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)

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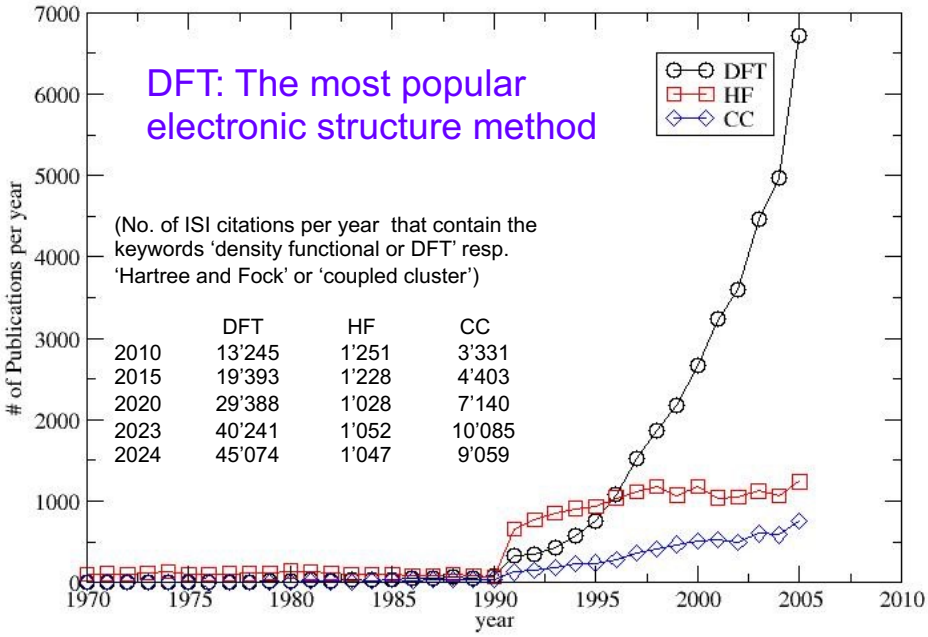


3

Walter Kohn and John Pople

1923-2016

Nobelprize in

Chemistry 1998

1925-2004

Schrödingers equations made easy with DFT!

4

Density Functional Theory (DFT)

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

$$H\Psi = E\Psi$$

Let's choose the electron density ρ(r) as central quantity:

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

3N variables → 3 variables

Integrate over N-1 variables!

Electron density ρ(r):

$$\rho = \frac{\#electrons}{V}$$

$$\rho(\vec{r}) = M \int \ldots \int \Psi^*(\vec{r}, \vec{r}_2, \vec{r}_3 \ldots \vec{r}_N) \Psi(\vec{r}, \vec{r}_2, \vec{r}_3 \ldots \vec{r}_N) d\vec{r}_2 \ldots d\vec{r}_N$$

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

Single particle system:

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

f_i: occupation (2,1,or 0)

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

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).

5

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 ρ(**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 ρ(**r**) (e.g. reactivity indices, hardness, softness etc…)
- can easily be combined with ab initio molecular dynamics

6

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?

7

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:

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

- $\hat{T}_e(\mathbf{r})$: kinetic energy operator
- $\hat{V}_{eN}(\mathbf{r},\mathbf{R})$: Electron-nuclei Coulomb potential
- $\hat{V}_{NN}(\mathbf{R})$: Nuclei-nuclei Interaction Potential (constant for fixed R)
- $\hat{V}_{ee}(\mathbf{r})$: Electron-electron repulsion potential

Convention:

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

External potential V_{ext}

9

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?

10

What is Density Functional Theory?

Conventional (wavefunction based) quantum chemical methods:

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

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!!

12

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

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

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

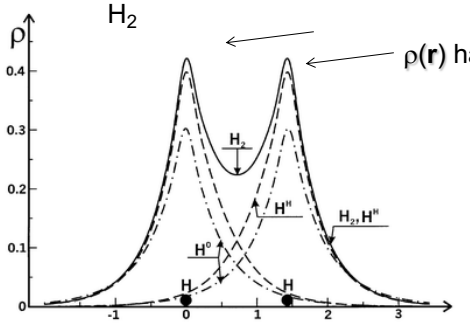
And vice versa: V_{ext} is determined within an additive constant by $\rho_0(\vec{r})$

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

13

Electron density distributions

H_2

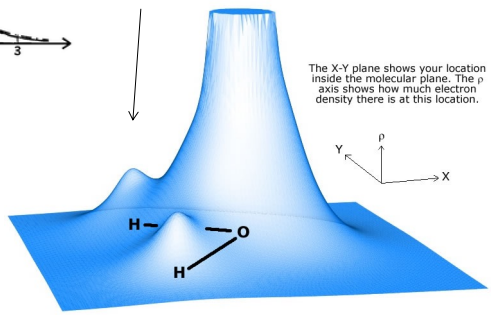


ρ(**r**) has cusp at nuclear positions

Kato's cusp condition:

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

H_2O



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

14

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 $\rho_0(\mathbf{r})$ $\Psi = \Psi[\rho]$

→ 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 $\rho_0(\mathbf{r})$

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

15

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 $\rho_0(\vec{r})$

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

16

2nd 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!!!

17

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

18

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?

19

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:

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

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

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

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

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]?

21

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 $\rho(\mathbf{r})$ (analogous to the Hartree term in the Hartree-Fock method):

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

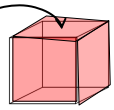
Thomas-Fermi Approximation: Exchange and correlation effects neglected

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:

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

N electrons homogeneus compensating positive charge: jellium

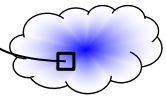


Homogeneous electron gas ρ = N/V = const

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

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

Inhomogeneous system



22

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**))

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

☹

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

This is very easy in a wavefunction formulation:

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

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

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

23

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

24

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)

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

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

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

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

$$T[\rho] = T_s[\rho] + T_c[\rho]$$

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

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

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

25

KS Energy Functional

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

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

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

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

26

Kohn-Sham equations

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

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

=> Solved self-consistently

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

Potential is the functional derivative of the energy

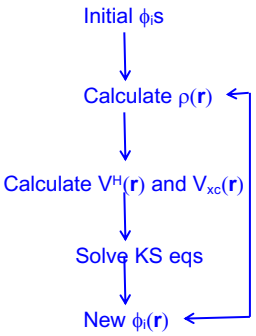
V_H: Hartree potential

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

V_{XC}: exchange-correlation potential

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

ε_{xc}: exchange-correlation energy per particle



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

27

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

28

Exchange-Correlation Functionals

Usually split into separate contributions from exchange and correlation

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

Rung 1: Local Density Approximation (LDA)

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

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

$\varepsilon_{xc}^{\text{hom}}[\rho(\vec{r})]$ 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 !

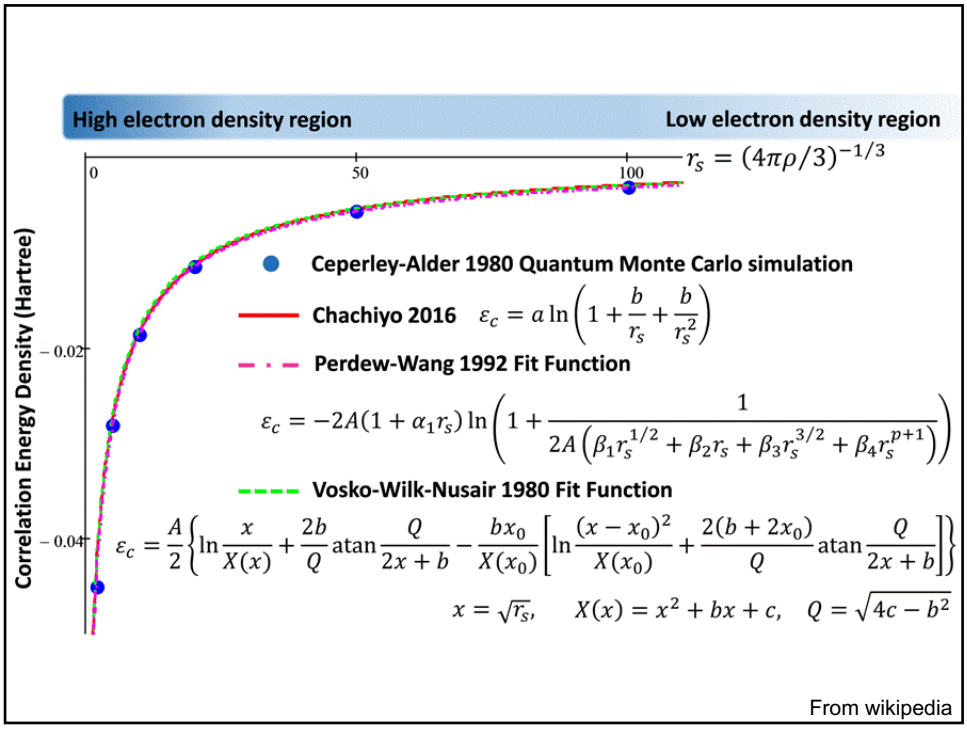
$$\varepsilon_x^{\text{hom}}[\rho(\vec{r})] = -C_x\rho^{\frac{1}{3}} \qquad C_x = \frac{3}{4}\left(\frac{3}{\pi}\right)^{\frac{1}{3}}$$

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)

29



30

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

31

Generalized Gradient Approximations (GGAs)

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

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..)

$$E_x^{B88}\left[\rho\right]=C_x\int d\vec{r}\,\rho^{4/3}\left(\vec{r}\right)F_x\left(s\right)$$

$$F_x^{B88}\left(s\right)=1+\frac{\gamma c_2 c_1^2 s^2}{1+6\gamma c_1 s\sinh^{-1}\left(c_1 s\right)}$$

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

enhancement factor

Fitted to exchange of 6 noble gases → γ =0.0042

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

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

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

32

Meta-GGAs, Hybrids and Double Hybrids

Rung 3: Meta functionals

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

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

Kinetic energy density

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

Rung 4: Hybrid functionals

use a fraction of exact exchange

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

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

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

33

Exchange-Correlation Functionals from Machine Learning

Direct Learning: ML models to predict xc energy or potential from $\rho(\mathbf{r})$
Delta Learning: ML models to correct/augment existing functionals
Direct prediction of properties

Neural Networks
Gaussian Process Regression
Kernel Ridge Regression

Requirements:
- Need for a lot of high-level data: CC calculations, QMC, exact models
- Representation of $\rho(\mathbf{r})$

Examples:
- DM21, SchNet for xc, NICE functionals, GradDFT etc..

Challenges:
- Accuracy, amount and diversity of training data
- Transferability across chemical space
- Physical constraints
- Computational efficiency

Literature:
Kalita et al. *Acc. Chem. Res.* 54, 818 (2021); Kirkpatrick et al. *Science* 374, 1385 (2021); Wang et al. *JACS AU* 8, 3205 (2024)

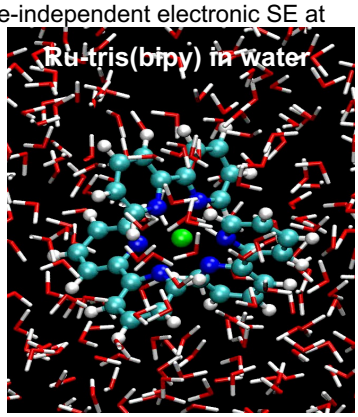
34

9. First-Principles Molecular Dynamics

35

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:

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

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

36

When Newton meets Schrödinger...

Sir Isaac Newton (1642 - 1727)

$$F = ma$$

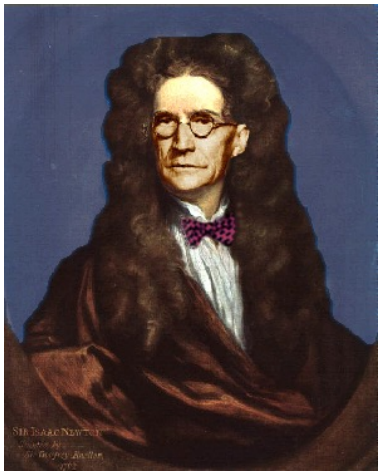
Erwin Schrödinger (1887 - 1961)

$$\hat{H}\Psi = \varepsilon\Psi$$

37

New-dinger

$F = ma$



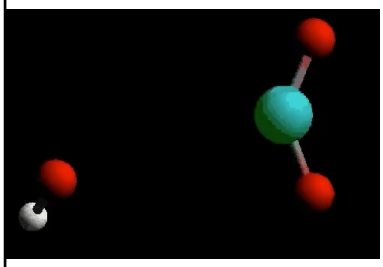
$\hat{H}\Psi = \varepsilon\Psi$

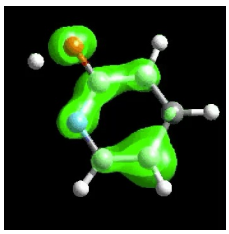
The ideal combination for

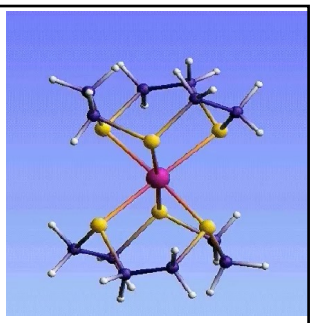
Ab Initio Molecular Dynamics

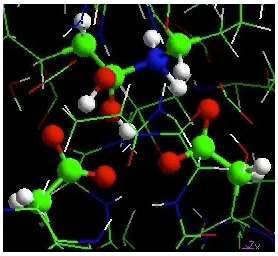
38

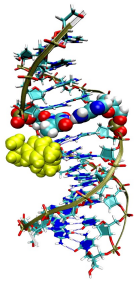
Chemical Reactions:

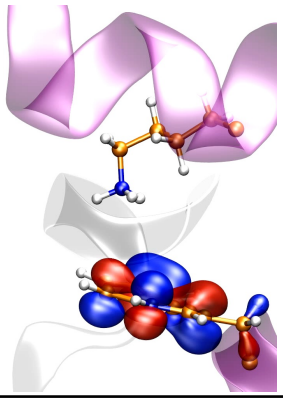












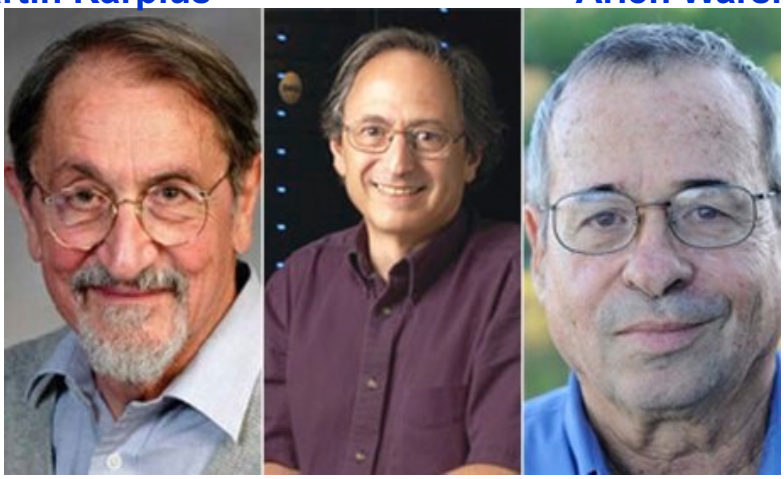
39

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

40

Nobelprize in Chemistry 2013

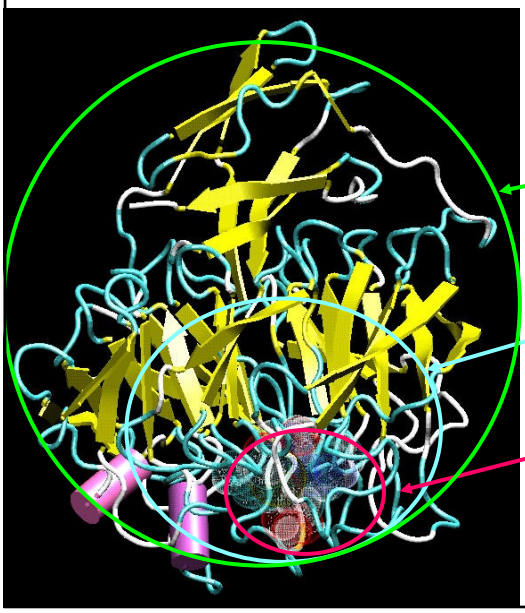
Martin Karplus | Michael Levitt | Arieh Warshel



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

41

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



MM part
> 1000 solute atoms
> 10000 solvent atoms

Interface region

QM part
~ 100 atoms
~ 400 electrons

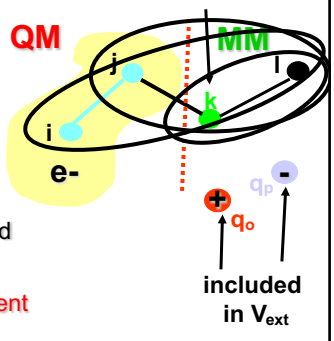
42

QM/MM coupling

monovalent pseudo potential

• **Bonded and van der Waals interactions: MM level**

$$U(\vec{R}) = \sum_{bonds} K_r(r - r_{eq})^2 + \sum_{angles} K_\theta(\theta - \theta_{eq})^2 + \sum_{dihedrals,n} \frac{V_n}{2}[1 + cos(n\phi - \gamma)] + \sum_{i<j} \frac{A_{ij}}{R_{ij}^{12}} - \frac{B_{ij}}{R_{ij}^{6}} + \sum_{i<j} \frac{q_i q_j}{\epsilon R_{ij}}$$



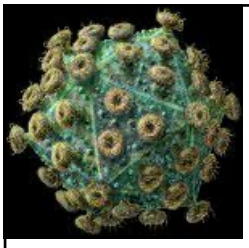
included in V_{ext}

• bonded interaction in which at least 1 MM atom involved
⇒ via classical force field

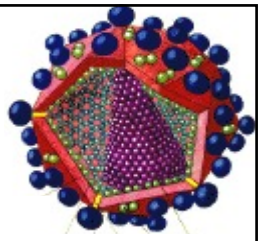
(bonds across QM/MM interface saturated via monovalent pseudopotentials)

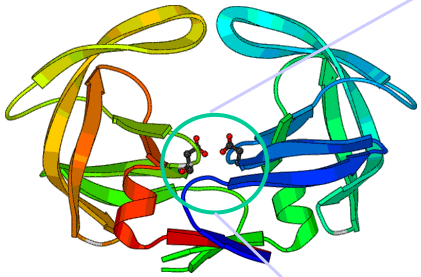
• van der Waals interactions:
- within MM and between QM and MM ⇒ via classical force field parameters
- within QM:
  - none
  - via addition of empirical C_6 term
  - via optimized effective atom centered potentials (OECPs)

43

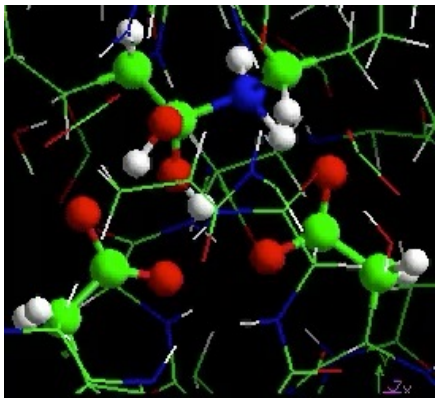


Watch Enzymes in Action..





HIV- I Protease



44

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?)

45

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

46