Overview of Modern Quantum Chemistry

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$$\hat{H}\Psi(x) = E\Psi(x)$$
, or to be precise $\hat{H}\Psi(x, t) = i\hbar \frac{\partial \Psi(x, t)}{\partial t}$
The Hamiltonian \hat{H} is pretty simple - kinetic motion and Coulomb interactions.
Quantum mechanics:

- Scale of atomic distances, energies and velocities
- It can describe atoms and molecules

- DFT is not the primarily topic of this school
- It is a nice idea, since wavefunction contains more information than needed
- Does universal exist?
- What will happened if tomorrow it will be discovered? Nothing. The complexity of the equations will return to the complexity of SE.
- Using DFT it is easier introduce approximations, but the problem here these approximations do not correspond to physics and there is no way to use them in a controllable way.
- Kohn-Sham DFT (an effective Hamiltonian in the form of Hartree-Fock)

Capability/limitations of different methods

method	parameters	system size	Scaling
MM/MD	pair parametrization	10 000 - 100 000	M^2
Semiempirical	atomic parametrization	1000 - 5000	$M^2 - M^4$
HF	parameter free	400 - 800	N^2-N^4
pure DFT	hidden parameters	600 - 1000	N ³
hybrid DFT	3-40 parameters	400 - 800	$N^{3} - N^{4}$
MP2	hidden parameters	400 - 600	N^5
Multiconfigurational CASSCF	parameter "free"	80 - 150	N^7
Coupled Cluster CCSDT	parameter free	10-20	N ⁸
Coupled Cluster CCSDTQ	parameter free	<10	N^{10}
Full CI	parameter free	<10	N!

N= number of orbitals, M= number of atoms

Estimations of a typical system size for each method are subjective!



Every method can give the "right" answer (sometime).

- Variational methods
- Ab initio (different meanings)
- Parameter-free
- Approximate methods
 - Perturbation theory
 - Semiempirical methods
 - Functionals with parameters

$$\Psi(1,2,...,N) = \varphi_1(1)\varphi_2(2)...\varphi_N(N)$$

Permutation property of the wavefunction. Density, $|\Psi|^2$, does not depend on the sign:

$$\Psi(1,2,..,n,..,m,..,N) = -\Psi(1,2,..,m,..,n,..,N)$$

Hartree-Fock wavefunction

$$\Psi(1,2,..,N) = \frac{1}{\sqrt{N!}} \det \begin{vmatrix} \varphi_i(x_1) & \varphi_j(x_1) & \dots & \varphi_n(x_1) \\ \varphi_i(x_2) & \varphi_j(x_2) & \dots & \varphi_n(x_2) \\ \dots & \dots & \dots & \dots \\ \varphi_i(x_n) & \varphi_j(x_n) & \dots & \varphi_n(x_n) \end{vmatrix}$$

We will discuss HF theory later ..

Key points:

- Single configuration (separation of orbitals to occupied and virtual)
- Good for description the ground state
- Well defined equations (unfortunately, analytical solutions exist only for 1D and 2D).

Example of ground and excited states





To compute an area we can use rectangles (note! we can control that we always get a result lower than the actual value!) We can also use Simpson-like method and use a more smooth approximation for the function value. The Simpson method converges faster, but requires additional calculations.

Finally, it is possible to use the Taylor expansion and use one point (value and all derivatives) as a single reference.

- Single reference $\Psi = \sum_{K} C_{K} \Phi_{K}$, Φ_{K} are constructed from the only reference
- Multi- reference $\Psi = \sum_{K} C_{K} \Phi_{K}$, Φ_{K} are fixed
- Multiconfigurational methods $\Psi = \sum_{K} C_{K} \Phi_{K}$

- Active space
- Restricted active space
- Generalized Active space
- Hand-made selection of excitations

- Full CI at limited basis set
- MRCI
- DMRG
- Stochastic Cl
- CAS-DFT

Spin-independent symmetry-adapted molecular orbitals are used. Divide the occupied orbitals into:

Inactive orbitalsAlways doubly occupiedActive orbitalsVarying occupation allowedSecondary orbitalsAlways virtual

The Complete Active Space (CAS) wave function includes all electronic configurations that are consistent with the given overall number of electrons, spin and space symmetry. The CASSCF method: Optimize the CI coefficients and the MO's for a CAS wave function.

Spin-independent symmetry-adapted molecular orbitals are used. Divide the occupied

orbitals into:	Inactive orbitals Ras1 orbitals Ras2 orbitals Ras3 orbitals	Always doubly occupied Max number of holes Varying occupation allowed Max number of electrons	This can be regarded
orbitals into:	Ras2 orbitals Ras3 orbitals	Varying occupation allowed Max number of electrons	I his can be regard

as a CAS with the additional possibility to excite out of some doubly occupied orbitals and into some virtual orbitals.

Note that RASSCF strictly speaking is not size consistent method, but the error is small

CASSCF: 12e/12o - laptop CASSCF: 14e/14e - desktop CASSCF: 16e/16e - supercomputer CASSCF: 18e/18o - only with symmetry RASSCF: 20/4/20 desktop size

How far CASSCF from Full CI?



19/21

CASPT2 is not a parameter-free method. The choice of zero-order Hamiltonian, IPEA-shift, selection of frozen orbitals, etc.

There are many alternative ways to correct dynamic correlation:

- XMS-CASPT2
- NEVPT2
- XMCQDPT2

