University of California, Berkeley
Professional Masters in Molecular Simulation and Software Engineering Online Degree

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Numerical Algorithms applied to Computational Quantum Chemistry
Chemistry 279, 3 Units / 15 week version.
Fall 2021.

Course description: An introduction to numerical algorithms, their application to computational quantum chemistry, and best practices for software implementation, and reuse. This course covers a toolbox of useful algorithms from applied mathematics that are used in physical simulations. They are illustrated via computer implementation of density functional theory for modeling chemical reaction mechanisms from quantum mechanics. Topics covered include local optimization, numerical derivatives and numerical integration, dense linear algebra the symmetric eigenvalue problem, the singular value decomposition, and the fast Fourier transform. More specialized topics as time permits. Students are guided through principles of procedural and object-oriented programming in C++, as well as usage of efficient numerical libraries.

Contribution of this course to the broader curricular objectives: Required course for all MSSE students.

Course format: Three 50 minute lectures of faculty led web-based instruction per week, and 3 hours of GSI-led, web-based discussions per week (split into a 2 hour computing lab and 1 hour of synchronous discussion) to complete the course in 15 weeks. Structured asynchronous graded discussion groups will expand on the lecture material and readings. Students will be given deadlines to make their individual posts and then reply to peer postings for each week's readings. All students will be required to participate. GSIs will also go over homework assignments and practice exercises that are quantitative, prepare students for their homework assignments and post answer guides to homework assignments after they are submitted, and provide detailed guidance and feedback about the final project (done over the last 5 weeks). Outside class work should comprise 3 hours a week, for a total of 9 hours per week.

Reading List and Resources:
Numerical Recipes: The Art of Scientific Computing, W.H. Press, S.A. Teukolsky, W.T. Vetterling, and B.P. Flannerty (3rd edition, Cambridge Univ. Press, 2007)
Introduction to Computational Chemistry, F.H. Jensen (3rd edition, Wiley, 2017).

Grading: There will be 7 well-staged programming assignments.

Prerequisites: the students will have had MSSE courses (1) C275A Intro to Programming, (2) C275B Software Best Practices, and (3) DS100 courses. In addition, undergraduate physical chemistry or permission of instructor is required.

Course requirements: Each student is required to view all of the online lectures, do all the online quizzes, submit all homework assignments, and discussion postings for grading. A laptop, workstation, or access to a LINUX account is required, as is installation of open source C++ development environment and libraries.

Office hours: The instructor will be available 1 hours per week for one on one consultation by appointment. The GSIs will be available 5 hours a week. These synchronous office hours will be posted on the course website. The instructor will also be available for synchronous open class discussion one hour per week. These will be archived and available to students.

Learning objectives for this course:
1. To introduce computer-based physical simulation via computational quantum chemistry.
2. To develop the core numerical algorithms needed to efficiently implement computational quantum chemistry methods, as well as other physical simulations.
3. To reinforce programming skills directed to sustainable software as well as intelligent use of optimized libraries to implement numerical kernels.

Detailed Course Syllabus and Schedule:

Week 1: Introduction to density functional theory (DFT). DFT as a theory of the many-electron problem via the Hohenberg-Kohn theorems. Thomas-Fermi theory. The kinetic energy problem and the Kohn-Sham equations.

Week 2: Numerical aspects of DFT: Local spin density approximation (LSDA) as the simplest possible functional. Sketch of the numerical steps involved in solving the Kohn-Sham equations as a roadmap to the rest of the course: operator matrix evaluation, exchange correlation quadrature, linear algebra, optimization, etc.

Week 3: Chemical aspects of DFT: DFT from an applications perspective, including the spectral approximation and basis sets, evaluation of nuclear forces to walk on potential energy surfaces, and classes of density functionals from simple to complicated. Examples of DFT calculations to solve chemical problems.

Week 4: Local optimization theory: Introduction to local optimization methods, using function evaluations only, and using gradients. Steepest descent, quasi-Newton and Newton methods. Application to molecular geometry optimization to find equilibrium structures and transition structures. Application to minimizing the DFT energy with respect to orbital variations.

Week 5: Numerical and analytical derivatives. Numerical differentiation via finite differences. Truncation error analysis. Application to force evaluation via energies. Analytical gradient theory. Evaluation of vibrational frequencies using analytic gradients.

Week 6: Numerical integration: Integrating functions in 1 dimension. Use of uniform grids versus adaptive quadrature. Generalization to 3 dimensions, using uniform grids.

Week 7: Numerical integration in DFT. Uniform grids versus atom-centered grids for integrating the exchange-correlation functional. Analytic derivatives of numerically integrated functions. Application to optimizing the DFT energy and DFT forces. Analytical evaluation of matrix elements over Gaussian basis functions for Coulomb and exchange integrals.

Week 8: Dense numerical linear algebra. Some considerations regarding efficient matrix multiplication vs matrix-vector multiplies. Solving dense linear equations by direct methods.

Week 9: Matrix decompositions. The symmetric eigenvalue problem, and efficient direct algorithms such as QR factorization. Application of the symmetric eigenvalue problem to updating the orbitals in DFT. Singular value decomposition and examples applications such as finding the corresponding orbitals.

Week 10: Fourier series and Fourier transforms. Basic theory and connections to periodic systems (real space vs reciprocal space). The Fast Fourier Transform, and efficient libraries that implement the FFT.

Week 11: DFT for periodic systems. Use of the FFT to evaluate Coulomb interactions in DFT. An overview of DFT for periodic systems such as crystals and solid surfaces. Bloch theorem, and band structure. Gamma point calculations and large unit cells.

Week 12,13: (Special topics) Methods to solve non-linear equations. Generalized Newton method. Generalized quasi-Newton methods, such as direct inversion in the iterative subspace (DIIS). Application to accelerating the iterative self-consistent field problem in DFT. Solving for saddle points of the SCF energy as a method to evaluate excited states. Algorithms for minimizing to saddle points such as square gradient minimization and the maximum overlap method.

Week 13,14: (Special topics) Iterative linear algebra for very large systems. Linear equations, via repeated matrix-vector multiplication. Pre-conditioning and condition number considerations. Application to the evaluation of the DFT hessian as required for analytical frequency calculations. Iterative eigensolvers for the lowest few eigenvalues of very large matrices. Application to electronic excited states.