

Computational Chemistry

- **Molecular Mechanics/Dynamics**

$$\mathbf{F} = \mathbf{M}\mathbf{a}$$

- **Quantum Chemistry**

Schrödinger Equation

$$H\psi = E\psi$$

Density-Functional Theory

Schrödinger Equation

$$\mathbf{H} \psi = \mathbf{E} \psi$$

Wavefunction

Hamiltonian

$$H = -(\hbar^2/2m_e)\sum_i \nabla_i^2 + \sum_i V(r_i) + \sum_i \sum_j e^2/r_{ij}$$

Energy

Text Book:

**Density-Functional Theory for Atoms and Molecules
by Robert Parr & Weitao Yang**

Hartree-Fock Method

1. Many-Body Wave Function is approximated by Slater Determinant

2. Hartree-Fock Equation

$$F \phi_i = \varepsilon_i \phi_i$$

F Fock operator

ϕ_i the i -th Hartree-Fock orbital

ε_i the energy of the i -th Hartree-Fock orbital

3. Roothaan Method (introduction of Basis functions)

$$\phi_i = \sum_k c_{ki} \psi_k \quad \text{LCAO-MO}$$

$\{ \psi_k \}$ is a set of atomic orbitals (or basis functions)

4. Hartree-Fock-Roothaan equation

$$\sum_j (F_{ij} - \epsilon_i S_{ij}) c_{ji} = 0$$

$$F_{ij} \equiv \langle \psi_i | F | \psi_j \rangle$$

$$S_{ij} \equiv \langle \psi_i | \psi_j \rangle$$

5. Solve the Hartree-Fock-Roothaan equation self-consistently

Basis set of GTFs

STO-3G, 3-21G, 4-31G, 6-31G, 6-31G*, 6-31G**

----->
complexity & accuracy

Minimal basis set: one STO for each atomic orbital (AO)

STO-3G: 3 GTFs for each atomic orbital

3-21G: 3 GTFs for each inner shell AO

2 CGTFs (w/ 2 & 1 GTFs) for each valence AO

6-31G: 6 GTFs for each inner shell AO

2 CGTFs (w/ 3 & 1 GTFs) for each valence AO

6-31G*: adds a set of d orbitals to atoms in 2nd & 3rd rows

6-31G**: adds a set of d orbitals to atoms in 2nd & 3rd rows
and a set of p functions to hydrogen

*Polarization
Function*

Diffuse/Polarization Basis Sets:

For excited states and in anions where electronic density is more spread out, additional basis functions are needed.

Polarization functions to 6-31G basis set as follows:

6-31G* - adds a set of polarized d orbitals to atoms
in 2nd & 3rd rows (Li - Cl).

6-31G** - adds a set of polarization d orbitals to atoms in
2nd & 3rd rows (Li- Cl) and a set of p functions
to H

Diffuse functions + polarization functions:

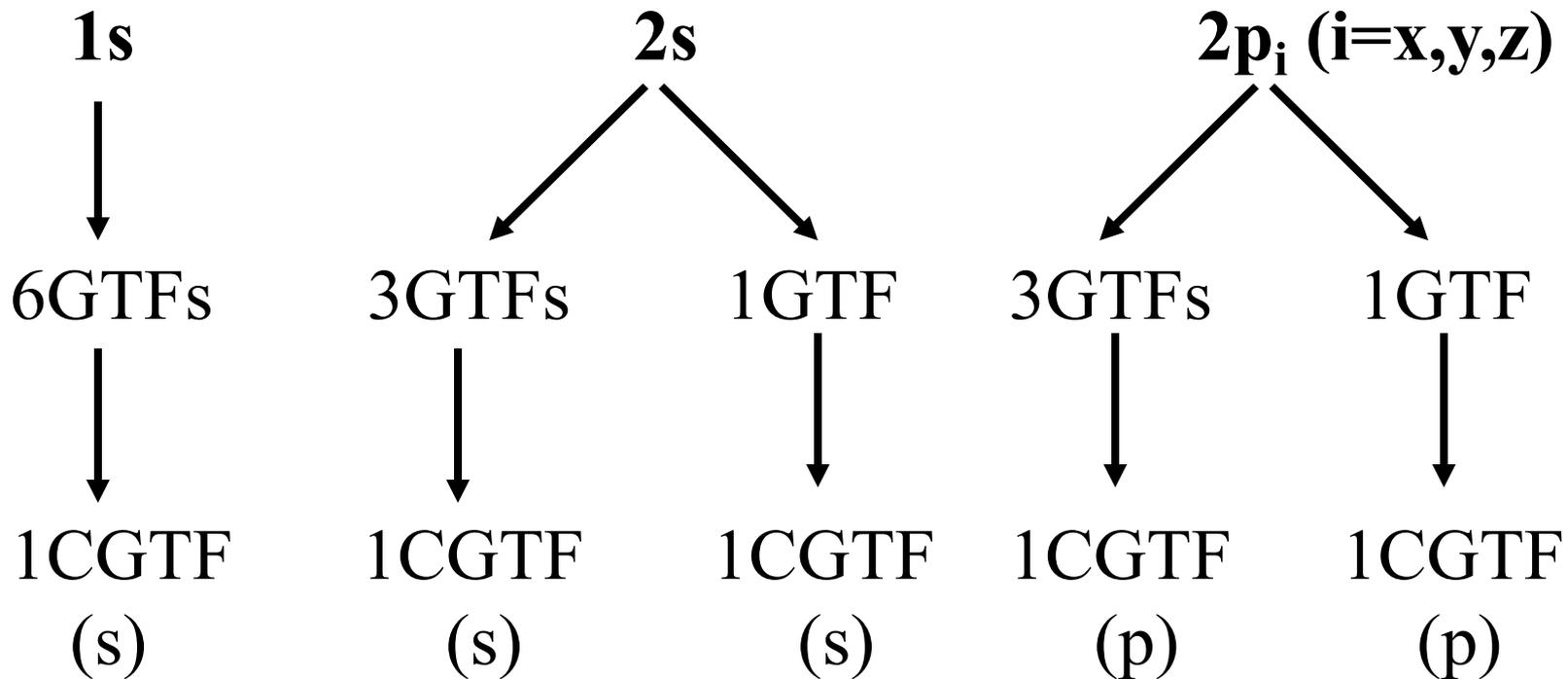
6-31+G*, 6-31++G*, 6-31+G** and 6-31++G** basis sets.

Double-zeta (DZ) basis set:

two STO for each AO

6-31G for a carbon atom:

$(10s12p) \rightarrow [3s6p]$



Hohenberg-Kohn Theorems

1st Hohenberg-Kohn Theorem: *The external potential $V(\mathbf{r})$ is determined, within a trivial additive constant, by the electron density $\rho(\mathbf{r})$.*

Implication: electron density determines every thing.

$$\begin{aligned} E_0 < \langle \Psi' | \hat{H} | \Psi' \rangle &= \langle \Psi' | \hat{H}' | \Psi' \rangle + \langle \Psi' | \hat{H} - \hat{H}' | \Psi' \rangle \\ &= E'_0 + \int \rho(\mathbf{r}) [v(\mathbf{r}) - v'(\mathbf{r})] d\mathbf{r} \end{aligned}$$

$$\begin{aligned} E'_0 < \langle \Psi | \hat{H}' | \Psi \rangle &= \langle \Psi | \hat{H} | \Psi \rangle + \langle \Psi | \hat{H}' - \hat{H} | \Psi \rangle \\ &= E_0 - \int \rho(\mathbf{r}) [v(\mathbf{r}) - v'(\mathbf{r})] d\mathbf{r}. \end{aligned}$$

$$E_0 + E'_0 < E'_0 + E_0$$

2nd Hohenberg-Kohn Theorem: *For a trial density, $\tilde{\rho}(\mathbf{r})$*

such that $\tilde{\rho}(\mathbf{r}) \geq 0$ and $\int \tilde{\rho}(\mathbf{r}) d\mathbf{r} = N$.

$$E_0 \leq E_v[\tilde{\rho}]$$

Implication: Variation approach to determine ground state energy and density.

$$\begin{aligned} E_v[\rho] &= T[\rho] + V_{ne}[\rho] + V_{ee}[\rho] \\ &= \int \rho(\mathbf{r})v(\mathbf{r}) d\mathbf{r} + F_{\text{HK}}[\rho] \end{aligned}$$

$$F_{\text{HK}}[\rho] = T[\rho] + V_{ee}[\rho]$$

$$V_{ee}[\rho] = J[\rho] + \text{nonclassical term}$$

$$\langle \tilde{\Psi} | \hat{H} | \tilde{\Psi} \rangle = \int \tilde{\rho}(\mathbf{r})v(\mathbf{r}) d\mathbf{r} + F_{\text{HK}}[\tilde{\rho}] = E_v[\tilde{\rho}] \geq E_v[\rho]$$

Kohn-Sham Equations

In analogy with the Hohenberg–Kohn definition of the universal functional $F_{\text{HK}}[\rho]$ (see §3.2 and §3.3), Kohn and Sham invoked a corresponding *noninteracting reference system*, with the Hamiltonian

$$\hat{H}_s = \sum_i^N \left(-\frac{1}{2}\nabla_i^2\right) + \sum_i^N v_s(\mathbf{r}_i)$$

in which there are no electron–electron repulsion terms, and for which *the ground-state electron density is exactly ρ* . For this system there will be an exact determinantal ground-state wave function

$$\Psi_s = \frac{1}{\sqrt{N!}} \det [\psi_1 \psi_2 \cdots \psi_N]$$

$$\rho(\mathbf{r}) = \sum_i^N \sum_s^2 |\psi_i(\mathbf{r}, s)|^2$$

$$\hat{h}_s \psi_i = \left[-\frac{1}{2}\nabla^2 + v_s(\mathbf{r})\right] \psi_i = \varepsilon_i \psi_i$$

The kinetic energy is $T_s[\rho]$ $T_s[\rho] = \langle \Psi_s | \sum_i^N \left(-\frac{1}{2}\nabla_i^2\right) | \Psi_s \rangle$

$$= \sum_{i=1}^N \langle \psi_i | -\frac{1}{2}\nabla^2 | \psi_i \rangle$$

the energy functional

$$E[\rho] = \int \rho(\mathbf{r})v(\mathbf{r}) d\mathbf{r} + F[\rho]$$

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

$$F[\rho] = T_s[\rho] + J[\rho] + E_{xc}[\rho]$$

exchange-correlation energy

$$E_{xc}[\rho] \equiv T[\rho] - T_s[\rho] + V_{ee}[\rho] - J[\rho]$$

The energy functional

$$\begin{aligned} E[\rho] &= T_s[\rho] + J[\rho] + E_{xc}[\rho] + \int v(\mathbf{r})\rho(\mathbf{r}) d\mathbf{r} \\ &= \sum_i^{N/2} \sum_s \int \psi_i^*(\mathbf{r})(-\frac{1}{2}\nabla^2)\psi_i(\mathbf{r}) d\mathbf{r} + J[\rho] + E_{xc}[\rho] + \int v(\mathbf{r})\rho(\mathbf{r}) d\mathbf{r} \end{aligned}$$

constrain the orbitals to be orthonormal, namely,

$$\int \psi_i^*(\mathbf{x}) \psi_j(\mathbf{x}) d\mathbf{x} = \delta_{ij}$$

Define the functional of the N orbitals

$$\Omega[\{\psi_i\}] = E[\rho] - \sum_i^N \sum_j^N \varepsilon_{ij} \int \psi_i^*(\mathbf{x}) \psi_j(\mathbf{x}) d\mathbf{x}$$

ε_{ij} are Lagrange multipliers for the constraints

$$\delta\Omega[\{\psi_i\}] = 0$$

which leads to the equations

$$\hat{h}_{\text{eff}} \psi_i = [-\frac{1}{2}\nabla^2 + v_{\text{eff}}] \psi_i = \sum_j^N \varepsilon_{ij} \psi_j$$

$$v_{\text{eff}}(\mathbf{r}) = v(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + v_{xc}(\mathbf{r})$$

$$v_{xc}(\mathbf{r}) = \frac{\delta E_{xc}[\rho]}{\delta \rho(\mathbf{r})}$$

Density Matrix

$$\gamma_1(\mathbf{x}'_1, \mathbf{x}_1) = N \int \cdots \int \Psi(\mathbf{x}'_1 \mathbf{x}_2 \cdots \mathbf{x}_N) \Psi^*(\mathbf{x}_1 \mathbf{x}_2 \cdots \mathbf{x}_N) d\mathbf{x}_2 \cdots d\mathbf{x}_N$$

$$\gamma_2(\mathbf{x}'_1 \mathbf{x}'_2, \mathbf{x}_1 \mathbf{x}_2)$$

$$= \frac{N(N-1)}{2} \int \cdots \int \Psi(\mathbf{x}'_1 \mathbf{x}'_2 \mathbf{x}_3 \cdots \mathbf{x}_N) \Psi^*(\mathbf{x}_1 \mathbf{x}_2 \mathbf{x}_3 \cdots \mathbf{x}_N) d\mathbf{x}_3 \cdots d\mathbf{x}_N$$

$$E = \text{tr}(\hat{H} \hat{\gamma}_N) = E[\gamma_1, \gamma_2] = E[\gamma_2]$$

$$= \int [(-\frac{1}{2}\nabla_1^2 + v(\mathbf{r}_1))\gamma_1(\mathbf{x}'_1, \mathbf{x}_1)]_{\mathbf{x}'_1=\mathbf{x}_1} d\mathbf{x}_1 + \iint \frac{1}{r_{12}} \gamma_2(\mathbf{x}_1 \mathbf{x}_2, \mathbf{x}_1 \mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2$$

$$\rho_1(\mathbf{r}'_1, \mathbf{r}_1) = \int \gamma_1(\mathbf{r}'_1 s_1, \mathbf{r}_1 s_1) ds_1$$

$$\rho_2(\mathbf{r}'_1 \mathbf{r}'_2, \mathbf{r}_1 \mathbf{r}_2) = \iint \gamma_2(\mathbf{r}'_1 s_1 \mathbf{r}'_2 s_2, \mathbf{r}_1 s_1 \mathbf{r}_2 s_2) ds_1 ds_2$$

$$\rho(\mathbf{r}_1) = \rho_1(\mathbf{r}_1, \mathbf{r}_1)$$

$$\rho_2(\mathbf{r}_1, \mathbf{r}_2) = \rho_2(\mathbf{r}_1 \mathbf{r}_2, \mathbf{r}_1 \mathbf{r}_2)$$

Local-density approximations

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

$$v_{xc}^{\text{LDA}}(\mathbf{r}) = \frac{\delta E_{xc}^{\text{LDA}}}{\delta \rho(\mathbf{r})} = \varepsilon_{xc}(\rho(\mathbf{r})) + \rho(\mathbf{r}) \frac{\delta \varepsilon_{xc}(\rho)}{\delta \rho}$$

the KS orbital equations read

$$\left[-\frac{1}{2} \nabla^2 + v(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + v_{xc}^{\text{LDA}}(\mathbf{r}) \right] \psi_i = \varepsilon_i \psi_i.$$

$$\varepsilon_{xc}(\rho) = \varepsilon_x(\rho) + \varepsilon_c(\rho)$$

$$\varepsilon_x(\rho) = -C_x \rho(\mathbf{r})^{1/3}, \quad C_x = \frac{3}{4} \left(\frac{3}{\pi} \right)^{1/3}$$

$$\varepsilon_c(r_s) = \frac{A}{2} \left\{ \ln \frac{x}{X(x)} + \frac{2b}{Q} \tan^{-1} \frac{Q}{2x+b} - \frac{bx_0}{X(x_0)} \left[\ln \frac{(x-x_0)^2}{X(x)} + \frac{2(b+2x_0)}{Q} \tan^{-1} \frac{Q}{2x+b} \right] \right\}$$

$$x = r_s^{1/2}, \quad X(x) = x^2 + bx + c, \quad Q = (4c - b^2)^{1/2} \quad c = 42.7198$$

$A = 0.0621814, \quad x_0 = -0.409286, \quad b = 13.0720$

The hybrid B3LYP functional is expressed as

$$E_{XC} = a_0 E_X^{\text{Slater}} + (1 - a_0) E_X^{\text{HF}} + a_X \Delta E_X^{\text{Becke}} + a_C E_C^{\text{LYP}} + (1 - a_C) E_C^{\text{VMN}},$$

$$E_X^{\text{Slater}} = - (1/\pi) \{3\pi^2 n(\mathbf{r})\}^{1/3} \quad a_0=0.80, a_X=0.72, a_C=0.81$$

E_X^{HF} is the exact exchange functional,

$$= E_X^{\text{LDA}} - \beta \sum_{\sigma} \int \rho_{\sigma}^{4/3} \frac{x_{\sigma}^2}{(1 + 6\beta x_{\sigma} \sinh^{-1} x_{\sigma})} d^3 \mathbf{r}$$

$$x_{\sigma} = \frac{|\nabla \rho_{\sigma}|}{\rho_{\sigma}^{4/3}}$$

$$E_C^{\text{LYP}} = -a \int \frac{1}{1 + d\rho^{-1/3}} \{ \rho + b\rho^{-2/3} [C_F \rho^{5/3} - 2t_W + (\frac{1}{9}t_W + \frac{1}{18}\nabla^2 \rho)] e^{-c\rho^{-1/3}} \} d\mathbf{r}$$

$$\epsilon_c(r_s) = A \left\{ \ln \frac{x^2}{X(x)} + \frac{2b}{Q} \tan^{-1} \frac{Q}{2x + b} - \frac{bx_0}{X(x_0)} \left[\ln \frac{(x - x_0)^2}{X(x)} + \frac{2(b + 2x_0)}{Q} \tan^{-1} \frac{Q}{2x + b} \right] \right\}$$

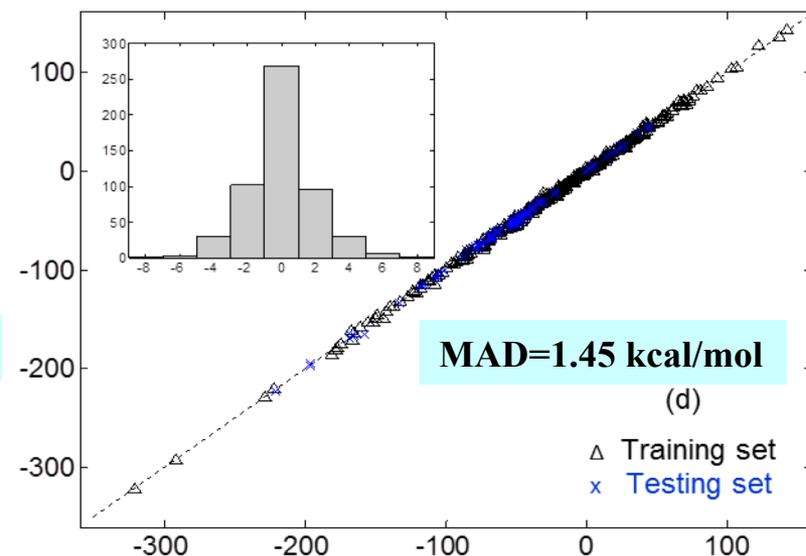
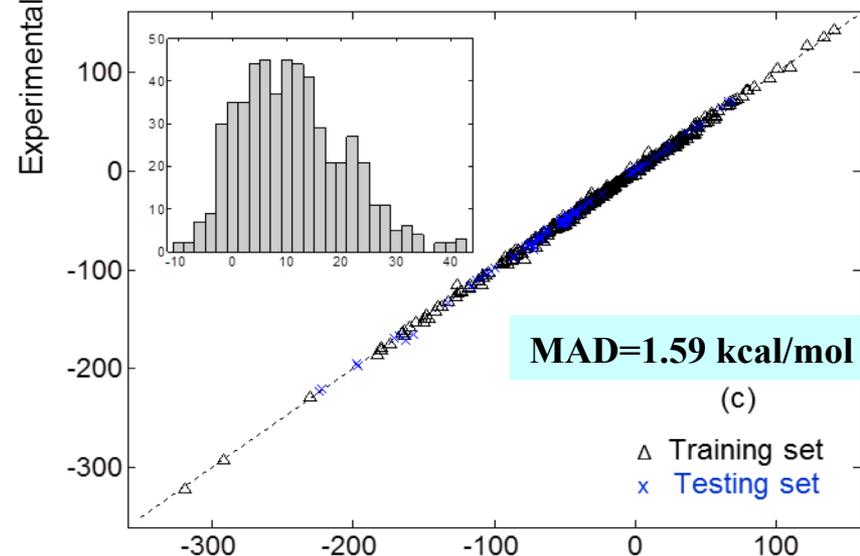
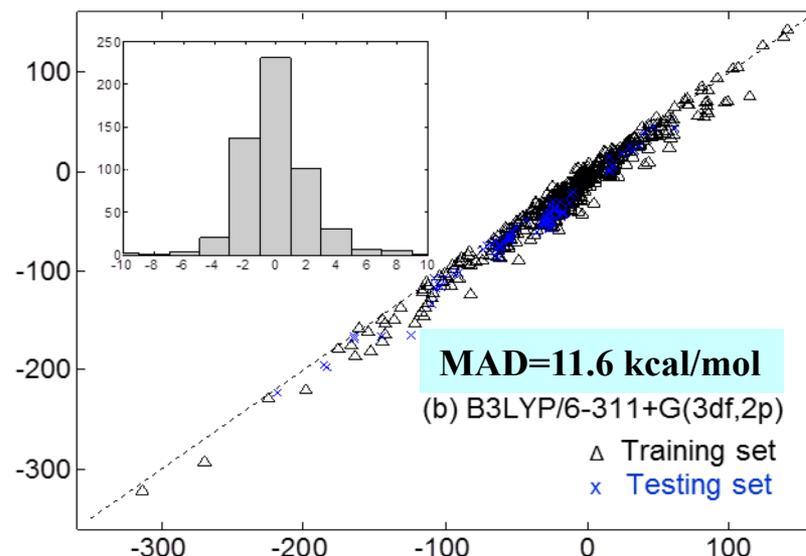
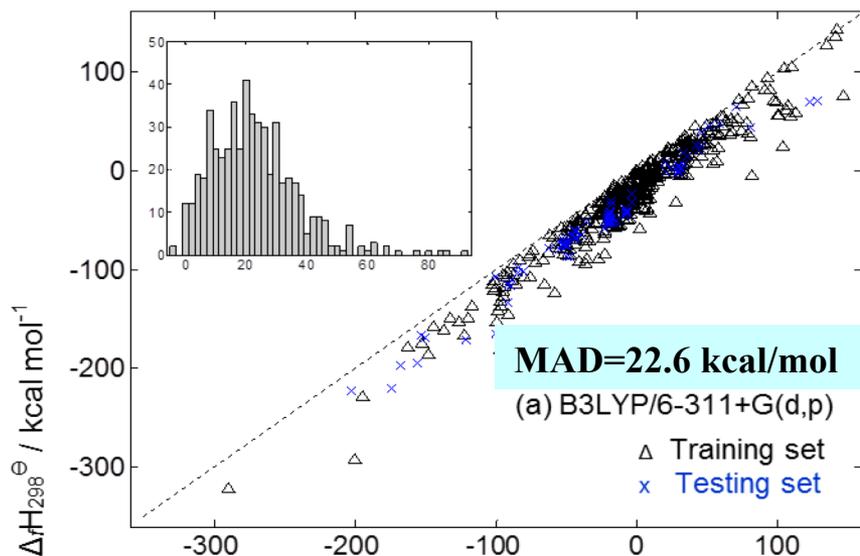
$$t_W(\mathbf{r}) = \frac{1}{8} \frac{|\nabla \rho(\mathbf{r})|^2}{\rho(\mathbf{r})} - \frac{1}{8} \nabla^2 \rho$$

$$A^{\text{P}} = 2A^{\text{F}} = 0.0621814 \quad x_0, b, c = 0.409286, 13.0720, \text{ and } 42.7198$$

1. Barrier heights: B3LYP was found²¹ to underestimate barrier heights by an average of 4.4 kcal/mol for a database of 76 barrier heights. This underestimation is usually ascribed to the self-interaction error (unphysical interaction of an electron with itself) in local DFT.
2. Noncovalent interactions: B3LYP is unable to describe van der Waals complexes bound by medium-range interactions, such as the interactions in methane dimers and benzene dimers. This inability of B3LYP (and most other popular functionals) to accurately describe medium-range XC energy limits their applicability for biological systems and soft materials where medium-range dispersion-like interactions play vital roles. Moreover, some recent studies have shown that inaccuracy for the medium-range XC energies leads to large systematic errors in the prediction of heats of formation of organic molecules^{22–29} and incorrect trends in the bond energies of organometallic catalytic systems.^{30,31}
3. Transition metal chemistry: B3LYP and many other hybrid functionals have been found to give unreliable results for transition metal chemistry,^{32–35} where better performance is often obtained with local functionals that are poor for main-group organic chemistry. For example, popular functionals containing Hartree–Fock exchange often overestimate the spin polarization of systems containing transition metals.

B3LYP/6-311+G(d,p)

B3LYP/6-311+G(3df,2p)



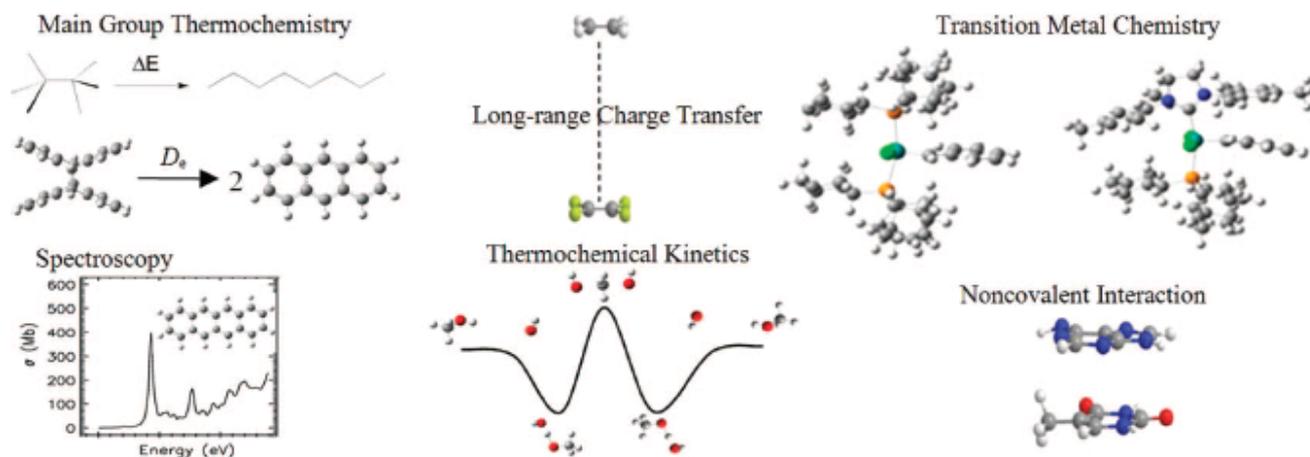
Calculated $\Delta_f H_{298}^\ominus / \text{kcal mol}^{-1}$

Density Functionals with Broad Applicability in Chemistry

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- (1) the M06-2X, BMK, and M05-2X functionals for main-group thermochemistry and kinetics
- (2) M06-2X and M06 for systems where main-group thermochemistry, kinetics, and noncovalent interactions are all important.
- (3) M06-L and M06 for transition metal thermochemistry.
- (4) M06 for problems involving multireference rearrangements or reactions where both organic and transition-metal bonds are formed or broken.
- (5) M06-2X, M05-2X, M06-HF, M06, and M06-L for the study of noncovalent interactions.
- (6) M06-HF when the use of full Hartree–Fock exchange is important, for example, to avoid the error of self-interaction at long-range.
- (7) M06-L when a local functional is required, because a local functional has much lower cost for large systems.

First-Principles Methods

**Usage: interpret experimental results
numerical experiments**

Goal: predictive tools

Inherent Numerical Errors caused by

Finite basis set

Electron-electron correlation

Exchange-correlation functional

In Principle:

DFT is exact for ground state

TDDFT is exact for excited states

To find:

Accurate / Exact Exchange-Correlation Functionals

Too Many Approximated Exchange-Correlation Functionals

System-dependency of XC functional ???

$$E_{XC}^{ex}[\rho] = E_{XC}[\rho] + \delta E_{XC}[\rho]$$

$E_{XC}[\rho]$: Existing Approx. XC functional

$$E_{XC}^{ex}[\rho] = (1 + a[\rho])E_{XC}[\rho]$$

$$a[\rho] = \delta E_{XC}[\rho] / E_{XC}[\rho]$$

When the exact XC functional is projected onto an existing XC functional, it should be system-dependent

The hybrid B3LYP functional is expressed as

$$E_{XC} = a_0 E_X^{Slater} + (1 - a_0) E_X^{HF} + a_X \Delta E_X^{Becke} + a_C E_C^{LYP} + (1 - a_C) E_C^{VMN}, \quad (1)$$

$$E_{XC}^{ex}[\rho] = E_{XC}[\rho] + \delta E_{XC}[\rho]$$

$$\delta E_{XC}[\rho] = \delta a_0[\rho] E_X^{Slater}[\rho] - \delta a_0[\rho] E_X^{HF}[\rho] + \delta a_X[\rho] \Delta E_X^{Becke}[\rho] + \delta a_C[\rho] E_C^{LYP}[\rho] - \delta a_C[\rho] E_C^{VMN}[\rho]$$

$$E_{XC}^{ex}[\rho] = a_0[\rho] E_X^{Slater}[\rho] + (1 - a_0[\rho]) E_X^{HF}[\rho] + a_X[\rho] \Delta E_X^{Becke}[\rho] + a_C[\rho] E_C^{LYP}[\rho] + (1 - a_C[\rho]) E_C^{VMN}[\rho]$$

$E_{XC}[\rho]$ is system-dependent functional of ρ

Any hybrid exchange-correlation functional is system-dependent

v - and N -representability

we define a density to be v -representable if

it is the density associated with the antisymmetric ground-state wave

The second Hohenberg–Kohn theorem simply states that for all v -representable densities,

$$E_v[\rho] \equiv F_{\text{HK}}[\rho] + \int v(\mathbf{r})\rho(\mathbf{r}) d\mathbf{r} \geq E_v[\rho_0] \quad (3.3.2)$$

where $E_v[\rho_0]$ is the ground-state energy of the Hamiltonian with $v(\mathbf{r})$ as external potential, and ρ_0 is its ground-state density.

What if a trial density is not v -representable?

A density is N -

v -representable if it can be obtained from some antisymmetric wave

a density $\rho(\mathbf{r})$ is N -representable if

$$\rho(\mathbf{r}) \geq 0, \quad \int \rho(\mathbf{r}) d\mathbf{r} = N, \quad \text{and} \quad \int |\nabla \rho(\mathbf{r})|^{1/2} d\mathbf{r} < \infty.$$

The Levy constrained-search formulation

there exist an infinite number of antisymmetric wave functions (not necessarily from ground states) that all give the same density. Given one of these functions that integrates to ρ_0 , say Ψ_{ρ_0} , how do we distinguish it from the true ground-state Ψ_0 ?

minimum-energy principle for the ground state gives

$$\langle \Psi_{\rho_0} | \hat{H} | \Psi_{\rho_0} \rangle \geq \langle \Psi_0 | \hat{H} | \Psi_0 \rangle = E_0$$

$$\langle \Psi_{\rho_0} | \hat{T} + \hat{V}_{ee} | \Psi_{\rho_0} \rangle + \int v(\mathbf{r})\rho_0(\mathbf{r}) d\mathbf{r} \geq \langle \Psi_0 | \hat{T} + \hat{V}_{ee} | \Psi_0 \rangle + \int v(\mathbf{r})\rho_0(\mathbf{r}) d\mathbf{r}$$

$$\langle \Psi_{\rho_0} | \hat{T} + \hat{V}_{ee} | \Psi_{\rho_0} \rangle \geq \langle \Psi_0 | \hat{T} + \hat{V}_{ee} | \Psi_0 \rangle$$

the ground state Ψ_0 minimizes the expectation value $\langle \hat{T} + \hat{V}_{ee} \rangle$

$$E_{\text{HK}}[\rho_0] = \langle \Psi_0 | \hat{T} + \hat{V}_{ee} | \Psi_0 \rangle$$

$$= \text{Min}_{\Psi \rightarrow \rho_0} \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle$$

Defining $E_{\text{HK}}[\rho_0]$ by (3.4.4) not only provides a new proof for the first theorem of Hohenberg and Kohn, but also eliminates the original Hohenberg–Kohn limitation that there be no degeneracy in the ground state. For in the constrained search, only one of a set of degenerate wave functions is selected, the one corresponding to ρ_0 .

$$\begin{aligned}
 E_0 &= \text{Min}_{\Psi} \langle \Psi | \hat{T} + \hat{V}_{ee} + \sum_i^N v(\mathbf{r}_i) | \Psi \rangle \\
 &= \text{Min}_{\rho} \left\{ \text{Min}_{\Psi \rightarrow \rho} \langle \Psi | \hat{T} + \hat{V}_{ee} + \sum_i^N v(\mathbf{r}_i) | \Psi \rangle \right\} \\
 &= \text{Min}_{\rho} \left\{ \text{Min}_{\Psi \rightarrow \rho} \left[\langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle + \int v(\mathbf{r})\rho(\mathbf{r}) d\mathbf{r} \right] \right\}
 \end{aligned}$$

constrained-search eliminates v -representability constraint

Spin-density-functional theory

$$\hat{H} = -\frac{1}{2} \sum_i^N \nabla_i^2 + \sum_{i<j}^N \frac{1}{r_{ij}} + \sum_i^N v(\mathbf{r}_i) + 2\beta_e \sum_i^N \mathbf{B}(\mathbf{r}) \cdot \mathbf{s}_i$$

$\beta_e = e\hbar/2mc$ is the Bohr magneton

$$E_0 = \text{Min}_{\Psi} \langle \Psi | \hat{T} + \hat{V}_{ee} + \sum_i^N v(\mathbf{r}_i) + 2\beta_e \sum_i^N b(\mathbf{r}_i) \cdot \mathbf{s}_z(i) | \Psi \rangle$$

$$= \text{Min}_{\rho^\alpha, \rho^\beta} \left\{ \text{Min}_{\Psi \rightarrow \rho^\alpha, \rho^\beta} \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle + \int [v(\mathbf{r})\rho(\mathbf{r}) - b(\mathbf{r})m(\mathbf{r})] d\mathbf{r} \right\}$$

$$= \text{Min}_{\rho^\alpha, \rho^\beta} \left\{ F[\rho^\alpha, \rho^\beta] + \int d\mathbf{r} [(v(\mathbf{r}) + \beta_e b(\mathbf{r}))\rho^\alpha(\mathbf{r}) + (v(\mathbf{r}) - \beta_e b(\mathbf{r}))\rho^\beta(\mathbf{r})] \right\}$$

$$F[\rho^\alpha, \rho^\beta] = \text{Min}_{\Psi \rightarrow \rho^\alpha, \rho^\beta} \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle$$

$$m(\mathbf{r}) = \beta_e [\rho^\beta(\mathbf{r}) - \rho^\alpha(\mathbf{r})]$$

$$E[\rho^\alpha, \rho^\beta] = \sum_{i\sigma} n_{i\sigma} \int d\mathbf{r} \phi_{i\sigma}^*(\mathbf{r}) \left(-\frac{1}{2} \nabla^2 \right) \phi_{i\sigma}(\mathbf{r}) + J[\rho^\alpha + \rho^\beta] + E_{xc}[\rho^\alpha, \rho^\beta] \\ + \int d\mathbf{r} [(v(\mathbf{r}) + \beta_e b(\mathbf{r})) \rho^\alpha(\mathbf{r}) + (v(\mathbf{r}) - \beta_e b(\mathbf{r})) \rho^\beta(\mathbf{r})]$$

The resulting Kohn–Sham equations are

$$\hat{h}_{\text{eff}}^\alpha \phi_{i\alpha}(\mathbf{r}) = \left[-\frac{1}{2} \nabla^2 + v_{\text{eff}}^\alpha(\mathbf{r}) \right] \phi_{i\alpha}(\mathbf{r}) \\ = \frac{\epsilon'_{i\alpha}}{n_{i\alpha}} \phi_{i\alpha}(\mathbf{r}) = \epsilon_{i\alpha} \phi_{i\alpha}(\mathbf{r}), \quad i = 1, 2, \dots, N^\alpha$$

$$\hat{h}_{\text{eff}}^\beta \phi_{j\beta}(\mathbf{r}) = \left[-\frac{1}{2} \nabla^2 + v_{\text{eff}}^\beta(\mathbf{r}) \right] \phi_{j\beta}(\mathbf{r}) \\ = \frac{\epsilon'_{j\beta}}{n_{j\beta}} \phi_{j\beta}(\mathbf{r}) = \epsilon_{j\beta} \phi_{j\beta}(\mathbf{r}), \quad j = 1, 2, \dots, N^\beta$$

$$v_{\text{eff}}^\alpha = v(\mathbf{r}) + \beta_e b(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \frac{\delta E_{xc}[\rho^\alpha, \rho^\beta]}{\delta \rho^\alpha(\mathbf{r})}$$

$$v_{\text{eff}}^\beta = v(\mathbf{r}) - \beta_e b(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \frac{\delta E_{xc}[\rho^\alpha, \rho^\beta]}{\delta \rho^\beta(\mathbf{r})}$$

$$E_x^{\text{LSD}}[\rho^\alpha, \rho^\beta] = 2^{1/3} C_x \int [(\rho^\alpha)^{4/3} + (\rho^\beta)^{4/3}] d\mathbf{r}$$

$$= \frac{1}{2} C_x \int \rho^{4/3} [(1 + \zeta)^{4/3} + (1 - \zeta)^{4/3}] d\mathbf{r}$$

$$= \int \rho \varepsilon_x(\rho, \zeta) d\mathbf{r} \quad \zeta = \frac{\rho^\alpha - \rho^\beta}{\rho} = \frac{\rho^\alpha - \rho^\beta}{\rho^\alpha + \rho^\beta}$$

$$\varepsilon_x(\rho, \zeta) = \varepsilon_x^0(\rho) + [\varepsilon_x^1(\rho) - \varepsilon_x^0(\rho)]f(\zeta)$$

$$\varepsilon_x^0(\rho) = \varepsilon_x(\rho, 0) = C_x \rho^{1/3}$$

$$\varepsilon_x^1(\rho) = \varepsilon_x(\rho, 1) = 2^{1/3} C_x \rho^{1/3}$$

$$f(\zeta) = \frac{1}{2} (2^{1/3} - 1)^{-1} [(1 + \zeta)^{4/3} + (1 - \zeta)^{4/3} - 2]$$

$$E_{xc}^{\text{LSD}}[\rho^\alpha, \rho^\beta] = E_x^{\text{LSD}}[\rho^\alpha, \rho^\beta] + E_c^{\text{LSD}}[\rho^\alpha, \rho^\beta]$$

$$\varepsilon_c(\rho, \zeta) = \varepsilon_c^0(\rho) + [\varepsilon_c^1(\rho) - \varepsilon_c^0(\rho)]f(\zeta)$$

$$\varepsilon_c(r_s) = \frac{A}{2} \left\{ \ln \frac{x}{X(x)} + \frac{2b}{Q} \tan^{-1} \frac{Q}{2x + b} \right.$$

$$\left. - \frac{bx_0}{X(x_0)} \left[\ln \frac{(x - x_0)^2}{X(x)} + \frac{2(b + 2x_0)}{Q} \tan^{-1} \frac{Q}{2x + b} \right] \right\}$$

$\forall = \frac{2}{3}(0.0051814)'$, $x^0 = -0.143580'$, $\rho = 50.1531'$, $\text{sup } c = 101.218'$, $\text{LH}26$
 $\forall = 0.0051814'$, $x^0 = -0.140580'$, $\rho = 13.0150'$, $\text{sup } c = 45.1108'$, $\text{LOL } \varepsilon_1^c(x^2)'$,
 $\text{MPLE } x = x_{15}^2$, $X(x) = x_5 + \rho x + c'$, $\text{sup } \bar{O} = (4c - \rho_5)_{15}$, $\text{LOL } \varepsilon_0^c(x^2)'$

Time-Dependent Density-Functional Theory (TDDFT)

Runge-Gross Extension: *Phys. Rev. Lett.* **52**, 997 (1984)

Time-dependent system

$\rho(r,t) \Rightarrow$ Properties P (e.g. absorption)

TDDFT equation: exact for excited states

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Density-Functional Theory for Time-Dependent Systems

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(Received 16 August 1983)

A density-functional formalism comparable to the Hohenberg-Kohn-Sham theory of the ground state is developed for arbitrary time-dependent systems. It is proven that the single-particle potential $v(\vec{r},t)$ leading to a given v -representable density $n(\vec{r},t)$ is uniquely determined so that the corresponding map $v \rightarrow n$ is invertible. On the basis of this theorem, three schemes are derived to calculate the density: a set of hydrodynamical equations, a stationary action principle, and an effective single-particle Schrödinger equation.

Theorem 1.—For every single-particle potential $v(\vec{r}t)$ which can be expanded into a Taylor series with respect to the time coordinate around $t = t_0$, a map $G:v(\vec{r}t) \rightarrow n(\vec{r}t)$ is defined by solving the time-dependent Schrödinger equation with a fixed initial state $\Phi(t_0) = \Phi_0$ and calculating the corresponding densities $n(\vec{r}t)$. This map can be inverted up to an additive merely time-dependent function in the potential.

$$i \frac{d}{dt} \langle \Phi(t) | \hat{O}(t) | \Phi(t) \rangle = \langle \Phi(t) | i \frac{\partial}{\partial t} \hat{O}(t) + [\hat{O}(t), \hat{H}(t)] | \Phi(t) \rangle. \quad (4)$$

Using $\vec{j}(\vec{r}, t) = \langle \Phi(t) | \hat{j}(\vec{r}) | \Phi(t) \rangle$ with

$$\hat{j}(\vec{r}) = (2i)^{-1} \sum_s [|\nabla \hat{\psi}_s^{\dagger}(\vec{r})\rangle \hat{\psi}_s(\vec{r}) - \hat{\psi}_s^{\dagger}(\vec{r}) |\nabla \hat{\psi}_s(\vec{r})\rangle],$$

one obtains

$$i \partial_t \vec{j}(\vec{r}, t) / \partial t = \langle \Phi(t) | [\hat{j}(\vec{r}), \hat{H}(t)] | \Phi(t) \rangle. \quad (5)$$

Since $\Phi(t)$ and $\Phi'(t)$ evolve from the same initial state Φ_0 , Eq. (5) leads to

$$i \frac{\partial}{\partial t} [\vec{j}(\vec{r}, t) - \vec{j}'(\vec{r}, t)]|_{t=t_0} = \langle \Phi_0 | [\hat{j}(\vec{r}), \hat{H}(t_0) - \hat{H}'(t_0)] | \Phi_0 \rangle = in(\vec{r}, t_0) \nabla [v(\vec{r}, t_0) - v'(\vec{r}, t_0)].$$

If the potentials differ at $t = t_0$ [i.e., if (3) holds for $k=0$] then the right-hand side of this equation will be different from zero and thus $\vec{j}(\vec{r}, t)$ and $\vec{j}'(\vec{r}, t)$ will become different infinitesimally later than t_0 . If the minimum integer k for which (3) holds is greater than zero then Eq. (4) has to be applied k times. Derivatives of the potentials with respect to space coordinates [as far as required to calculate the commutators in (4)] are assumed to exist. After some straightforward algebra one obtains

$$\left(i \frac{\partial}{\partial t} \right)^{k+1} [\vec{j}(\vec{r}, t) - \vec{j}'(\vec{r}, t)]|_{t=t_0} = in(\vec{r}, t_0) \nabla \left\{ \left[i \frac{\partial}{\partial t} \right]^k [v(\vec{r}, t) - v'(\vec{r}, t)]|_{t=t_0} \right\} \neq 0.$$

Again this means that $\vec{j}(\vec{r}, t)$ and $\vec{j}'(\vec{r}, t)$ will become different infinitesimally later than t_0 which completes the proof for the current vectors.

Next we consider the corresponding densities. By use of the continuity equation we have

$$(\partial/\partial t)[n(\vec{r}, t) - n'(\vec{r}, t)] = -\text{div}[\vec{j}(\vec{r}, t) - \vec{j}'(\vec{r}, t)].$$

Taking the $(k+1)$ st derivative of this equation and using the above result for the current densities we obtain

$$\frac{\partial^{k+2}}{\partial t^{k+2}} [n(\vec{r}, t) - n'(\vec{r}, t)]|_{t=t_0} = -\text{div} n(\vec{r}, t_0) \cdot \nabla \left\{ \frac{\partial^k}{\partial t^k} [v(\vec{r}, t) - v'(\vec{r}, t)]|_{t=t_0} \right\}. \quad (6)$$

It remains to be shown that the right-hand side of (6) cannot vanish if (3) holds. The proof is by *reductio ad absurdum*: Assume that $\text{div}[n(\vec{r}, t_0) \nabla u(\vec{r})] = 0$ with $u(\vec{r}) \neq \text{const}$; then

$$0 = \int d^3r u(\vec{r}) \text{div}[n(\vec{r}, t_0) \nabla u(\vec{r})] = - \int d^3r n(\vec{r}, t_0) [\nabla u(\vec{r})]^2 + \frac{1}{2} \oint n(\vec{r}, t_0) [\nabla u^2(\vec{r})] \cdot d\vec{r}.$$

If the initial density $n(\vec{r}, t_0)$ falls off rapidly enough to ensure that the surface integral vanishes we can conclude $n(\vec{r}, t_0) [\nabla u(\vec{r})]^2 \equiv 0$. This is in contradiction to $u(\vec{r}) \neq \text{const}$ provided $n(\vec{r}, t_0)$ is reasonably well behaved (we merely have to exclude that the initial density vanishes in precisely those subregions of space where $u = \text{const}$, if such regions exist at all). Thus, the right-hand side of (6) cannot vanish which proves that the densities $n(\vec{r}, t)$ and $n'(\vec{r}, t)$ become different infinitesimally later than t_0 .

Proof.—Let $v(\vec{r}, t)$ and $v'(\vec{r}, t)$ be two potentials which differ by more than a td function, i.e., $v(\vec{r}, t) - v'(\vec{r}, t) \neq c(t)$. This does of course not exclude that the potentials are identical at $t = t_0$. However, since the potentials can be expanded into a Taylor series around t_0 , there must exist some minimal nonnegative integer k such that

$$\frac{\partial^k}{\partial t^k} [v(\vec{r}, t) - v'(\vec{r}, t)]|_{t=t_0} \neq \text{const}. \quad (3)$$

The only thing to prove is that the densities $n(\vec{r}, t)$ and $n'(\vec{r}, t)$ corresponding to $v(\vec{r}, t)$ and $v'(\vec{r}, t)$ are different if (3) is fulfilled with some $k \geq 0$. In a first step, we show that the corresponding current densities $j(\vec{r}, t)$ and $j'(\vec{r}, t)$ are different. It should be noted that the particle and current densities corresponding to $v(\vec{r}, t)$ and $v'(\vec{r}, t)$ are of course identical at the initial time t_0 since we consider only wave functions which evolve from a fixed initial state Φ_0 .

The time evolution of the current density is most easily discussed by means of the equation of motion

Theorem 2.—There exists a three-component density functional $\bar{P}[n](\bar{r}t)$ which depends parametrically on $(\bar{r}t)$ such that the exact particle and current densities can be determined from a set of “hydrodynamical” equations

$$\partial n(\bar{r}t)/\partial t = -\text{div } \vec{j}(\bar{r}t), \quad (7)$$

$$\partial \vec{j}(\bar{r}t)/\partial t = \bar{P}[n](\bar{r}t), \quad (8)$$

with initial conditions $n(\bar{r}t_0) = \langle \Phi_0 | \hat{n}(\bar{r}) | \Phi_0 \rangle$ and $\vec{j}(\bar{r}t_0) = \langle \Phi_0 | \hat{\vec{j}}(\bar{r}) | \Phi_0 \rangle$.

Proof.—Since the exact particle and current densities always satisfy the continuity equation (7) it is sufficient to prove Eq. (8). From theorem 1 we know that the potential is determined by the density up to an additive td function $C(t)$. This in turn fixes the wave function within a td phase factor: $\Phi(t) = e^{-i\alpha(t)}\Psi[n](t)$ where $\Psi[n](t)$ is defined as the wave function obtained for the choice $C(t) = 0$. By insertion into (5) the desired Eq. (8) is immediately obtained if the functional \bar{P} is chosen as

$$\begin{aligned} \bar{P}[n](\bar{r}t) \\ = -i \langle \Psi[n](t) | [\hat{\vec{j}}(\bar{r}), \hat{H}(t)] | \Psi[n](t) \rangle. \end{aligned} \quad (9)$$

Theorem 3.—The action integral (2) can be represented as a functional of the density $A[n]$. If the potential $v(\bar{r}t)$ is chosen such that no additive time-dependent function can be split, the total action can be written as

$$A[n] = B[n] - \int_{t_0}^{t_1} dt \int d^3r n(\bar{r}t)v(rt), \quad (10)$$

where $B[n]$ is a *universal* functional of the density in the sense that the same dependence on $n(\bar{r}t)$ holds for all external potentials $v(\bar{r}t)$. $A[n]$ has a stationary point at the exact density of the system, i.e., the exact density can be computed from the Euler equation

$$\delta A / \delta n(\bar{r}t) = 0. \quad (11)$$

Proof.—Although the wave function $\Phi(t)$ is fixed by the density only within a td phase factor, the matrix element

$$\langle \Phi(t) | i\partial/\partial t - \hat{T} - \hat{W} - \hat{V}(t) | \Phi(t) \rangle$$

is *uniquely* determined since the function $C(t)$ contained in the potential $\hat{V}(t)$ is precisely cancelled by the time derivative of the phase $\dot{\alpha}(t) = C(t)$ [see discussion following Eq. (1)]. Therefore, the action (2) is a unique functional of the density and can be written as (10) if $B[n]$ is chosen as

$$B[n] = \int_{t_0}^{t_1} dt \langle \Psi[n](t) | i\partial/\partial t - \hat{T} - \hat{W} | \Psi[n](t) \rangle. \quad (12)$$

The universality of B follows trivially from the construction. Since the action (2) is stationary for the exact solution of the td SE (1), the corresponding density functional (10) must be stationary for the exact td density of the system.

Theorem 4.—The exact time-dependent density of the system can be computed from

$$n(\vec{r}t) = \sum \phi_j^*(\vec{r}t)\phi_j(\vec{r}t),$$

where the single-particle orbitals $\phi_j(\vec{r}t)$ fulfill the time-dependent Schrödinger equation

$$(i\partial/\partial t + \frac{1}{2}\nabla^2)\phi_j(\vec{r}t) = v_{\text{eff}}[\vec{r}t; n(\vec{r}t)]\phi_j(\vec{r}t)$$

with an effective one-particle potential given by

$$v_{\text{eff}}[\vec{r}t, n(\vec{r}t)] = v(\vec{r}t) + \int d^3r' n(\vec{r}'t)w(\vec{r}, \vec{r}') + \delta A_{\text{xc}}/\delta n(\vec{r}t).$$

$$A_{\text{xc}}[n] = \int_{t_0}^{t_1} dt \langle \Psi[n](t) | \hat{W} | \Psi[n](t) \rangle - \frac{1}{2} \int_{t_0}^{t_1} dt \int d^3r \int d^3r' n(\vec{r}t)w(\vec{r}, \vec{r}')n(\vec{r}'t) + S_0[n] - S_W[n]$$

$$S[n] = \int_{t_0}^{t_1} dt \langle \Psi[n](t) | i\partial/\partial t - \hat{T} | \Psi[n](t) \rangle$$

Proof.—With use of the definition of the exchange-correlation functional (14), the stationary action principle (11) yields

$$\delta A/\delta n(\vec{r}t) = 0 = \delta S_0/\delta n(\vec{r}t) - [v(\vec{r}t) + \int d^3r' n(\vec{r}'t)w(\vec{r}, \vec{r}') + \delta A_{\text{xc}}/\delta n(\vec{r}t)].$$

Casida equation

- ▶ (Non-linear) eigenvalue equation for excitation energies

$$\Omega \mathbf{F}_j = \omega_j^2 \mathbf{F}_j$$

with

$$\Omega_{ia\sigma,jb\tau} = \delta_{\sigma,\tau} \delta_{i,j} \delta_{a,b} (\epsilon_a - \epsilon_i)^2 + 2\sqrt{(\epsilon_a - \epsilon_i)} K_{ia\sigma,jb\tau} \sqrt{(\epsilon_b - \epsilon_j)}$$

and

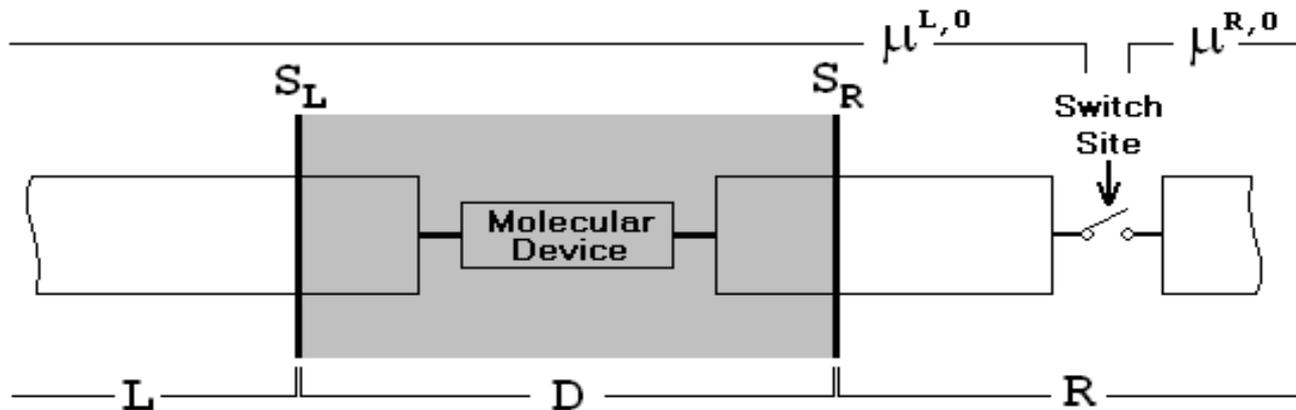
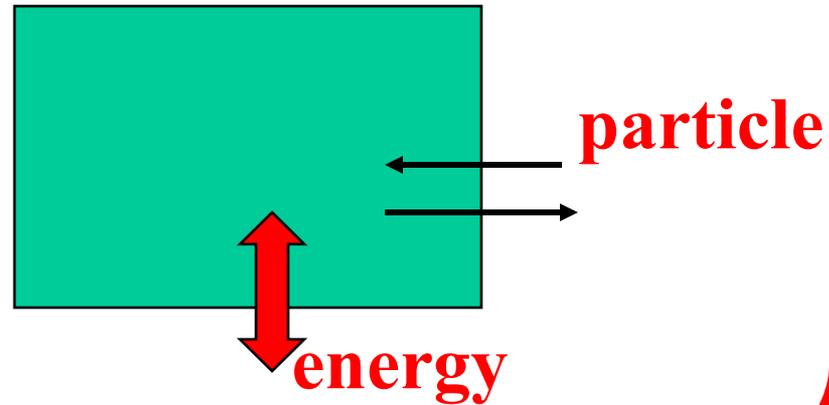
$$K_{ia\sigma,jb\tau}(\omega) = \int d^3r \int d^3r' \phi_{i\sigma}(\mathbf{r}) \phi_{j\sigma}(\mathbf{r}) \left[\frac{1}{|\mathbf{r} - \mathbf{r}'|} + f_{xc}(\mathbf{r}, \mathbf{r}', \omega) \right] \phi_{k\tau}(\mathbf{r}) \phi_{l\tau}(\mathbf{r})$$

- ▶ Eigenvalues ω_j are exact vertical excitation energies
- ▶ Eigenvectors can be used to compute oscillator strength
- ▶ Drawback: need occupied and unoccupied orbitals

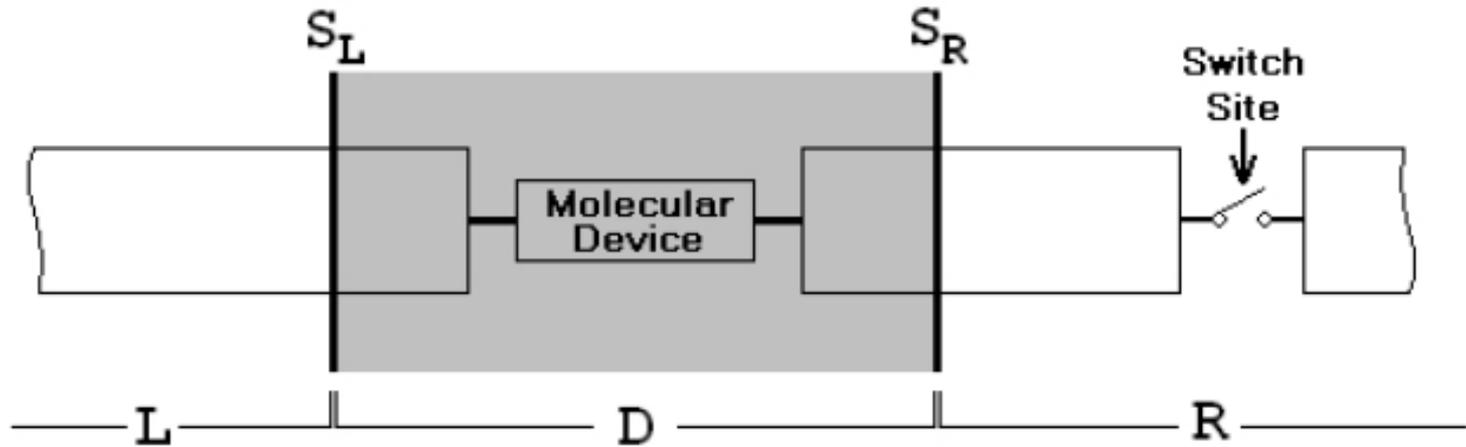
Time-dependent density-functional theory for open systems

Open Systems

$$\mathbf{H} = \mathbf{H}_S + \mathbf{H}_B + \mathbf{H}_{SB}$$



⊛ First-principles method for open systems?



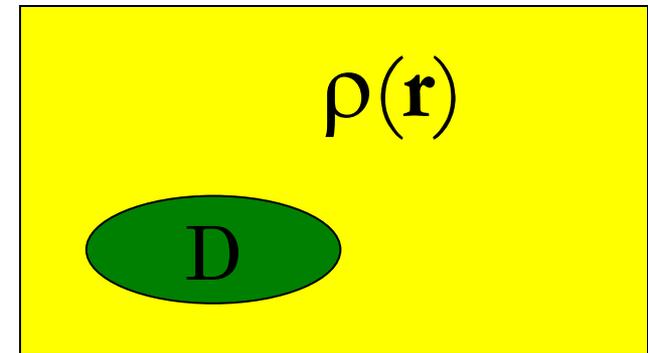
$\rho_D(\vec{r}, t) \Rightarrow$ open system properties

Is the **electron density function** of any physical system a **real analytical function** ?

A real function is said to be analytic if it possesses derivatives of all orders and agrees with its Taylor series in the neighborhood of every point.

Analyticity of basis functions

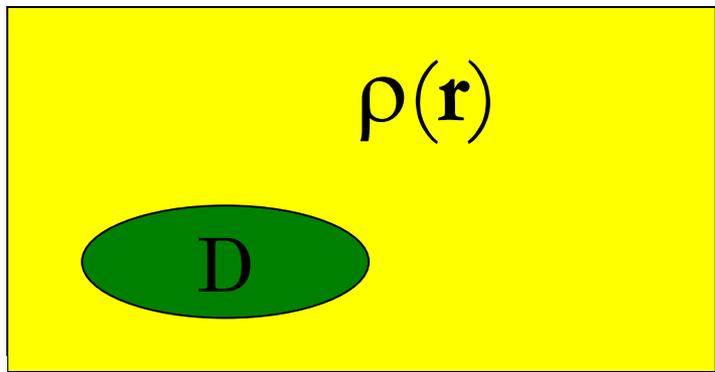
- Gaussian-type orbital
- Slater-type orbital
- Plane wave
- **Linearized augmented plane wave (LAPW)**



⚙️ Holographic electron density theorem for time-independent systems

- Riess and Munch (1981)
- Mezey (1999)
- Fournais (2004)

$$H\Psi = E\Psi$$



Ark. Mat., 42 (2004), 87–106
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Analyticity of the density of electronic wavefunctions

Søren Fournais, Maria Hoffmann-Ostenhof, Thomas Hoffmann-Ostenhof and Thomas Østergaard Sørensen

Theorem 1.1. Let $\psi \in L^2(\mathbf{R}^{3N})$ satisfy the equation

$$H\psi = E\psi.$$

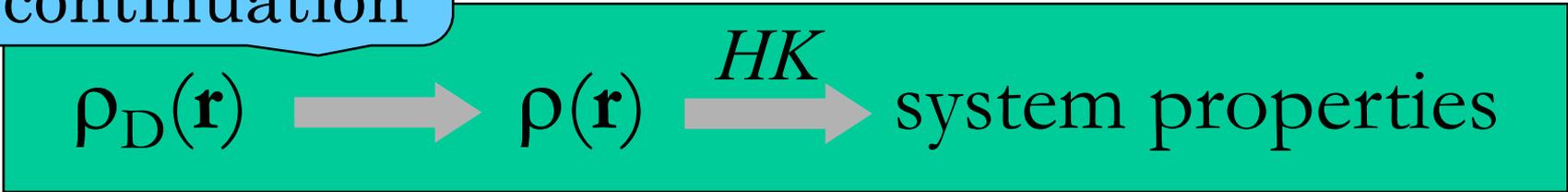
with $E \in \mathbf{R}$ and H given by (1.1). Let the density ρ be defined as in (1.6). Then ρ is a real analytic function in $\mathbf{R}^3 \setminus \{R_1, \dots, R_L\}$.

$$(1.6) \quad \rho(x) = \int_{\mathbf{R}^{3N-3}} |\psi(x, x_2, \dots, x_N)|^2 dx_2 \dots dx_N.$$

Abstract. We prove that the electronic densities of atomic and molecular eigenfunctions are real analytic in \mathbf{R}^3 away from the nuclei.

$$(1.1) \quad H = H_{N,L}(\mathbf{R}, \mathbf{Z}) = \sum_{j=1}^N \left(-\Delta_j - \sum_{l=1}^L \frac{Z_l}{|x_j - R_l|} \right) + \sum_{1 \leq i < j \leq N} \frac{1}{|x_i - x_j|} + \sum_{1 \leq l < k \leq L} \frac{Z_l Z_k}{|R_l - R_k|}.$$

Analytical continuation



HOLOGRAPHIC ELECTRON DENSITY THEOREM

Ark. Mat., **42** (2004), 87–106

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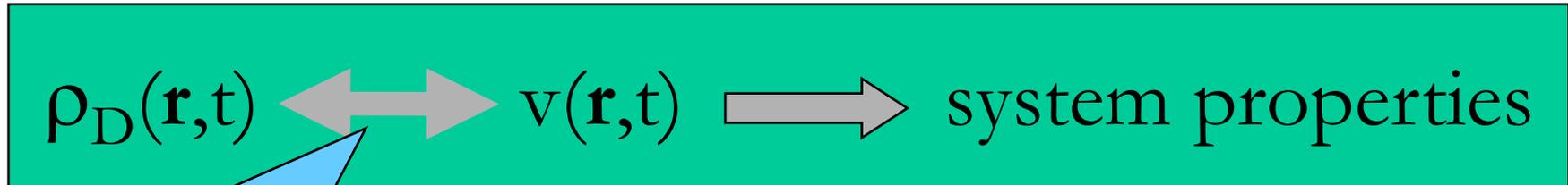
Analyticity of the density of electronic wavefunctions

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and Thomas Østergaard Sørensen

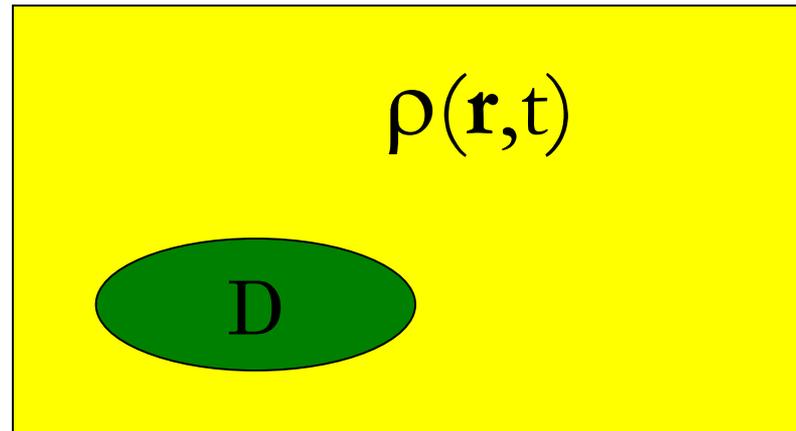
Abstract. We prove that the electronic densities of atomic and molecular eigenfunctions are real analytic in \mathbf{R}^3 away from the nuclei.

⚙️ Holographic electron density theorem for time-dependent systems

It is difficult to prove the analyticity for $\rho(\mathbf{r},t)$ rigorously!



Holographic electron density theorem



X. Zheng and G.H. Chen, *arXiv:physics/0502021* (2005);

Yam, Zheng & Chen, *J. Comput. Theor. Nanosci.* 3, 857 (2006);

Recent progress in computational sciences and engineering, Vol. 7A, 803 (2006);

Zheng, Wang, Yam, Mo & Chen, *PRB* (2007).

Time-dependent density-functional theory for open systems

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Theorem. If the electron density function of a real finite physical system at t_0 , $\rho(\mathbf{r}, t_0)$, is real analytic in \mathbf{r} space, the corresponding wave function is $\Phi(t_0)$, and the system is subjected to a real analytic (in both t space and \mathbf{r} space) external potential field $v(\mathbf{r}, t)$, the time-dependent electron density function on any finite subspace D , $\rho_D(\mathbf{r}, t)$, has a one-to-one correspondence with $v(\mathbf{r}, t)$ and determines uniquely all electronic properties of the entire time-dependent system.

Proof: Let $v(\mathbf{r}, t)$ and $v'(\mathbf{r}, t)$ be two real analytic potentials in both t -space and \mathbf{r} -space which differ by more than a constant at any time $t \geq t_0$, and their corresponding electron density functions are $\rho(\mathbf{r}, t)$ and $\rho'(\mathbf{r}, t)$, respectively. Therefore, there exists a minimal nonnegative integer k such that the k -th order derivative differentiates these two potentials at t_0 :

$$\left. \frac{\partial^k}{\partial t^k} [v(\mathbf{r}, t) - v'(\mathbf{r}, t)] \right|_{t=t_0} \neq \text{const.} \quad (15)$$

Following exactly the Eqs. (3)-(6) of Ref. [3], we have

$$\left. \frac{\partial^{k+2}}{\partial t^{k+2}} [\rho(\mathbf{r}, t) - \rho'(\mathbf{r}, t)] \right|_{t=t_0} = -\nabla \cdot u(\mathbf{r}), \quad (16)$$

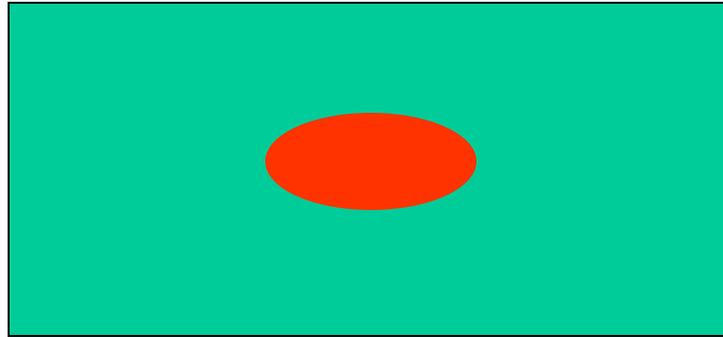
where

$$u(\mathbf{r}) = \rho(\mathbf{r}, t_0) \nabla \left\{ \left. \frac{\partial^k}{\partial t^k} [v(\mathbf{r}, t) - v'(\mathbf{r}, t)] \right|_{t=t_0} \right\}. \quad (17)$$

Due to the analyticity of $\rho(\mathbf{r}, t_0)$, $v(\mathbf{r}, t)$ and $v'(\mathbf{r}, t)$, $\nabla \cdot u(\mathbf{r})$ is also real analytic in \mathbf{r} -space. It has been proven in Ref. [3] that it is *impossible* to have $\nabla \cdot u(\mathbf{r}) = 0$ on the entire \mathbf{r} -space. Therefore it is also impossible that

³E. Runge and E. K. U. Gross, *Phys. Rev. Lett.* **52**, 997 (1984).

The electron density distribution of the reduced system determines all physical properties or processes of the entire system!



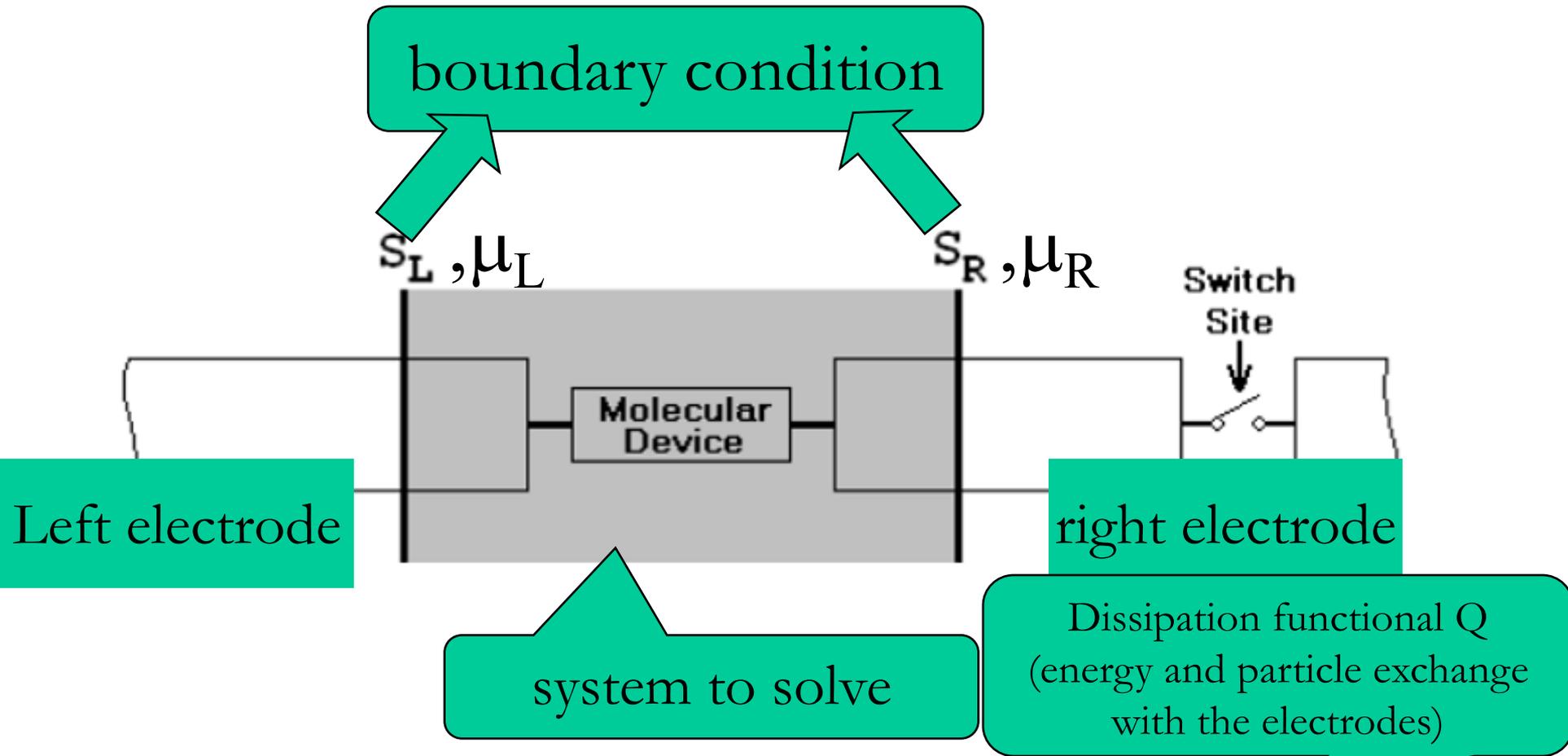
Existence of a rigorous TDDFT for Open System

$$i\dot{\sigma}(t) = [h(t), \sigma(t)],$$

$$\sigma = \begin{bmatrix} \sigma_L & \sigma_{LD} & \sigma_{LR} \\ \sigma_{DL} & \sigma_D & \sigma_{DR} \\ \sigma_{RL} & \sigma_{RD} & \sigma_R \end{bmatrix},$$

$$\begin{aligned} i\dot{\sigma}_D &= [h_D, \sigma_D] + \sum_{\alpha=L,R} (h_{D\alpha}\sigma_{\alpha D} - \sigma_{D\alpha}h_{\alpha D}) \\ &= [h_D, \sigma_D] - i \sum_{\alpha=L,R} Q_\alpha, \end{aligned}$$

⚙️ Time-Dependent DFT for Open Systems



$$i\dot{\sigma}_D = \left[h_D[\mathbf{r}, t; \rho_D(\mathbf{r}, t)], \sigma_D \right] - i \sum_{\alpha=L,R} Q_\alpha[\mathbf{r}, t; \rho_D(\mathbf{r}, t)]$$

Poisson Equation with boundary condition via potentials at S_L and S_R

Zheng, Wang, Yam, Mo & Chen, Phys. Rev. B 75, 195127 (2007)