Preface

This material was presented in a Fall 2009 class taken by first year graduate students in Physical and Theoretical Chemistry at USC. There were also several (more senior) auditors who sometimes livened, but never dominated, classroom participation. Typed notes were distributed throughout the semester at intervals of a few weeks. I agreed to organize and refine them into something resembling a finished product not too long after the end of the term — hence this document.

Myriad handouts of clipped together pages (to say nothing of my custom of distributing improved versions without notice) had resulted in a high entropy situation. It is tedious to say the least to navigate mounds of paper — pages that appear similar at first glance, pagination that does not match from one handout to the next, nearly always undated, missing passages, mathematical notation that changes en route, and so on. This document will eliminate such annoyances.

Professor George Flynn (Columbia University) has been a superb host during my Spring 2010 sabbatical, when this organization and refinement took place. He also shared with me his own adventures with one-dimensional periodic lattices. My wife Michele and I have had many wonderful dinners with George and Jeanie Flynn, where discussions ranged from vacations in France to the joys of proposal writing.

These notes are not (nor were they ever) intended for stand-alone use, in the sense, say, of a textbook. It is assumed that they accompany lectures. Indeed, hundreds of PowerPoint slides were used in the course lectures. In addition, assigned exercises and tricky items were dealt with in the discussion sessions, and individual projects were presented at the Phonon-Photon-Fest. I suspect that by themselves these notes will come across as dry and overly focused on mathematical detail. Also, be warned: they are more-or-less a first draft. The material in Chapter 1 had been presented previously, albeit piecemeal, but this was the first time I lectured on the material in Chapters 2-4. Consequently, you can expect the writing to be unpolished, no doubt with numerous errors, most small but probably some egregious ones as well. The use of cut-and-paste is a great time saver. Unfortunately, in my case, it results in errors that are hard to spot.

The material in Chapter 4 was presented after the semester officially ended in mid-December. Professor Alex Benderskii commenced lectures on complementary topics on November 1. These continued for six weeks, i.e., until the end of term. Following final exams, the material that comprises Chapter 4 was presented in a series of three lectures in as many days that tested the mettle of even the hardiest.

Much of the material is off the beaten track; at least that was the intent. Graduate curricula in physical chemistry (chemical physics, theoretical chemistry) touch many topics but rarely the ones addressed at the end of Chapter 2 and all of Chapters 3 and 4. It strikes me as curious that a person will spend years as a graduate student and postdoc coaxing atoms, molecules, solids, liquids, etc. to absorb photons, yet display an allergic reaction to learning what a photon might be.

The figures have been prepared in nearly all cases by me. About 5% were downloaded from the web or taken from books and journal articles, with proper references provided. Often my figures are little more than sketches or educated guesses. Notable exceptions
are some artwork done by Minh To about five years ago, when he was preparing QuickTime animations of the now infamous Gilbert (Hilbert) Bunny traipsing about on non-Euclidean surfaces. A highly dedicated graduate student, George Kumi, carried out numerous calculations and prepared many of the figures in Chapter 1, certainly the important ones. Photos of my brother's artwork (which also can be viewed and downloaded online at no charge) and pictures of rabbits are interspersed.

Putting these notes together has had the beneficial effect of forcing me to organize them. Organization is not my strong suit, so, despite the considerable time investment, the net effect is positive. I have another batch of typed notes, also ~ 300 pages, and these are now better organized as well. A book may well emerge, but this will require time and patience and a reason for doing it.

Curt Wittig
March 2010

"People often ask themselves the right questions. Where they fail is in answering the questions they ask themselves, and even there they do not fail by much. A single avenue of reasoning followed to its logical conclusion would bring them straight home to the truth. But they stop just short of it, over and over again. When they have only to reach out and grasp the idea that would explain everything, they decide that the search is hopeless. The search is never hopeless. There is no haystack so large that the needle in it cannot be found. But it takes time, it takes humility and a serious reason for searching."

Time Will Darken It
William Maxwell
Table of Contents

Overview
Comments .................................................. 11
Synopses .................................................. 12

Chapter 1. Electrons in periodic potentials
Preliminary comments ........................................ 18
  Periodic potentials ........................................ 18
  Occupancy ............................................... 19
1. Particle on a ring ........................................ 21
   Identical sites .......................................... 21
   Weak $V(\phi)$ .......................................... 22
   Wave vector ........................................... 24
2. Diagonalization ........................................... 26
   $n$-fold potentials .................................... 27
   Pairwise interaction .................................... 29
   Threefold symmetry .................................... 30
   Less symmetrical potentials ......................... 32
   Bands of low lying levels ............................ 33
   Strong binding ......................................... 34
   Summary for Section 2 .................................. 37
3. Transfer matrices ........................................ 38
   Boundary condition ...................................... 40
   Allowed $k$ values ...................................... 41
   Transfer matrices ....................................... 42
   Rectangular well ........................................ 44
   Transcendental .......................................... 45
   Degenerate pairs ....................................... 46
   Higher $n$ .................................................. 47
   Summary for Section 3 .................................. 48
4. The Hückel model ........................................ 49
   The model ................................................ 50
   Allyl and cyclopropenyl ............................... 52
   Butadiene and cyclobutadiene ....................... 53
   Benzene .................................................. 54
   Closed chains ........................................... 55
   Open chains ............................................. 58
   Density of states ....................................... 61
   Particle in a box ....................................... 61
   Particle on a ring ...................................... 62
   Hückel density of states ............................. 63
5. Infinite one dimensional lattice ....................... 67
Allowed $k$ values ........................................ 71
Brillouin zones ............................................ 72
Energy eigenvalues ......................................... 74
Fourier analysis ............................................ 75
Zone boundary ............................................. 77
Nearly free electron ....................................... 78
Tight binding ................................................ 81

6. Simple molecular orbital view ........................................ 86
   Threefold symmetry ........................................ 86
   Sixfold symmetry ........................................... 88
   Bloch theorem applied to six orbitals ..................... 89
   Linear chains .............................................. 90
   Two dimensions ............................................ 90

Bibliography .................................................. 93
Exercises ...................................................... 94
Projects ...................................................... 96

Chapter 2. Phonons and their interactions

1. Lattice vibrations in one dimension .................................. 100
   Site-to-site phase progression ................................ 102
   $k$-space representation of $H$ ................................ 111
   Dispersion relation .......................................... 112
   Second quantization ........................................ 113
   Interpretation .............................................. 116

2. Ionic lattice .................................................... 122
   Displacements ............................................... 125
   Acoustic branch ............................................ 125
   Optical branch ............................................. 126

3. Heat capacity and thermal conductivity ............................ 128
   Canonical ensemble of bosons .............................. 128
   Heat capacity ............................................... 130
   One dimensional monatomic lattice ......................... 130
   Three dimensional lattice ................................ 131
   Debye model ................................................ 135
   Thermal conductivity ...................................... 138
   Model adapted from gas phase kinetics .................... 138
   Phonon crystal momentum ................................ 140
   Bragg scattering .......................................... 141
   A phonon is created ...................................... 143
   Phonon-phonon scattering ................................ 143
   High temperature limit .................................... 144
   Low temperature limit .................................... 145

4. Interaction with radiation: infrared spectroscopy ................ 147
   TO and LO branches: wave vector conservation .......... 148
Charge oscillation: plasma frequency .................................................. 148
Polarized ionic lattice ........................................................................ 151
Polarizability: electron densities of the ions .................................. 152
Polarizability: ion displacements ..................................................... 153
Vibrational resonance ..................................................................... 154
Dielectric function: $\varepsilon(\omega)$ ................................................... 155
Clausius-Mossotti and $\varepsilon(\omega)$ ................................................ 156
Optical branches: interaction with an electromagnetic field .......... 156
Lyddane-Sachs-Teller relation ......................................................... 157
Polaritons ......................................................................................... 159
Mixed photon/phonon character ..................................................... 160
Avoided crossing ............................................................................ 160
5. Continuous mass distribution: the elastic limit ....................... 165
   Plasma oscillation revisited .......................................................... 172
   Surface plasmon/polariton ............................................................ 173
6. Time dependence ......................................................................... 175
7. Three dimensional space ............................................................. 178
   Infinite volume limit .................................................................. 179
8. Extension to covariant field theory ............................................. 180
   Klein-Gordon equation ............................................................... 181
   Non-Hermitian fields .................................................................. 183
Bibliography .................................................................................. 184
Exercises ......................................................................................... 185
Projects .......................................................................................... 186

**Chapter 3. Photons: quanta of the electromagnetic field**

1. Equations of James Clerk Maxwell ............................................. 190
   Gauge transformation .................................................................. 192
   Lorenz gauge ............................................................................... 193
   Coulomb gauge .......................................................................... 194
2. Transverse waves ......................................................................... 196
   Electromagnetic energy density ................................................ 197
3. Quantization ................................................................................. 198
   Commutation relations ............................................................... 199
   Summary for the quantized electromagnetic field ..................... 200
4. Absorption and emission of photons ........................................... 201
   Perturbation ............................................................................... 203
   Electric dipole approximation .................................................... 204
Bibliography .................................................................................. 206
Exercises ......................................................................................... 207

**Chapter 4. Aharonov-Bohm effect**

Preliminary comments .................................................................. 210
1. The main issue
   Quantum versus classical

2. \( E \) and \( B \) versus \( \phi \) and \( A \)

3. Particle-on-a-ring

4. Solution for \( A \neq 0 \)

5. Vector potential appears in a phase factor

6. Topology

7. Aharonov-Bohm

8. Extensions and generalizations
   Covariant derivative
   Local gauge invariance

9. Variation on the main theme
   Electron in a box

10. Born-Oppenheimer approximation and local gauge invariance
    Phase and flux
    Surface integral
    Two states and degeneracy
    Spin in a magnetic field

11. Geometric phase
    General situation
    Choosing phase
    Magnetic monopole: a mathematical curiosity

12. Summary

Appendices
1. Transfer matrices
   Impurities

2. Schrödinger, Heisenberg, and interaction pictures
   Preliminary comments
   1. Schrödinger, Heisenberg, and interaction pictures
      Schrödinger picture
      Heisenberg picture
      Interaction picture
   2. Perturbation
   3. Level decay via adiabatic switching
      Second order transitions

3. Classical particle mechanics including electromagnetism
   Adding the electromagnetic field
   Interaction terms

8
There is nothing so complicated that it cannot, with sufficient effort, be made more complicated.

old adage
Overview

*Fundamental ideas play the most essential role in forming a physical theory. Books on physics are full of complicated mathematical formulae. But thought and ideas, not formulae, are the beginning of every physical theory. The ideas must later take the mathematical form of a quantitative theory, to make possible comparison with experiment.*

A. Einstein and L. Infeld
*The Evolution of Physics (1938)*

Comments

These lectures will be successful if you emerge from them emotionally intact and with an improved understanding of the theoretical foundations that underlie modern chemical physics. The latter goal is ambitious, vague to be sure, but ambitious. Hopefully the former is not. It is likely that you have encountered much of the material previously, though probably in different contexts and less depth. Despite any familiarity, the course will most likely prove challenging.

Repetition is valuable if not taken to extremes, and quantum mechanics is an excellent example. One cannot master a difficult subject such as this in a first encounter, even with a rigorous course, excellent teacher, and comprehensive textbook. The material needs to be revisited, and not just once. At the same time, one cannot master quantum mechanics (or for that matter any serious scientific subject) in depth — say well enough to teach it to others — by repeated readings of introductory texts. It is necessary to dig as deeply as possible.

In line with these premises, a *from-the-ground-up* approach will be used in these lectures to examine several topics in the quantum mechanics of particles and fields. The topics are chosen with the intention of complementing what you have learned, or will learn, in other courses. They are challenging, but not esoteric. You may encounter them repeatedly in graduate school, and even throughout your career. The material is divided into four chapters whose themes are:

(i) Electrons in one dimensional (1D) periodic lattices, including: particle-on-a-ring with a periodic potential $V(\phi)$, solved using the complementary methods of matrix diagonalization and transfer matrices; the Hückel model for closed and open chains; the infinite 1D lattice from the perspective of solid state physics; qualitative molecular orbital approach to molecular crystals.

(ii) Quantization of lattice vibrations (phonons), including: an introduction to Fock space and second quantization; heat capacity; thermal conductivity; plasmons (bulk and surface); polaritons; polarons; infrared spectroscopy; elastic limit; extensions to field theories.

(iii) Quantization of the electromagnetic field, including: spontaneous and stimulated emission; interaction of radiation with matter; electric dipole approximation; magnetic dipole and electric quadrupole transitions.
Aharonov-Bohm effect, including: topology; gauge fields; local gauge invariance (gauge principle) and an introduction to gauge field theory; relation to adiabatic separation, Michael Berry's approach; application to the geometric phase encountered in the Born-Oppenheimer approximation.

You will find that these seemingly disparate topics are, in fact, related to a significant, perhaps surprising, extent.

To master the material and get the most out of the course you must not fall behind. This is, without doubt, the most important sentence in this handout. Consequently, problems will be assigned weekly, and one day per week has been set aside for a grand participatory discussion. A firm grasp of the subject matter of these lectures will serve you well in years to come.

Synopses

Chapter 1 is relatively light hearted. It will be covered in four weeks. Of all the chapters, it is the one that contains the topics you are most likely to have encountered previously. It is purposely repetitious. Sections 1 – 3 solve the problem of a particle-on-a-ring with a periodic potential \( V(\phi) \). This is a convenient way to introduce regimes, limiting cases, and phenomena through straightforward adjustments of \( V(\phi) \). Two complementary approaches will be used and compared: brute force matrix diagonalization in which \( V(\phi) \) is expanded in a Fourier series, and the use of transfer matrices to express site-to-site phase shifts of site functions. The latter approach can be used to describe 1D potentials of virtually any shape through piecewise linear approximation. The transfer matrix algorithm is a nice thing to have at your disposal for a broad range of applications, including ones that go beyond the topics covered in this course.

Section 4 presents the Hückel model for closed and open linear chains. Connections to the results of Sections 1 – 3 are plentiful and elaborated. Section 5 presents the infinite 1D lattice. This is similar to the approach that would be encountered in introductory solid state physics. Many terms that are commonplace in the solid state physics approach have parentage in the finite dimensional systems examined in Sections 1 – 4 (Brillouin zones, energy bands, band gaps, dispersion relations, group and phase velocities, crystal momentum, Bloch theorem, Bloch functions, nearly free electron limit, tight binding limit). Section 6 is short — an introduction to the Hückel-type molecular orbital approach to molecular crystals. It is included to whet your appetite.

Chapter 2 is mainly about lattice vibrations. It will be covered in six weeks. It begins with a 1D lattice comprised of mass points bound harmonically to their respective equilibrium sites, as well as to one another through nearest neighbor harmonic interactions. The quantum mechanical version is solved using second quantization, thereby yielding the acoustic and optical phonons of the 1D lattice. Little imagination is required to add time dependence and extend the 1D model to 3D, then to all of space, and these extensions will be carried out. The great thing about a toy model like this is that it is conjured, not because it mimics one or another real physical system, but because its solution illustrates phenomena and trends, and it provides insights into other areas of science.

Numerous texts are available that cover the vibrations of periodic lattices. So what is special about the model introduced in the beginning of Chapter 2? The answer is that,
though introduced in the context of a periodic lattice with harmonic restoring forces, it is easily extended to field theories for electromagnetism and massive fields. Insight into these theories is facilitated (in my opinion greatly) by the familiarity with harmonic oscillators, Fourier analysis, molecular vibrations, etc. gained throughout the chapter.

To do justice to lattice dynamics, models such as the ionic lattice (e.g., NaCl) will be presented, analyzed, and discussed, including dispersion, infrared spectroscopy, phonon momentum, transport, and parallels with polyatomic molecules. This material is valuable on its own, and it complements the band theory of electrons in periodic structures introduced in Chapter 1.

The discrete lattice serves to introduce, in a way that is transparent from start to finish, the strategy and useful mathematics of Fock space. After solving this model, the lattice is converted to a continuous mass distribution. This is called the elastic limit. Next: time dependence is determined; the 1D system is extended to 3D; and the finite volume is taken to infinity. These innocuous maneuvers leave us with a quantum field theory for massive scalar fields. With a few substitutions it becomes a relativistic quantum field theory — an impressive feat for a few weeks effort and considering the simple model used to obtain it.

Though we are not going to study relativistic quantum mechanics, extension of the lattice model into this regime is an excellent way to introduce field theory in general, because important points are developed from the ground up. Many results that will be obtained would appear opaque and confounding if thrown without warning at the reader, as often happens. The material is a wonderful starting point for Chapters 3 and 4.

Many of the topics presented toward the end of Chapter 2 (bulk and surface plasmons, polaritons, polarons, infrared spectroscopy) are subjects of current day research, especially the nanoscale versions. Graduate students in physical, inorganic, and materials chemistry who are doing, or plan to do, research in this area might benefit from this material, with the caveat that it could prove out of reach without adequate background.

Chapter 3 addresses the quantization of the electromagnetic field. This strikes close to home. Experimental chemical physics exploits the use of radiation in one form or another (usually involving lasers) to carry out a broad range of basic scientific studies. For example, laser spectroscopy is ubiquitous in our graduate program. It spans a broad range of applications, includes frequencies from the vacuum ultraviolet to the far infrared, and takes many forms: high spectral resolution, ultrafast time resolution, parametric amplification and oscillation, resonant and nonresonant multiple photon ionization, laser induced fluorescence, cavity-ring-down spectroscopy, stimulated scattering, sum and difference frequency generation, four wave mixing, nonlinear optics, imaging, and so on. The use of lasers and spectroscopy occupies center stage.

Then there is the classroom. The dominant pedagogical approach has been to treat the electromagnetic field as classical in all respects other than acknowledging that photons are absorbed and emitted. This gives good results for most cases, but leaves gaps, for example: (i) Everyone knows that spontaneous emission is responsible for lighting up the world we live in. Yet, it cannot be explained theoretically without quantization of the electromagnetic field. (ii) The use of time dependent perturbation theory to calculate spectroscopic transition rates is widespread. However, with a classical electromagnetic field, energy is not conserved. (iii) The stimulated emission that makes lasers work is
based on the boson nature of the photon. The larger the number of photons in a cavity mode, the higher the probability that newly emitted photons will enter that mode.

Our approach departs from the paradigm embodied in the widespread use of the classical electromagnetic field. We shall quantize the electromagnetic field and then explore the properties of its quantum, the photon. This will be achieved using an approach that puts physical content up front, and is replete with examples from experimental science. There is subtlety when it comes to quantizing the electromagnetic field, mainly because of something called gauge, and the massless nature of the field. I decided to use a derivation that gets us the answer quickly, with no subtlety to speak of. This opens the door to examples, exercises, and discussion. There is insufficient time to explore nuances of quantization of the electromagnetic field. This will have to wait, say until a special topics course. Then, the derivation will then be repeated, but including the subtleties. Chapter 3 will be covered in two weeks.

Pragmatism notwithstanding, spending a few weeks exploring the quantization of the electromagnetic field is one of those intellectual exercises that are eminently worthwhile in their own right.

The fourth and final chapter deals with the Aharonov-Bohm effect. In my first encounter with conical intersections and geometric phase, I worked through many papers in the chemical physics literature. Only later did I see and appreciate the Aharonov-Bohm effect. It is a great exercise because it links, and is germane to, so many things. Any time that you invest in its study will be repaid many-fold. Geometric phases in molecules will be rendered intuitive. Gauge field theory will fall into place, at least for electrodynamics. Flux quantization in superconductivity will be obvious, and so on.

As far as background material goes, it is necessary to know something about electromagnetic theory. Familiarity with Maxwell's equations, including gauge transformations, will suffice. It should be possible, with a reasonable E&M text (e.g., Griffiths, portions of Jackson if you are brave) to come up to speed in a couple weeks.

Had there been more time, I would have included a chapter on fermion fields. This is more challenging, but one can sneak up on it by starting with the Schrödinger field. This is a scalar field, so it does not carry the correct spin statistics. This needs to be imported. Nonetheless, working through this system is enlightening, and practical as well. For

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1 Hermann Weyl introduced the term gauge into quantum mechanics. The story of how this came about is interesting. Weyl was fascinated by relativity, and he was trying to figure out how quantum mechanical wave functions are affected when a gauge transformation is applied to an electromagnetic field. These transformations had been around since their introduction by Ludwig Lorenz in the 1860’s (though not with the name gauge), but melding them with quantum mechanics had not yet been done. After all, this was the early age of quantum mechanics. Weyl derived a formula in which the wave function is multiplied by a factor: \( e^{i\gamma} \), where \( \gamma \) is real. This is amazing, because this would make the wave function get larger or smaller depending on the sign in the exponent. We now know that this makes no sense, but at the time Weyl thought that this change of size was acceptable because of Lorentz contraction in relativity. Thus, he introduced the term gauge — a simple analogy with a mechanical gauge that indicates the increase or decrease of some quantity through the movement of a pointer. Einstein pointed out that the exponent had to be imaginary: \( e^{i\gamma} \), in which case \( |e^{i\gamma}| = 1 \). Nonetheless the name gauge caught on and is used to this day.
example, it illustrates how second quantization works in the context of electronic structure theory. This chapter would also contain an introduction to the Dirac field. This is a spinor field, so fermion statistics are built in. If I find the time, I will write this up and send you a PDF file.

Comments about units and nomenclature are in order. Conventions $\hbar = 1$ and $c = 1$ are used when it is unlikely this would result in ambiguity. Said differently, no particular care has been taken to conform to a convention regarding $\hbar$, $c$, or units in general. I do not think this creates a problem. For example, it is unlikely that one would come up with a numerical estimate that is off by a factor of $\hbar$ or $c$, though I have seen undergraduates do this. In Chapter 2 carets are placed atop operators. You might consider this unnecessary: why write $\hat{x}$ and $\hat{p}$ when $x$ and $p$ do just as well? The reason is that, as we move from discrete mass points to a continuous mass field, the role of coordinate shifts from one of operator to one of parameter. In other words, the $x$ and $r$ that are familiar operators in the quantum mechanics of particles appear as parameters in their counterpart displacement field operators $\hat{q}(x)$ and $\hat{\phi}(r)$. This important distinction will be belabored. Vector quantities in 3-space are indicated with boldface type. Spacetime uses standard 4D notation: $x = (ct, r)$, metric (+ − − −), contravariant-covariant contractions: $a^\mu b_\mu = a^0 b_0 + a^i b_i = a^0 b^0 - a^i b^i$, the gauge field for electromagnetism: $A^\mu = (A^0, A^1, A^2, A^3) = (\phi, A) = (\phi, A_x, A_y, A_z) = (A_0, -A_1, -A_2, -A_3)$, etc.

It is assumed that you have had a course in quantum mechanics (e.g., Sakurai, Landau and Lifschitz, Griffiths, Atkins and Friedman). Along the way, aspects of classical mechanics and electromagnetism will be encountered. Please review things like: action principle, Lagrangian, Hamiltonian, Poisson brackets, Maxwell's equations, electromagnetic energy density, Poynting vector, and, most importantly, Fourier analysis.
There is a story about two friends, who were classmates in high school, talking about their jobs. One of them became a statistician and was working on population trends. He showed a reprint to his former classmate. The reprint started, as usual, with a Gaussian distribution and the statistician explained to his former classmate the meaning of the symbols for the actual population, for the average population, and so on. His classmate was a bit incredulous and was not quite sure whether the statistician was pulling his leg.

"How can you know that?" was his query. "And what is this symbol here?" "Oh," said the statistician, "this is $\pi$." "What is that?" "The ratio of the circumference of the circle to its diameter." "Well, now you are pushing your joke too far," said the classmate, "surely the population has nothing to do with the circumference of the circle."

Eugene P. Wigner

"I am not a plane Figure, but a Solid. You call me a Circle, but in reality I am not a Circle, but an infinite number of Circles, of size varying from a Point to a Circle of thirteen inches in diameter, one placed on top of the other. When I cut through your plane as I am now doing, I make in your plane a section which you, very rightly, call a Circle. For even a Sphere—which is my proper name in my own country—if he manifest himself at all to an inhabitant of Flatland—must needs manifest himself as a Circle."

Edwin Abbott Abbott
Flatland (1884)