8. Density Functional Theory (DFT)

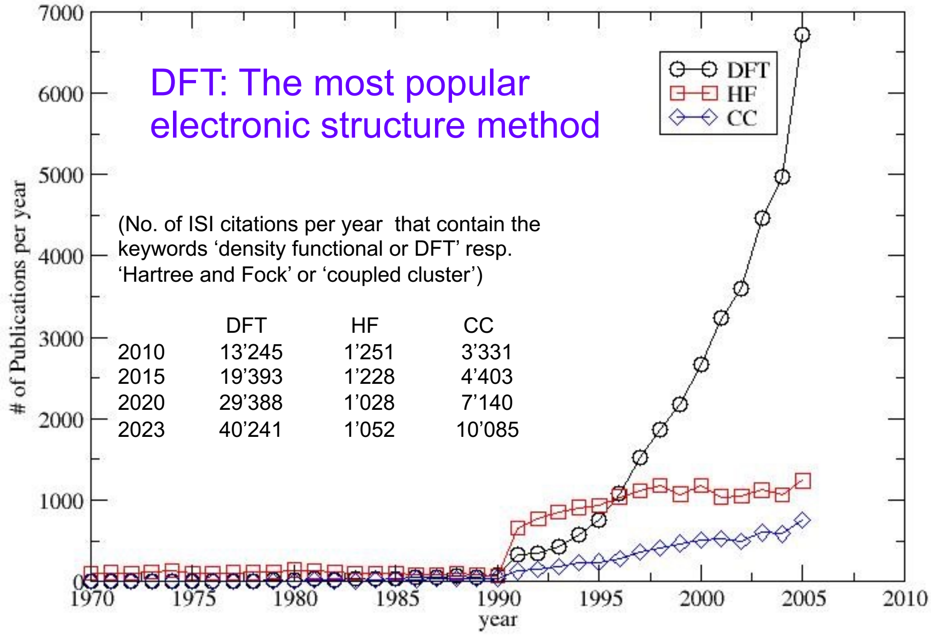
1

Literature on Density Functional Theory

1. R. M. Dreizler and E. K. U. Gross, *Density Functional Theory*, Springer, Berlin, 1990.
2. R. G. Parr and W. Yang, *Density-Functional Theory of Atoms and Molecules*, Oxford University Press, Oxford, 1989.
3. W. Koch and M. C. Holthausen, *A Chemist's Guide to Density Functional Theory*, John Wiley & Sons, New York, 2001.
4. R. O. Jones and O. Gunnarsson, *Rev. Mod. Phys.* 61, 689 (1989).
5. J. M. Seminario (Ed.), *Recent Developments and Applications of Modern DFT*, Elsevier, Amsterdam, 1996.

Recent review orbital-free DFT: Mi et al. Chem Rev. 123, 12039-21204 (2023)

2



	DFT	HF	CC
2010	13'245	1'251	3'331
2015	19'393	1'228	4'403
2020	29'388	1'028	7'140
2023	40'241	1'052	10'085

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Walter Kohn and John Pople

1923-2016

Nobelprize in

Chemistry 1998

1925-2004

Schrödingers equations made easy with DFT !

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Density Functional Theory (DFT)

An alternative possibility to find an approximate solution of the electronic Schrodinger equation

$$\boxed{H\Psi = E\Psi}$$

Let's choose the electron density $\rho(r)$ as central quantity:

$$\boxed{\Psi(\vec{r}_1, \vec{r}_2, \vec{r}_3 \ldots \vec{r}_N) \rightarrow \rho(\vec{r})}$$

3N variables → 3 variables

Integrate over N-1 variables!

Electron density $\rho(r)$:

$$\boxed{\rho = \frac{\#\,electrons}{V}} \qquad \boxed{\rho(\vec{r}) = M \int \ldots \int \Psi^*(\vec{r}, \vec{r}_2, \vec{r}_3 \ldots \vec{r}_N) \Psi(\vec{r}, \vec{r}_2, \vec{r}_3 \ldots \vec{r}_N) d\vec{r}_2 \ldots d\vec{r}_N}$$

M: normalization constant, Ψ is normalized in such a way that

$$\boxed{\int \rho(\vec{r}) d\vec{r} = N}$$

Single particle system:

$$\boxed{\rho(\vec{r}) = \sum_i f_i \phi_i^*(\vec{r}) \phi_i(\vec{r})}$$

f_i: occupation

Measure for the probability of finding electrons (i.e. any electron) at a specific location.
The electron density is an observable (can be measured in e.g. an x-ray diffraction experiment).

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Reasons for the Popularity of DFT Methods

Practical Reasons

To store the many-electron wavefunction for an oxygen atom (8 electrons, 24 variables) with only 10 entries per coordinate and 1 byte per entry, we would need:

10^{24} bytes
5×10^9 bytes per DVD → 2×10^{14} DVDs
10g per DVD → 2×10^9t DVDs

Whereas to store $\rho(\mathbf{r})$, we only need 10^3 bytes !

Physical Reasons

- DFT is computationally very efficient: typical system sizes are 100 – 1000 atoms
- DFT is fairly accurate (bond lengths typically predicted within 1-2%, energies within few kcal/mol) even for systems with strong electron correlation effects, such as e.g. transition metals!
- many chemical concepts can be directly expressed in terms of $\rho(\mathbf{r})$ (e.g. reactivity indices, hardness, softness etc…)
- can easily be combined with ab initio molecular dynamics

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Quiz XVII: Functionals

1) What is the difference between a function and a functional?
2) Why is the method called Density Functional Theory?
3) What is a functional derivative?

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What is Density Functional Theory?

Solution of the many-electron electronic Schrödinger equation that includes all (in principle), approximate (in practice) exchange and correlation effects.

Electronic Schrödinger equation for fixed nuclear geometry:

Collective variables for all electronic (**r**) and all nuclear (**R**) position variables

$$\left[-\frac{1}{2}\sum_i \nabla_i^2 - \sum_{I,i}\frac{Z_I}{|\mathbf{R}_I - \mathbf{r}_i|} + \sum_{I>J}\frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|} + \sum_{i>j}\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}\right]\Psi(\mathbf{r},\mathbf{R}) = E_{el}\Psi(\mathbf{r},\mathbf{R})$$

In a more compact form:

$$\left[\hat{T}_e(\mathbf{r}) + \hat{V}_{eN}(\mathbf{r},\mathbf{R}) + \hat{V}_{NN}(\mathbf{R}) + \hat{V}_{ee}(\mathbf{r})\right]\Psi(\mathbf{r},\mathbf{R}) = E_{el}\Psi(\mathbf{r},\mathbf{R})$$

kinetic energy operator

Electron-nuclei Coulomb potential

Nuclei-nuclei Interaction Potential (constant for fixed R)

Electron-electron repulsion potential

Convention:

$$v(\mathbf{r}) = v(\mathbf{r},\mathbf{R}) \qquad \mathbf{R}_I \ \ (\mathbf{R} = (\mathbf{R}_1, \mathbf{R}_2, \ldots, \mathbf{R}_{Nu})$$

External potential V_{ext}

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Quiz XVIII: Universal vs system specific terms

1) Given 2 systems with the same total number of electrons N = 10 (e.g. H_2O and NH_3):

Which term in the electronic Hamiltonian is different, i.e. which term determines that we are doing a calculation of a water molecule and not of an ammonia molecule?

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What is Density Functional Theory?

Conventional (wavefunction based) quantum chemical methods:

$$v(\mathbf{r}, \mathbf{R}) \stackrel{SE}{\Longrightarrow} \Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_n) \stackrel{\langle\Psi|\ldots|\Psi\rangle}{\Longrightarrow} \text{observable}$$

given external potential
(determined by geometry of the nuclei)

e.g. electron density $\rho(\mathbf{r})$

Density Functional theory:

$$\rho(\mathbf{r}) \Longrightarrow \Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_n) \Longrightarrow v(\mathbf{r})$$

Unique relation between $\rho(\mathbf{r})$ and $v(\mathbf{r})$, all observables (including the (ground state) many-electron wavefunction can be calculated from $\rho(\mathbf{r})$!!!!)

$v(\mathbf{r})$ is the only system-dependent term,

$\hat{T}_e$ and $\hat{V}_{ee}(\mathbf{r})$ are universal operators!!

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Theoretical foundations of DFT: Hohenberg-Kohn Theorems

First Hohenberg Kohn Theorem (1964)

(Hohenberg&Kohn, Phys.Rev. 136, 864B, 1964)

Pierre Hohenberg (1934-2017)

Walter Kohn (1923 -2016)

The ground state energy of a nondegenerate system with N electrons in an external potential V_{ext} is a unique functional of the electron density

$$\boxed{E = E[\rho(\vec{r})]}$$

=> V_{ext} determines $\hat{H}$ and $\hat{H}$ determines the exact Ψ_0 determines $\rho_0(\vec{r})$

And vice versa: V_{ext} is determined within an additive constant by $\rho_0(\vec{r})$

=>The ground state expectation value of any observable is a unique functional of the ground state density $\rho_0(\vec{r})$

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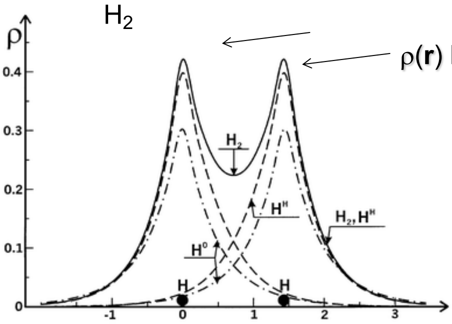
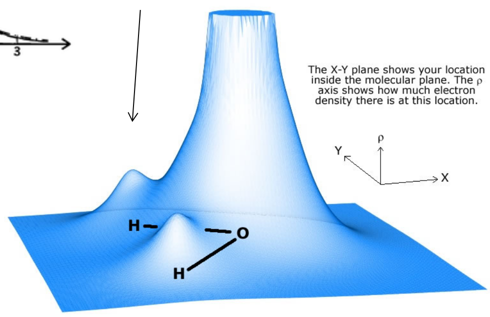
Electron density distributions

H_2



$\rho(\mathbf{r})$ has cusp at nuclear positions

H_2O



Kato's cusp condition:

$$\boxed{Z_J = -\frac{a_0}{2\rho(\vec{r})}\frac{d\rho(\vec{r})}{d\vec{r}}\bigg|_{\vec{r}\to\vec{R}_J}}$$

Pictures taken from:
http://www.reed.edu/chemistry/roco/density/images/

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1st HK Theorem (cont'd)

In other words: the relation

$$\rho(\mathbf{r}) = M \int \dots \int \Psi(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N)\, \Psi^*(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N)\, d\mathbf{r}_2 \dots d\mathbf{r}_N$$

can be inverted, i.e. if the ground state density $\rho_0(\mathbf{r})$ is known, it is possible to calculate the ground state many-electron wavefunction .

$$\Psi_0(\mathbf{r}_1, \mathbf{r}_2 \dots, \mathbf{r}_N)$$

Ψ_0 is a functional of $\rho_0(\mathbf{r})$ $\quad \Psi = \Psi[\rho]$

→ any ground state observable is a functional of $\rho_0(\mathbf{r})$

The ground state wavefunction Ψ_0 is the one that minimizes the ground state energy and reproduces the ground state density $\rho_0(\mathbf{r})$

$$E_{v,0} = \min_{\Psi \to \rho_0} \langle \Psi | \hat{T} + \hat{V}_{ee} + \hat{V}_{eN} | \Psi \rangle$$

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Theoretical foundations of DFT: Hohenberg-Kohn Theorems

Second Hohenberg and Kohn Theorem:

- Variational principle:

The total energy is minimal for the ground state density of the system $\rho_0(\vec{r})$

$$\boxed{E[\rho(\vec{r})]_{\min} = E_0 = E[\rho_0(\vec{r})]}$$

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2^{nd} HK Theorem (cont'd)

For an arbitrary density $\rho(\mathbf{r})$

$$E_v[\rho] = \min_{\Psi\to\rho} \langle\Psi|\hat{T} + \hat{V}_{ee} + \hat{V}_{eN}|\Psi\rangle$$

If $\rho(\mathbf{r}) \neq \rho_0(\mathbf{r})$ then $\Psi \neq \Psi_0$ and $E_v > E_0$. Variational principle for the ground state density!
One can write the total energy also as:

$$E_v[\rho] = \min_{\Psi\to\rho} \Psi|\hat{T} + \hat{V}_{ee}|\Psi\rangle + \int d^3r\, \rho(\mathbf{r})v(\mathbf{r})$$
$$=: F[\rho] + V[\rho]$$

$$F[\rho] = \min_{\Psi\to\rho} \langle\Psi|\hat{T}+\hat{V}_{ee}|\Psi\rangle$$

Internal energy functional,
Independent of v(**r**), universal!!!

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Some (subtle) remarks about the HK theorems

V-Representability of $\rho(\mathbf{r})$
Can all electron density distributions be associated with a Hamiltonian with an external potential $V_{ext}(\mathbf{r})$ (V-representability)? => not necessarily: e.g. electron density distribution in an electronically excited state
=> HK1 valid for v-representable densities
=> HK2: The minimization of the total energy with respect to the density has to be performed under the condition that $\rho(\mathbf{r})$ remains V-representable (i.e. that there is a corresponding $V_{ext}(\mathbf{r})$).

N-Representability $\rho(\mathbf{r})$
Can all electron densities be derived from an antisymmetric wavefunction (N-representability)?
=> The minimization of the total energy with respect to the density has to be performed under the condition that $\rho(\mathbf{r})$ remains N-representable
=> Lieb&Levy constrained search

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Quiz IXX: Total Energy as a functional of ρ(r)

1) Try to find expressions for the different terms of the total energy in terms of the electron density distribution ρ(**r**):
   a) The kinetic energy
   b) The electron-nuclei interaction
   c) The classical part of the electron-electron interaction
   d) The exchange and correlation energy?

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Precursors of Kohn-Sham DFT: The 'true' (orbital-free) Density Functional Methods

The total energy of the system (and any other observable) is expressed as a functional of the density only:

$$\boxed{E_v[\rho] = T[\rho] + V_{ee}[\rho] + V_{eN}[\rho] = F[\rho] + V_{eN}[\rho]}$$

Some of these terms are easy to calculate, e.g. $V_{eN}[\rho]$:

$$v_{eN}(\mathbf{r}) = v_{ext}(\mathbf{r}) \qquad \hat{V}_{ext}(\mathbf{r}) = \sum_I \frac{Z_I}{|\mathbf{r} - \mathbf{R}_I|}$$

$$\boxed{V_{ext}[\rho] = \int d^3r\, \rho(\mathbf{r}) v_{ext}(\mathbf{r})}$$

Classical electrostatic energy of a charge distribution ρ(**r**) in a potential v_{ext}(**r**).

Classical electrostatic potential energy:

$$U(\vec{r}) = q\Phi(\vec{r})$$

$$U = q\int d\vec{r}\,\Phi(\vec{r})$$

$\Phi(\vec{r})$: electrostatic potential at $\vec{r}$

What is the form of the universal terms T[ρ] and V_{ee}[ρ]?

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Llewellyn Hilleth Thomas (1903-1992)

Precursors of Kohn-Sham DFT: The Thomas-Fermi Model (1927)

Enrico Fermi (1901-1953)

The electron-electron interaction is approximated by the classical Coulomb energy of a charge distribution ρ(**r**) (analogous to the Hartree term in the Hartree-Fock method):

$$\boxed{V_{ee} \approx V_{HF} = \frac{1}{2}\int d^3r \int d^3r' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}}$$

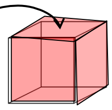
Thomas-Fermi Approximation: Exchange and correlation effects neglected

It turns out that the most difficult term to express as a functional of the density, is the kinetic energy T[ρ].

Thomas and Fermi suggested a first approximation for this term in the form of a local density approximation for the kinetic energy functional:

$$\boxed{T[\rho] \approx T^{LDA}[\rho] = \int t^{hom}(\rho(\mathbf{r}))d^3r}$$

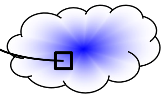
N electrons
homogeneus compensating positive charge: jellium



Homogeneous electron gas
ρ = N/V = const

Where t^{hom}(ρ(**r**) is the kinetic energy density (kinetic energy per unit volume) of a homogeneous electron gas with constant density ρ(**r**).

$$t = \frac{T}{V} \qquad \boxed{t^{hom}\left(\rho(\vec{r})\right) = C^F \rho(\vec{r})^{5/3}} \qquad C^F = \frac{3\hbar}{10m}\left(3\pi^2\right)^{2/3}$$



Inhomogeneous system

Precursors of Kohn-Sham DFT: The Thomas-Fermi Method

Unfortunately, it turns out that this approximation is not very useful in chemistry: atoms have no shell structure, molecules are not bound !!!! ☹
Many, more sophisticated approximations have been suggested for T[ρ] but so far no sufficiently accurate *'pure'* density functional expression of T has been found!

e.g. Weizsäcker correction (1935): gradient expansion
T[ρ] = t(ρ(**r**),∇ρ(**r**))

$$\boxed{T^W = \frac{\hbar^2}{8m}\int \frac{\left|\nabla\rho(\vec{r})\right|^2}{\rho(\vec{r})}d\vec{r}}$$

☹

How can we calculate the kinetic energy of an interacting many electron system?

This is very easy in a wavefunction formulation:

$$\boxed{T = -\frac{1}{2}\left\langle \Psi \middle| \nabla^2 \middle| \Psi \right\rangle}$$

And in the case of noninteracting electrons, T is simply the sum of the kinetic energy of each electron:

$$\boxed{T = -\frac{1}{2}\sum_i \left\langle \phi_i \middle| \nabla^2 \middle| \phi_i \right\rangle}$$

Literature on Density Functional Theory

1. R. M. Dreizler and E. K. U. Gross, *Density Functional Theory*, Springer, Berlin, 1990.
2. R. G. Parr and W. Yang, *Density-Functional Theory of Atoms and Molecules*, Oxford University Press, Oxford, 1989.
3. W. Koch and M. C. Holthausen, *A Chemist's Guide to Density Functional Theory*, John Wiley & Sons, New York, 2001.
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5. J. M. Seminario (Ed.), *Recent Developments and Applications of Modern DFT*, Elsevier, Amsterdam, 1996.

Recent review orbital-free DFT: Mi et al. Chem Rev. 123, 12039-21204 (2023)

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Walter Kohn (1923 -2016)

Kohn and Sham Formulation of DFT

(Kohn&Sham, Phys. Rev. 1140, 1133A, 1965)

Lu Jeu Sham (1938)

- re-introduce some wavefunctions (single particle orbitals)
- The many-electron problem can be mapped exactly onto:

• an auxiliary *noninteracting* reference system with the same density (i.e. the exact ground state density)

$$\boxed{\rho(\vec{r}) = 2\sum_i \phi_i^*(\vec{r})\phi_i(\vec{r})} \qquad \boxed{\int d\vec{r}\,\rho(\vec{r}) = N}$$

kinetic energy of the noninteracting single-particle system $T_s[\rho]$ is

$$\boxed{T_s[\rho] = -\frac{1}{2}\sum_i^N \int d^3r\, \phi_i^*(\mathbf{r})\nabla^2\phi_i(\mathbf{r})}$$

kinetic energy of the interacting system $T[\rho]$ is

$$\boxed{T[\rho] = T_s[\rho] + T_c[\rho]}$$

• each electron moves in an effective 1-particle-potential due to all the other electrons

$$\boxed{v_s(\vec{r}) = v_{ext}(\vec{r}) + v_{ee}(\vec{r})}$$

$$\boxed{v_s(\mathbf{r}) = v_{ext}(\mathbf{r}) + v_H(\mathbf{r}) + v_{xc}(\mathbf{r})}$$

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KS Energy Functional

$$E^{KS}\left[\{\phi_i\}\right] = -\sum_i \int d\vec{r}\,\phi_i^*(\vec{r})\nabla^2\phi_i(\vec{r}) - \int V_{ext}(\vec{r})\rho(\vec{r})d\vec{r} + \frac{1}{2}\int \frac{\rho(\vec{r})\rho(\vec{r}')}{\vec{r}-\vec{r}'}d\vec{r}d\vec{r}' + E_{xc}\left[\rho(\vec{r})\right] + E_{ion}\left(\{\vec{R}_I\}\right)$$

Kinetic energy of the non interacting system
External potential due to ionic cores
Hartree-term ~ classical Coulomb energy

exchange-correlation energy functional (includes also T_c)
core -core interaction

Find $\rho_o(\mathbf{r})$, ϕ_i: minimize $E^{KS}\left[\{\phi_i\}\right]$ under orthonormality constraints for ϕ_i's

$$L = E^{KS}\left[\{\phi_i\}\right] + \sum_i\sum_j \varepsilon_{ij}\left(\int d\vec{r}\,\phi_i^*(\vec{r})\phi_j(\vec{r}) - \partial_{ij}\right)$$

ε_i: Lagrange multipliers associated with N orthogonality constraints

$$\frac{\partial L}{\partial \phi_i^*} = \frac{\partial E^{KS}\left[\{\phi_i\}\right]}{\partial \phi_i^*} - \sum_j \varepsilon_{ij}\phi_j$$

=> N single particle equations

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Kohn-Sham equations

N coupled Schrödinger equations (1 for each effective one-particle orbital):

$$\left[-\frac{1}{2}\nabla^2 + V_{ext}(\vec{r}) + V_H(\vec{r}) + V_{xc}(\vec{r})\right]\phi_i(\vec{r}) = \varepsilon_i\phi_i(\vec{r})$$

=> Solved self-consistently

$$V(\vec{r}) = \frac{\partial E\left[\rho(\vec{r})\right]}{\partial \rho(\vec{r})}$$

Potential is the functional derivative of the energy

V_H: Hartree potential

$$V^H(\vec{r}) = \frac{\partial E^H\left[\rho(\vec{r})\right]}{\partial \rho(\vec{r})} = \int d\vec{r}\,'\frac{\rho(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}$$

V_{XC}: exchange-correlation potential

$$V_{xc}(\vec{r}) = \frac{\partial E_{xc}\left[\rho(\vec{r})\right]}{\partial \rho(\vec{r})} \qquad V_{xc}(\vec{r}) = \varepsilon_{xc}[\rho] + \rho(\vec{r})\frac{\partial \varepsilon_{xc}[\rho]}{\partial \rho}$$

ε_{XC}: exchange-correlation energy per particle

Initial ϕ_is
↓
Calculate $\rho(\mathbf{r})$
↓
Calculate $V^H(\mathbf{r})$ and $V_{xc}(\mathbf{r})$
↓
Solve KS eqs
↓
New $\phi_i(\mathbf{r})$

We have to find suitable approximations for E_{xc}!

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Types of $E_{xc}[\rho]$ Approximations

virtual ϕ_i	⋮	Double hybrids
Exact HF exchange Occupied ϕ_i		hybrids meta hybrids
$\rho(\vec{r}), \nabla\rho(\vec{r}), \tau(\vec{r}) = \frac{1}{2}\sum_i \left|\nabla\phi_i(\vec{r})\right|^2$		meta
$\rho(\vec{r}), \nabla\rho(\vec{r})$		GGAs
$\rho(\vec{r})$		LDA

Perdew's Jacob's Ladder

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Exchange-Correlation Functionals

Usually split into separate contributions from exchange and correlation

$$\boxed{\varepsilon_{xc}[\rho] = \varepsilon_x[\rho] + \varepsilon_c[\rho]}$$

Rung 1: Local Density Approximation (LDA)

Purely local density functional ! (i.e. only dependent on the local position)

$$\boxed{E_{xc}^{LDA}[\rho] = \int d\vec{r}\,\rho(\vec{r})\,\varepsilon_{xc}^{\text{hom}}[\rho(\vec{r})]}$$

$\varepsilon_{xc}^{\text{hom}}[\rho(\vec{r})]$ exchange-correlation energy per particle of a homogeneous electron gas with uniform density

Exchange contribution

(P.A.M. Dirac, Proc. Cambridge Phil. Soc. 26, 376 (1930), E.P. Wigner, Trans. Faraday Soc. 34, 678 (1987))

can be determined exactly !

$$\boxed{\varepsilon_x^{\text{hom}}[\rho(\vec{r})] = -C_x\rho^{\frac{1}{3}}} \qquad \boxed{C_x = \frac{3}{4}\left(\frac{3}{\pi}\right)^{\frac{1}{3}}}$$

Correlation contribution $\varepsilon_c^{\text{hom}}[\rho(\vec{r})]$:

(D.M. Ceperly, B.J. Alder, Phys. Rev. Lett. 45, 566 (1980), G.Ortiz, P. Ballone, Phys. Rev. B 50, 1391 (1994))

Accurate (numerical) results available from Quantum Monte Carlo simulations for discrete values of the density Parameterized analytic forms that interpolate between different density regimes are available: e.g. J.P. Perdew, A. Zunger, Phys. Rev. B. 23, 5084 (1981)

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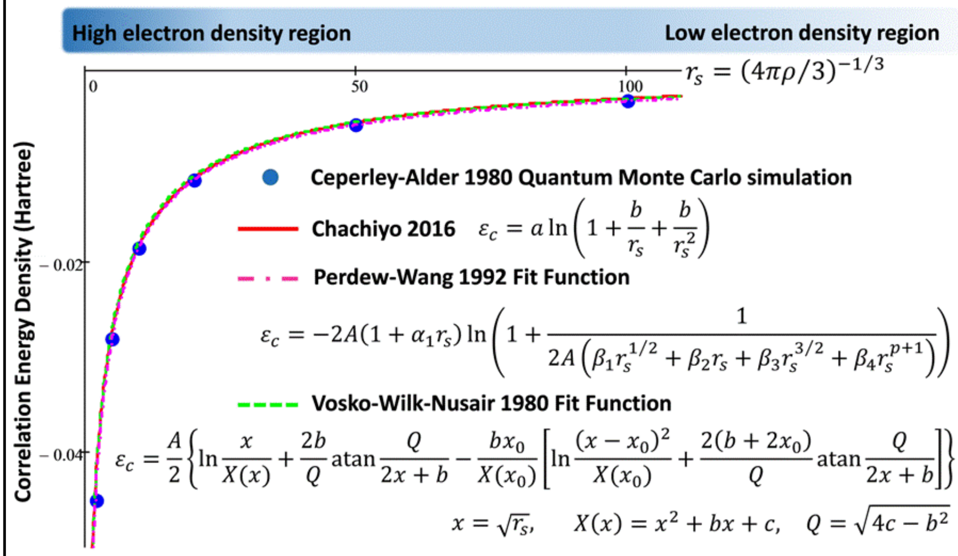

From wikipedia

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Performance of LDA

In principle LDA is a very crude approximation! Molecules do not have a homogeneous electron density!!!
E_{xc} of a non uniform system locally approximated by results of the uniform electron gas results, should 'work' only for systems with almost constant or slowly varying density!

But: atoms and molecules are highly inhomogeneous systems

However LDA works remarkably well in practice:
☺ in general good structural properties:

- bond lengths up to 1-2%
- bond angles ~ 1-2 degrees
- torsional angles ~ a few degrees

☺ vibrational frequencies
~ 10% (phonon modes up to few %)

Cr_2

	Re [Å]	De (eV)
HF	1.465	-19.4
CCSD	1.560	-2.9
CCSD(T)	1.621	0.5
DFT	1.59	1.5
exp	1.679	1.4

☺ cheap and good method for transition metals !
e.g. Cr_2, Mo_2 in good agreement with experiment (not bound in HF, UHF!)

☺ F_2 r_e within 3% (not bound in HF)

😐 atomization, dissociation energies over estimated (mainly due to errors for atoms), typically by 10-20%

☹ hydrogen-bonding overestimated

☹ van der Waals-complexes: strongly overestimated binding (e.g. noble gas dimers, Mg_2, Be_2: factor 2-4

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Generalized Gradient Approximations (GGAs)

$$E_{xc}^{GGA}[\rho] = \int d\vec{r}\, f_{xc}\left(\rho(\vec{r}), \nabla\rho(\vec{r})\right)$$

f_{xc} : analytic function that contains a number of adjustable parameters

Determination of parameters:

- fully non empirical
- fit to exact Ex-Corr energies for atoms
- fit to experimental data (empirical)

⇒ many different forms (B88, P86, LYP, PW91, PBE, BLYP, BP86 etc..)

$$E_x^{B88}[\rho] = C_x \int d\vec{r}\, \rho^{4/3}(\vec{r}) F_x(s) \qquad F_x^{B88}(s) = 1 + \frac{\gamma c_2 c_1^2 s^2}{1 + 6\gamma c_1 s \sinh^{-1}(c_1 s)}$$

$s = \frac{|\nabla\rho(\vec{r})|}{\rho(\vec{r})}$ Reduced gradient

enhancement factor

Fitted to exchange of 6 noble gases → $\gamma = 0.0042$

$C_x = 3/4(3/\pi)^{1/3}$

$c_1 = 2(6\pi^2)^{1/3}$

$c_2 = \left(2^{1/3} C_x\right)^{-1}$

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Meta-GGAs, Hybrids and Double Hybrids

Rung 3: Meta functionals

$$E_{xc}^{meta}[\rho] = \int d\vec{r}\, g_{xc}\left(\rho(\vec{r}), \nabla\rho(\vec{r}), \tau(\vec{r})\right)$$

$$\tau(\vec{r}) = \frac{1}{2}\sum_i^{occ} \left|\nabla\phi_i(\vec{r})\right|^2$$

Kinetic energy density

e.g. TPSS, SCAN, M06-L etc.

Rung 4: Hybrid functionals

use a fraction of exact exchange

$$E_x^{hybrid}[\rho] = aE_x^{EXX}[\phi_i] + (1-a)E_x^{GGA}[\rho]$$

$$E_x^{EXX}[\phi_i] = -\frac{1}{2}\sum_{i,j}^{occ} \int\int \frac{\phi_i(\vec{r})\phi_i^*(\vec{r}\,')\phi_j(\vec{r}\,')\phi_j^*(\vec{r})}{|\vec{r}-\vec{r}\,'|} d\vec{r}\, d\vec{r}\,'$$

e.g. B3LYP, PBE0, HSE, M06 etc.

$$E_x^{B3LYP} = E_x^{LDA} + a_0\left(E_x^{EXX} - E_x^{LDA}\right) + a_x\left(E_x^{GGA} - E_x^{LDA}\right) + a_c\left(E_c^{GGA} - E_c^{LDA}\right)$$

$a_0 = 0.2$, $a_x = 0.72$, $a_c = 0.81$

Rung 5: make use of unoccupied orbitals

e.g. RPA, double hybrids =>mix in a fraction of exact HF exchange and a fraction of MP2 correlation energy

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9. First-Principles Molecular Dynamics

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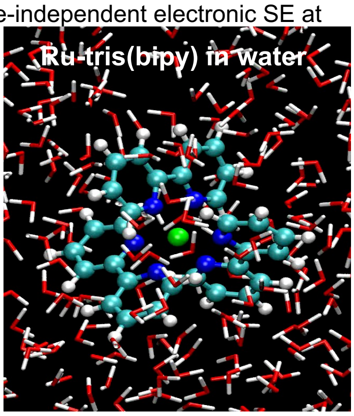
When the nuclei start to move: Ab initio Molecular Dynamics

- in principle => time-dependent Schrödinger eq.
- Within Born-Oppenheimer approximation: solve time-independent electronic SE at each nuclear configuration during dynamics
- Nuclei move classically => semiclassical methods



Classical dynamics of nuclei ($M_I >>> m_e$):

Newton's equations:

$$\boxed{M_I \ddot{R}_I = -\frac{\partial E}{\partial R_I}} \leftarrow E^{KS}[\rho(r)]$$

1) Do DFT calculation for a given geometry {R}-> E^{KS}{R}
2) Calculate forces acting on every nuclei I as dE^{KS}/dR_I
3) Integrate equations of motion to get new positions of nuclei at time $t = t_o+\Delta t$
4) Go to 1)

Born-Oppenheimer Molecular Dynamics

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10. Mixed Quantum Mechanical/Molecular Mechanical (QM/MM) Simulations

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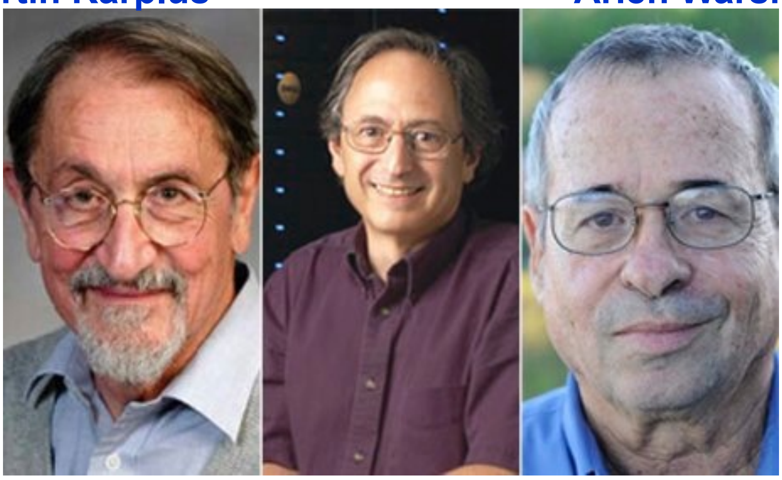
Nobelprize in Chemistry 2013

Martin Karplus **Michael Levitt** **Arieh Warshel**



***"for the development of multiscale models for complex chemical systems"*: mixed quantum mechanical/molecular mechancial (QM/MM) simulations**

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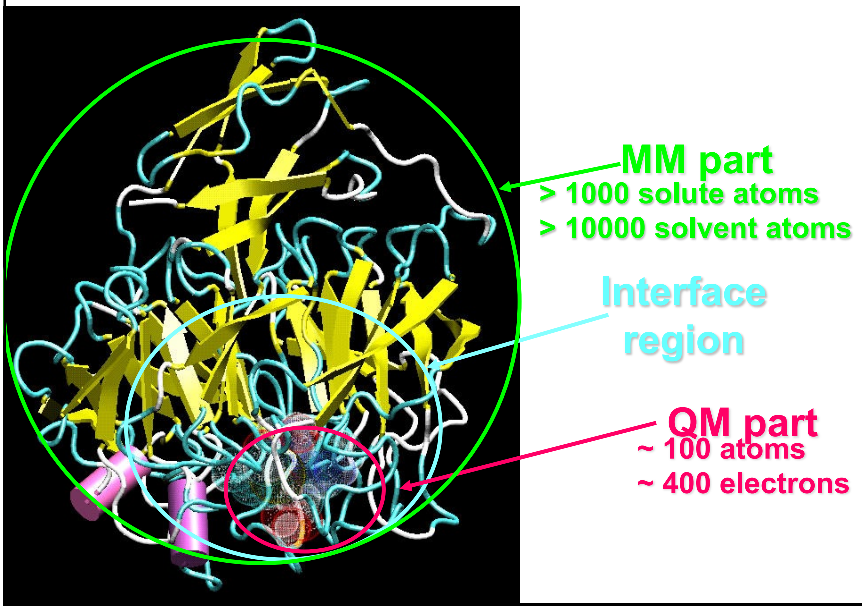
Mixed Quantum Mechanical / Molecular (QM/MM) Mechanical Methods



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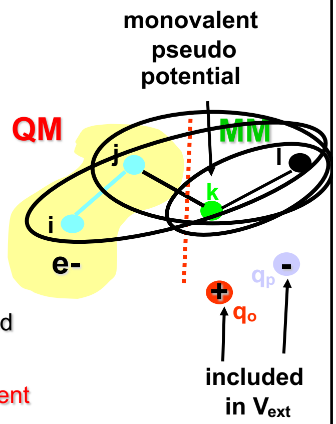
QM/MM coupling



• Bonded and van der Waals interactions: MM level

$$U(\vec{R}) = \sum_{bonds} K_r (r - r_{eq})^2 + \sum_{angles} K_\theta (\theta - \theta_{eq})^2$$

$$+ \sum_{dihedrals,n} \frac{V_n}{2}[1 + cos(n\phi - \gamma)] + \sum_{i<j} \frac{A_{ij}}{R_{ij}^{12}} - \frac{B_{ij}}{R_{ij}^{6}} + \sum_{i<j} \frac{q_i q_j}{\epsilon R_{ij}}$$

• bonded interaction in which at least 1 MM atom involved
$\Rightarrow$ via classical force field

(bonds across QM/MM interface saturated via monovalent pseudopotentials)

• van der Waals interactions:
- within MM and between QM and MM $\Rightarrow$ via classical force field parameters
- within QM:
  - none
  - via addition of empirical C_6 term
  - via optimized effective atom centered potentials (OECPs)

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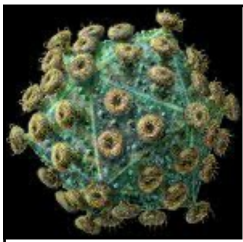
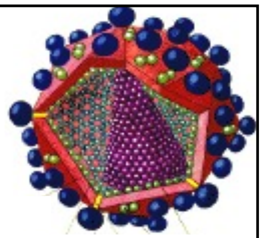
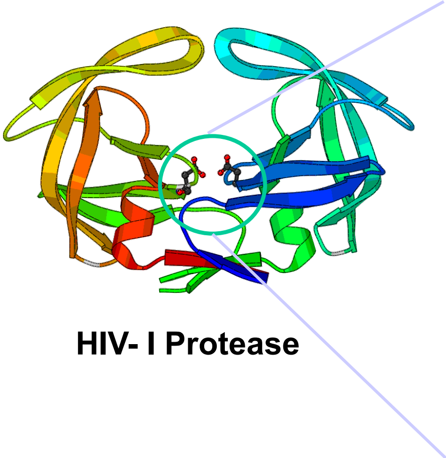
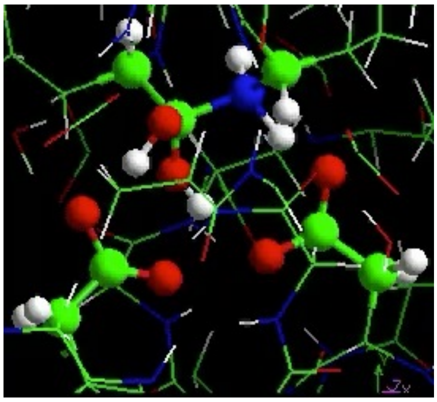


Watch Enzymes in Action..





HIV- I Protease



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Overview

Some important features of electronic structure methods:

- what is the Ansatz for the wavefunction?
- how are exchange and correlation treated?
- can static correlation/multireference problems be treated?
- is the method variational (i.e. is E always ≥ E_{true})?
- is the method size consistent (i.e. is the energy of two noninteracting systems the sum of the single systems?)
- can excited states be treated with the same method?
- what is the scaling of the method (i.e. how does the computational cost grow if I double the system size?)

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Method	wavefunction	exchange	correlation	variational?	Size-consistentt?	multi-ref?	Excited states?	Scaling
HF	1 determinant	exact	none	yes	yes	no	no	N^2-N^4
MPn	contributions from excited determinants through perturbation	exact	some	no	yes	CAS-PT2	CAS-PT2	MP2 N^5 MP3 N^6 MP4 N^7
Truncated CI	selected determinants	exact	some	yes	no	no	yes	e.g. CISD N^6
CASSCF	selected dets determinants	exact	little	yes	no	yes	yes	exp, $N_{act}*N_{det}^4$
CC	contribution of selected excitations through infinite order	exact	some	no	yes	no	EOM-CC CC2	CCSD N^6 CCSD(T) N^7 CCSDT N^8 CCSDTQ N^{10}
Full CI	exact wf within basis set, linear combination of all possible excited determinants	exact	all	yes	yes	yes	yes	$N!/N_{el}!(N-N_{el})!$
Exact DFT	electron density	exact	exact	yes	yes	no	TDDFT	N
Orbital-free DFT	electron density	some	some	no	yes	no	TDDFT	N
KS-DFT	electron density	some	some	no	yes	no	TDDFT	N^2-N^3

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