The State of Computational Quantum Chemistry

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Acknowledgements

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- They showed me the forest and the trees
  - even the mushrooms growing on the forest floor.

Overview of the talk

- Molecule = nuclei + electrons
- Mean-field theory
- Many-body theory
- Density functional theory
- Time dependent theory
- Science: experiment, simulation, theory
- Mission: Impossible?

Message of the talk

There is a lot of

- exciting
- transformative

work to be done for a new generation of scientists and engineers

Molecules = n + e

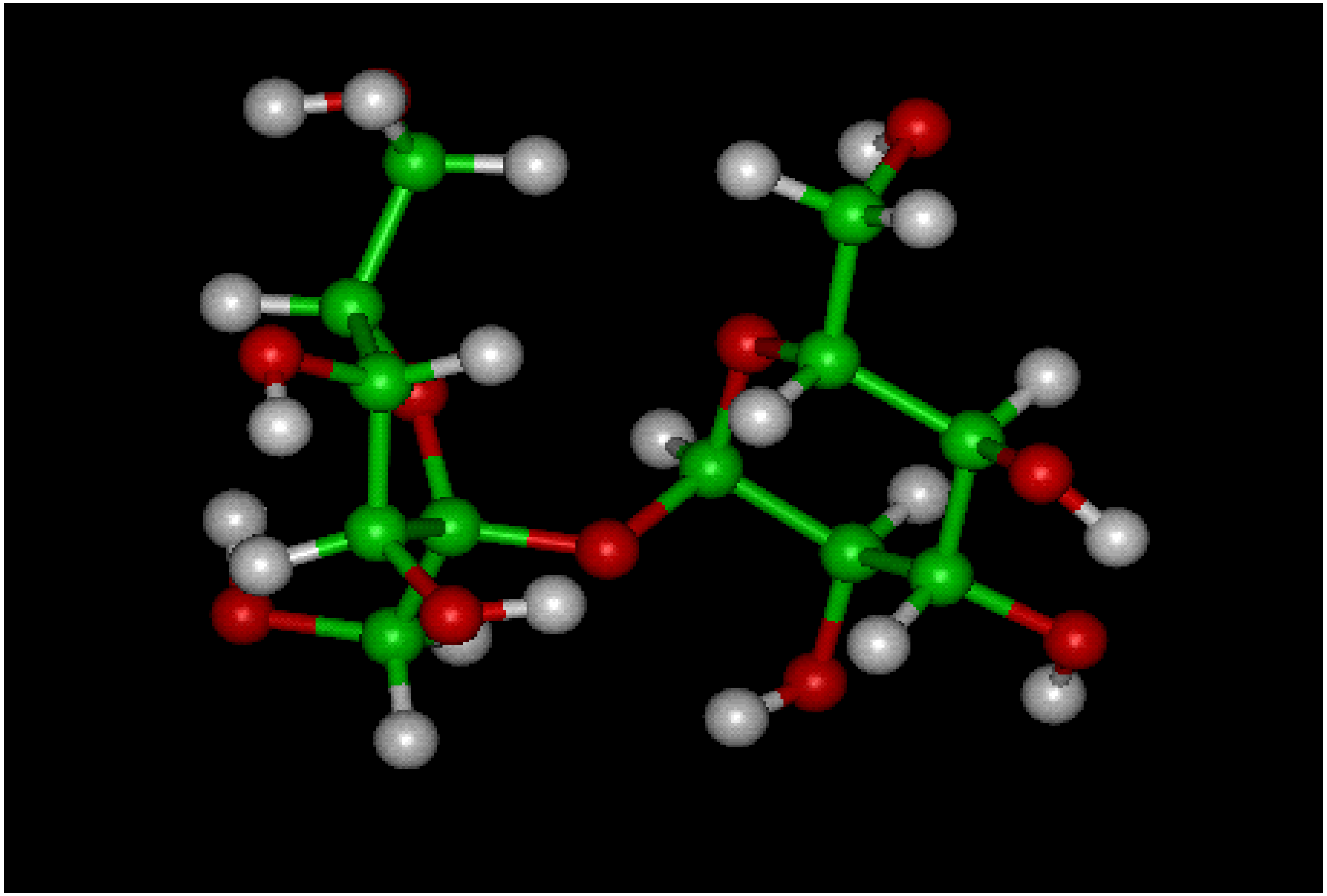
- Atomic nuclei
  - Heavy
    - Hydrogen is 2,000 times heavier than e
  - Atomic charge Z
- Electrons are light and fast
  - 1 a.u. of speed is 1/137th of speed of light

Born-Oppenheimer approximation

- Fix nuclei at molecular geometry
  - $H = T_n + V_{nn} + T_e + V_{NA} + V_{ee}$
- Solve electronic structure/motion first
  - $H_{el} = V_{nn} + T_e + V_{NA} + V_{ee}$
  - $H_{el}\, \varphi(r|R) = V(R)\varphi(r|R)$
- Solve nuclear motion next
  - $(T_n + V(R))\, \chi(R) = E\chi(R)$
- Result wave function $\Psi(r,R) = \chi(R)\varphi(r|R)$

Molecular structure of Sucrose

from www.chemcases.com/olestra/images/sucrose.jpg



Nuclei-electron correlation

- Correlation between nuclei and electrons
  - is **very strong**
  - electrons bunch up close to atomic nuclei
  - BO parameter $\kappa^2=1/\sqrt{M}$ = .02 to .01
  - Non-adiabatic corrections are small
- Diabatic approximation
  - Nuclei and electrons as independent particles
  - is a **poor starting point** for molecules

Mean-field theory

- Electrons have spin
  - – Spin up is α, spin down is β
- Electronic wave function
  - – Independent particle model
  - – Pauli Exclusion Principle
    - Only one electron in every state

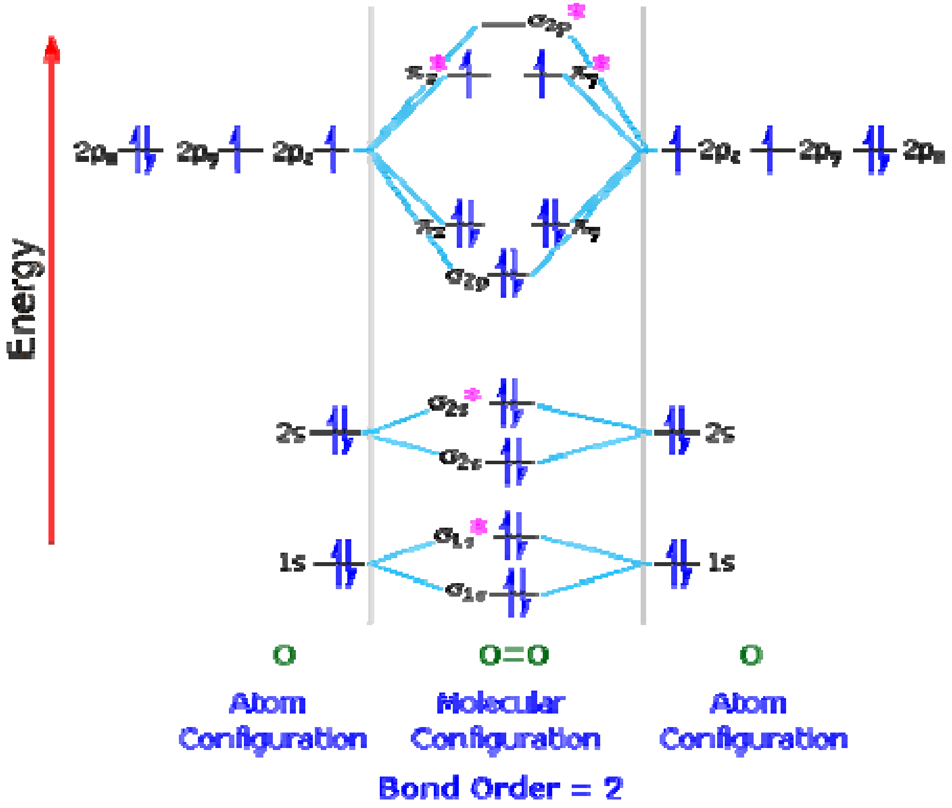
      → $\varphi(r|R)$ antisymmetric

Hartree-Fock theory

- $\varphi(r|R)$ = determinant of spin-orbitals
- Spin-orbitals are solutions of
  - $F\ \psi_i(r) = \varepsilon_i\ \psi_i(r)$
  - ε_i are the spin-orbital energies
  - F is the Fock operator
  - F depends on all occupied $\psi_i(r)$, $i=1,\ldots,N$
- Equation is solved iteratively
  - Self-consistent field (SCF) method

Molecular orbital diagram for O_2

http://infinity.usanethosting.com/Tuition/MolecularOrbitalTheory_OxygenMolecule.gif



Hartree-Fock 2

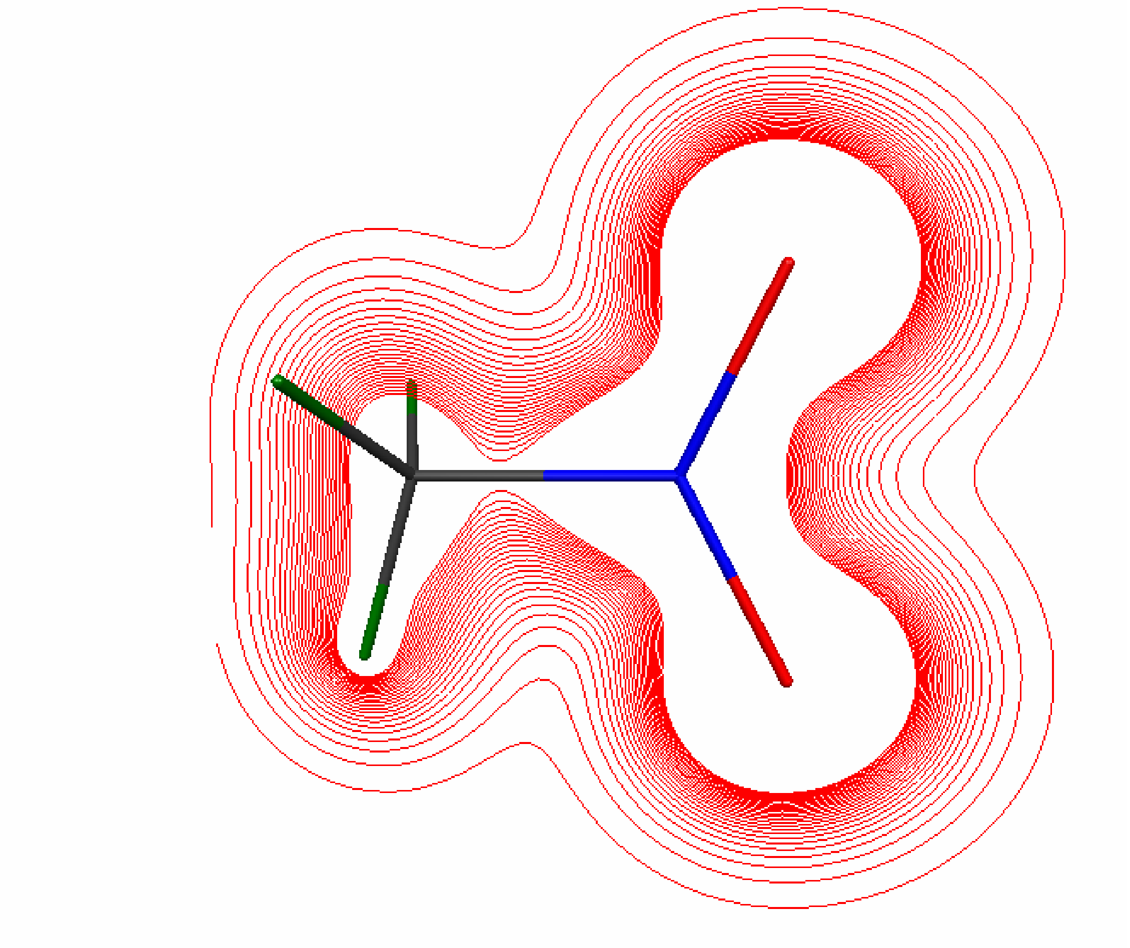
- The wave function φ(r|R)
  - Is invariant under transformations of occupied orbitals
  - This follows from properties of determinants

Restricted Hartree-Fock

- RHF: Uses same spatial function for both spin states
  - Most commonly used
- Unrestricted HF (UHF)
  - Different orbitals for different spins
- Restricted Open-shell HF (ROHF)
  - Same orbitals for core α and β spin-orbitals
  - Different orbitals for unmatched α spins

HF electron density for CH_3NO_2

produced by Ann Melnichuk – contour values 0.2



Overview of many-body theory

- Wave function theory
- Density functional theory
- Other theories
- Electronic correlation

Wave function theory

- Many-body (MB) perturbation theory (PT)
  - $H = H_0 + \lambda V$
  - $H_0\ \Psi_{0n} = E_{0n}\ \Psi_{0n}$
  - $\varphi(r|R) = \Psi_{00} + \lambda\Psi_1 + \lambda^2\Psi_2 + \ldots$
  - $E_1 = < \Psi_{00}\ |V|\ \Psi_{00} >$
  - With HF as reference Ψ_{00}
    - first order vanishes
    - Hence MBPT(2) is the first order that matters

Wave function theory 2

- Configuration Interaction (CI)
  - Build configurations from HF reference
  - $\varphi(r|R) = c_0\Psi_0 + c_i^a \Psi_i^a + c_{ij}^{ab} \Psi_{ij}^{ab} + \ldots$
  - Diagonalize the big Hamiltonian super matrix
  - $H\,\varphi(r|R) = E\,\varphi(r|R)$
  - To determine the c's
- The full CI wave function $\varphi(r|R)$
  - Does not depend on the reference orbitals

Wave function theory 3

- Multi-reference theory
  - Multi-configuration self-consistent field (MCSCF)
  - Complete active Space (CAS) MCSCF
  - Multi-reference (MR) CI
  - MR-PT

Wave function theory 4

- Coupled Cluster theory
  - Uses an infinite subsequence of configurations
  - Nonlinear equations must be solve iteratively
  - CCSD(T) considered “best of breed”
    - (T) means perturbative triples
- MR-CC has been formulated
  - Many flavors
  - None completely satisfactory

Wave function theory 5

- R_{12} theory
  - – Adds explicit factors depending on
  - – Inter-electron distance $R_{12}=|r_1 - r_2|$
  - – Like $\exp(-a\ R_{12})$
  - – To the many-electron wave function
- Approximations must be used to evaluate some many-electron integrals
- Improves quality of results a lot

Density Functional Theory

- Determine electron density
  - Include correlation effects
  - Functional is not exactly known
    - Some functionals have empirical content
- Single determinant **representation** of the density
  - Kohn-Sham problem is similar to Hartree-Fock problem
  - Determines energies ε_i and orbitals $\psi_i(r)$

Analytical or numerical?

- Wave function and density
  - Are built with single particle orbitals
  - These can be analytical
    - Expanded in gaussian type orbitals
  - Or numerical
    - Represented on a grid

Other theories

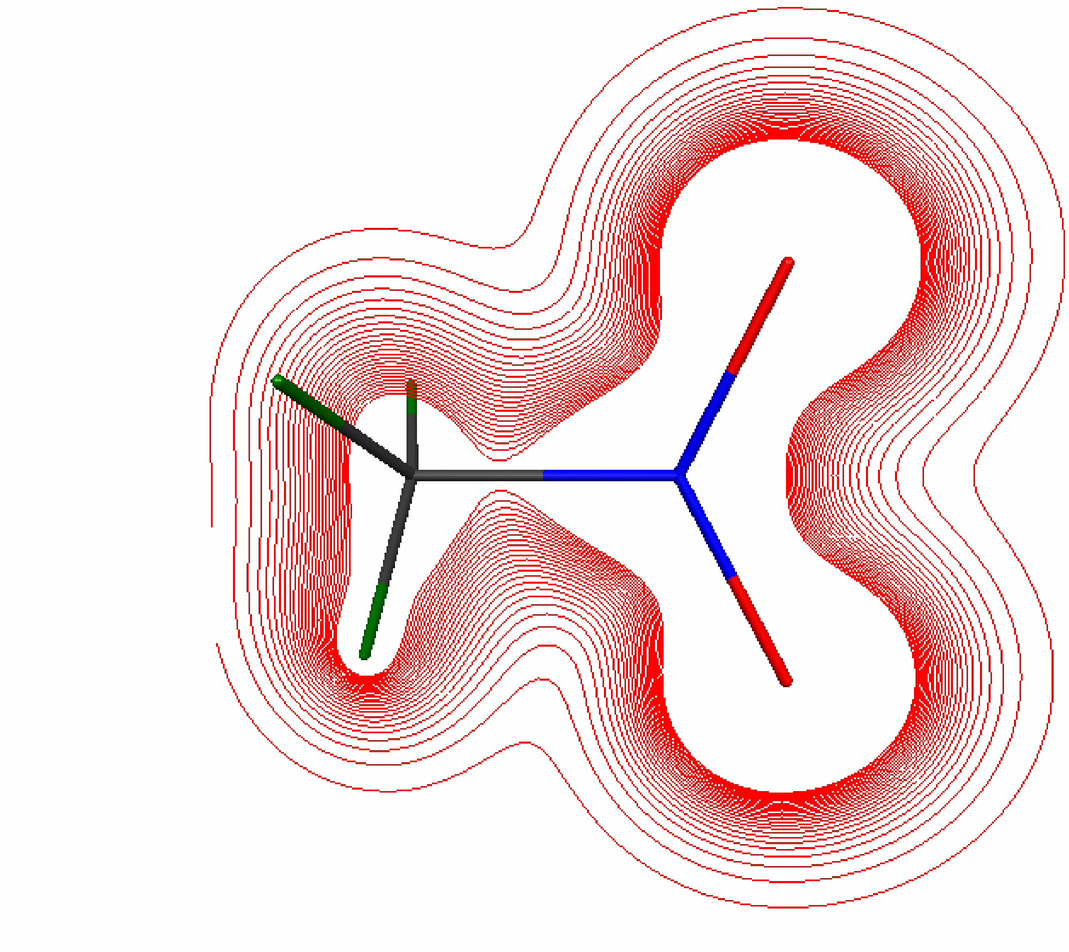
- Quantum Monte-Carlo (MC) methods
  - Previous methods use basis functions
  - Diffusion MC is most successful for quantum chemistry
- Density matrix theory
- Cumulant theory
- Renormalization group theory
- Semi-empirical theories
  - Model Hamiltonians

Density of electrons

- The electronic density $\rho(\mathbf{x})=\rho(x,y,z)$
  - Is dominated by mean field behavior
  - The **difference** between SCF and CCSD densities in the next plot **cannot be seen!**
- DFT
  - Has correlation implicit, not explicit
  - Density looks the same as SCF and CCSD

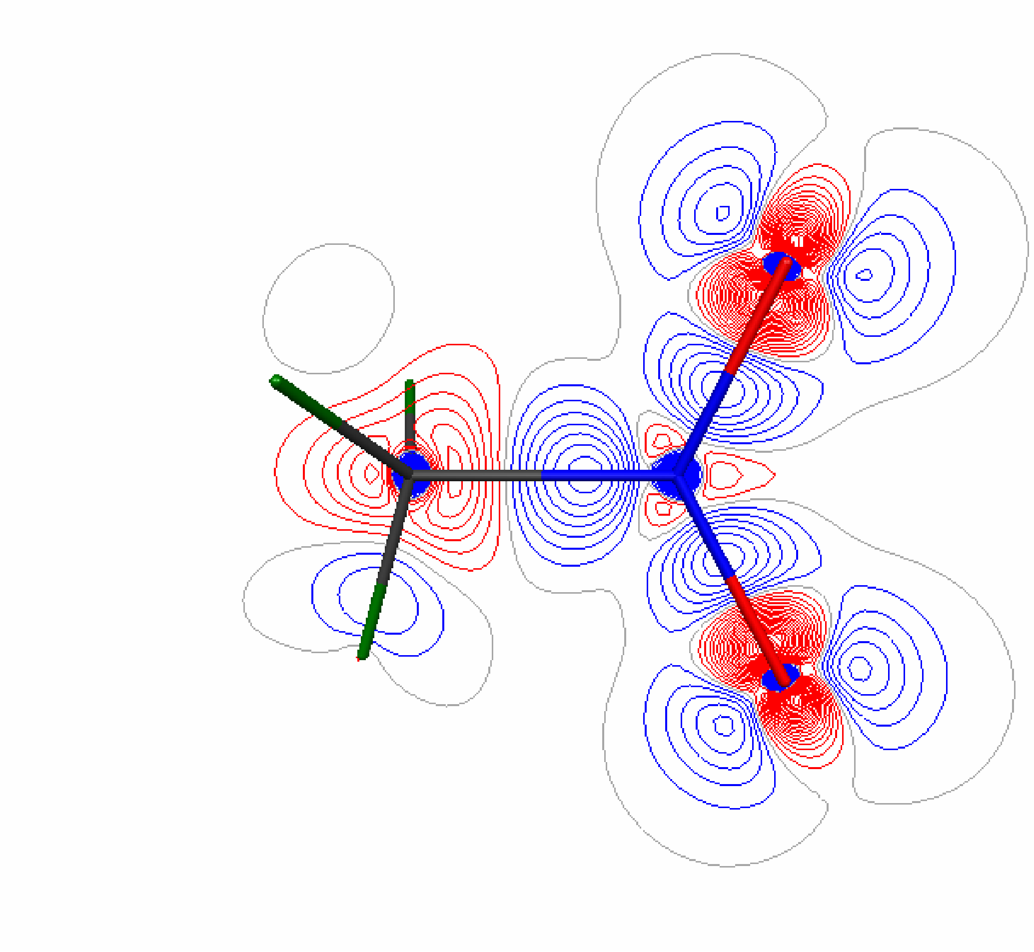
HF electron density for CH_3NO_2

produced by Ann Melnichuk – contour values 0.2



HF-CCSD density diff for CH_3NO_2

produced by Ann Melnichuk- contour values 0.02



Electronic correlation

Classified into three types

- Essential correlation
- Dynamic correlation
- Polarization correlation

Essential correlation

- Describes quantum entanglement effects
- Needs multi-reference wave functions for rapid convergence
- CI, PT and CC often need very high order expansions to describe MR character

Dynamic correlation

- Describes electrons avoiding each other because of Coulomb repulsion
  - inside electron-filled medium
- PT and CC describe this correlation very well
- DFT describes this correlation implicitly
  - Any density functional is consistent with a matching correlation hole

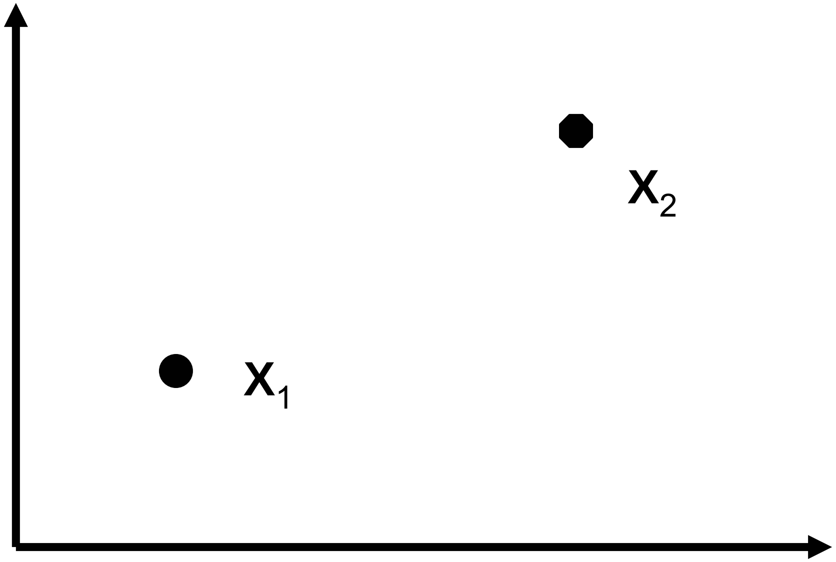
Polarization correlation

- Can be viewed as a special case of dynamic correlation
- Describes electrons avoiding each other because of Coulomb repulsion
  - Through vacuum, as opposed to in bulk
  - Carries across a long distance
  - Creates van der Waals force

Correlation hole

- How to study correlation?
  - two-point function (statistics)
  - two-electron density (quantum mechanics)
    - One density $\rho(\mathbf{x_1})$ shows probability to find an electron at $\mathbf{x}_1$. We can show this in 3D.
    - Two density $\Gamma(\mathbf{x}_1,\mathbf{x}_2)$ shows probability to find one electron at $\mathbf{x}_1$ and another at $\mathbf{x}_2$ at some time
    - To show this, we pick $\mathbf{x}_1$ and plot $\Gamma(\mathbf{x}_1,\mathbf{x}_2)$ as a function of $\mathbf{x}_2$ in 3D.

Correlation hole 2



A two-dimensional cut through a two density or two-point function

One point is the reference point, the other point is the variable

Correlation hole 3

- Hartree wave function (not for electrons)
  - $\Gamma(\mathbf{x}_1,\mathbf{x}_2) = \rho(\mathbf{x}_1)\,\rho(\mathbf{x}_2)$
  - Pure product → no statistical correlation
- HF wave function (anti-symmetric)
  - $\Gamma(\mathbf{x}_1,\mathbf{x}_2)= \rho(\mathbf{x}_1)\,\rho(\mathbf{x}_2) - \gamma(\mathbf{x}_1, \mathbf{x}_2)\,\gamma(\mathbf{x}_2, \mathbf{x}_1)$
  - Involves the one-density matrix $\gamma(\mathbf{x}, \mathbf{x}')$
  - Not a product → statistical correlation
  - Not called correlation in quantum mechanics

Correlation hole 4

- Why is it a hole?
  - Electrons repel each other with the Coulomb force
  - The chance to find electron 2 close to electron 1 is less than to find it some distance away
  - At very large distances the chance goes down again because both electrons are bound in the molecule

Time dependence

- Ab-initio molecular dynamics
  - Newtonian dynamics of nuclei on any ab-initio potential energy surface (PES)
    - including DFT
    - Up to 1,000 atoms
- Quantum molecular dynamics
  - Full quantum mechanical wave packet propagation on PES
    - Limited to 4 or 5 atoms

Time Dependence 2

- Electron Nuclear Dynamics
  - Newtonian dynamics of nuclei
  - With full quantum dynamics of the electrons
    - In a dynamic, complex wave function
      - single determinant
      - multi-configuration CAS
    - Not a stationary state for nuclear geometry
    - Electrons have momentum too
    - 10 to 20 atoms

5 keV impact: H^+ -> $(H_2O)_2$

produced by Olivier Quinet

- Show movies with Windows Media Player in full-screen mode
  - Impact: H++H2Odimer-Q3-3.25.mpg
  - Breakup: H++H2Odimer-Q4-4.02.mpg
  - Published in IJQC 2008

Scientific method

- Experiment and simulation
  - Have become very similar in practice
  - Used to understand complex scientific problems
  - Prepare the problem
  - Validate assumptions
  - Perform experiment/simulation
  - Draw conclusions
  - Repeat

Scientific method 2

- Simulation
  - There is need for reliable and practical estimate of accuracy
- Theory
  - Development of new methods is still needed
  - E. g. known accuracy estimates are
    - Too expensive
    - Too hard to implement

Summary: accomplishments

- Good practical methods exist
  - Electronic density
  - Molecular geometry
  - Vibrations, electronic excitations, molecular dynamics
  - DFT is most useful
    - Correlation hole is implicit
  - Wave functions give correlation details
    - Too expensive

Mission: Impossible?

- Is it all done?
- Did the "old guard" finish all interesting problems?
- Is there anything left that is exciting?

YES! A LOT!

Mission: open problem 1

- Correlation hole
  - Accurate and practical description
  - Base configurations with explicit correlation hole

Mission: open problem 2

- Protein folding
  - Locality in space and time
  - Speed of light limits BO approximation
  - At the speed of light one side of a protein is 1 fs away from the other side
  - Mean field is the wrong starting point
  - Instantaneous force fields miss important physics and are too “bouncy”

Please take on the challenge!