

**CHEM 6325****Introduction to ab initio Calculations: Hartree-Fock Theory, Fall/2011**

Lectures, time and location:	TBD
Course period and start:	1st period
Instructor:	Dieter Cremer, 325 FOOSC, ext 8-1300, dcremer@smu.edu
Office Hours:	By appointment
Units:	3
Grading:	ABC Letter Grade

**1. Rationale:**

Quantum chemical calculations of the ab initio type all start with a Hartree-Fock calculation. Hartree-Fock theory is the basic knowledge each student in quantum chemistry has to acquire before starting with the more advanced electron correlation theories. This course provides an introduction into Hartree-Fock theory. It describes the construction of the wave function from one-electron functions and Slater determinants, the description of electron-electron interaction in form of mean-field potential, the derivation of the Hartree-Fock equations and their transformation into a computer program. Essential terms such as basis sets, initial guess, self-consistent field, convergence enforcement, etc. are explained so that the student is prepared to use Hartree-Fock theory for solving chemical problems.

**2. Course Recommendations**

The course is important for all students interested in computational chemistry, molecular modeling, and molecular simulations, who want to use quantum chemical programs for solving chemical problems. Special care will be taken that students with different background can follow the course. There is no need to have advanced knowledge in quantum mechanics and mathematics. There will be an intensive computer lab accompanying the course that will give participants ample training possibilities to carry out Hartree-Fock calculations.

**3. Texts**

- Textbook: A. Szabo, N. S. Ostlund, Modern Quantum Chemistry, Introductory to Advanced Electronic Structure Theory, McGraw Hill, New York, 2008.
- Handouts.

**4. Course Aims and Objectives:**

The course will discuss Hartree-Fock theory and its realization in computer programs to lay in this way a basis for solving chemical problems with the help of quantum chemical calculations. Each student will learn about basic Hartree-Fock theory, how it is realized in a computer program, and how Hartree-Fock calculations are carried out. It will be trained what type of basis set and what type of method (restricted closed shell, unrestricted open shell, restricted open shell) has to be used for a given chemical problem.

***Specific Learning Objectives:***

By the end of this course, students  
will be in the position to have a basic understanding of Hartree-Fock theory;

will be able to understand its advantages and its shortcomings;  
will be able to use the appropriate basis set for a given problem;  
will be able to solve convergence problems in a Hartree-Fock calculation;  
will be able to apply restricted, unrestricted, and restricted open shell methods;  
will be able to analyze a Hartree-Fock wave function.

**General Education Learning outcomes:**

1. Students will be able to demonstrate basic facility with the methods and approaches of scientific inquiry and problem solving.
2. Students will be able to explain how the concepts and findings of science in general, or of particular sciences, shape our world.

## 5. Course Outline

In 11 chapters, the course will develop essential features of modern Hartree Fock theory:

### 1. Introduction

Introduction into Linear Algebra: vector space, Hilbert space, basis vectors; scalar product, operators, dyadic product, projection operator, Hermitian operator, turn-over rule, unitary operator, eigenvalue problem, Hamilton operator; - Definition of the term *ab initio*, goals; advantages; size-extensivity, approximations involved; limitations, classification; difference between empirical, semiempirical, and nonempirical methods; What is calculated? Comparison with experimental measurements; acronyms; units; conventions; history

### 2. The independent particle model

Born-Oppenheimer approximation, single determinant wavefunction, what is an orbital? spin orbitals and space orbitals; Variational principle, Hartree product; antisymmetry principle, Slater determinant; matrix elements for Slater determinants; Slater-Condon rules, exchange and Coulomb operator, Fock operator, Hartree-Fock equations; canonical form, orbital energy, separation of spin, energy for closed-shell system, restricted HF (RHF), LCAO approach; basis functions, metric of a non-orthogonal basis, overlap integrals, Fock matrix, Roothaan-Hall equations, energy expressions, density matrix

### 3. What is needed for a Hartree-Fock (HF) calculation?

Flow chart for *ab initio* calculations; input; choice of the coordinates; Cartesian and internal coordinates, z-matrix formalism; dummy atoms; puckering coordinates; determination of symmetry, number of independent internal coordinates, molecular framework group, what *ab initio* programs are available? How to get them; how to use them?

### 4. The basis functions

Building-block principle, H-type functions and H-type orbitals; Slater-type functions and Slater-type orbitals; the exponent zeta; diffuse and compact basis functions, Slater rules; Gaussian-type functions and Gaussian-type orbitals, cusp problem, energy of the H atom; difference between STFs and GTFs, Cartesian Gaussians; advantages and disadvantages; first order and second order GTF, Gaussian lobe functions;

### 5. The basis set

Minimal zeta basis; double zeta basis; choice of the exponent, split valence basis, extended basis sets; isotropic limit, HF limit, augmented basis sets; hidden variables; floating functions; bond functions; polarisation functions (p, d, f, g, h, i); radial and angular polarization, notation for augmented basis sets, weight, size, and position of a basis function, uncontracted and contracted basis sets; contraction criteria; segmented and generalized contraction, the scaling theorem; notation; Huzinaga-Dunning basis sets; Pople basis sets; shell constraints; addition of diffuse functions; even-tempered basis sets, basis sets for special molecular properties,

## 6. Calculation of integrals

Single bar and double bar integrals, physical and chemical notation of integrals; number of integrals; shell structure; one-electron integrals; overlap integrals, Cartesian Gaussian functions, spherical Gaussians, transformation from cartesian to spherical Gaussians, Gaussian product theorem, Laplace transform of  $r_{12}^{-1}$ , incomplete Gamma functions, shift of angular momentum, differentiation of Gaussian functions, recurrence relationships, Cartesian Hermite Gaussian-type functions, translational invariance, Gaussian Quadrature, two-electron repulsion integrals (ERIs), prescreening of ERIs, McMurchie-Davidson scheme, Dupuis-King-Rys scheme, Rys polynomials, Pople-Hehre scheme, exponent sharing, PRISM algorithm, contraction and scaling, Resolution of the identity (RI) method, canonical ordering, sequential and random storing, batch processing, packing and unpacking of ERI labels, synchronous/asynchronous IO, buffering of ERIs

## 7. Solution of the Self-Consistent Field (SCF) problem

Conventional Roothaan-Hall SCF, the trial and error method, iterative solution of the Roothaan-Hall equations, initial guess, diagonalization of the core hamiltonian, extended Hückel type guess, INDO and MNDO guess, guess from atomic densities, basis set expansion, solution of the pseudo-eigenvalue problem, canonical orthonormalization, spectral form of S, Schmidt orthonormalization, symmetric orthonormalization, density matrices, projector idempotency constraint, Jacobi diagonalization, Givens-Householder diagonalization, stationary state conditions (with regard to orbitals and basis functions), unitary transformation of MOs, mixing of occupied and virtual orbitals, orbital rotation, energy gradient with regard to expansion coefficients, Brillouin theorem, construction of the Fock matrix, permutational symmetry of ERIs, supermatrix formalism, Raffanetti ordering, timings for construction of the F matrix

## 8. Convergence of SCF calculations

Convergence criteria for SCF, convergence problems, oscillations, state switching, divergence, counteractions, convergence acceleration, state loyalty, univariate search methods, Fock matrix partitioning, pseudocanonical orbitals,  $\lambda$ -dependent form of F, mixing coefficient, energy gradient with regard to  $\lambda$ , Bessel equation, overlap of spinorbitals, Camp-King method, unitary transformation by an exponential matrix, diagonalization of a rectangular matrix, orbital rotation, extrapolation methods, Hartree damping, dynamic damping, 3-point extrapolation, Aitken  $\delta^2$  method, 4-point extrapolation, level shifting, starting and termination strategies, Pulay's DIIS, linear dependence of changes in F and P, errors in P and stationary state conditions, ADEM-DIOS, QC-SCF, linear convergence, quadratic convergence, orbital mixing expressed by a CI formalism, Newton-Raphson formulation of the SCF problem,

## 9. SCF for open shell cases

Different open shell cases, generalized Brillouin theorem, generalized HF equations, coupling terms, generalized Roothaan-Hall equations, partitioned HF (PHF); ROHF according to Roothaan; the McWeeny method for ROHF; unrestricted HF (UHF); Pople-Nesbet equations; properties of the UHF energy; dissociation problem by RHF and UHF; UHF wave function; the expectation value of  $S^2$ ; spin contamination; spin projection methods; UHF electron and spin densities;

## 10. General HF Theory

Complex GHF, real GHF, complex UHF, real UHF, complex RHF, real RHF, form of general spinorbitals, possible constraints, internal and external stability, stability test, form of the Hessian, symmetry dilemma of UHF, singlet instability, non-singlet instabilities, complex HF, the  $O_2$  molecule, complex orbitals vs. real orbitals, complex Fock matrix, complex HF equations, eigenvalues for the complex problem, flow chart diagram,

## 11. Direct SCF methods for large molecules

$M^4$ -myth, number of ERIs for large molecules, storage problem, recalculation of ERIS; prescreening of two-electron integrals; batch processing, recurrence formula for the Fock

matrix; cost for an ERI in dependence of  $l$ , selective storage of integrals; minimization of errors; changes in the number of ERIs per iteration step

## 6. Student Responsibilities:

- a) Students have to attend each lecture and actively participate in them.
- b) Students have to hand in homework for each hour and present their reading tasks in short oral or written summaries.
- c) In addition to the final exam, there will be 4 quizzes, one after each second or third chapter. Students have to pass quizzes and exams to pass the course. Questions regarding grades should be brought to the instructor's attention within 2 days after receiving back the quiz or the exam.

## 7. Final Examination: Spring 2011, TBD

## 8. Grading Procedures:

Final grades will be calculated according to the following scheme:

Final exam	30%
Quizzes	30%
Homework	30%
Special assignments	10%

Grading Table	A	100 – 90 %
	B	89 – 80 %
	C	79 – 70 %
	D	69 - 60 %
	F	59% and below

## 9. Statement of Honor Code:

All SMU Dedman College students are bound by the honor code. The applicable section of the code reads: "All academic work undertaken at the University shall be subject to the guidelines of the Honor Code. Any giving or receiving of aid on academic work submitted for evaluation, without the express consent of the instructor, or the toleration of such action shall constitute a breach of the Honor Code." A violation of the Code can result in an F for the course and an Honor Code Violation recorded on a student's transcript. Academic dishonesty includes plagiarism, cheating, academic sabotage, facilitating academic dishonesty and fabrication. Plagiarism is prohibited in all papers, projects, take-home exams or any other assignments in which the student submits another's work as being his or her own. Cheating is defined as intentionally using or attempting to use unauthorized materials, information or study aids in any academic exercise. Academic sabotage is defined as intentionally taking any action, which negatively affects the academic work of another student. Facilitating academic dishonesty is defined as intentionally or knowingly helping or attempting to help another to violate any provision of the Honor Code. Fabrication is defined as intentional and unauthorized falsification or invention of any information or citation in an academic exercise.

## 10. Disability Accommodations:

Students needing academic accommodations for a disability must first contact Ms. Rebecca Marin, Director, Services for Students with Disabilities (214-768-4557) to verify the disability and establish eligibility for accommodations. They should then schedule an appointment with the professor to make appropriate arrangements.

**11. Religious Observance:**

Religiously observant students wishing to be absent on holidays that require missing class should notify their professors in writing at the beginning of the semester, and should discuss with them, in advance, acceptable ways of making up any work missed because of the absence.

**12. Excused Absences for University Extracurricular Activities:**

Students participating in an officially sanctioned, scheduled University extracurricular activity should be given the opportunity to make up class assignments or other graded assignments missed as a result of their participation. It is the responsibility of the student to make arrangements with the instructor prior to any missed scheduled examination or other missed assignment for making up the work.

**13. Assessment:**

In accordance with University regulations copies of student work may be retained to assess how the learning objectives of the course are being met.

**14. Course Schedule**

Will be discussed in the first meeting and adjusted, as far as possible, to the student needs.