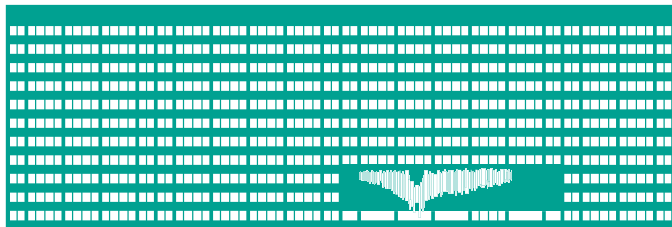


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A brief introduction to electronic structure calculations

Seminar on Applied Mathematics

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- $|\psi\rangle$ – element of \mathbb{V} , state of a quantum system.
- $\langle\phi|$ – element of \mathbb{V}^* , linear form.
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- Take Hilbert space \mathbb{V} (one point particle) and element $|\psi\rangle$.
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System of N electrons and M nuclei is described by wavefunction

$$\Psi(\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_M, \mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) \in L^2(\mathbb{R}^{3(M+N)}). \quad (1)$$

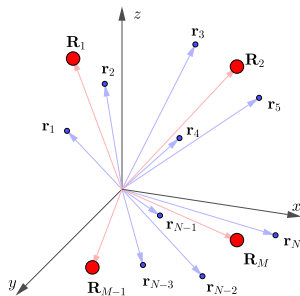


Figure: System of N electrons and M nuclei

$|\Psi|^2$ has the meaning of probability density.



Stationary Schrödinger Equation:

$$\hat{H}\Psi = E\Psi \quad (2)$$

with Hamiltonian (including the electrostatic interaction)

$$\hat{H} = \underbrace{-\sum_{n=1}^M \frac{\Delta_n}{2m_n}}_{\hat{T}_n} + \underbrace{\sum_{\substack{m,n=1 \\ m < n}}^M \frac{Z_m Z_n}{\|\mathbf{R}_m - \mathbf{R}_n\|}}_{V_{nn}} - \underbrace{\sum_{i=1}^N \frac{\Delta_i}{2}}_{\hat{T}_e} + \underbrace{\sum_{\substack{i,j=1 \\ i < j}}^N \frac{1}{\|\mathbf{r}_i - \mathbf{r}_j\|}}_{V_{ee}} - \underbrace{\sum_{i=1}^N \sum_{n=1}^M \frac{Z_n}{\|\mathbf{r}_i - \mathbf{R}_n\|}}_{V_{en}}. \quad (3)$$

An eigenproblem with point and/or continuous spectrum. Lowest eigenvalue = ground state energy. Energy formula:

$$E[\Psi] = \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle}. \quad (4)$$

The problem of finding the Ground State Energy is equivalent to the solution of the minimization problem

$$E_{GS} = \min E[\Psi]. \quad (5)$$



Problem (2) practically intractable (dimensionality, hidden symmetry in Ψ).

Idea: The mass of the electron is several orders of magnitude lower than the mass of the proton – an electron responds almost instantly to a change of a nucleus position. Separation of the total wavefunction:

$$\Psi(\mathbf{R}_1, \dots, \mathbf{R}_M, \mathbf{r}_1, \dots, \mathbf{r}_N) = \psi(\mathbf{r}_1, \dots, \mathbf{r}_N) \varphi(\mathbf{R}_1, \dots, \mathbf{R}_M). \quad (6)$$

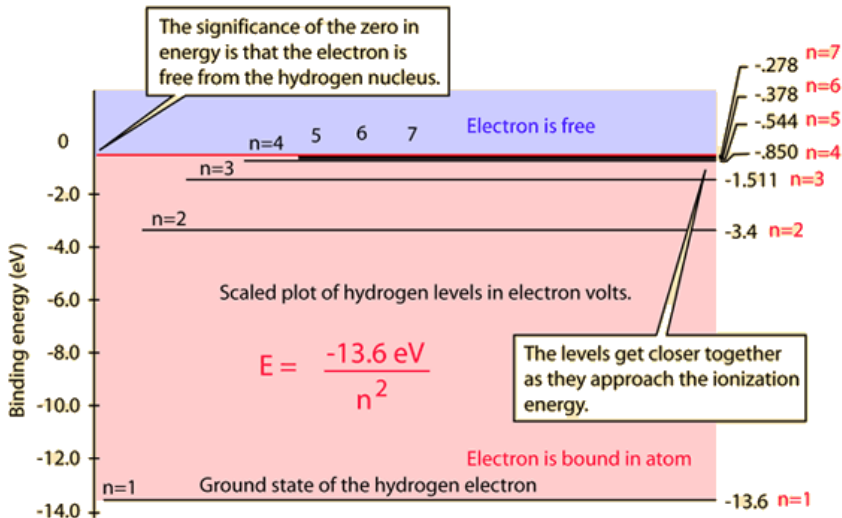
The original Schrödinger Equation (2) splits into the set of equations

$$\left\{ \begin{array}{l} \left(\hat{T}_e + V_{ee} + V_{en} + V_{nn} \right) \psi = E_{\text{elec}} \psi, \end{array} \right. \quad (7a)$$

$$\left\{ \begin{array}{l} \left(\hat{T}_n + E_{\text{elec}}(\mathbf{R}_1, \dots, \mathbf{R}_M) \right) \varphi = E \varphi. \end{array} \right. \quad (7b)$$

Equation (7a) is the electronic part. For now we forget the second one.

Example - hydrogen atom



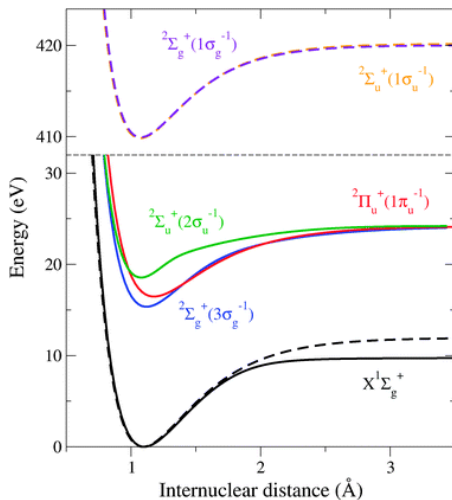
Example - hydrogen atom



$$\left(-\frac{1}{2}\Delta - \frac{1}{\|\mathbf{r}\|}\right)\psi(\mathbf{r}) = E \cdot \psi(\mathbf{r}). \quad (8)$$

| | s ($\ell=0$) | p ($\ell=1$) | | | d ($\ell=2$) | | | | f ($\ell=3$) | | | | | | | | |
|-------|----------------|----------------|-----------|-------|----------------|-----------|----------|-----------|----------------|-----------|------------|------------|-----------|------------------|-------------------|-------------------|--|
| | $m=0$ | $m=0$ | $m=\pm 1$ | | $m=0$ | $m=\pm 1$ | | $m=\pm 2$ | $m=0$ | $m=\pm 1$ | | $m=\pm 2$ | | $m=\pm 3$ | | | |
| | s | p_z | p_x | p_y | d_{z^2} | d_{xz} | d_{yz} | d_{xy} | $d_{x^2-y^2}$ | f_{z^3} | f_{xz^2} | f_{yz^2} | f_{xyz} | $f_{z(x^2-y^2)}$ | $f_{x(x^2-3y^2)}$ | $f_{y(3x^2-y^2)}$ | |
| $n=1$ | | | | | | | | | | | | | | | | | |
| $n=2$ | | | | | | | | | | | | | | | | | |
| $n=3$ | | | | | | | | | | | | | | | | | |
| $n=4$ | | | | | | | | | | | | | | | | | |
| $n=5$ | | | | | | | | | | ... | ... | ... | ... | ... | ... | ... | |
| $n=6$ | | | | | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | |
| $n=7$ | | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | |

Example - potential energy curves





We have to include another quantum coordinate associated with each electron – spin. Consider one electron. Its wavefunction χ consists of two parts:

- 1 Spatial part – orbital $\phi(\mathbf{r}) \in L^2(\mathbb{R}^3)$.
- 2 Spin part – $\sigma(s) \in \mathbb{S} = \mathbb{R}^2$. Basis:

$$\sigma_{\downarrow}(s) = \begin{cases} 0, & s = \frac{1}{2} \\ 1, & s = -\frac{1}{2} \end{cases}, \quad \sigma_{\uparrow}(s) = \begin{cases} 1, & s = \frac{1}{2} \\ 0, & s = -\frac{1}{2} \end{cases} \quad (9)$$

The total wavefunction (spin-orbital) is given as

$$\chi(\mathbf{x}) = \phi(\mathbf{r}) \cdot \sigma(s), \quad \mathbf{x} = (\mathbf{r}, s), \quad (10)$$

which is an element of the tensor-product Hilbert space

$$\mathbb{V} = L^2(\mathbb{R}^3) \otimes \mathbb{S} \quad (11)$$

with induced dot product

$$\langle \chi | \chi' \rangle = \langle \phi | \phi' \rangle \cdot \langle \sigma | \sigma' \rangle. \quad (12)$$



Basis $\{\chi_1, \chi_2, \dots\}$ is generated as

$$\chi_{2k-1}(\mathbf{x}) = \phi_k(\mathbf{r}) \cdot \sigma_{\uparrow}(s), \quad (13)$$

$$\chi_{2k}(\mathbf{x}) = \phi_k(\mathbf{r}) \cdot \sigma_{\downarrow}(s), \quad (14)$$

where $k = \{1, 2, 3, \dots\}$ and ϕ_k form a basis of $L^2(\mathbb{R}^3)$.

Now, consider a system of N electrons described by wavefunction $\psi(\mathbf{x}_1, \dots, \mathbf{x}_N) \in \mathbb{W}$, where \mathbb{W} is also defined as a tensor-product space

$\mathbb{W} = \bigotimes_{\ell=1}^N \mathbb{V}^{(\ell)}$, ($\mathbb{V}^{(\ell)} = \mathbb{V}$) equipped with dot product

$$\langle \psi | \psi' \rangle = \prod_{\ell=1}^N \langle \chi^{(\ell)} | \chi'^{(\ell)} \rangle \quad (15)$$

defined for rank-1 elements (elementary tensors) as

$$\psi(\mathbf{x}_1, \dots, \mathbf{x}_N) = \prod_{\ell=1}^N \chi^{(\ell)}(\mathbf{x}_{\ell}). \quad (16)$$



Let $\{\chi_1, \chi_2, \dots\}$ be basis of \mathbb{V} . Then any general wavefunction can be written as

$$\psi(\mathbf{x}_1, \dots, \mathbf{x}_N) = \sum_{\mathbf{i}=1}^{\infty} C_{\mathbf{i}} \cdot \prod_{\ell=1}^N \chi_{i_{\ell}}(\mathbf{x}_{\ell}), \quad (17)$$

where $\mathbf{i} = (i_1, \dots, i_N)$. A wavefunction is antisymmetric when following symmetry property is fulfilled:

$$C_{P(\mathbf{i})} = \text{sgn}(P) \cdot C_{\mathbf{i}} \quad (18)$$

for all possible permutations P . NOTE: This condition also implies the Pauli exclusion principle (any nonzero contribution must contain distinct basis functions). The contributions belonging to a given expansion coefficient can be grouped into Slater determinants

$$\psi_{\mathbf{i}}^{\text{SD}}(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) = \begin{vmatrix} \chi_{i_1}(\mathbf{x}_1) & \cdots & \chi_{i_1}(\mathbf{x}_N) \\ \vdots & \ddots & \vdots \\ \chi_{i_N}(\mathbf{x}_1) & \cdots & \chi_{i_N}(\mathbf{x}_N) \end{vmatrix} \quad (19)$$



Using the Slater determinants, we can write an equivalent expansion

$$\psi(\mathbf{x}_1, \dots, \mathbf{x}_N) = \sum_{\substack{i_1 = 1 \\ i_{\ell+1} > i_\ell \\ \ell = 1, \dots, N-1}}^{\infty} C_{\mathbf{i}} \cdot \psi_{\mathbf{i}}^{\text{SD}}(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N). \quad (20)$$

This gives us a method of generating basis of Slater determinants for constructing any ψ . Theoretically, we may choose a basis of \mathbf{V} , construct all the possible Slater determinants and find coefficients $C_{\mathbf{i}}$ representing the GS wavefunction. However, there are many obstacles:

- We have to make a cutoff to get a finite dimensional basis. How many SDs do we need?
- What is the best basis to get the lowest number of SDs for reaching a given accuracy?



Idea: Instead of minimizing the coefficients with a fixed basis, take only one Slater determinant and find a "basis" which minimizes the energy. ψ is considered in a form of single Slater determinant

$$\psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(\mathbf{x}_1) & \cdots & \chi_1(\mathbf{x}_N) \\ \vdots & \ddots & \vdots \\ \chi_N(\mathbf{x}_1) & \cdots & \chi_N(\mathbf{x}_N) \end{vmatrix} \quad (21)$$

generated from unknown orthonormal spin-orbitals χ_i ($\langle \chi_i | \chi_j \rangle = \delta_{ij}$). By taking the orthonormality as a constraint, we may write down the Lagrangian function

$$L[\{\chi_i\}, \{\lambda_{ij}\}] = \langle \psi^{\text{SD}} | \hat{H} | \psi^{\text{SD}} \rangle + \sum_{i,j=1}^N (\langle \chi_i | \chi_j \rangle - \delta_{ij}) \quad (22)$$

Constrained minimum is reached if the first variation with respect to orbitals vanishes, i.e.

$$\delta L[\{\chi_i\}, \{\lambda_{ij}\}] = 0. \quad (23)$$



Given a manifold \mathbb{M} of continuous functions $\rho(\mathbf{r})$ and functional $F : \mathbb{M} \mapsto \mathbb{R}$, the functional derivative of $F[\rho]$ is defined via the first variation as

$$\delta F[\rho][\phi] = \int \underbrace{\frac{\delta F}{\delta \rho(\mathbf{r})}}_{\text{func.der.}} \cdot \phi(\mathbf{r}) d\mathbf{r} = \lim_{\varepsilon \rightarrow 0} \frac{F[\rho + \varepsilon \phi] - F[\rho]}{\varepsilon} = \left[\frac{d}{d\varepsilon} F[\rho + \varepsilon \phi] \right]_{\varepsilon=0} \quad (24)$$

Examples:

$$F[\rho] = \frac{1}{2} \int \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{\|\mathbf{r} - \mathbf{r}'\|} d\mathbf{r} d\mathbf{r}' \quad \rightarrow \quad \frac{\delta F}{\delta \rho(\mathbf{r})} = \int \frac{\rho(\mathbf{r}')}{\|\mathbf{r} - \mathbf{r}'\|} d\mathbf{r}' \quad (25)$$

$$F[\rho] = \rho(\mathbf{r}') = \int \rho(\mathbf{r}) \cdot \delta(\mathbf{r}' - \mathbf{r}) d\mathbf{r} \quad \rightarrow \quad \frac{\delta F}{\delta \rho(\mathbf{r})} = \delta(\mathbf{r}' - \mathbf{r}) \quad (26)$$

$$F[\rho] = \int f(\mathbf{r}, \rho(\mathbf{r}), \nabla \rho(\mathbf{r})) d\mathbf{r} \quad \rightarrow \quad \frac{\delta F}{\delta \rho(\mathbf{r})} = \frac{\partial f}{\partial \rho} - \nabla \cdot \frac{\partial f}{\partial \nabla \rho} \quad (27)$$

The first variation is equal to zero if

$$\forall i \in \{1, \dots, N\} : \frac{\delta L [\{\chi_i\}, \{\lambda_{jk}\}]}{\delta \chi_i(\mathbf{x}_1)} = 0. \quad (28)$$

NOTE: We may diagonalize the matrix of Lagrange multipliers using a unitary transformation (we use the same notation for orbitals, $\{\lambda_{jk}\} \rightarrow \{\varepsilon_m\}$). After doing some work we get HF equations (closed-shell form with $2N$ electrons)

$$\forall k \in \{1, \dots, N\} : \left(\underbrace{-\frac{1}{2}\Delta}_{\hat{T}} - \underbrace{\sum_{i=1}^M \frac{Z_i}{\|\mathbf{R}_i - \mathbf{r}\|}}_{V_N(\mathbf{r})} + 2 \underbrace{\sum_{i=1}^N \int_{\mathbb{R}^3} \frac{|\phi_i(\mathbf{r}')|^2}{\|\mathbf{r}' - \mathbf{r}\|} d^3\mathbf{r}'}_{V_H(\mathbf{r})} \right) \phi_k(\mathbf{r}) - \underbrace{\sum_{i=1}^N \int_{\mathbb{R}^3} \frac{\phi_i^*(\mathbf{r}') \phi_k(\mathbf{r}')}{\|\mathbf{r} - \mathbf{r}'\|} d^3\mathbf{r}'}_{V_X \phi_k(\mathbf{r})} \phi_i(\mathbf{r}) = \varepsilon_k \phi_k(\mathbf{r}). \quad (29)$$



Within a finite-dimensional "basis", each spatial part of a one-electron orbital is expanded as

$$\phi_i(\mathbf{r}) = \sum_{j=1}^{N_b} c_{ji} \mu_j(\mathbf{r}). \quad (30)$$

Applying the Galerkin method to HF Equations leads to the Roothaan-Hall matrix equation

$$\mathbf{F}(\mathbf{C}) \mathbf{C} = \mathbf{M} \mathbf{C} \mathbf{\Lambda}, \quad (31)$$

where $\mathbf{\Lambda} \in \mathbb{R}^{N \times N}$ is diagonal matrix of eigenvalues ε_i ,

$$[\mathbf{M}]_{kj} = \int_{\mathbb{R}^3} \mu_k(\mathbf{r}) \mu_j(\mathbf{r}) \, d^3\mathbf{r} \quad (32)$$

is the overlap matrix,

$$\mathbf{F}(\mathbf{C}) = \mathbf{H} + \mathbf{J}(\mathbf{C}) + \mathbf{K}(\mathbf{C}). \quad (33)$$



Core Hamiltonian matrix:

$$[\mathbf{H}]_{ij} = \int_{\mathbb{R}^3} \frac{1}{2} \nabla \mu_i(\mathbf{r}) \cdot \nabla \mu_j(\mathbf{r}) - \sum_{k=1}^M \frac{Z_k \mu_i(\mathbf{r}) \mu_j(\mathbf{r})}{\|\mathbf{R}_k - \mathbf{r}\|} d^3\mathbf{r}. \quad (34)$$

Hartree matrix:

$$[\mathbf{J}]_{ij} = 2 \cdot \sum_{k=1}^{N_b} \sum_{l=1}^{N_b} z_{lk} \cdot b_{ijkl}. \quad (35)$$

Exchange matrix:

$$[\mathbf{K}]_{ij} = - \sum_{k=1}^{N_b} \sum_{l=1}^{N_b} z_{lk} \cdot b_{ikjl}. \quad (36)$$

Two-electron integrals:

$$[\mathbf{B}]_{ijkl} = b_{ijkl} = \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{\mu_i(\mathbf{r}) \mu_j(\mathbf{r}) \mu_k(\mathbf{r}') \mu_l(\mathbf{r}')}{\|\mathbf{r} - \mathbf{r}'\|} d^3\mathbf{r} d^3\mathbf{r}'. \quad (37)$$

Density matrix $\mathbf{Z} = \mathbf{C}\mathbf{C}^T$, $[\mathbf{Z}]_{lk} = z_{lk}$.



Hartree-Fock equations give us only an approximate solution to the electronic SE:

$$E = \langle \psi | \hat{H} | \psi \rangle \leq \langle \psi_{\text{HF}} | \hat{H} | \psi_{\text{HF}} \rangle = E_{\text{HF}} \quad (38)$$

(This is the case when we choose an infinite-dimensional Galerkin basis).

Solution:

- After the E_{HF} and orbital basis is calculated, we may consider more Slater determinants that include unoccupied orbitals – post-HF methods (Configuration Interaction, Coupled Clusters, Møller-Plesset perturbation theory)
- Instead one SD we may consider more of them from the beginning – Multi-configurational SCF.
- Combination of both previous approaches – Multireference configuration interaction

NOTE: All these methods are very expensive – usually applicable on systems of few atoms.



Different philosophy: Instead of the wavefunction, the main quantity is the electronic density

$$\rho(\mathbf{r}_1) = N \sum_{\substack{s_i = \frac{1}{2}, -\frac{1}{2} \\ i=1, \dots, N}} \int_{\mathbb{R}^3} \cdots \int_{\mathbb{R}^3} |\psi(\mathbf{r}_1, s_1, \dots, \mathbf{r}_N, s_N)|^2 d^3\mathbf{r}_2 \cdots d^3\mathbf{r}_N. \quad (39)$$

The mapping $\psi \mapsto \rho$ is evident. However, it can be reversed! The first Hohenberg-Kohn theorem says:

The external potential $V_N(\mathbf{r})$ (up to a constant) and hence the total energy E , is a unique functional of the ground state electronic density $\rho^{\text{GS}}(\mathbf{r})$.

The dependence of the energy on the GS density:

$$E [\rho^{\text{GS}}] = \langle \psi [\rho^{\text{GS}}] | \hat{T}_e + V_{\text{en}} + V_{\text{ee}} | \psi [\rho^{\text{GS}}] \rangle. \quad (40)$$

It is not difficult to realize that it can be reformulated in terms of ρ^{GS} as

$$E [\rho^{\text{GS}}] = \underbrace{\int_{\mathbb{R}^3} \rho^{\text{GS}}(\mathbf{r}) \cdot V_{\text{N}}(\mathbf{r}) \, d^3\mathbf{r}}_{\langle \psi[\rho^{\text{GS}}] | V_{\text{en}} | \psi[\rho^{\text{GS}}] \rangle} + \underbrace{F[\rho^{\text{GS}}]}_{\langle \psi[\rho^{\text{GS}}] | \hat{T}_e + V_{\text{ee}} | \psi[\rho^{\text{GS}}] \rangle}. \quad (41)$$

Functional F is universal! It does not depend on the number of the nuclei and their positions. However, its closed form is not known. The practical usage of the energy formula is given by the second Hohenberg-Kohn theorem:

The ground state density of a system in a particular external potential can be found by minimizing an associated energy functional.



Reorganization of the original functional:

$$F[\rho] = \underbrace{\frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{\rho(\mathbf{r}) \cdot \rho(\mathbf{r}')}{\|\mathbf{r} - \mathbf{r}'\|} d^3\mathbf{r} d^3\mathbf{r}'}_{E_{\text{H}}[\rho]} + T[\rho] + E_{\text{ncl}}[\rho]. \quad (42)$$

Now we replace our N electrons by a fictitious system of N noninteracting particles. These particles are described by Kohn-Sham orbitals and form single Slater determinant. Using KS orbitals, the density is calculated as:

$$\rho(\mathbf{r}) = 2 \sum_{i=1}^N \left| \phi_i^{\text{KS}}(\mathbf{r}) \right|^2. \quad (43)$$

NOTE: No direct correspondence between the KS wavefunction and the original one. Generally, the kinetic energy of the KS system is different from the original one.



However, we are able to write it down using the one-particle orbitals (as an implicit functional of the density):

$$T_s[\rho] = - \sum_{i=1}^N \int_{\mathbb{R}^3} \phi_i^{\text{KS}}(\mathbf{r}) \Delta \phi_i^{\text{KS}}(\mathbf{r}) d^3\mathbf{r}. \quad (44)$$

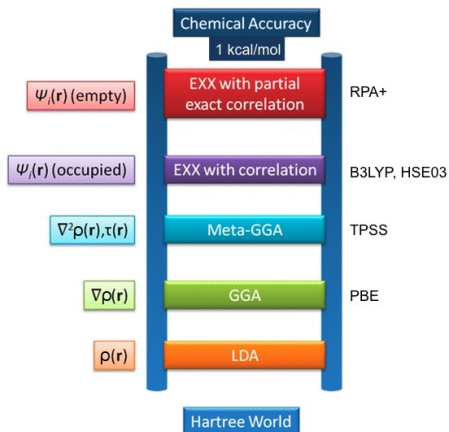
Now, let us do some reordering of the terms in the energy functional:

$$F[\rho] = T_s[\rho] + E_H[\rho] + \underbrace{T[\rho] - T_s[\rho] + E_{\text{ncl}}[\rho]}_{E_{\text{xc}}[\rho]}, \quad (45)$$

The xc term is still not known, but it represents a relatively small contribution – approximations.



$$E_{xc}[\rho] = \int_{\mathbb{R}^3} f(\rho(\mathbf{r}), \nabla\rho(\mathbf{r}), \dots) d^3\mathbf{r}, \quad (46)$$





Idea (equivalent to HF eqs.): Constrained minimization of energy functional (orthonormal KS orbitals). We use the functional derivative chain rule

$$\frac{\delta F[\rho]}{\delta \phi_i^{\text{KS}}(\mathbf{r})} = 4 \frac{\delta F[\rho]}{\delta \rho(\mathbf{r})} \phi_i^{\text{KS}}(\mathbf{r}) \quad (47)$$

to derive the set of KS equations:

$$\left(\underbrace{-\frac{1}{2}\Delta}_{\hat{T}} - \underbrace{\sum_{i=1}^M \frac{Z_i}{\|\mathbf{R}_i - \mathbf{r}\|}}_{V_{\text{N}}(\mathbf{r})} + \underbrace{\int_{\mathbb{R}^3} \frac{\rho(\mathbf{r}')}{\|\mathbf{r} - \mathbf{r}'\|} d^3\mathbf{r}'}_{V_{\text{H}}(\mathbf{r})} + \underbrace{\frac{\delta E_{\text{xc}}[\rho]}{\delta \rho(\mathbf{r})}}_{V_{\text{xc}}[\rho(\mathbf{r})]} \right) \phi_i^{\text{KS}}(\mathbf{r}) = \varepsilon_i \phi_i^{\text{KS}}(\mathbf{r}). \quad (48)$$



After the introduction of a basis, we get the matrix equation

$$\mathbf{F}(\mathbf{C})\mathbf{C} = \mathbf{M}\mathbf{C}\mathbf{\Lambda}, . \quad (49)$$

Similar to HF RH equations, however, matrix \mathbf{F} is slightly different

$$\mathbf{F}(\mathbf{C}) = \mathbf{H} + \mathbf{J}(\mathbf{C}) + \mathbf{V}_{\text{xc}}(\mathbf{C}). \quad (50)$$

Each evaluation of \mathbf{V}_{xc} requires a numerical integration.

The coefficient matrix represent the KS orbitals – no direct correspondence to the original electronic wavefunction. It only generates the same density.



- Plane-wave basis

$$\psi_n(\mathbf{r}) = \sum_{\mathbf{G}} c_{n,\mathbf{k},\mathbf{G}} e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}, \quad (51)$$

NOTE: Suitable (not only) for periodic systems.

- Localized Gaussian-type orbitals (GTO):

$$\mu_{ijk}^{\text{CGTO}}(\mathbf{r}) = N \cdot x^i y^j z^k e^{-\alpha\|\mathbf{r}\|^2}, \quad (52)$$

or

$$\mu_{lm}^{\text{SGTO}}(\mathbf{r}) = N \cdot Y_{lm}(x, y, z) \|\mathbf{r}\|^l e^{-\alpha\|\mathbf{r}\|^2}, \quad (53)$$

NOTE: Analytical evaluation of integrals.



- Physically inspired Slater-type orbitals (STO):

$$\mu_{nlm}^{\text{STO}}(\mathbf{r}) = N \cdot \|\mathbf{r}\|^{n-l-1} \cdot \tilde{Y}_{lm}(\mathbf{r}) \cdot e^{-\alpha\|\mathbf{r}\|}. \quad (54)$$

- Coulomb-Sturmian functions

$$\mu_{nlm}^{\text{CS}}(\mathbf{r}) = N_{\text{CS}} \cdot L_{n-l-1}^{2l+1}(\alpha\|\mathbf{r}\|) \cdot \tilde{Y}_{lm}(\mathbf{r}) \cdot e^{-\frac{\alpha}{2}\|\mathbf{r}\|}. \quad (55)$$

- Laguerre functions

$$\mu_{nlm}^{\text{LF}}(\mathbf{r}) = N_{\text{LF}} \cdot L_{n-l-1}^{2l+2}(\alpha\|\mathbf{r}\|) \cdot \tilde{Y}_{lm}(\mathbf{r}) \cdot e^{-\frac{\alpha}{2}\|\mathbf{r}\|}. \quad (56)$$

All the cases require a numerical integration – very expensive, special mathematical methods have to be used.



How to solve the NEVP

$$\mathbf{F}(\mathbf{C}) \mathbf{C} = \mathbf{M} \mathbf{C} \mathbf{\Lambda} \quad (57)$$

Idea: linearization and iterative solution – Self-consistent field (SCF) iteration

$$\mathbf{F}(\mathbf{C}^{k-1}) \mathbf{C}^k = \mathbf{M} \mathbf{C}^k \mathbf{\Lambda}^k. \quad (58)$$

Problems:

- Two possible scenarios – convergence or oscillation between two states (much more common)
- Choice of the initial guess.

Alternative – mixing of matrices from previous iterations (\mathbf{Z} or \mathbf{F}).

Example:

$$\mathbf{F}^* = \alpha \mathbf{F}^k + (1 - \alpha) \mathbf{F}^{k-1}. \quad (59)$$

More sophisticated mixing is done by Direct inversion of the iterative subspace (DIIS) – minimization of a suitable error estimate (residual) in the sense of the least squares. No proves of the convergence exist.



The alternative optimization approach is based on the direct minimization of the energy functional. Instead of the coefficient matrix we consider the density matrix

$$\mathbf{Z} = \mathbf{C}\mathbf{C}^T \quad (60)$$

as a variable. The objective function can be written as

- HF Equation (quadratic function):

$$E^{\text{HF}}(\mathbf{Z}) = \text{Trace} [2\mathbf{H}\mathbf{Z} + (\mathbf{J}(\mathbf{Z}) + \mathbf{K}(\mathbf{Z}))\mathbf{Z}], \quad (61)$$

- KS Equation (generally nonlinear function):

$$E^{\text{KS}}(\mathbf{Z}) = \text{Trace} [2\mathbf{H}\mathbf{Z} + \mathbf{J}(\mathbf{Z})\mathbf{Z}] + E_{\text{xc}}[\rho_{\mathbf{Z}}]. \quad (62)$$

Minimization is done over the set of all feasible density matrices \mathbf{Z} (can be represented by equality constraints).



It is useful to use the transformation $\mathbf{X} = \mathbf{M}^{\frac{1}{2}}\mathbf{Z}\mathbf{M}^{\frac{1}{2}}$ which leads to optimization problem

$$\text{find } \min f(\mathbf{X}) = E\left(\mathbf{M}^{-\frac{1}{2}}\mathbf{X}\mathbf{M}^{-\frac{1}{2}}\right). \quad (63)$$

with equality constraints that can be easily written as

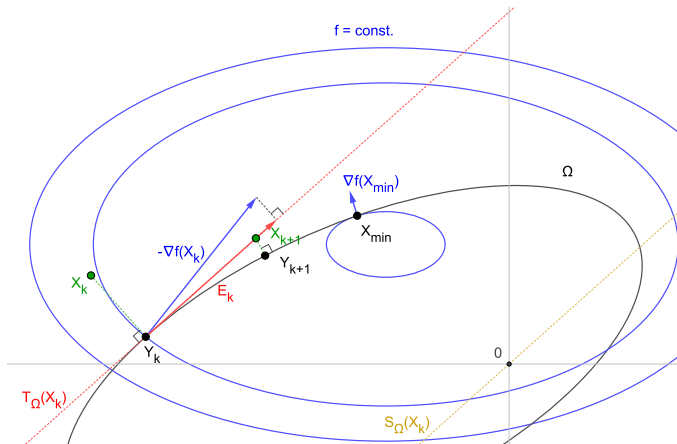
$$\mathbf{X} = \mathbf{X}^T, \quad (64)$$

$$\mathbf{X}\mathbf{X} = \mathbf{X}, \quad (65)$$

$$\text{Trace}[\mathbf{X}] = N. \quad (66)$$

Such quadratically constrained problems require specific algorithms to be solved.

Inexact Restoration Method (IRM):



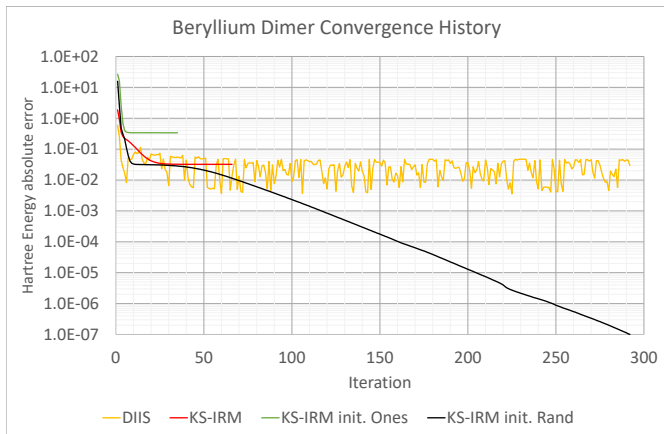
Many alternatives exist...



Finally, the end of the theoretical torture!!!! Some of my results will follow.

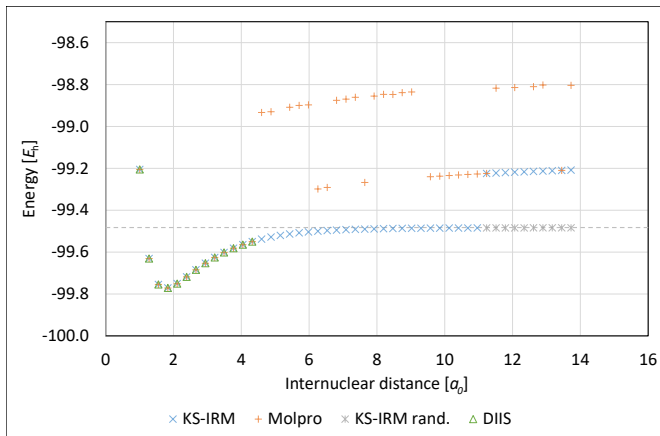


Some systems are known to have convergence issues (SCF) or there are present local minima and/or saddle points. An example - Beryllium dimer:

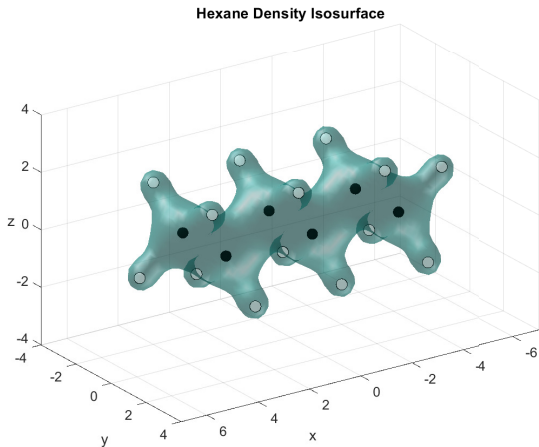




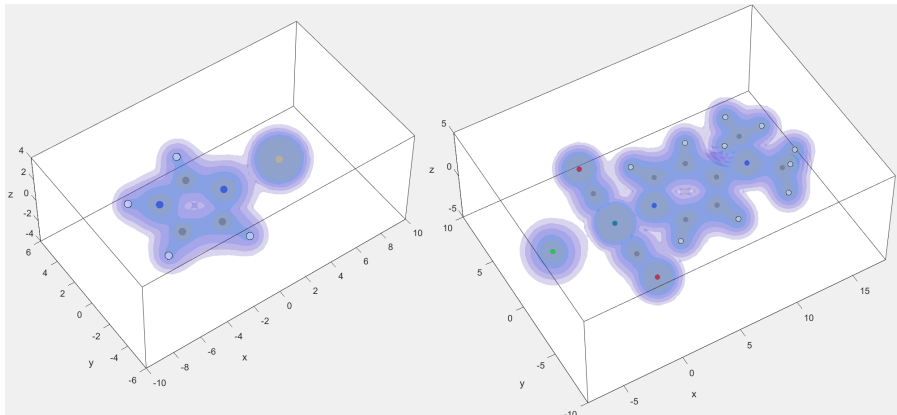
Example - HF molecule potential curve (dependence of the electronic energy on the internuclear distance):



Density-contour plot (1 contour):



Density-contour plot (more contours):





- 1 Yousef Saad, James R. Chelikowsky, and Suzanne M. Shontz: *Numerical Methods for Electronic Structure Calculations of Materials* (DOI: 10.1137/060651653) – **paper** – **brief overview of ESC**
- 2 Richard M. Martin: *Electronic Structure Basic Theory and Practical Methods* – **book** – **ESC in more detail**
- 3 Wolfgang Hackbusch: *Tensor Spaces and Numerical Tensor Calculus* – **book** – **tensor-product Hilbert spaces and much more**
- 4 N. D. Woods, M. C. Payne, and P. J. Hasnip: *Computing the self-consistent field in Kohn–Sham density functional theory* – **paper** – **nice overview of numerical approaches to solve KS (or HF) NEVP**

Thank you for your attention

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