Some formulae require painstaking effort in their derivation. This was the case, for example, in the coupled cluster method, p. 546.

To begin with

It is suggested that the reader start with the following.

- A study of the TREE diagram.
- Read the table of contents and compare it with the TREE.
- Address the question of what is *your* goal, i.e. why you would like to read such a book?
- Choose a personal path on the TREE, the suggested itineraries may be of some help.[23]
- Become acquainted with the organization of any chapter.

CHAPTER ORGANIZATION

Once an itinerary is chosen the student will cover different chapters. All the chapters have the same structure, and are divided into sections.

- **Where are we**
  In this section readers are made aware of their current position on the TREE diagram. In this way, they know the relationship of the current chapter to other chapters, what chapters they are expected to have covered already, and the remaining chapters for which the current chapter provides a preparation. The current position shows *whether they should invest time and effort in studying the current chapter*. Without the TREE diagram it may appear, after tedious study of the current chapter, that this chapter was of little value and benefit to the reader.
- **An example**
  Here the reader is confronted with a practical problem that the current chapter addresses. Only after posing a clear-cut problem without an evident solution, will the student see the purpose of the chapter and how the material presented sheds light on the stated problem.
- **What is it all about**
  In this section the essence of the chapter is presented and a detailed exposition follows. This may be an occasion for the students to review the relationship of the current chapter to their chosen path. In surveying the subject matter of a given chapter, it is also appropriate to review student expectations. Those who have chosen a special path will find only some of the material pertinent to their needs. Such recommended paths are also provided within each chapter.

[23]This choice may still be tentative and may become clear in the course of reading this book. The subject index may serve as a significant help. For example a reader interested in drug design, that is based in particular on enzymatic receptors, should cover the chapters with ▲ (those considered most important) and then those with △ (at the very least, intermolecular interactions). They will gain the requisite familiarity with the energy which is minimized in computer programs. The reader should then proceed to those branches of the TREE diagram labelled with □. Initially they may be interested in force fields (where the above mentioned energy is approximated), and then in molecular mechanics and molecular dynamics. Our students may begin this course with only the □ labels. However, such a course would leave them without any link to quantum mechanics.

- **Why is this important**

  There is simply not enough time for a student to cover and become familiar with all extent textbooks on quantum mechanics. Therefore, one has to choose a set of important topics, those that represent a key to an understanding of the broad domains of knowledge. To this end, it often pays to master a complex mathematical apparatus. Such mastery often leads to a generalization or simplification of the internal structure of a theory. Not all chapters are of equal importance. At this point, the reader has the opportunity to judge whether the author's arguments about the importance of a current chapter are convincing.
- **What is needed**

  It is extremely disappointing if, after investing time and effort, the reader is stuck in the middle of a chapter, simply for lack of a particular theoretical tool. This section covers the prerequisites necessary for the successful completion of the current chapter. Material required for understanding the text is provided in the Appendices at the end of this book. The reader is asked not to take this section too literally, since a tool may be needed only for a minor part of the material covered, and is of secondary importance. This author, however, does presuppose that the student begins this course with a basic knowledge of mathematics, physics and chemistry.
- **Classical works**

  Every field of science has a founding parent, who identified the seminal problems, introduced basic ideas and selected the necessary tools. Wherever appropriate, we mention these classical investigators, their motivation and their most important contributions. In many cases a short biographical note is also given.
- **The Chapter's Body**

  The main body of each chapter is presented in this section. An attempt is made to divide the contents logically into sub-sections, and to have these sections as small as possible in order to make them easy to swallow. A small section makes for easier understanding.
- **Summary**

  The main body of a chapter is still a big thing to digest and a student may be lost in seeing the logical structure of each chapter.[24] A short summary gives the motivation for presenting the material at hand, and why one should expend the effort, what the main benefits are and why the author has attached importance to this subject. This is a useful point for reflection and consideration. What have we learnt, where are we heading, and where can this knowledge be used and applied?
- **Main concepts, new terms**

  New terms, definitions, concepts, relationships are introduced. In the current chapter they become familiar tools. The reader will appreciate this section (as well as sections *Why is this important* and *Summaries*) just before an examination.

[24] This is most dangerous. A student at *any* stage of study has to be able to answer easily what the purpose of each stage is.

- **From the research front**
  It is often ill advised to present state of the art results to students. For example, what value is it to present the best wave function consisting of thousands of terms for the helium atom? The logistics of such a presentation are difficult to contemplate. There is significant didactic value in presenting a wavefunction with one or only a few terms where significant concepts are communicated. On the other hand the student should be made aware of recent progress in generating new results and how well they agree with experimental observations.
- **Ad futurum...**
  The reader deserves to have a learned assessment of the subject matter covered in a given chapter. For example, is this field stale or new? What is the prognosis for future developments in this area? These are often perplexing questions and the reader deserves an honest answer.
- **Additional literature**
  The present text offers only a general panorama of quantum chemistry. In most cases there exists an extensive literature, where the reader will find more detailed information. The role of review articles, monographs and textbooks is to provide an up-to-date description of a particular field. References to such works are provided in this section, often combined with the author's comments on their appropriateness for students.
- **Questions**
  In this section the reader will find ten questions related to the current chapter. Each question is supplied with four possible answers. The student is asked to choose the correct answer. Sometimes the answer will come easily. In other cases, the student will have to decide between two or more similar possibilities that may differ only in some subtle way. In other cases the choice will come down to the truth or an absurdity (I beg your pardon for this). Life is filled with situations where such choices have to be made.
- **Answers**
  Here answers to the above questions are provided.

WEB ANNEX http://www.chem.uw.edu.pl/ideas

The role of the Annex is to expand the readers' knowledge *after* they read a given chapter. At the heart of the web Annex are useful links to other people's websites. The Annex will be updated every several months. The Annex adds at least four new dimensions to my book: colour, motion, an interactive mode of learning and connection to the web (with a plethora of possibilities to go further and further). The *living erratum* in the Annex (with the names of those readers who found the errors) will help to keep improving the book after it was printed.

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Without my dearest wife Basia this book would not be possible. I thank her for her love and patience.

Izabelin,
in Kampinos Forest (central Poland),
hot August 2006

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