Supercomputers and Quantum Chemistry

Dalton Tutorial

Patrick Norman
National Supercomputer Centre

Quantum Mechanics

Wave function

A system of N electrons is described by a wave function with $4N$ degrees of freedom

$$\psi = \psi(\mathbf{x}_1, \ldots, \mathbf{x}_N), \tag{1}$$

where $\mathbf{x} = (\mathbf{r}, \omega)$ summons spatial and spin degrees of freedom. The spin of the single electron may be either "up" or "down", often denoted by the functions $\alpha(\omega)$ and $\beta(\omega)$, respectively. The Pauli principle states that the interchange of any two electrons in the wave function should correspond to a sign change.

Energy Levels

The energy levels E_n of a system of bound electrons are discrete and given as eigenvalues to the energy-operator, or the Hamiltonian H (the eigenvalue equation is known as the the time-independent Schrödinger equation)

$$H\psi_n = E_n\psi_n, \tag{2}$$

where, for a molecule with M atomic centra, the Hamiltonian is given by

$$H = \sum_{i=1}^{N} \left[-\frac{1}{2}\nabla_i^2 - \sum_{A=1}^{M} \frac{Z_A}{r_{iA}} \right] + \sum_{i>j} \frac{1}{r_{ij}}. \tag{3}$$

The state corresponding to the lowest energy E_0 is referred to as the ground state ψ_0 and others as excited states. Transitions between states may be induced by absorption and emission of photons, and the study of transitions is known as spectroscopy.

Potential Energy Surfaces

To plot the energy values corresponding to a particular state but for different positions of the atomic nuclei is to generate a so-called *potential energy surface* (PES). The equilibrium structure corresponds to the global minimum of the PES. Thermal energies may ignite walkabouts on the PES and even induce conformational changes. A *chemical reaction* is the passing from one minimum to another on the PES, and the ridge is known as the *transition state*. Proton transfer is one example

$$\mathrm{CH_3O} \longleftrightarrow \mathrm{CH_2OH} \tag{4}$$

Approximate State Theory

Variational State Theory

The expectation value of the Hamiltonian is greater than E_0 for *all* approximate wave functions

$$\langle H \rangle \geq E_0. \tag{5}$$

In approximate state theory, the wave function depends on a set of parameters λ that are varied subjected to the condition that the wave function remains normalized. The *best* representation of the ground state is defined to be given by the wave function $\psi(\lambda_0)$ that minimizes the expectation value of the energy

$$\left.\frac{\partial\langle H\rangle}{\partial\lambda}\right|_{\lambda=\lambda_0} = 0. \tag{6}$$

The Hartree–Fock Approximation

In Hartree–Fock (HF) theory, the N-electron wave function is formed as the determinant of a set of orthogonal single electron wave functions

$$\psi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(\mathbf{x}_1) & \ldots & \psi_N(\mathbf{x}_1) \\ . & & . \\ . & & . \\ . & & . \\ \psi_1(\mathbf{x}_N) & \ldots & \psi_N(\mathbf{x}_N) \end{vmatrix}. \tag{7}$$

Since the interchange of two electrons corresponds to the interchange of two rows in the determinant, the so-called Slater determinant fulfills the Pauli principle. The functions ψ_i are formed as

$$\psi_{2i-1}(\mathbf{x}) = \phi_i(\mathbf{r})\alpha(\omega), \tag{8}$$
$$\psi_{2i}(\mathbf{x}) = \phi_i(\mathbf{r})\beta(\omega), \tag{9}$$

where the $N/2$ spatial functions ϕ_i are known as *molecular orbitals* and can be occupied by two electrons each.

Basis Set

It is common procedure to express the molecular orbital as a linear combination of Gaussian functions that form a basis set

$$\phi(\mathbf{r}) = \sum_{\alpha=1}^{n} c_\alpha g_\alpha(\mathbf{r}). \tag{10}$$

The coefficients c_α are optimized variationally to determine the Hartree–Fock wave function.

Computational Scaling

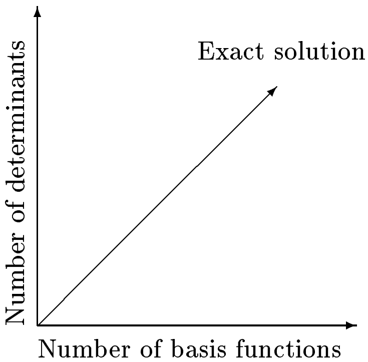
Each time $\langle H \rangle$ is evaluated in the iterative optimization of the HF state in a basis set of n Gaussian functions, there are n^4 so-called two-electron integrals to be evaluated. Beyond small systems, neither memory nor disk storage can be used for the complete set of integrals. The re-evaluation of integrals therefore makes quantum chemical calculations CPU intensive but inexpensive with respect to storage. A two-electron integral is of the form

$$\int g_\alpha(\mathbf{r}_1) g_\beta(\mathbf{r}_1) \frac{1}{r_{12}} g_\gamma(\mathbf{r}_2) g_\delta(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2. \qquad (11)$$

In principle, we desire a complete basis set, but, in practice, we are restricted to a finite number of basis functions.

Post Hartree–Fock Methods

The Hartree–Fock approximation is not always adequate, so a plethora of post HF methods have been developed and we speak about inclusion of *electron correlation* in the calculation. Some methods are based on multi-determinant wave functions.



Much of the beauty of quantum chemistry lies in the fact that there exist a well-defined way to approach the exact solution to Eq. (2).

Iso-density surfaces

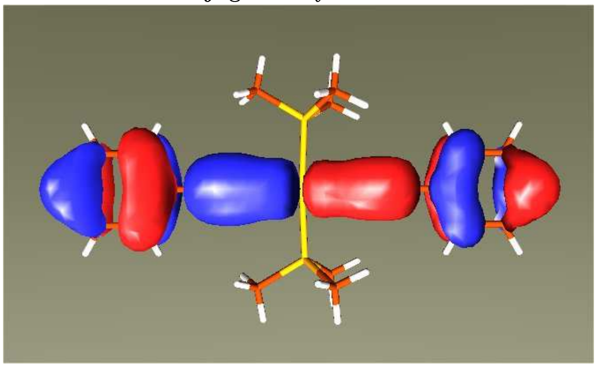
Knowledge of the distribution of electrons in the molecule is important in order to rationalize and understand the experiments. Electron mobility is largely connected with charge conjugation, and plots of the electron densities, i.e., the squared modulus of the molecular orbitals, are used in this context, see Figure 1 for an illustration.

Laboration

The goal in this exercise is to find the equilibrium structure and the hydrogen bond dissociation energy of water. We will use the quantum chemical program Dalton[1].

[1] http://www.kjemi.uio.no/software/dalton/dalton.html

Figure 1: The highest-occupied molecular orbital (HOMO) in an organometallic molecule. Platinum is the center atom which is electronically well connected to the conjugated hydrocarbon backbone.



Monolith access

The laboration will be run on Monolith[2], you get access with secure shell to `k_dalton@monolith.nsc.liu.se` and password `lcsc2003`.

Dalton execution

Create the two input files, e.g., `hf.dal` and `h2o.mol`. Execute Dalton with the command

```
/usr/local/chem/dalton/dalton -t /var/tmp/ hf h2o
```

The output is found in the file `hf_h2o.out` after the calculation is finished.

Exercises

We will do selected exercises in a more extensive laboration course[3]. Use the course homepage to access the laboration pamphlet. Start on exercise 1 on page 16, and continue with exercises 3–6 if time permits.

Results

My best estimate for the selected properties of water are

Property	My result	Experiment
O–H bond length		0.957 Å
H–O–H bond angle		104.5°
H dissociation energy		9.5 eV

[2] http://www.nsc.liu.se/systems/monolith/
[3] http://www.ifm.liu.se/~panor/courses/Kvantkemi/