Introduction to Electronic Structure Methods

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Chapter 1

Introduction to computational quantum chemistry

Computational quantum chemistry is a branch of theoretical chemistry whose major goal is to create efficient mathematical approximations and computer programs to calculate the properties of molecules such as their total energy, dipole and quadrupole moments, potential energy (free energy) surfaces, vibrational frequencies, excitation energies and other diverse spectroscopic quantities, reactivity behavior, the involved reaction mechanism and reaction dynamics. The term is also sometimes used to cover the areas of overlap between computer science and chemistry.

Theoretical vs. computational chemistry. The term theoretical chemistry may be defined as a mathematical description of chemistry, whereas computational chemistry is usually used when a mathematical method is sufficiently well developed that it can be automated for implementation on a computer. Note that the word exact does not appear here, as very few aspects of chemistry can be computed exactly. Almost every aspect of chemistry, however, can be and has been described in a qualitative or approximate quantitative computational scheme.

Accuracy vs. efficiency. It is, in principle, possible to use a very accurate method and apply it to all molecules. Although such methods are well-known and available in many computer programs, the computational cost of their use grows exponentially with the number of electrons. Therefore, a great number of approximate methods strive to achieve the best trade-off between accuracy and computational cost. Present computational chemistry can routinely and very accurately calculate the properties of molecules that contain no more than 40-50 electrons. The treatment of molecules that contain up to 1’000 electrons or more is computationally tractable by some relatively accurate methods like Density Functional Theory (DFT).

The main target of this course is to introduce the basic notions
of computational quantum chemistry, which allow to explore the properties of molecular systems to understand chemical and biochemical reaction mechanisms and predict and rationalize observations of laboratory experiments. To this end, we will discuss the basic theoretical concepts and approximations of different quantum chemical methods and we learn how to apply them to run calculations on computers.

Computational quantum chemistry methods can provide use with many useful informations. They can for example be applied to:

- compute physical and chemical properties of molecules (structure and dynamics)
- identify correlations between chemical structures and properties
- understand reaction mechanisms and thermodynamic properties
- determine potential energy surfaces and quantum forces on the nuclei to perform \textit{ab initio} molecular dynamics simulations.
- help in the efficient synthesis of compounds
- design molecules that interact in specific ways with other molecules (e.g. drug design)

Quantum chemical methods can also be applied to solid state physics problems. The electronic structure of a crystal is in general described by a band structure, which defines the energies of electron orbitals for each point in the Brillouin zone.

1.1 \textbf{Ab Initio Methods}

The programs used in quantum chemistry are based on different quantum-mechanical methods that solve the molecular Schrödinger equation associated with the molecular Hamiltonian. Methods that do not include empirical or semi-empirical parameters in their equations - are derived directly from theoretical principles, with no inclusion of experimental data - are generally called \textit{ab initio} methods. However, the same term is also used to design theories that are derived from exact quantum mechanical equations but which also assume a certain level of approximation. The approximations made in these cases are usually mathematical in nature, such as using a simpler functional form or getting an approximate solution for a complicated differential equation.
1.1.1 Electronic structure

One of the primary goals of quantum chemical methods is to determine the electronic structure, e.g., the probability distribution of electrons in chemical systems. The electronic structure is determined by solving the Schrödinger equation associated with the electronic molecular Hamiltonian. In this process, the molecular geometry is considered as a fixed parameter. Once the optimal electronic wavefunction is determined, one can access the gradient on each nuclei (as the derivative of the total energy with respect to the positions of the nuclei) and update their positions accordingly until the process reaches convergence. This is how we obtain optimized molecular geometries. Usually the basis set (which is usually built from the LCAO ansatz) used to solve the Schrödinger equation is not complete and does not span the full Hilbert space associated to the system. However, this approximation allows one to treat the Schrödinger equation as a "simple" eigenvalue equation of the electronic molecular Hamiltonian with a discrete set of solutions. The problem of dealing with function (functionals) and operators can be therefore translated into a linear algebra calculation based on energy matrices and state vectors. The obtained eigenvalues are functions of the molecular geometry and describe the potential energy surfaces. Many optimized linear algebra packages have been developed for this purpose (e.g., LAPACK – Linear Algebra PACKage: http://www.netlib.org/lapack).

The most common type of an ab initio electronic structure approach is called the Hartree-Fock (HF) method, in which the Coulombic electron-electron repulsion is taken into account in an averaged way (mean field approximation). This is a variational calculation, therefore the obtained approximate energies, expressed in terms of the system's wavefunction, are always equal to or greater than the exact energy, and tend to a limiting value called the Hartree-Fock limit. Many types of calculations begin with a HF calculation and subsequently correct for the missing electronic correlation. Møller-Plesset perturbation theory (MP) and Coupled Cluster (CC) are examples of such methods.

An alternative stochastic approach is Quantum Monte Carlo (QMC), in its variational, diffusion, and Green’s functions flavors. These methods work with an explicitly correlated wavefunction and evaluate integrals numerically using a Monte Carlo integration. Such calculations can be very time consuming, but they are probably the most accurate methods known today.

Density Functional Theory (DFT) methods are often considered to be ab initio methods for determining the molecular electronic structure, even though one utilizes functionals usually derived from empirical data, properties of the electron gas, calculations on rare gases or more complex higher level approaches. In DFT, the total energy is expressed in terms of the total electron density, rather than the wavefunction.

The Kohn-Sham formulation of DFT introduces a set of non-interacting fictitious molecular orbitals, which makes the chemical interpretation of DFT
simpler, even though their nature is different from the real-HF ones. In addition, KS based DFT has the advantage to be easily translated into an efficient computer code.

The most popular classes of ab initio electronic structure methods are:

- Hartree-Fock
- Generalized Valence Bond
- Møller-Plesset Perturbation Theory
- Multi-Configurations Self Consistent Field (MCSCF)
- Configuration Interaction
- Multi-Reference Configuration Interaction
- Coupled Cluster
- Quantum Monte Carlo
- Reduced Density Matrix Approaches
- Density functional theory

Ab initio electronic structure methods have the advantage that they can be made to converge systematically to the exact solution (by improving the level of approximation). The convergence, however, is usually not monotonic, and sometimes - for a given property - a less accurate calculation can give a better result (for instance the total energy in the series HF, MP2, MP4, ...).

The drawback of ab initio methods is their cost. They often take enormous amounts of computer time, memory, and disk space. The HF method scales theoretically as $N^4$ ($N$ being the number of basis functions) and correlated calculations often scale much less favorably (correlated DFT calculations being the most efficient of this lot).

### 1.1.2 Quantum dynamics

Once the electronic and nuclear motions are separated (within the Born-Oppenheimer approximation), the wave packet corresponding to the nuclear degrees of freedom can be propagated via the time evolution operator associated with the time-dependent Schrödinger equation (for the full molecular Hamiltonian). The most popular methods for propagating the wave packet associated to the molecular geometry are

- the split operator technique for the time evolution of a phase-space distribution of particles (nuclei) subject to the potential generated by the electrons (Liouville dynamics),
• the Multi-Configuration Time-Dependent Hartree method (MCTDH), which deals with the propagation of nuclear-wavepackets of molecular system evolving on one or several coupled electronic potential energy surfaces.

• Feynman path-integral methods. In this approach the quantum partition function describing the dynamics of \( N \) nuclei is mapped into a classical configurational partition function for a \( N \times P \)-particle system, where \( P \) are discrete points along a cyclic path.

**The semiclassical approach.** In this case one adopts a classical molecular mechanics propagation of the nuclear dynamics (where the equation of motion is given by Newton’s law) combined with any treatment of the time-dependent Schrödinger equation for the electrons. The combination of classical molecular dynamics with an efficient scheme for the computation of the potential energy surface, like for instance DFT, allows for *ab initio* MD simulations of systems of the size of few hundreds of atoms. Non-adiabatic effects\(^1\) can also be introduced by means of the *fewest switches surface hopping* scheme of Tully et. al. or a *mean-field* approximation (Ehrenfest dynamics).

Different numerical schemes for the update of the electronic state at each molecular step are possible

• wavefunction optimization at the new nuclear configuration. This method is often called Born-Oppenheimer Molecular Dynamics (BO MD).

• within DFT, the electronic density can be propagated using the "fictitious" electronic dynamics obtained from the Car-Parrinello extended Lagrangian scheme. In this way one saves the cost of a full wavefunctions optimization at each MD step. The method is referred to as Car Parrinello Molecular Dynamics (CP MD).

• propagation of the electronic wavefunction using an approximate solution of the time-dependent Schrödinger equation. Due to the small mass of the electrons (compared to the one of the nuclei) the time step for the propagation of the electrons is necessary much smaller than the one required for the solution of the Newton’s equations for the ions.

1.2 Semiempirical methods

1.2.1 Electronic structure

The most expensive term in a Hartree-Fock calculation, are the so-called two-electron integrals. Semiempirical methods are based on the HF method

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\(^1\)Non-adiabatic effects describe the quantum phenomena that arise when the dynamics reaches regions in phase space where two or more adiabatic potential energy surfaces are approaching each other.
but the costly two-electrons integrals are approximated by empirical data or omitted completely. In order to correct for this approximation, semiempirical methods introduce additional empirical terms in the Hamiltonian which are weighted by a set of a priori undefined parameters. In a second step, these are fitted in order to reproduce results in best agreement with experimental data.

Semiempirical calculations are much faster than their ab initio counterparts. Their results, however, can be badly wrong if the molecule being computed is not similar enough to the molecules in the database used to parameterize the method.

Semiempirical calculations have been very successful in the description of organic chemistry, where only a few elements are used extensively and molecules are of moderate size.

Semiempirical methods also exist for the calculation of electronically excited states. These methods, such as the Pariser-Parr-Pople (PPP) method, can provide good estimates of the electronic excited states, when parameterized well. Indeed, for many years, the PPP method outperformed ab initio excited state calculations. Large scale ab initio calculations have confirmed many of the approximations of the PPP model and explain why the PPP-like models work so well in spite of its simple formulation.

1.3 Mixed Quantum Mechanical/Molecular mechanical (QM/MM) Methods

The combination of quantum chemical methods (QM) with a classical molecular mechanical (MM) treatment of the environment enables the investigation of larger systems in which the chemical active region (QM) is confined in a localized volume surrounded by MM atoms. This approach is particularly suited for the analysis of enzymatic reactions in proteins.

1.4 Software packages

A number of software packages that are self-sufficient and include many quantum-chemical methods are available. The following is a table (not complete) illustrating the capabilities of various software packages:

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