Syllabus for CHEM667601: Physical Chemistry Principles and Applications
Core Curriculum (Fall Semester, 2021)

Class schedule: Monday, Wednesday, Friday 8:00 AM – 8:50 AM

Location: Merkert 130

Course website: https://www.lucasbaogroup.com/chem-course-1

I may update the course syllabus and problem sets on the course website. Solutions to the problem sets may be posted on *Canvas*. The recorded videos for course material are accessible with the link I shared with the class. All students must obey the university academic integrity policies and cannot distribute any part of course material (including, but not limited to, videos, problem sets, exams, and solutions) to anyone outside this class under any circumstance.

Instructor: Prof. Lucas Bao (email: lucas.bao@bc.edu)

Office hours: Monday, 9:00–11:00 AM (Starting from Sept. 13)

Office: Merkert 224

TA: Mr. Hao Liang (email: hao.liang@bc.edu)

Office hours: Friday, 3:00–5:00 PM (Starting from Sept. 10)

Office: Merkert 315A

Prerequisites. This course is **theory/math-intensive** and involves **active learning**, and thus I strongly recommend students who are **well prepared** in introductory quantum mechanics (one-semester undergraduate-level quantum mechanics or equivalent) and in math (multivariable calculus and linear algebra) to take this course.

Description and scope of the course. This course intends to build a solid and rigorous foundation for physical-chemistry graduate students to understand chemistry and materials at the microscopic level, and study the physical nature of bonding and chemical reaction dynamics quantitatively. We focus on fundamental principles of quantum mechanics, and their connections to chemistry and chemical physics. Topics covered in this course include principles of quantum mechanics, the connections between classical and quantum dynamics, exactly solvable systems, variational principle, introductory perturbation theory, and Hartree-Fock theory. We will also cover some necessary mathematical tools that are tremendously useful in understanding modern physical chemistry.

The vast majority of the topics chosen in this course are generally useful for all physical-chemistry and chemical-physics graduate students. Due to time limitation and the goal of this one-semester course, we won't be able to cover many exciting and important topics such as time-dependent perturbation theory and selection rules, density-functional theory (DFT), solid-state theory and band structures, scattering, groups, etc. This course merely serves as a gateway for digesting physical-chemistry literature and appreciating the physical principles underlying a variety of spectroscopic techniques and computational programs. Nevertheless, students who find themselves in need of these theories in their research should not have too much trouble learning these topics after taking this course.

Course style. In order to create a flexible and more interactive learning experience for this graduate-level course, we adopt a ***flipped classroom*** strategy. **My teaching of the course material (i.e., lectures) is recorded as videos and delivered online, not in the classroom**. These videos are accessible via the link I shared with you in email. To avoid my speaking and writing being out of sync when recording the videos, I intentionally slow down my talking. You could choose to view the videos at a higher speed (e.g., 1.5×). Please do not share the videos and course material with other people outside the class.

In-class sessions focus on discussions of the key concepts covered in the videos and the problems that address both the conceptual and quantitative understandings. Students are responsible for **watching the videos and studying the course material *before* each in-class discussion**. This is ***active learning*** (a must for all PhDs). I recommend you bring your laptop and notes you've taken to the in-class discussion.

I highly recommend **watching the videos and studying the reading material *ahead* of our schedule** (i.e., the course outline presented on page 5 and thereafter) since it requires a substantial time investment to digest the lecture notes (on average, ~ 5–6 hours per week). Students are expected to participate in the in-class discussions.

Since this is a 3-credit course, I expect, on average, you will spend ~ 5–6 hours watching the videos or studying the course material and ~ 3–4 hours on problem sets every week. If you find yourself spending far more time than this expectation (especially for most of the material covered in lectures 2–9, which you should feel comfortable with after undergraduate training), it probably means that you may have missed a couple of pieces of the puzzle in undergraduate quantum mechanics and mathematics (this is perhaps due to different curriculum focus implemented at various schools). Don't panic! You could first focus on grasping the big picture and key ideas rather than on the detailed mathematical derivations. Nevertheless, I don't believe it is possible to truly understand and apply quantum mechanics without going through the math. Different students come in with different backgrounds. Everybody will advance in understanding at a different rate. That is expected; that is graduate school.

Textbooks (required):

1. P. Atkins and R. Friedman, *Molecular Quantum Mechanics* (Fifth edition), Oxford University Press

Comment: This is a very good textbook for *chemists* to learn quantum mechanics and its applications in chemistry and materials science. The potential drawback is that sometimes the authors skip several mathematical derivations and leave the readers to fill in the gaps. To help you go through the details, Shankar's book (see below) is a must to read.

2. R. Shankar, *Principles of Quantum Mechanics* (Second edition), Plenum Press

Comment: A classic textbook on quantum mechanics. The derivations, the logic of the presentation, and the physical pictures are all fantastically clear. The only drawback is that it does not cover the connection between quantum mechanics and chemistry, and thus, Atkins' book (see above) is a perfect complement.

References (optional):

<u>Principles of quantum mechanics</u>:

1. J. J. Sakurai and J. J. Napolitano, *Modern Quantum Mechanics* (Second edition), Cambridge University Press

Comment: The first three chapters present the logic and motivation behind fundamental postulates of quantum mechanics brilliantly.

2. P. A. M. Dirac, *The Principles of Quantum Mechanics* (Fourth edition), Clarendon Press

Comment: This *bible* is written by one of the founding fathers of quantum mechanics.

<u>Molecular quantum mechanics</u>:

3. T. Helgaker, P. Jørgensen, and J. Olsen, *Molecular Electronic-Structure Theory*, Wiley

Comment: All you need to know about wavefunction methods!

4. R. G. Parr and W. Yang, *Density-Functional Theory of Atoms and Molecules*, Oxford University Press

Comment: All you need to know about functional variations and density-functional theory (DFT)!

Reference mathematics book:

If you have trouble understanding course material due to a lack of related mathematic background, I highly recommend you use the following book (which is written by a physical chemist) as your reference.

D. A. McQuarrie, *Mathematical Methods for Scientists and Engineers*, University Science Books

Note: In this course, I will assume you have studied multivariable calculus, linear algebra and are familiar with complex numbers and basic ordinary differential equations. It is perfectly fine to study these topics or refresh your memory along with the lectures.

Written exams and grading:

- Exam 1 (Date: 10/08): In-class, closed-note/closed-book, 1-hour test — 30 points (in total)
- Exam 2 (Date: 11/05): In-class, closed-note/closed-book, 1-hour test — 30 points (in total)
- Exam 3 (Date: 11/22): In-class, closed-note/closed-book, 1-hour test — 30 points (in total)
- Final exam (Date: 12/20): In-class, open-note/closed-book, 4-hour test — 150 points (in total)
- Problem set — 600 points (in total)

Final score *X*

$$X = (\text{Exam 1} + \text{Exam 2} + \text{Exam 3}) \times \frac{4}{9} + 40 \times \left(\frac{\text{Final exam}}{150}\right) + 20 \times \left(\frac{\text{Problem set}}{600}\right)$$

Grade: **A**: $X \geq 85$; **A–**: $85 > X \geq 76$; **B+**:$76 > X \geq 68$; **B**: $68 > X \geq 58$; **B–**: $58 > X \geq 48$; **C+**: $48 > X \geq 40$;
C: $40 > X \geq 35$; **C–**: $35 > X \geq 30$; **D+**: $30 > X \geq 25$; **D**: $25 > X \geq 20$; **D–**: $20 > X \geq 15$; **F**: $X < 15$.

(Alternatively, the final course grade may be assigned based on a curved final score.)

Please mark the exam date and the due date on your calendar.

The one-hour midterm exams (i.e., exams 1, 2, and 3) usually include 3–4 long questions or a hybrid of multiple fill-in-the-blank short questions and a few long questions. You are not allowed to use any notes or textbooks during the midterms. The four-hour final exam includes 7–8 long questions. (You should be able to finish all questions within three hours. Nevertheless, I give you one more hour.) For the long questions, you must show all of your work for full credits. You are allowed to bring handwritten notes (*not exceeding 5 single-sided letter pages*) for the final exam. Nontrivial and complicated formulas and mathematical results will be provided in the questions when necessary.

Students must turn in both the written solution (i.e., answer pages) and the printed question pages.

The final exam is scheduled for the final exam week, from **8 AM** to noon. **The final exam is an open-note/closed-book exam.** You are allowed to use the handwritten notes (***not exceeding 5 single-sided letter pages***) during the **4-hour final exam**. Other resources (lecture notes, textbooks, laptops, etc.) are NOT allowed.

All the exams emphasize your fundamental understandings of the course material rather than challenging your mathematical skills; however, testing a certain amount of your mathematical ability cannot be avoided. Mastering the essential mathematical techniques is indispensable for any physical-chemistry researcher.

Homework. Homework (HW) usually includes reading assignments and a problem set (PS). In the lectures and the in-class discussion sessions, I sometimes skip some details in derivations. It is your responsibility to fill these gaps with the help of reading material. PSs are designed to be pedagogical (and perhaps, challenging to some students); in other words, you can learn a lot (including some important topics that I did not cover in the lectures) by working out questions in PSs. PSs will be graded, and solutions will be posted on *Canvas*. (TA will only grade a subset of the questions so that we can return your written solutions ASAP.) You are highly encouraged to work *independently* on PSs.

The due date of each PS is listed in the course outline. PSs are collected at the beginning of the in-class discussion sessions. If you choose to submit a scanned version of your written HW solutions, please email your file as a *single* PDF to the course TA *before* the deadline. **Start these well ahead of their due dates as they require a substantial time investment to complete** (on average, ~ 3–4 hours every week). I am certain that you will NOT be able to solve all problems within 24 hours. No homework will be accepted after the class period in which it is due.

For any physical chemistry course, the key to understand and master the course material is to practice on problems. You are highly recommended (but not obligated) to study the exercises and problems in your textbooks and/or in your reading assignments. Please contact the course TA regarding any concerns about the grading of your homework or exams.

Academic Integrity Policies. Please refer to https://www.bc.edu/bc-web/academics/sites/university-catalog/policies-procedures.html#academic_integrity_policies for a statement about the importance of academic integrity and a reference to the university's academic integrity policy.

Course outline:

Date	#Lecture	Discussion topics [a]	Assignment
M 08/30	1	**No class (No class gathering)!** (In-class discussions start on Wednesday) **Active learning starts!** A recap of classical Hamiltonian mechanics; Sommerfeld quantization; from classical Poisson bracket to Dirac canonical quantization	**Problem set 1 (PS1)** Reading: Shankar, 2.5, 2.7, 2.8, 3.1–3.5.
W 09/01		**In-class session begins** Discussions of Lecture 1	
F 09/03	2	Linear operators; eigenfunctions; time-independent Schrödinger equation; Dirac notation; superposition, expectation	Reading: Shankar, 1.1–1.3, 1.5; Atkins, 4.1, 4.2, 4.8.
M 09/06	No Class (Labor Day)		
W 09/08	3	Time-dependent Schrödinger equation; fundamental postulates of quantum mechanics; Heisenberg picture.	Reading: Atkins, 1.1–1.14.
F 09/10		More Discussions	
M 09/13 (Due: PS1) [b]	4	Ehrenfest theorem; virial theorem; Hellman-Feymann theorem; uncertainty principle; matrix mechanics	**Problem set 2 (PS2)** Reading: Atkins, 1.15–1.19, 2.1–2.6.
W 09/15	5	Matrix mechanics and its applications: spin in an external magnetic field (magnetic resonance); harmonic oscillator	Reading: Shankar, 1.6, 1.8., 7.1, 7.2, 7.4.
F 09/17		More Discussions	
M 09/20	6	Free particle and wave packet; position and momentum representations; phase velocity and group velocity; Gaussian wave packet	Reading: Shankar, 9.3, 5.1, 5.2; Atkins, 2.10, 2.11.
W 09/22	7	Separation of variables: Particle in a 3D box; nuclear motion in a free diatomic molecule (two-body system); particle on a ring.	Reading: Atkins, 2.12, 2.13, 3.1–3.12.
F 09/24	8	Bound states and scattering states; 1D tunneling and chemical kinetics.	Reading: Atkins, 2.7–2.9.
M 09/27 (Due: PS2)		More Discussions	
W 09/29	9	Power series solutions to ODE; eigenfunctions of the harmonic oscillator	**Problem set 3 (PS3)** Atkins, 2.14–2.16; Shankar, 7.3.

[a] We may cover less or (unlikely) more topics depending on class performance and participation. Watch the lecture video first! [b] Problem set (PS) is collected at the beginning of in-class discussion session (If you choose to submit a scanned version of your written PS solutions, please send your file as a *single* PDF to the course TA *before* the deadline).

Date	#Lecture	Discussion topics	Assignment
F 10/01		More Discussions	
M 10/04	10	Eigenvalues and eigenfunctions of angular momentum; addition of angular momenta	Reading: Atkins, Chapter 4, 7.19–7.21, 10.3.
W 10/06	11	Central potential; atomic orbital basis (Slater functions, Gaussian functions)	Reading: Atkins, 3.13–3.16, 7.8; Shankar, Chapter 13.
F 10/08		**Exam 1** (In-class, **CLOSED-NOTE/CLOSED-BOOK**, 1-hour) [a] You will be tested on the material covered in lectures **1–11**.	
M 10/11		No Class (Columbus Day)	
T 10/12 (Substitute Monday class schedule)	12	Molecular harmonic vibrations: Classical coupled oscillators, normal modes, and quantization	**Problem set 4 (PS4)** Reading: Shankar, Example 1.8.6 in chapter 1; Atkins, 10.7, 10.9, 10.11.
W 10/13		More Discussions	
F 10/15	13	Variational principle in geometry and classical mechanics; functional variations	Reading: Shankar, 2.1–2.4.
M 10/18 (Due: PS3)		More Discussions	
W 10/20	14	Variational principle in quantum mechanics; linear variation of the parameters; upper-bound theorem	Reading: Atkins, 6.5–6.6; Shankar, 16.1.
F 10/22		More Discussions	
M 10/25	15	He atom; H_2^+ molecule: the exact solutions and the linear variational solutions (LCAO-MO); Hückel theory	Reading: Atkins, 7.8, 8.2, 8.3, 8.6–8.9, 9.17, 9.18.
W 10/27	16	Born-Oppenheimer approximation; adiabatic approximation; concepts of the adiabatic and diabatic surfaces	**Problem set 5 (PS5)** Reading: Atkins, 8.1; Encyclopedia of Physical Science and Technology (3rd Ed.), 2003, 9–17 [b]
F 10/29		More Discussions	
M 11/01 (Due: PS4)	17	Adiabatic invariant; adiabatic theorem; geometric phase	Optional reading: [b] (1) *Am. J. Phys.* 1990, 58, 337; (2) *J. Chem. Phys.* 1977, 67, 4640: I – III; (3) *Proc. R. Soc. Lond. A*, 1932, 137, 696; (4) *Proc. R. Soc. Lond. A*, 1984, 392, 45.
W 11/03	18	Spin; Pauli matrices; identical particles; Slater determinant; spin orbital; Fermi hole (Fermi correlation)	Reading: Shankar, 10.3, Chapter 14; Atkins, 7.11.
F 11/05		**Exam 2** (In-class, **CLOSED-NOTE/CLOSED-BOOK**, 1-hour) You will be tested on the material covered in lectures **12–16** primarily. Nevertheless, material covered in the previous lectures cannot be avoided in the test.	
M 11/08	19	Spin states of He atom; exchange interactions; determinantal energy; Slater-Condon rule	**Problem set 6 (PS6)** Reading: Atkins, 7.15
W 11/10		More Discussions	

[a] Notes or textbooks are NOT allowed. At the end of the examination, please turn in both the question page and the answer page. [b] Reading material is accessible via *Canvas*. The optional reading list is not mandatory.

Date	#Lecture	Discussion topics	Assignment
F 11/12	20	Restricted Hartree-Fock theory; Roothaan equations	Reading: Atkins, 7.16, 9.1–9.3
M 11/15		More Discussions	
W 11/17	21	H_2 molecule (MO vs. VB); the concept of electron Coulomb correlation	Reading: Atkins, 8.4
F 11/19		More Discussions	
M 11/22 (Due: PS5)		**Exam 3** (In-class, **CLOSED-NOTE/CLOSED-BOOK**, 1-hour) You will be tested on the material covered in lectures **17–21** primarily. Nevertheless, material covered in the previous lectures cannot be avoided in the test.	
W 11/24		No Class (Thanksgiving Holidays)	
F 11/26			
M 11/29		More Discussions	
W 12/01	22	Theorems in Hartree-Fock theory; unrestricted Hartree-Fock; limitations of Hartree-Fock theory and the concept of configuration interaction	Reading: Atkins, 7.17, 8.5, 9.5–9.8
F 12/03		More Discussions	
M 12/06 (Due: PS6)	23	Solving algebraic equations by perturbation theory; time-independent perturbation theory (non-degenerate); vibrational anharmonicity for 1D oscillator; introduction to Møller–Plesset perturbation theory; the first-order spin-orbit coupling	Reading: Atkins, 6.1–6.3, 7.4–7.5, 7.22–7.24
W 12/08		More Discussions	
F 12/10		More Discussions & Final-Exam Heads-Up	
M 12/20 **(8:00 AM – Noon)**		**Final exam** (In-class, **Open-note/Closed-book**, 4-hour test) You will be tested on the material covered in all lectures. The handwritten note must ***not exceed 5 single-sided letter pages***. Textbooks, lecture notes, laptops, etc. are NOT permitted.	