



## Content

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### Chem3621 Fall 2018 Syllabus and Office Hour Information



### (31 Aug) First day of class; Complex Numbers; Intro to QM states

Attached Files: [Worksheet: Complex numbers; QM states](#) (105.765 KB)

#### Learning goals:

- Overview of expectations for the class and syllabus
- Review of complex numbers
- Introduction to quantum states of the spin-1/2 particle

#### Reading to review (after class...since this is the first day of class...normally these would be assigned before class):

- McQuarrie, Quantum Chemistry ("McQ"), Math Chapter A (pp. 45-49)

#### Homework problems (turn these in on Tuesday):

- Install Mathematica on your computer: <https://play.web.fordham.edu/software/>
- McQuarrie problems A-2, A-3, A-4 (on McQ p. 49)
- Complete any unfinished problems on the worksheet shared in class

#### Supplementary materials (if you need more review):

- Khan Academy tutorial on complex number algebra (includes videos and exercises) <https://www.khanacademy.org/math/algebra-home/alg-complex-numbers>



### (04 Sep) QM Operators; Vectors; Intro to Programming

Attached Files: [Worksheet on vectors & QM operators](#) (66.37 KB)

#### Learning Goals:

- Review of vector algebra
- Introduction to computer programming concepts: Variables and arithmetic operations
- Introduction to quantum mechanical operators and their properties (Pauli operators for the Spin-1/2 particle)

#### Reading (please read these before class):

- McQ Math Chapter C ("Vectors") (pp. 129-139). Work through the examples in the reading with a pencil and paper when preparing before class.
- Intro to Computational Physical Chemistry ("ICPC") Appendix A.1-A.4.2/Order of Operations (pp. 405-412) Be sure to try the examples in Mathematica. Work through the examples in the reading in Mathematica before coming to class

**Homework problems:** (do this after class and turn them in next Tuesday)

- McQ C-1, C-4, C-8 (do these "by hand") (on McQ pp. 139-140)
- McQ C-7 (do this using Mathematica. Recall that the "." (period) operator corresponds to the dot product, whereas the "\*" (asterisk) operator performs an element-by-element multiplication.
- Complete any unfinished problems on the in-class worksheet.

**Supplementary material** (if you need extra review or practice):

- Khan Academy Vector intro <https://www.khanacademy.org/math/linear-algebra/vectors-and-spaces#vectors>



## (05 Sep) Matrices; QM Experiments

Attached Files:  02MatricesMoreOperators.pdf (158.123 KB)

**Learning goals:**

- Explain and compute of quantum measurement outcomes (Born postulate) for the Spin-1/2 particle
- Explain Nuclear Magnetic Resonance experiments using the Spin-1/2 model (intro to Hamiltonians and eigenstates)
- Review matrix algebra
- Introduction to programming: Logical operators; using and defining functions

**Readings** (before class):

- McQ Math Chapter G (pp. 367-375)—"Matrices"
- ICPC Appendix A.4.2-A.4.4 (pp.411-418)—more operations and functions

**Homework problems** (after class, turn them in next Tuesday):

- McQ Problems G-1, G-2 (on McQ p. 376) (do these "by hand", then also do them with Mathematica) Please complete these problems before the next class
- McQ Problem G-16 (on McQ p. 378) (try this "by hand", then also do this with Mathematica using the matrix Inverse[] function or the LinearSolve[] function; use the help function to learn more about this)
- ICPC Problem A-2 (on ICPC p. 426)
- Complete any worksheet problems that we did not finish in class

**Additional resources:**

- For additional review of matrix algebra: <https://www.khanacademy.org/math/precalculus/precalc-matrices>



## (07 Sep) Linear algebraic representations of QM; Programming loops, conditionals, and visualization

Attached Files:  03LinearAlgebraProgramming.pdf (57.562 KB)

**Learning goals:**

- Continued discussion of QM measurement; single-spin NMR example
- Represent and perform computations on quantum mechanical states and operators using linear algebra
- Intro to Programming: loops, conditionals, and plotting

**Readings:**

- ICPC Appendix A.5-A.8 (pp. 419-426); you can skip the material on postfix operators for now. Be sure to try the examples in the text as you go along, and feel free to modify them to test your understanding.

**Homework problems:** (turn these in next Tuesday) (We didn't get a chance to work on this, so please wait on these. We'll pick up with this in Tuesday's class)

- ICPC Problems A-8, A-10 (p. 427)
- Unfinished problems from the in-class worksheet

- Erratum: Problem 3.(v) should read "Starting with the QM state with  $\alpha = 1/\sqrt{2}$ "...

Please note: Worksheet 03, problem 3.(v) is missing a "1/" in the constant (without this, the state will not be normalized). The problem should read:

"Starting with the QM state with  $\alpha = 1/\sqrt{2}$ ..."

- 



## (11 Sep) Linear algebraic representations of QM; Programming (continued)

### Learning goals:

- Represent and perform computations on quantum mechanical states and operators using linear algebra
- Intro to Programming: loops, conditionals, and plotting

### Readings:

- ICPC Appendix A.5-A.8 (pp. 419-426); you can skip the material on postfix operators for now. Be sure to try the examples in the text as you go along, and feel free to modify them to test your understanding.
- Rather than rereading this material, as preparation try working on the problems in ICPC and the in-class worksheet

### Homework problems: (turn these in next Tuesday)

- ICPC Problems A-8, A-10 (p. 427)
- Unfinished problems from the in-class worksheet
  - **Erratum:** Worksheet03, 3.iv should read "If  $\text{RandomReal}[] < p_{\text{up}}$ , then..."



## (12 Sep) Stern-Gerlach Experiment; Data Handling

Attached Files: [Worksheet 04--Stern-Gerlach Experiment](#) (77.148 KB)  
 [04SternGerlach.pdf](#) (77.148 KB)

### Learning Goals:

- Discuss how the Stern-Gerlach experiment violates the classical understanding of the world
- Discuss how a quantum mechanical treatment (using spin-1/2 particles) explains the Stern-Gerlach experiment
- Learn basic data handling and fitting techniques

### Reading:

- ICPC Appendix B
- "Stern-Gerlach experiment" (Wikipedia) [https://en.wikipedia.org/wiki/Stern-Gerlach\\_experiment](https://en.wikipedia.org/wiki/Stern-Gerlach_experiment) (be sure to watch the video)

### Problems:

- ICPC Problem B-3 (p. 440)
- Unfinished problems from worksheet

### Supplementary reading ("How the heck did they figure this out?"):

- Friedrich & Herschbach, "Stern and Gerlach: How a Bad Cigar Helped Reorient Atomic Physics" (Physics Today 56, 12, 53 (2003); <https://doi.org/10.1063/1.1650229>)



## (14 Sep) Multiple Spin Problems—NMR Spectroscopy

Attached Files: [Mini Lecture: 04C-Kronecker Product.pdf](#) (1.376 MB)

**Learning Goals:**

- Extend QM models to treat multiple, non-identical, interacting spins (with the Kronecker product)
- Model multiple-spin nuclear magnetic resonance (NMR) experiments
- Practice linear algebraic representation of quantum mechanics
- Practice Mathematica programming

**Reading:**

- ICPC Appendix B.1

**Problems:**

- Finish worksheet problems from class

**Supplementary Reading:**

- I've attached a brief video-lecture on the essential properties of the Kronecker product, for your review. You can watch it using Adobe Reader.
- More than you wanted to know about the Kronecker product [https://en.wikipedia.org/wiki/Kronecker\\_product](https://en.wikipedia.org/wiki/Kronecker_product)

**(18 Sep) Experimental evidence of quantized states**

Attached Files:  [06QuantizedEnergy.pdf](#) (32.357 KB)

**Learning Goals**

- What are the basic experiments indicating that we need Quantum Mechanics to understand the world/chemistry?
- Review of: Photoelectric effect, Hydrogen atom spectrum (Rydberg, Bohr)
- Review of: Basic calculations related to light (e.g., wavelength to energy, etc.)

**Reading:**

- McQ Chapter 1-1.9 (pp. 1-25)

**Problems:**

- McQ Problems 1-15, 1-16, 1-19, 1-26, 1-30, 1-33 (p. 38-39); [don't worry, these are lot of short numerical calculations]
- ICPC Problem B-7 (p. 442)

**Interactive Demonstrations of Experiments Discussed in the Reading:**

(you can run these in Mathematica without installing any additional software)

Blackbody radiation as a function of temperature: <https://demonstrations.wolfram.com/BlackbodyRadiation/>

Photoelectric effect: <https://demonstrations.wolfram.com/ThePhotoelectricEffect/>

Einstein solid (heat capacity): <https://demonstrations.wolfram.com/EinsteinSolid/>

Hydrogen atom spectrum: <https://demonstrations.wolfram.com/BalmerSeriesForTheBohrAtom/>

**(19 Sep) Experimental evidence that matter is wavelike; Probability**

Attached Files:  [07WaveParticleDuality.pdf](#) (33.044 KB)

**Learning Goals:**

- Review of evidence that matter has wavelike properties (e.g., de Broglie waves, two slit experiment)
- Review of discrete and continuous probability calculations

**Readings:**

- McQ 1.10-1.14
- McQ Math Chapter B (be sure to "pencil through" the examples in this chapter yourself)

**Problems:**

- McQ Problem 1-38, 1-42, 1-48
- McQ Problems B-1, B-3 (certainly use Mathematica, if you wish)

**Demonstrations/animations:**

Electron waves in the Bohr Atom <https://demonstrations.wolfram.com/ElectronWavesInBohrAtom/>

Constructive and destructive interference of waves, through two-slits:

<https://demonstrations.wolfram.com/ConstructiveAndDestructiveInterference/>

Two-Slit Experiment: <https://demonstrations.wolfram.com/WaveParticleDualityInTheDoubleSlitExperiment/>

Bragg's Law: <https://demonstrations.wolfram.com/BraggsLaw/>

Wave scattering in 3D crystals (i.e., where does Figure 1.13 come from):

<https://demonstrations.wolfram.com/XRayReflectionByPlanesOfAtomsInACubicLattice/>



**(21 Sep) Schrödinger equation; 1D Particle in a Box**

**Learning Goals:**

- Introduction to the Schrödinger formulation of QM, using the particle-in-a-box (PIB) problem as an example.
- Symbolic and numerical computational strategies for working with the PIB solutions.

**Readings:**

- McQ 3.1-3.6
- ICPC 1.1 (try the code yourself)

**Problems:**

- McQ Problem 3-3, 3-6, 3-9 (you are always encouraged to use Mathematica...or the integral tables in the back of McQ)
- ICPC Problem 1-1
- There are no problems to turn in on the worksheet...but do try to think through the back page on your own, without referring to the book or other notes. (You can use Mathematica or the integral tables in the back of McQ to help you do any integrals you need.)



**(25 Sep) More PIB**

**Learning Goals:**

- Computation of expectation values for the PIB
- Generalization to 2D- and 3D-PIB problem
- Computational approaches to integration

**Readings:**

- McQ 3.7-3.9
- ICPC 1.2-1.4 — Note: Minor [errata](#).

**Homework Problems:**

- McQ 3-15, 3-32, 3-33\*
- ICPC 1-5, 1-6
- Any unfinished worksheet problems (we'll work on these on class again on Wednesday)

\* "direct substitution" means...assume that the proposed wavefunction is true, substitute it into the Schrödinger equation and demonstrate that the results are consistent.



## (26 Sep) Postulates of Quantum Mechanics

### Learning Goals:

- Formal statement of the postulates of quantum mechanics, expressed in Schrödinger wave formalism
- Continued practice with mathematical/computational operations relevant to wave mechanics

### Reading:

- McQ 4.1-4.3.
- As you are doing this reading, go back and reorganize your notes from the first weeks of class. Try expressing the spin-1/2 particle calculations that we performed in terms of the postulates and wave-based expressions discussed in the reading. It may be helpful to construct a table showing the "parallels" between the two approaches

### Problems:

- McQ 4-1\*, 4-3\*\*
- ICPC Problems 1-7, 1-9
- [worksheet problems from last time]

\* feel free to use Mathematica

\*\* One way to approach this problem is to think about the problems this would cause if it were *not* the case



## (28 Sep) Formal properties of QM Operators

### Learning Goals:

- Formal properties of QM operators.
- What does it mean that an operator is "Hermitian", and why is this important for QM?
- Computing and utilizing operator commutation relationships
- Visualization of QM states and generation (e.g., point cloud distributions)

### Readings:

- McQ Section 4.4 - 4.7
  - Again, take a few minutes to review your notes on the Pauli spin-1/2 operators that we discussed in the first weeks of class and look for parallels)
- ICPC 1.5
  - Input and run the code as you go along. Be sure to "rotate" your 3D plots

### Problems:

- McQ 4-11\*, {4-12, 4-13}\*\*, 4-18\*, 4-22
- ICPC 1-10
- Bonus problem for the mathematically inclined: McQ 4-20

\* Because the goal is to show that these are true for *any* function that they apply to, it is probably best to do them "by hand", applying the functions to a "generic" function  $f(x)$ . (There are ways to do this with Mathematica, but it is a bit more sophisticated.)

\*\* I consider these one problem



## (02 Oct) Connecting the Linear-Algebraic and Wave-Equation pictures— The Finite Difference Method (part 1)

Attached Files:  [A brief video lecture introducing the Finite Difference Method](#) (3.456 MB)

**Note:** I am at a conference today, and will not be in class. I encourage you all to attend and work together on debugging your code and working on Problem 2-2. I will be back for Friday's class.

**Learning Goals:**

- Compute finite difference solutions to the Schrödinger equation of arbitrary potentials.
- Identify connections between the linear algebraic and Schrödinger wave equation formulations of quantum mechanics.
- Practice computational skills related to list and matrix generation

**Readings:**

- ICPC 2.1-2.2

**Problems:**

- ICPC 2-2

**Supplementary Materials:**

- I've recorded a brief video lecture that introduces this material, which can be downloaded above. You will need Adobe Reader to view the animation.



**(03 Oct) Midterm 1**



**(05 Oct) Finite Difference, continued**

**Learning Goals:**

- Continued practice of the finite difference method, and application to new potentials
- ...(with a sneak peak at the quantum harmonic oscillator)

**Readings:**

- ICPC 2.3 (and get the code running)

**Problems:**

- ICPC 2-4, 2-6 (we'll work on the first of these in class)
- For the mathematically inclined: McQ 4-54 (I suggest everyone take a look at it...so that you can see why the Finite Difference method is actually easier than the alternative)



**(09 Oct) State decompositions and time-dependent Schrödinger equation**

**Learning Goals:**

- Review of Midterm 1
- Decompose arbitrary states into a convenient basis (e.g., Fourier decomposition) to facilitate calculation
- Perform and interpret time-dependent Schrödinger calculations

**Readings:**

- McQ 4.8-4.10
- ICPC 1.6-1.7

**Problems:**

- McQ 4-26, 4-28\*, 4-32\*\*

- ICPC 1-12
- Bonus problems for the mathematically-inclined: McQ 4-43, 4-44
- Bonus problem for the computationally-inclined: ICPC 1-13

\* This is really an exercise in following along the "steps" described in the problem for yourself.

\*\* "Show" here means that if you substitute in the value for  $\Psi$ , that the time-dependent Schrödinger equation "works"



### (10 Oct) Wrap up finite differences and postulates

#### Learning Goals:

- A final look at the finite difference method, with time spent performing and debugging calculations for the QHO
- A look ahead at the quantum harmonic oscillator
- (bring a laptop)

**Readings:** Review ICPC Chapter 2...but more importantly, work through the code.

**Problems:** ICPC 2-4, 2-5, 2-6



### (12 Oct) Series expansions; Intro to the Quantum Harmonic Oscillator (QHO)

#### Learning Goals:

- Build mathematical skill in computing series expansions
- Introduce the quantum harmonic oscillator (QHO)

#### Readings:

- McQ Math Chapter D
- McQ 5.1-5.6

#### Problems:

- McQ D-1, D-3
- McQ 5-9, 5-14
- Last Friday you computed trends in the energy as a function of  $m$  and  $k$  values. How do your results compare to the exact solution to the QHO eigenenergies?

#### Supplementary Materials:

Demo: Solutions of the

QHO <https://demonstrations.wolfram.com/QuantizedSolutionsOfThe1DSchroedingerEquationForAHarmonicOs>



### (16 Oct) Molecular Vibrations and IR Spectroscopy

#### Learning Goals:

- Introduce QHO eigenfunctions
- Introduce use of symmetry to simplify quantum mechanical problems
- Application of QHO to vibrational (IR) spectroscopy
- Introduce anharmonic vibrations, polyatomic vibrations.

#### Readings:

- McQ 5.7-5.12

#### Problems:

- McQ 5-16, McQ 5-22\*, 5-29\*\*, 5-30\*\*\*, 5-42



\* It is trivial to do this with Mathematica; I suggest you try it by hand, taking advantage of the even/odd properties

\*\* Hint: Use the "useful properties" described in McQ 5-10

\*\*\* Hint: Use the idea of "separability". Namely, that functions that don't contain a variable  $x$  are "invisible" to an operator that acts only on  $x$ . This will allow you to decompose this into a set of three independent 1D-QHO problems, in only a few lines of algebra.

#### Supplementary materials:

- <https://demonstrations.wolfram.com/EnergyLevelsOfAMorseOscillator/>

#### A Note:

For a first course in quantum chemistry, it is not necessary to derive the QHO eigenfunctions and eigenvalues from scratch. However, I would encourage those of you interested in physical chemistry and/or math to give it a try. For this, there are two readings that illustrate two different approaches. The Appendix to McQ Chpt 5 describes how to do this using the operator methods we introduced in a previous problem set. The PDF online shows how to derive this using a recursion relationship (which McQ disparages in his Appendix, but can also be done elegantly).



### (19 Oct) Spherical Coordinates; Intro to the Quantum Rigid Rotator

Attached Files:  [12A-Spherical Coordinates.pdf](#) (2.46 MB)

#### Learning Goals:

- Review of spherical coordinate systems
- Introduction to the quantum rigid rotator (QRR) model

#### Readings:

- McQ Math Chapter E
- McQ Section 6.1

#### Problems:

- McQ E-2, E-7\*, E-9\*
- McQ 6-2

\* Don't forget to include the proper volume element. Try each of these for 10 minutes (set a timer) "by hand", before you switch to Mathematica. Utilize the trigonometric integral relationships on the inside cover of McQ to help you see which integrals go to zero.

#### Supplementary videos:

- A short video lecture on spherical coordinates (link above)



### (17 Oct) Computational IR Spectroscopy

Attached Files:  [webmo\\_basics\\_v3.1.pdf](#) (1.32 MB)

#### Learning Goals:

- Compute dipole transition strengths for the QHO and Morse Potential using Finite Differences
- Use Quantum Chemistry software packages to compute and visualize molecular vibrations and simulate IR spectra

#### Readings:

- Review McQ Chapter 5
- Review ICPC Chapter 2
- **Read:** ICPC Appendix D (and try the WebMO calculations)...we'll get to rotational spectroscopy as our next topic so just keep those in the background for now.

**WebMO access:**

<http://ace-linux01.ds.fordham.edu/>

(please note...you must be on the Fordham \*wired\* network, e.g., in the computer labs. It does not work on Wireless...this is a Fordham network security thing...if you need to work off wireless, you can try the webmo.net server for short jobs)

- Username: Your email username.
- Password: Your Fordham ID number (e.g., "A1234") (please change this)

**Problems:**

- Compute the dipole transition integrals for the QHO and Morse Potential (ICPC 2-4, 2-5) solutions using finite differences. Report  $\langle n|x|m\rangle$  where n and m go from the ground state to the first 5 states. Comment on the presence of selection rules and overtones.
- ICPC D-3: Only compute the equilibrium bond length and vibrational energy and compare to experiment.
- ICPC D-8: Compute the equilibrium bond length and vibrational energy for HCl.

**Supplementary (optional) reading:** Prof. Paul Smith has written a brief tutorial on some of the other features of WebMO. We'll touch on a few of these briefly later in this class. Consider this a reference...or as another perspective on how to run the vibrational calculations.

**(23 Oct) QRR Continued, and applications to spectroscopy****Learning Goals:**

- Apply QRR model to understand rotational (microwave) spectroscopy
- Properties of the QRR eigenfunctions (Spherical Harmonic functions)
- Commutation relations of the angular momentum operators

**Reading:**

- McQ 6.2-6.8

Don't get too bogged down by the mathematical details of McQ 6.6-6.7. The most important thing to take away from this is that the spherical harmonic functions for an orthonormal set (and as such, you can do the usual tricks with them, of setting their bra-ket sandwiches to zero or one. Like the Hermite polynomials that form the solution to the QHO problem, they also have a simple selection rule.

You will notice that the commutation relationships of the angular momentum operators has a similar structure to that of the spin-1/2 operators. For those of you who like math: the abstract algebras of their groups (SO(3) and SU(2), respectively) have an isomorphism.

**Problems:**

- McQ 6-7, 6-15, 6-21\*, 6-40\*\*, 6-43

\*Refer back to ICPC Appendix B to help you perform the fit.

\*\*Use the  $L^2$  operator defined in eqn (6.10). Please be sure to address McQ's question: "Do you find anything interesting about the result?" in your submitted papers. In particular, what is the relationship between these functions and the operator? Explain briefly (1 or 2 sentences) as part of your solution.

**(24 Oct) Rovibrational IR spectroscopy ; Sneak Preview of the Hydrogen Atom****Learning Goals:**

- Gain practice with separable wavefunctions (in this case: separability of rotational and vibrational degrees of freedom)
- Interpret rovibrational spectra
- Generate simulated rovibrational spectra using computational techniques
- The hydrogen atom as a separable problem...

**Reading:**

- Re-read McQ 6.3
- Review ICPC Appendix D

**Problems:**

- ICPC D-3 (this time include the rotational states and compute the transitions)
- ICPC D-8; you do not have to repeat the WebMO calculations; merely extract the relevant data from the calculations you performed last week.
- Using your values obtained from the ICPC calculations to generate the collection of R(0), R(1), P(1), P(2) lines (use the Mathematica function you wrote for ICPC D-3 to do this for you)
- McQ 6-17

**(26 Oct) The Hydrogen Atom, part 1****Learning Goals:**

- Introduce the hydrogenic Hamiltonian, eigenfunctions, and eigenenergies
- Understand ways of describing the spatial distributions and symmetries of the hydrogen atom wavefunctions predicted by QM

**Readings:**

- McQ 7.1-7.2

**Problems:**

- McQ 7-9, 7-10, 7-12\*
- I recommend that you set these up by hand and try working them out by hand for 10 minutes each, before resorting to Mathematica. Use the integrals inside the rear cover of McQ. The goal of these problems is not only to learn a little about the nature of the hydrogen atom, but also to practice working with the spherical integrals.

\* Don't use the "canned" result in Table 7.4, but rather work these out for yourself for the specific examples stated, and then compare your result to those found in the table...otherwise there is no fun in this problem.

**(30 Oct) The Hydrogen Atom, part 2****Learning Goals:**

- Continued practice with hydrogenic atom wavefunctions (extending to p orbitals)
- Understand hydrogenic energy levels in an external magnetic field
- Review spin in the context of the hydrogenic atom (the Stern-Gerlach experiment revisited)
- Introduction to spin-orbital coupling
- Introduction to atomic energy level term symbols

**Readings:**

- McQ 7.3-7.9
  - McQ 7.3 is really just an extension of what we talked about last time to p-orbitals
  - McQ 7.5 revisits the Stern-Gerlach experiment. Alpha and beta are just up and down spins. Personally, I find the use of integrals over " $d\sigma$ " in eqn 7.53 a bit goofy, but it is helpful to be able to write out the products of spatial and spin states as is done in eqn. 7.61.
  - McQ 7.7 (term symbols) are just a way of describing the states. This is actually useful for those of you doing atomic absorption (AA) spectroscopy. Note the selection rules!

**Problems:**

- McQ 7-18\*, 7-24\*\*, 7-28\*\*\*, 7-30\*\*\*, 7-35\*\*\*, 7-46\*\*
- Optional problems if you really like atomic-absorption spectroscopy: McQ 7-38, 7-41

\* try this by hand for 10 minutes (using the integral tables), before resorting to Mathematica

\*\* really, this can be done by hand. It's just a bit of algebra. Separate the radial and angular parts of the wavefunction, and it will practically solve itself

\*\*\* short numerical calculations to get a feel for the relevant energy scales. be careful of units.



### (31 Oct) Approximation methods—The Variational Method

#### Learning goals:

- (wrap up spin-orbit coupling)
- Introduce the variational method for estimating the ground state of quantum systems
- Introduce computational strategies for performing variational optimizations

#### Readings:

- McQ 8.1
- ICPC 4.1-4.2

#### Problems:

- ICPC 4-1
- McQ 8-3. Set this up by hand and go as far as you can by hand. Allocate 20 minutes (set a timer) You don't have to finish it, but I want you to see the process and how it compares to the numerical approach you implemented in ICPC 4.2.
- Optional bonus problem for the math lovers: McQ 8-1



### (02 Nov) Approximation methods (part 2): Linear variational theory

Attached Files: [15B-Linear Variational Method.pdf](#) (3.198 MB)

#### Learning goals:

- Identify how restricting the variational method to linear functions reduces the calculation to a matrix eigenvalue problem
- Perform practical linear variational solutions to problems in orthonormal and non-orthonormal bases

#### Readings:

- ICPC 4.3
- McQ 8.2-8.3 (just skim this...all the business of secular determinants makes for messy algebra)

#### Problems:

- ICPC 4-6 (also try writing out the setup for each of the problems "by hand"...further analytical solution is possible but the algebra is rather lengthy)

**Supplementary reading/viewing:** As mentioned in class, a recorded mini-lecture on the derivation of the linear variational method that I recorded a few years ago. You will need to open this file in Adobe Reader (with flash enabled) to hear the audio and animations.



### (06 Nov) Approximation methods (part 3)—Perturbation theory; Determinants

#### Learning goals:

- Introduction to first-order perturbation theory
- Revisit and review spectroscopic selection rules by deriving from perturbation theory
- Introduce/review the mathematical properties of *determinants*

#### Readings:

- McQ 8.4-8.6 (we'll limit ourselves to first-order perturbation theory in this class...this section looks long, but it is mainly the step-by-step proofs)
- McQ Math Chapter F

**Problems:**

- McQ 8-38. Remember, this is just a first-order perturbation to the  $v=0$  QHO wavefunction. The perturbing potential is comprised of only the terms that are *not* the QHO Hamiltonian.
- McQ F-1, F-2, F-7. Do these "by hand" to get a feel for the properties of determinants. I promise that you won't have to do F-7 again (if you want to know how I *really* feel about this, see the footnote on p. 77 of ICPC)

**(07 Nov) Midterm 2—Review Session****(09 Nov) Midterm 2****(13 Nov) Many-Electron atoms (part 1)—basic principles****Learning Goals:**

- Introduce the problem of many-electron quantum mechanics for atoms
- Apply variational and perturbative approaches to the helium atom ground state
- Distinguish between bosonic and fermionic particles, and the requirements these impose for many-particle wavefunctions
- Introduce the Hartree-Fock (mean field) method interacting many-electron systems

**Readings:**

- McQ 9.1-9.6...all this business of matrices should be starting to look familiar

**Problems:**

- McQ 9-4, 9-14, 9-21, 9-22

**(14 Nov) Atomic Hartree-Fock Theory in Practice**

Attached Files: [19C-Hartree-Fock Theory--Mean Field Operators.pdf](#) (3.478 MB)  
[19D-Hartree-Fock Theory---Computational Aspects.pdf](#) (2.954 MB)

**Learning Goals:**

- Deepen your understanding of Hartree-Fock theory
- Learn how to apply Hartree-Fock theory to atoms by implementing a solution in Mathematica
- Solve the Helium atom problem using Hartree-Fock theory
- Generalize the solution to atoms with higher  $Z$ , more electrons, large number of basis functions






**Readings:** ICPC 5.1; Be sure to get the code operational before class.

**Problem:** ICPC 5-5 (for part (d), you might read the text of problem 5-3 to remind you)

**Supplementary Material:** I've added some supplementary video mini-lectures describing the formalism of the mean field operators, and a brief summary of the computational process.

**(16 Nov) Many electron atoms (part 2)—Correlation, term symbols, Gaussian orbitals**

Attached Files: [17C-Atomic Term Symbols revisited.pdf](#) (3.733 MB)

-  17D-Hund's Rules.pdf (2.051 MB)
-  17E-Atomic Selection Rules.pdf (2.644 MB)
-  19E-Hartree-Fock Theory--Problems and Configuration Interaction.pdf (3.183 MB)
-  22A-Gaussian Type Orbitals.pdf (3.571 MB)
-  Worksheet 27 (18.678 KB)

#### Learning Goals:

- Deepen your understanding of many-electron atoms
- Identify limitations of Hartree-Fock theory
- Introduction to atomic term symbols (just a way of naming atomic states)
- Introduce Gaussian-type orbital (GTO) basis functions as a replacement for Slater orbitals

#### Readings:

- McQ 9.7-9.13. If you have time, review McQ 9.1-9.6, in light of our computational work in the last class
- ICPC 5.2.1 —we'll be using these for molecules....did you ever wonder why the program within WebMO is called "Gaussian"?

#### Problems:

- McQ 9-26, 9-31, 9-49\*, 9-52\*, 9-55\*
- Bonus computational problem: ICPC 5-7

\* just some short numerical calculations

#### SNOW DAY:

Classes at FCRH are canceled (until 11am today). I've uploaded some short mini-lectures on the material to Blackboard. For those of you who are on campus and have nothing better to do, I'll be available during our scheduled class time to help you with any problems (e.g., Mathematica code) you have.



### (20 Nov) One electron chemical bonds—the H<sub>2</sub><sup>+</sup> molecule

#### Learning Goals:

- Introduce the Born-Oppenheimer approximation
- Use H<sub>2</sub><sup>+</sup> as a model for chemical bonding principles
- Introduction to molecular orbital (MO) theory using the linear combination of atomic orbitals (LCAO) method

**Readings:** McQ 10.1-10.6

**Problems:** McQ 40-2, 10-5, 10-25, 10-26 (use symmetry arguments to avoid messy integrals), *and answer the Generalization questions on part 3 of today's worksheet. You need not come to a numerical value for these—you can leave integrals unevaluated. Focus on qualitative answers to these questions. We'll discuss this in the next class.*  
[edited: 20 Nov 2018]



### (21 Nov)—No Class Today

**Reminder:** There is no class today at FCRH



### (23 Nov)—No class today



### (27 Nov) Two electron chemical bonds—The H<sub>2</sub> Molecule

#### Learning goals:

- Extend LCAO-MO theory to the H<sub>2</sub> molecule

- Introduce Molecular term symbols.
- Configuration interaction revisited
- Hartree-Fock theory revisited (and extended to molecules)

**Readings:** McQ 10.7-10.10

**Problems:** McQ 10-37\*, 10-47, 10-48

\*there is nothing conceptually difficult in this problem...just a lot of algebra. It's a good proof, but will take too long to do in class. If you don't do it, it's not the end of the world.



## (28 Nov) Molecular Hartree-Fock Theory in Practice

### Learning Goals:

- Use of Gaussian basis sets for solving molecular problems
- Construct and perform a Hartree-Fock calculation for the H<sub>2</sub> molecule that can be generalized to more complex molecules

### Readings:

- ICPC 5.2 (and be sure to get the code working before class)
- *After class:* Read McQ 12.1-12.3 (this is really just a review of topics that you've read in other places, but framed in new language)

### Problems:

- ICPC 5-10
- At least one of the following: ICPC 5-17, ICPC 5-19
- Bonus problems: Do both of the above. Then try 5-22



## (30 Nov) Qualitative Theory of Chemical Bonding

### Learning goals:

- Use molecular orbital theory as a conceptual framework for understanding chemical bonds of homonuclear and heteronuclear diatomic molecules
- Use symmetry arguments to understand which atomic orbitals can contribute to which molecular orbitals
- Use molecular term symbols to denote symmetry properties of molecular orbitals
- Represent diatomic molecule Hamiltonians using matrices and obtain qualitative molecular orbital information from the eigenvalues.
- Interpret photoelectron spectra to determine molecular orbital energy levels

**Readings:** McQ 11.1-11.5. This is really just general chemistry, but stated in much more precise language. You have already seen concepts of bond order, *aufbau* principle, etc. It all comes from quantum mechanics, and can be calculated.

### Problems:

McQ 11-5, 11-7, 11-9, 11-13, 11-16, 11-19, 11-24 (These are short calculations, and are mostly refreshers from general chemistry.)

Bonus problem: BF and CO are isoelectronic, yet their molecular orbitals are very different. Use WebMO to optimize the geometry for each molecule and compute/visualize the molecular orbitals. Why are they different? Describe the symmetry of the molecular orbitals. How can you rationalize this using the non-interacting electron (matrix) model discussed in class?

**Reference:** Table of Effective Nuclear Charges (Clementi *et al.*)

[https://en.wikipedia.org/wiki/Effective\\_nuclear\\_charge](https://en.wikipedia.org/wiki/Effective_nuclear_charge)



## (04 Dec) Hückel Theory (part 1)—Introduction and basic calculations

### Learning goals:

- Introduction to the Hückel approximation for the molecular orbital theory of aromatic hydrocarbons.
- Calculation of total energy and bond order in Hückel theory.
- Computational strategies for obtaining and visualizing Hückel theory results

### Readings:

- McQ 11.6, 11.8 (yes, skip 11.7)
- ICPC 6.1-6.3 (as usual: be sure that you get the code working. this should be relatively familiar to you...it's the usual process of building a matrix representation and finding eigenvalues. the only wrinkle is the need to sort these)
- McQ 11.7 (go back only after you are finished with ICPC reading)

### Problems:

- McQ 11-44
  - (Note that here the basis are the s-orbitals, instead of the p-orbitals that are more frequently associated with Hückel theory. Set up the matrix in Mathematica, and then use Mathematica to compute the Eigenvalues[]. Compute the total energy as described in the text, or in ICPC Problem 6-1.)
- ICPC 6-1, 6-3, 6-4
  - (Note: do them in this order; the function that you write for the total energy is used in the first problem is used in the second and third. These are mostly exercises in setting up Hamiltonian matrices, and the underlying computation is mostly the same.)



## (05 Dec) Hückel Theory, part 2—Heteroaromatics and Chemical Reactivity

### Learning goals:

- Extended Hückel theory to heteroaromatic molecules
- Apply Hückel theory to compute charge distributions (and related properties) of aromatic molecules
- Introduce theories of chemical reactivity
- Use Hückel theory to make predictions about chemical reactivity.

### Readings:

- Reread McQ 11.7
- ICPC 6.4-6.7 (as usual, be sure to get the code working)

### Problems:

- ICPC 6-12(b)(c), 6-13
- If you really love organic chemistry : ICPC 6-17



## (07 Dec) Qualitative Valence Bond and MO Theory of Polyatomic Molecules

Attached Files: [Engel\\_pp267-83.pdf](#) (7.859 MB)  
[McQuarrie&Simon Chpt 10 Excerpt.pdf](#) (8.273 MB)

### Learning Goals:

- Formal statement of valence bond theory
- Comparison of theoretical differences between valence bond and molecular orbital theory.
- Use of Bent's Rule and Walsh Correlation Diagrams to predict molecular geometries relevant to organic and inorganic structures.

### Readings:

Excerpts from [Engel](#) Chapter 13 and [Mcquarrie & Simon](#) Chapter 10 (download PDFs for both of these below). Read Engel, and then come back to McQ&S for a more detailed discussion of the mathematics.



- Engel: 13.1-13.2 --> McQ & S 10-1
- Engel: 13.3-13.4 --> McQ & S 10-2
- Engel: 13.5 --> McQ & S 10-3
- Engel 13.6 --> (no counterpart in McQ & S)

**Problems:**

McQ & S (in the pdf) 10-3, 10-18, 10-20, 10-23\*

\* be careful with the number of electrons, particularly as you occupy the doubly degenerate MOs.

[these are just a few short qualitative problems]



**Practice problems, ahead of tomorrow's class.**

## Blackboard

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