
Electronic Structure Calculations

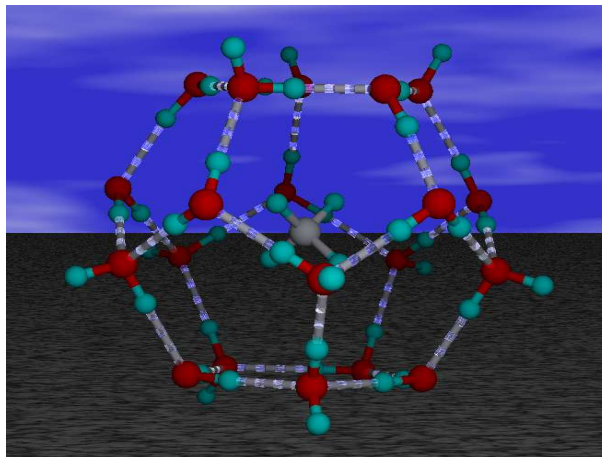
A survey on numerical methods

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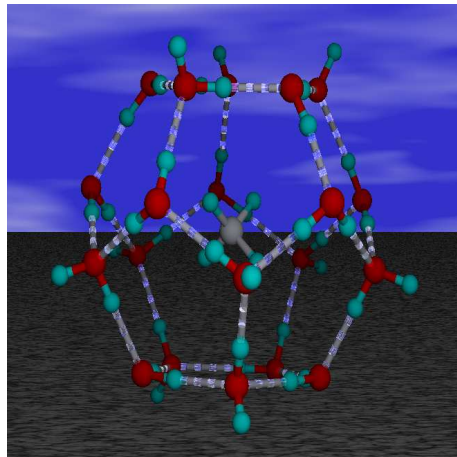
joint with H.J. Flad (MATHEON), and W. Hackbusch, MIS MPG Leipzig



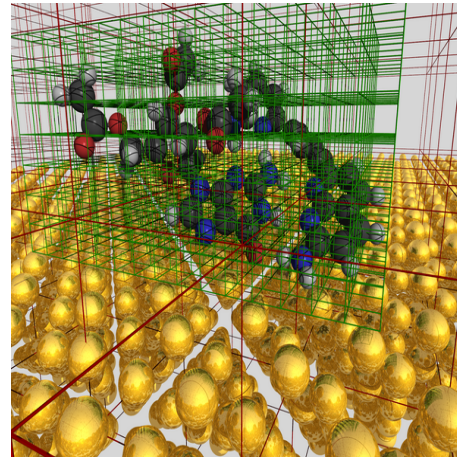
Ab Initio Computation

In future technology we need the computation of **molecular phenomena**: chemistry, molecular biology, semiconductor devices, material science etc.

Ab initio computation is based on **first principles** of quantum mechanics



small systems - high accuracy



large systems restricted accuracy

Stationary Schrödinger equation for *H*-atom Hydrogen

(Schrödinger 1925)

Describes one electron inside an electrical field of a single proton with Coulomb potential $\mathcal{V}(\mathbf{x}) = \frac{1}{|\mathbf{x}|}$.

$$\mathcal{H}\Psi(\mathbf{x}) := (\mathcal{T} + \mathcal{V})\Psi(\mathbf{x}) = \left[-\frac{1}{2}\Delta - \frac{1}{|\mathbf{x}|}\right]\Psi(\mathbf{x}) = E\Psi(\mathbf{x}) \quad , \quad \mathbf{x} \in \mathbb{R}^3$$

(in atomic units)

Eigenvalue problem for a linear 2nd order PDE

Analytical solution has been obtained by Schrödinger 1925.

spin s introduced by Pauli (1926)

Explained (almost): spectral lines of Hydrogen and vaguely quantum (discrete) effects, periodic system, etc.

Generalization to a **single atom** with **nuclear charge Z** centered at $\mathbf{R} = \mathbf{0}$ and **N electrons** (Dirac 1927)

$$\mathcal{H}\Psi = \sum_{i=1}^N \left[-\frac{1}{2}\Delta_i - \frac{Z}{|\mathbf{x}_i|} + \frac{1}{2} \sum_{j \neq i}^N \frac{1}{|\mathbf{x}_i - \mathbf{x}_j|} \right] \Psi = E\Psi$$

where the sought *state-function*

$$\Psi(\mathbf{x}_1, s_1; \dots; \mathbf{x}_N, s_N) \quad , \quad \Psi : \mathbb{R}^{3N} \otimes \mathcal{S}^N \rightarrow \mathbb{C} \quad , \quad \langle \Psi, \Psi \rangle = 1$$

satisfies the **Pauli's antisymmetry principle** (Dirac 1927):

$$\Psi(\mathbf{x}_1, s_1; \dots; \mathbf{x}_i, s_i; \dots; \mathbf{x}_j, s_j; \dots; \mathbf{x}_N, s_N) = -\Psi(\mathbf{x}_1, s_1; \dots; \mathbf{x}_j, s_j; \dots; \mathbf{x}_i, s_i; \dots; \mathbf{x}_N, s_N)$$

Model assumptions: In the sequel, we will neglect **relativistic** and **non-Born Oppenheimer effects** and consider only the **(real valued) stationary electronic Schrödinger equation** in atomic units.

Electronic Schrödinger Equation

- System of N identical non-relativistic particles with spin s_i is described by a *state-function*

$$\Psi(\mathbf{X}_1, \dots, \mathbf{X}_N) = \Psi(\mathbf{x}_1, s_1; \dots; \mathbf{x}_N, s_N) \quad , \quad \Psi : \mathbb{R}^{3N} \otimes \mathcal{S}^N \rightarrow \mathbb{C} \quad , \quad \langle \Psi, \Psi \rangle = 1$$

Pauli's antisymmetry principle:

$$\Psi(\mathbf{x}_1, s_1; \dots; \mathbf{x}_i, s_i; \dots; \mathbf{x}_j, s_j; \dots; \mathbf{x}_N, s_N) = -\Psi(\mathbf{x}_1, s_1; \dots; \mathbf{x}_j, s_j; \dots; \mathbf{x}_i, s_i; \dots; \mathbf{x}_N, s_N)$$

- Ψ satisfies the (stationary) Schrödinger equation with an Hamiltonian \mathcal{H}

$$\mathcal{H}\Psi = E_0\Psi \quad , \quad E_0 = \min_{\langle \Psi, \Psi \rangle = 1} \langle \mathcal{H}\Psi, \Psi \rangle$$

Born-Oppenheimer-approximation: The Hamiltonian \mathcal{H} for N electrons is given by

$$\mathcal{H} = \sum_{i=1}^N \left[-\frac{1}{2} \Delta_i - \sum_{j=1}^M \frac{Z_j}{|\mathbf{x}_i - \mathbf{R}_j|} + \frac{1}{2} \sum_{j \neq i}^N \frac{1}{|\mathbf{x}_i - \mathbf{x}_j|} \right]$$

Input: Z_j - charge of nucleon at position \mathbf{R}_j in atomic units, N number of electrons.

Major interest in **Output**: ground-state energy: Ritz variational principle

$$E_0 = \min_{\langle \Psi, \Psi \rangle = 1} \langle \mathcal{H}\Psi, \Psi \rangle, \quad \Psi = \operatorname{argmin}_{\langle \Psi, \Psi \rangle = 1} \langle \mathcal{H}\Psi, \Psi \rangle$$

Using **Born Oppenheimer energy** $E(\mathbf{R}_1, \dots, \mathbf{R}_N) = E_0(\mathbf{R}_1, \dots, \mathbf{R}_N) + \sum_{k=1}^M \sum_{j < k} \frac{Z_j Z_k}{|\mathbf{R}_j - \mathbf{R}_k|}$, this is the **basis for computing** \rightsquigarrow

Bonding energies, molecule geometries, forces, ionization energies, spectroscopical, electrical, mechanical, optical and thermal properties of molecules and crystals etc..

Dirac 1927: *Quantum Mechanics of Many Electron Systems*

... The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws lead to equations too much too complicated to be soluble.

It therefore becomes desirable that **approximate practical methods of applying quantum mechanics** should be developed, which can lead to an explanation of the main features of complex atomic systems without too much computation.

Is chemistry (and solid state physics) a part of mathematics?

Analytical results (simplified):

- Kato, ... (.. 60..) , energy space: $\Psi \in H^1((\mathbb{R}^3 \times \{\pm \frac{1}{2}\})^N)$.
- HVZ-Theorem (..60..), existence: $-\infty < E_0 < \sigma_{ess}(\mathcal{H})$
- Agmon (.. 70 ..), decay: $\Psi(\mathbf{x}) = O(e^{-a\|\mathbf{x}\|})$ if $\|\mathbf{x}\| \rightarrow \infty$.
- Kato (1957), Thomas - von Ostenhoff et al. (98), cusp-singularities:

$$\Psi(\mathbf{x}) = \phi(\mathbf{x})e^{F(\mathbf{x})},$$

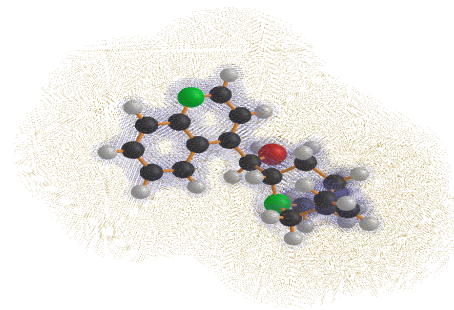
$$\phi \in C^\alpha, \Delta F = \sum_{i=1}^N \left(\sum_{j=1}^M \frac{Z_j}{|\mathbf{x}_i - \mathbf{R}_j|} + \frac{1}{2} \sum_{j \neq i}^N \frac{1}{|\mathbf{x}_i - \mathbf{x}_j|} \right)$$

and analytical outside the set of singularities.

Numerical approximation

- linear problem, but extremely **high-dimensional** + anti-symmetry constraints + **singularities**.
- traditional approximation methods (FEM, Fourier series, polynomials, MRA etc.): approximation error in \mathbb{R}^1 : $\lesssim n^{-s}$, s -regularity \rightsquigarrow , \mathbb{R}^{3N} : $\lesssim n^{-\frac{s}{3N}}$ **curse of dimension**
- Existing deterministic methods are scaling exponentially with N , if convergence is considered.

For large systems $N \gg 1$ the electronic Schrödinger equation seems to be intractable!? Impressive success after 70 years of progress in quantum chemistry was awarded by the Nobel price 1998 in Chemistry: Kohn, Pople



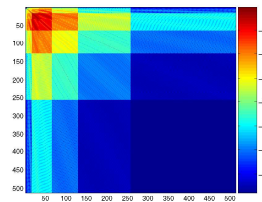
BigDFT discretization for $C_{19}H_{22}N_2O$

In most successful methods replace the original linear problem by a nonlinear problem.

Approximation in \mathbb{R}^d

Due to the *curse of dimension*: $\text{error} \lesssim n^{-\frac{s}{3N}}$. Recently, avoiding the *curse of dimension* is a **major challenge** of modern **Numerical Mathematics** due to computational bottlenecks for many problems: Machine Learning (Data Mining), Computational Finance, PDE's with stochastic data, Multi- scale phenomena etc... *DFG priority program SPP 1324: Extraction of essential information out of complex data*

- **Sparse grid** or **hyperbolic cross approximation**: e.g. Smolyak, Telmyakov, Zenger, Griebel,



- **Tensor product approximation**: e.g. Golub, Beylkin, Mohlenkamp, Hackbusch, Tyrtishnikov

$$f(x_1, \dots, x_d) \approx \sum_{k=0}^r \bigotimes_{i=1}^d f_{i,k}(x_i)$$

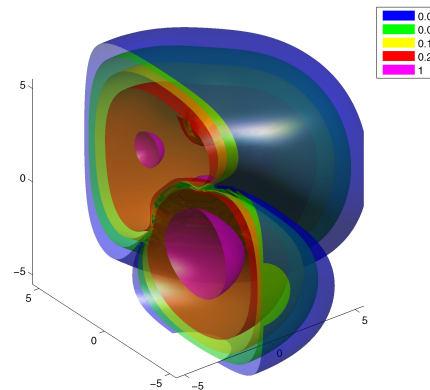
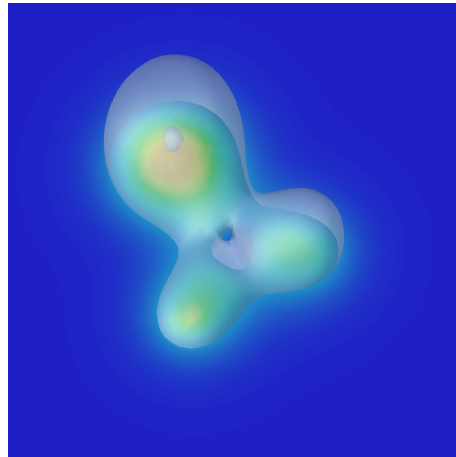
, complexity is $O(dr \dim V_{h,1-D})!!!$

Tensor product approximation of wave functions

Approximation by sums **anti-symmetric** tensor products (**separation of variables**): $\Psi = \sum_{k=1}^{\infty} c_k \Psi_k$

$$\Psi_k(\mathbf{x}_1, s_1, \dots, \mathbf{x}_N, s_N) = \varphi_{1,k} \wedge \dots \wedge \varphi_{N,k} = \frac{1}{\sqrt{N!}} \det(\varphi_{i,k}(\mathbf{x}_j, s_j))_{i,j=1}^N, \quad \langle \varphi_{i,k}, \varphi_{j,k} \rangle = \delta_{i,j}$$

Slater determinant: $\Psi_k = \Psi_k[1, \dots, N]$ is an (anti-symmetric) product of N ortho-normal functions φ_i , $i = 1, \dots, N$ called **spin orbitals** $\varphi_i : \mathbb{R}^3 \times \{\pm \frac{1}{2}\} \rightarrow \mathbb{C}$, $i = 1, \dots, N$.



orbital functions

Hartree Fock approximation

Simplest approximation by one Slater-determinant $\Psi \approx \Psi_{SL} = \Psi_0 = \Psi_{HF}$ minimization of $E_{FH} = \langle \Psi_0, \mathcal{H}\Psi_0 \rangle$

Hartree-Fock (1929,1933) and closed shell model:

$$E_{HF} = J_{HF}(\Phi) = \sum_{i=1}^N \frac{1}{2} \langle \nabla \phi_i, \nabla \phi_i \rangle + \langle \mathcal{V}_{core} \phi_i, \phi_i \rangle + \frac{1}{2} \langle \mathcal{V}_H \phi_i, \phi_i \rangle - \frac{1}{4} \langle \mathcal{W} \phi_i, \phi_i \rangle$$

First order nesc. conditions are

$$\mathcal{F}_\Phi \check{\phi}_i = \lambda_i \check{\phi}_i, \quad \lambda_0 \leq \dots \leq \lambda_i \leq \dots \leq \lambda_N < \lambda_{N+1}$$

with the (Hamilton-) **Fock operator**

$$\mathcal{F} = \mathcal{F}_\Phi = -\frac{1}{2}\Delta + \mathcal{V}_{core} + \mathcal{V}_{H,\Phi} - \frac{1}{2}\mathcal{W}_\Phi$$

With the **Hartree potential** \mathcal{V}_H and the **exchange energy** term $\rho(\mathbf{x}, \mathbf{y}) = \sum_i \phi_i(\mathbf{x})\phi_i(\mathbf{y})$, $n(\mathbf{x}) = \rho(\mathbf{x}, \mathbf{x})$

$$\Delta \mathcal{V}_H(\mathbf{x}) = -4\pi n(\mathbf{x}), \quad \mathcal{W}u(\mathbf{x}) = \int_{\mathbb{R}^3} \frac{\rho(\mathbf{x}, \mathbf{y})}{|\mathbf{x} - \mathbf{y}|} u(\mathbf{y}, s') d\mathbf{y}$$

Existence result if $Z = \sum Z_j \geq N$ Lieb-Simon (1977), P.L. Lions (1998), Lieb, Bach: $E_{HF} \rightarrow E_0$ for $Z \rightarrow \infty$

Effective single particle model

If you don't know the answer, change the problem

The Hartree-Fock model is a prototype for improved approximations e.g. Kohn-Sham equation etc.

Kohn-Hohenberg theorem (1960): **Ground state energy** depends only on the **electron density** $n(\mathbf{x})$

$$J_{KS}(\Phi) = \sum_{i=1}^N \frac{1}{2} \langle \nabla \varphi_i, \nabla \varphi_i \rangle + \langle \mathcal{V}_{core} \varphi_i, \varphi_i \rangle + \frac{1}{2} \langle \mathcal{V}_H \varphi_i, \varphi_i \rangle + \alpha \langle \mathcal{V}_{XC} \varphi_i, \varphi_i \rangle - \beta \frac{1}{4} \langle \mathcal{W} \varphi_i, \varphi_i \rangle$$

Kohn Sham equations (1963), e.g. **closed shell**: each orbital is for a pair of electron with opposite spin

$$\mathcal{H}_{\Phi} \varphi_i = \frac{-1}{2} \Delta \varphi_i + \mathcal{V}_{core} \varphi_i + \mathcal{V}_H \varphi_i + \alpha \mathcal{V}_{XC} \varphi_i - \beta \frac{1}{2} \mathcal{W} \varphi_i = \lambda_i \varphi_i$$

The exchange correlation energy term

$$\mathcal{V}_{XC}(\mathbf{x}) = -C_{TF} n(\mathbf{x})^{1/3} + \dots \text{ correction terms}$$

is not known explicitly!

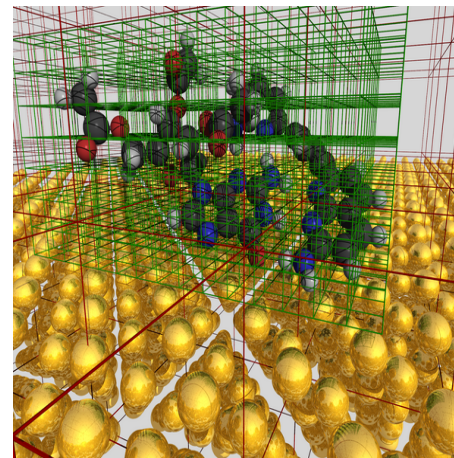
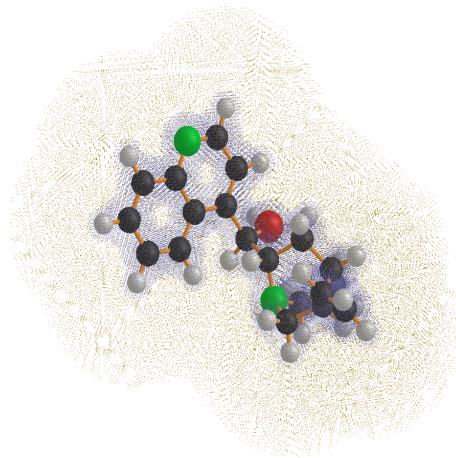
This yields a nonlinear one particle Schrödinger system of eigenvalue type for N functions $\Phi = (\varphi_1, \dots, \varphi_N)$
Complexity (roughly) $O(N^2 \dim V_{h,3-D})$.

But, there remains a **modeling error!!!**, Typically 2-3 digits relative accuracy

Recent Project **BigDFT**: high performance (linear scaling) wavelet code for density functional (DFT) computation of large molecules

http://www-drfmc.cea.fr/sp2m/L_Sim/BigDFT/

included in the newest version of **ABINIT** **ABINIT**: <http://www.abinit.org> (open source software)
($\sim 10^3 - 10^5$ atoms are computable).



Best N-Term Approximation

Consider a Riesz basis $\Psi = (\psi_\lambda)_{\lambda \in I}$ in some Hilbert space H . For $v \in H$, the **error of best n-term approximation**

$$\sigma_{n,H,\Psi}(v) = \min \left\{ \left\| v - \sum_{\lambda \in \mathcal{T}} w_\lambda \psi_\lambda \right\| : w_\lambda \in \mathbb{C}, \mathcal{T} \subset I, \#\mathcal{T} = n \right\}$$

$$A^s(H, \Psi) := \{v \in H : \sigma_{n,H,\Psi}(v) \lesssim n^{-s}\}$$

Theorem: (Hackb., Flad , S. 05, Flad, S., Schulze 07) For $s > 0$ there exists a wavelet basis Ψ of $L_2(\mathbb{R})$, s.t. the orbitals $\varphi_i, i = 1, \dots, N$ satisfy

$$\varphi_i \in A^s(L_2(\mathbb{R}^3), \bigotimes_{i=1}^3 \Psi_i) \quad , \quad \varphi_i \in A^{s-1}(H^1(\mathbb{R}^3), \bigotimes_{i=1}^3 \Psi_i)$$

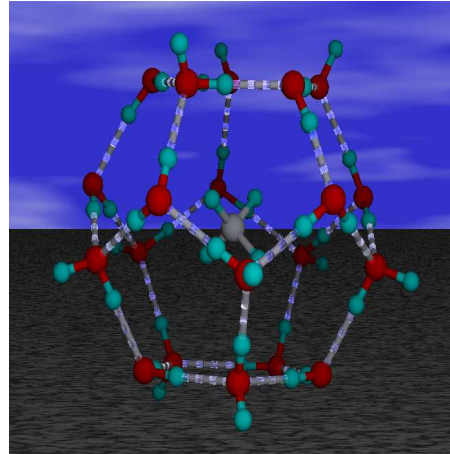
This result can be obtained using *Mellin calculus of pseudo differential operators* together with convergent SCF iteration from Cancès, LesBris, for the nonlinear HF equations. The density matrices ρ satisfy

$$\rho \in A^{s/3}(L_2(\mathbb{R}^6), \Psi_{\mathbb{R}^3} \times \Psi_{\mathbb{R}^3}) \quad , \quad \rho \in A^s((L_2(\mathbb{R}^6), \bigotimes_{i=1}^6 \Psi_i)$$

For all $s > 0, \frac{1}{\tau} = s + \frac{1}{2}$, there holds

$$\varphi_i \in \bigotimes_{i=1}^3 B_{\tau,\tau}^s(\mathbb{R}) \quad , \quad \rho \in \bigotimes_{i=1}^6 B_{\tau,\tau}^s(\mathbb{R})$$

Wave function methods



- Moller Plesset Perturbation Theory
- Configuration Interaction (CI)
- Multi Configuration Self Consistent Field Method (MCSCF)
- Coupled Cluster (CC)
- Density matrix minimization

CI Configuration interaction

Full CI \Leftrightarrow Galerkin method for

$$\mathcal{V}_h = \mathcal{V}_{CI} = \bigwedge_{i=1}^N X_{h,i} = \text{span}\{\Psi_{SL} = \Psi[\mathbf{v}_1, \dots, \mathbf{v}_N]\}, \quad X_h := \text{span} := \{\phi_i : i = 1, \dots, \mathcal{N}\}$$

$$\dim X_h = \mathcal{N}, \quad \dim \mathcal{V}_h = \binom{\mathcal{N}}{N} = \frac{\mathcal{N}!}{N!(\mathcal{N}-N)!} \sim O(\mathcal{N}^N).$$

Galerkin method leads to a linear eigenvalue problem

$$\mathbf{H} = (\langle \Psi_k, \mathcal{H}\Psi_k \rangle), \quad \Psi = c_0 \Psi_0 + \sum c_k \Psi_k, \quad \mathbf{H}\mathbf{c} = E\mathbf{c}, \quad \dim \mathcal{V}_h = \binom{\mathcal{N}}{N}$$

Theorem Let E_0 be a single eigenvalue and $H\Psi = E_0\Psi$ and $E_{0,h}$, $\Psi_h \in \mathcal{V}_h$ the Galerkin solution

$$\|\Psi - \Psi_h\|_{\mathcal{V}} \leq c \inf_{\phi_h \in \mathcal{V}_h} \|\Psi - \phi_h\|_{\mathcal{V}}$$

$$E_{0,h} - E_0 \leq C \inf_{\phi_h \in \mathcal{V}_h} \|\Psi - \phi_h\|_{\mathcal{V}}^2.$$

Since $\dim \mathcal{V}_h = O(\mathcal{N}^N)$, (curse of dimension), the full CI method is infeasible for large N or \mathcal{N} !!!!

Canonical orbitals $\varphi_i, i = 1, \dots, \mathcal{N}$ are eigenfunctions of the discretized Fock operator $\mathcal{F} := \mathcal{F}_h = \sum_{k=1}^N F_k$

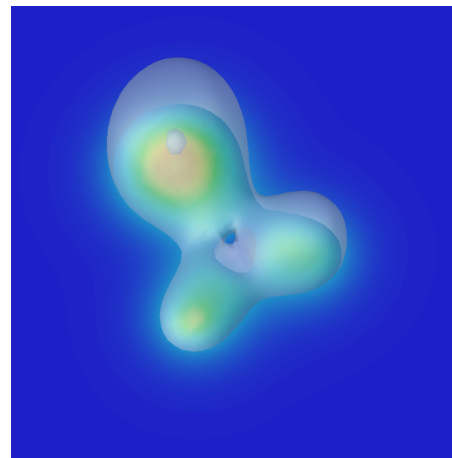
$$F\varphi_i = \lambda_i\varphi_i$$

The first N eigenfunctions φ_i are called **occupied orbitals** the others are called **unoccupied orbitals**

$$\varphi_1, \dots, \varphi_N, \varphi_{N+1}, \dots, \varphi_{\mathcal{N}}$$

Remark: Let $\Psi = \Psi_{SL} = \Psi[\mathbf{v}_1, \dots, \mathbf{v}_N]$ be a Slater determinant of canonical orbitals, then

$$\mathcal{F}\Psi = \varepsilon\Psi, \quad \varepsilon = \sum_{i=1}^N \lambda_{\mathbf{v}_i}$$



orbital

Excitation operators

$$\begin{array}{ll}
 \Psi^2 = X_j^a \Psi^1 & \Psi^1 = \Psi[\dots, \mathbf{v}_i, \mathbf{v}_j, \dots] \\
 \text{single excitations} & \Psi^2 = \Psi[\dots, \mathbf{v}_i, \mathbf{v}_a, \dots] \\
 \Psi^1 = X_{i,j}^{a,b} \Psi^2 & \Psi^1 = \Psi[\dots, \mathbf{v}_i, \mathbf{v}_j, \dots] \\
 \text{double excitations} & \Psi^2 = \Psi[\dots, \mathbf{v}_a, \mathbf{v}_b, \dots] \\
 \text{or higher excitations} & \Psi^2 = \Psi[\dots, \mathbf{v}_a, \mathbf{v}_b, \mathbf{v}_c, \dots] \quad \text{etc. for higher excitations}
 \end{array}$$

Single excitation operator e.g. X_j^a acts on Slater determinants

$$\Psi^2 = X_j^a \Psi^1, \quad \Psi^1 = \Psi[\dots, i, j, \dots], \quad \Psi^2 = \Psi[\dots, i, a, \dots] = X_j^a \Psi^1$$

and $X_j^a := 0$ if the orbital φ_j is not contained in Ψ^1 . General excitation operator:

$$X_\mu := X_{l_1, \dots, l_k}^{b_1, \dots, b_k} = \prod_{i=1}^k X_{l_i}^{b_i}, \quad 1 \leq l_i < l_{i+1} \leq N, \quad N < b_i < b_{i+1}, \quad i = 1, \dots, k \leq N.$$

Decomposition of the Hamilton operator into single particle and two particle operators

$$\mathcal{H} = h + G = \mathcal{F} + U,$$

$$\text{e.g. } h = \sum_{i=1}^N h_i = \sum_{i=1}^N \left(\frac{1}{2} \Delta_i + \sum_{j=1}^M \frac{-Z_j}{|\mathbf{x}_i - \mathbf{R}_j|} \right), \quad G = \sum_i^N \sum_{j>i}^N \frac{1}{\|\mathbf{x}_i - \mathbf{x}_j\|},$$

Slater-Condon Rules — computation of $\langle \Psi^2, H\Psi^1 \rangle$, e.g.

Single particle operators
e.g.: h or Fock operator \mathcal{F}

$$\langle \Psi^2, F\Psi^1 \rangle = 0$$

if $\Psi^2 = X_{i,j}^{a,b}\Psi^1$
or higher excitations

Two particle operators
e.g.: G or fluctuation potential U

$$\langle \Psi^2, U\Psi^1 \rangle = 0$$

if $\Psi^2 = X_{i,j,l}^{a,b,c}\Psi^1$
or higher excitations

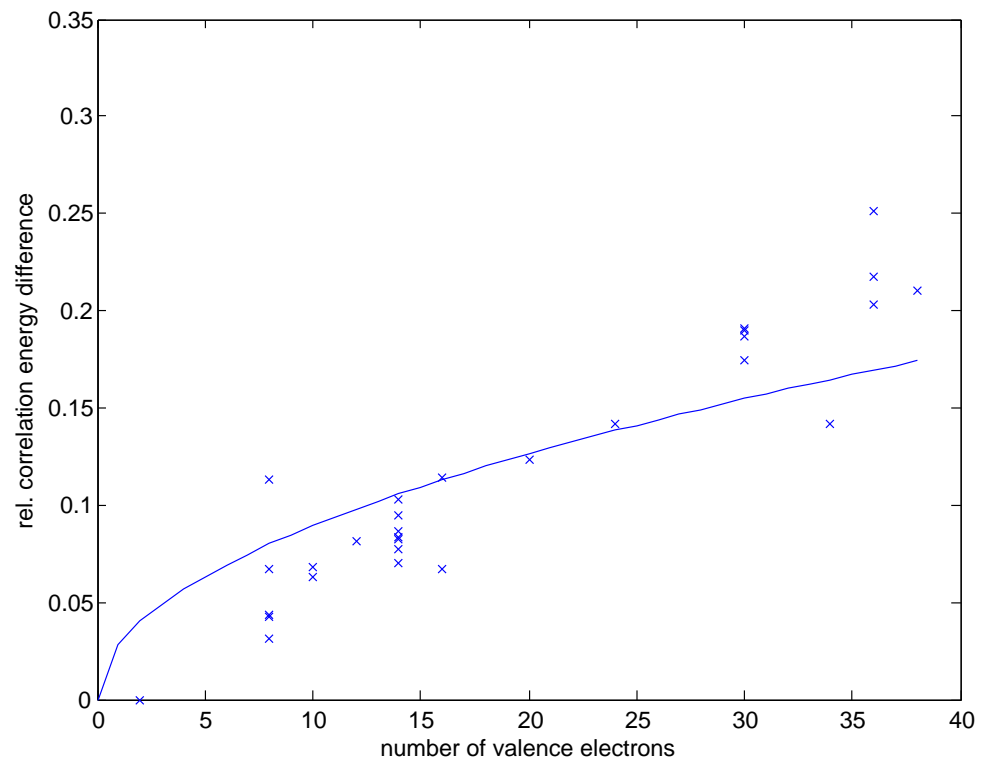
Truncated CI Method Let $\mathcal{J}_h \subset \mathcal{J}$ be a subset of all indices for the Slater determinants. A truncated CI solution, i.e. a Galerkin solution according to the ansatz $\Psi_h = c_0\Psi_0 + \sum_{\mu \in \mathcal{J}_h} c_\mu\Psi_\mu$ can be written by

$$\Psi_h = c_0\Psi_0 + \sum_{\mu \in \mathcal{J}_h} c_\mu X_\mu \Psi_0$$

Usually one truncated w.r.t the excitation level $\Psi_{\text{CISD}} = c_0\Psi_0 + T_1\Psi_0 + T_2\Psi_0$.

These truncations are NOT **size consistent**, i.e.

for M independent systems $E_{\text{cor}} := E_0 - E_{\text{HF}} = O(M)$, but CISD $E_{\text{cor,CISD}} := E_{\text{CISD}} - E_{\text{HF}} = \sqrt{M}$!



Coupled Cluster Approximation - Exponential-Ansatz

Idea: Instead of an $\#J_h$ dimensional linear space one approximate Ψ by an $\#J_h$ dimensional manifold.

Nowadays CC is the most powerful methods for high accuracy computations! Typically 4-6 digits relative accuracy for $\lesssim 10^2$ electrons.

Theorem (S. 06) Let Ψ_0 be a reference Slater determinant, e.g. $\Psi_0 = \Psi_{HF}$ and $\Psi \in \mathcal{V}_{CI}$ be the ground state wave function satisfying

$$\langle \Psi, \Psi_0 \rangle = 1 \quad \text{intermediate normalization .}$$

Then there exists an excitation operator (T_1 - single-, T_2 - double- , ... excitation operators)

$$T = \sum_{i=1}^N T_i = \sum_{\mu \in \mathcal{J}} t_{\mu} X_{\mu} \quad \text{such that}$$

$$\text{Exponential-ansatz } \Psi = e^T \Psi_0.$$

History: Kümmel (1960), discovered by Paldus Czichak (1965) for QC,

Simplified ansatz

Instead of a general operator consider a multiplication operator.

Exponential ansatz for the symmetric **Jastrow factor**

$$\Psi \approx \Phi_0 F = \Phi_0 e^\tau$$

with an **ANOVA type approximation**

$$\tau(\mathbf{x}_1, s_1, \dots, \mathbf{x}_N, s_N) \approx \sum_{i=1}^N \tau_1(\mathbf{x}_i, s_i) + \sum_{j < i} \tau_2(\mathbf{x}_1, s_1, \mathbf{x}_2, s_2) + \dots$$

corresponding to CCSD \rightsquigarrow size consistency !!!

τ is approximated by minimizing the corresponding ground state energy.

The reference function Φ_0 must not be a single determinant!!!

Perturbation approach recently by Luo, Flad and Hackbusch.

There remains an error due to the set of zeros of Φ_0 is fixed (fixed node approximation).

Projected Coupled Cluster Method

The Projected Couple Cluster method consists in the ansatz

$$T = \sum_{k=1}^l T_k = \sum_{\mu \in \mathcal{J}_h} t_\mu X_\mu, \quad 0 \neq \mu \in \mathcal{J}_h \subset \mathcal{J}$$

e.g. CCSD $T = T_1 + T_2 = T(\mathbf{t})$ satisfying

$$0 = \langle \Psi_\mu, e^{-T} H \Psi \rangle = \langle \Psi_\mu, e^{-T} H e^T \Psi_0 \rangle =: f_\mu(\mathbf{t}), \quad \mathbf{t} = (t_\nu)_{\nu \in \mathcal{J}_h}, \quad \mu, \nu \in \mathcal{J}_h$$

These are $L = \#\mathcal{J}_h$ nonlinear equations for L unknown excitation amplitudes $t_\mu, \mu \in \mathcal{J}_h$.

Computable: Due to the Slater Condon rules, the Baker Cample Hausdorff expansion terminates after the 4th term! Projected CC is size consistent!!!

Ground State Energy

Let $\Psi \in \mathcal{V}$ satisfying

$$\mathcal{H}\Psi := \mathcal{H}_h\Psi = E_0\Psi,$$

then, due to the Slater Condon rules and $\langle \Psi, \Psi_0 \rangle = 1$

$$E = \langle \Psi_0, \mathcal{H}\Psi \rangle = \langle \Psi_0, \mathcal{H}(I + T_2 + \frac{1}{2}T_1^2)\Psi_0 \rangle$$

Observation:

$$E = \mathcal{J}(\mathbf{t}) \quad \text{subordinated to} \quad \mathbf{f}(\mathbf{t}) = \mathbf{0}$$

Convergence

Theorem (S. 06) (a priori estimate) If $\mathbf{f}(\mathbf{t}) = \mathbf{0}$ and \mathbf{f} is (locally) strictly monotone at \mathbf{t} and solution of projected CC \mathbf{t}_h satisfies $\|\mathbf{t} - \mathbf{t}_h\|_V \leq \delta$, then it there holds

$$\|\mathbf{t} - \mathbf{t}_h\|_V \lesssim \inf_{\mathbf{v} \in \mathbb{R}^{\#J}} \|\mathbf{t} - \mathbf{v}_h\|_V.$$

Additionally, we have

$$\|\Psi - \Psi_h\|_{H^1} \lesssim \inf_{\mathbf{v} \in \mathbb{R}^L} \|\Psi - e^{\sum_{\mu \in \mathcal{J}_h} v_\mu X_\mu} \Psi_0\|_{H^1}.$$

Crucial was the proof of the property

$$\|\mathbf{t}\|_V \sim \|e^T \Psi_0\|_{H^1}$$

Theorem (S. 06) The error in the energy $E = J(\mathbf{t})$ and the discrete energy $E_h = J(\mathbf{t}_h)$ can be estimated by

$$\begin{aligned} |E - E_h| &\lesssim \|\mathbf{t} - \mathbf{t}_h\|_V \|\mathbf{a} - \mathbf{a}_h\|_V + (\|\mathbf{t} - \mathbf{t}_h\|_V)^2 \\ &\lesssim \inf_{\mathbf{u}_h \in V_h} \|\mathbf{t} - \mathbf{u}_h\|_V \inf_{\mathbf{b}_h \in V} \|\mathbf{a} - \mathbf{b}_h\|_V + \\ &\quad + \left(\inf_{\mathbf{u}_h \in V_h} \|\mathbf{t} - \mathbf{u}_h\|_V \right)^2. \end{aligned}$$

All constants involved above are uniform w.r.t. $\mathcal{N} \rightarrow \infty$.

Improved estimate

$$\begin{aligned} |E - E_h| &\lesssim \|\mathbf{t} - \mathbf{t}_h\|_V \|\mathbf{a} - \mathbf{a}_h\|_V \\ &\lesssim \inf_{\mathbf{u}_h \in V_h} \|\mathbf{t} - \mathbf{u}_h\|_V \inf_{\mathbf{b}_h \in V} \|\mathbf{a} - \mathbf{b}_h\|_V \end{aligned}$$

Proof by using *dual weighted residual method* (Rannacher)

A posteriori error estimator are available if the residual can be computed.

Tractability

- **Theorem (Yserentant 05)** : The wave function is in the space

$$H^{1, \frac{1}{2}}(\mathbb{R} \times \{\pm \frac{1}{2}\}^{3N}) := \left\{ \int |\widehat{\Psi}(\xi)|^2 (1 + |\xi|^2) \prod (1 + |\xi_i|) < \infty \right\}$$

. With a sparse grid approximation (theoretically) an order

$$O(n^{-s}), \forall s < \frac{1}{6}, n \simeq \text{DOF}$$

can be achieved for approx. Ψ , and twice the rate for the energy.

- **Theorem (Flad, Hackbusch, Schneider '05)** For every $0 < s < 1/2$ the singularity $\Theta \approx |\mathbf{x} - \mathbf{y}|$ of an electron-electron cusp (Kato, Thomas Ostenhoff et al.) could be approximated by a rate

$$O(n^{-s}), \forall s < \frac{1}{2}, n \simeq \text{DOF}$$

- **Conjecture**: This is also true for the wave function Ψ . More over a better rate with orbital approximation is not possible.
- **Question**. What is the (ideal) complexity for the solution $O(n)$? How to achieve this practically?

Error decay rates for the ground state energy

- Multiscale bases and sparse grids: n basis functions, n determinants

Hyperbolic cross (Yserentant '04, '05, '07) $O(n^{-1/6})$ ($O(n^{-1/3})$)

Adaptive sparse grids (H., F., S.)

$O(n^{-1})$ for all $s < 1$

$O(n^{-2})$ using $r_{1,2}$ singularity functions

Demand: linear complexity $O(n)$ is in progress

- GTO bases: basis set of size \mathcal{N} , $n \sim \mathcal{N}^2$ determinants in SD

e.g. CCSD

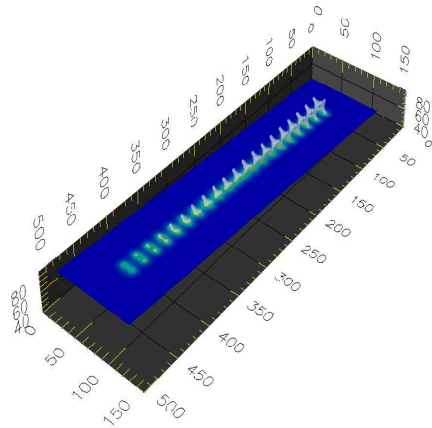
$O(n^{-1/2})$

Complexity is $O(N^2 \times n^5)$ (naively)!

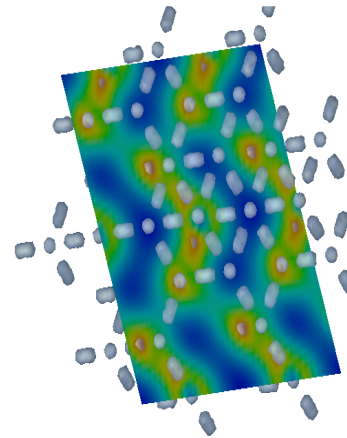
Improvements: $r_{1,2}$ ($f_{1,2}$)-Methods in CCSD (Klopper) and Linear scaling CCSD (Schütz, Werner)

Not mentioned:

- MCSCF (Multi-Configuration Self Consistent Field Method)
- perturbation theory
- p-particle density matrix optimization (Mazziotti)
- Quantum Monte Carlo methods
- many other important items ...



electron density of C₄₀H₈₂



electron density in a silicon