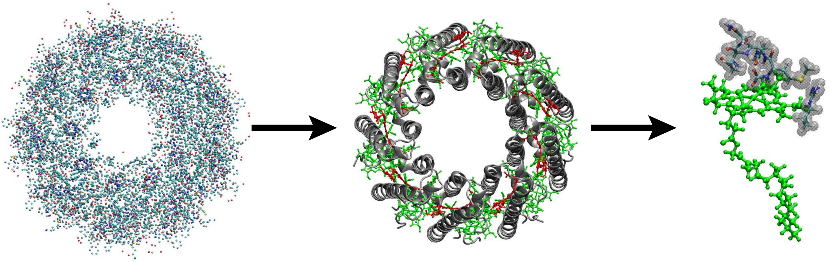
Subsystem Quantum Chemistry



Johannes Neugebauer

Graduate Course on Theoretical Chemistry and Spectroscopy

Han-sur-Lesse, December 2009

I. Non-Separability of Quantum Systems!?

Description of Quantum Systems

To describe a quantum system, we have to

- construct a Hamiltonian:
  - add kinetic-energy operators for all elementary particles
    (in chemistry: electrons and nuclei)
  - add interaction operators for all interactions between elementary particles
    (in chemistry: Coulomb interactions)

Description of Quantum Systems

To describe a quantum system, we have to

- construct a Hamiltonian:
  - add kinetic-energy operators for all elementary particles
    (in chemistry: electrons and nuclei)
  - add interaction operators for all interactions between elementary particles
    (in chemistry: Coulomb interactions)
- find wavefunction Ψ that fulfills Schrödinger Equation with this Hamiltonian

Description of Quantum Systems

To describe a quantum system, we have to

- construct a Hamiltonian:
    - add kinetic-energy operators for all elementary particles (in chemistry: electrons and nuclei)
    - add interaction operators for all interactions between elementary particles (in chemistry: Coulomb interactions)
- find wavefunction Ψ that fulfills Schrödinger Equation with this Hamiltonian
- note: $\Psi = \Psi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_n, \mathbf{X}_1, \mathbf{X}_2, \ldots, \mathbf{X}_N, t)$

$\mathbf{x}$ = electronic coordinates (incl. spin), $\mathbf{X}$ = nuclear coordinates, t = time

Non-Separability of Quantum Systems

- *all* charged particles interact via Coulomb forces

⇒ in a strict sense, there are no isolated systems
(and we have to find the wavefunction of the universe)

- but: experimental evidence shows that systems can be treated as if they were isolated
- Can we separate a quantum system into “parts” (electrons, atoms, functional groups, molecules, . . .)?
  ⇒ *a posteriori* approach
- Can we calculate the electronic structure of a big quantum chemical system based on its constituents? ⇒ *a priori* approach

Simplification of the Wavefunction

- for stationary states, we can separate t from $\mathbf{x}, \mathbf{X}$
- Born–Oppenheimer approximation:
  allows to separate $\mathbf{x}$ from $\mathbf{X}$
- harmonic oscillator approximation:
  allows to obtain $3N$ separate equations for nuclear coordinates
- common problem in quantum chemistry:
  find $\Psi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_n)$ for fixed coordinates $\mathbf{X}_1, \mathbf{X}_2, \ldots, \mathbf{X}_N$

⇒ find eigenfunctions of

$$\begin{aligned}\hat{H}_\mathrm{e} &= \hat{T}_\mathrm{e} + \hat{V}_\mathrm{ne} + \hat{V}_\mathrm{ee} \\ &= -\sum_i^n \frac{\nabla_i^2}{2} - \sum_I^N \sum_i^n \frac{Z_I}{|\mathbf{R}_I - \mathbf{r}_i|} + \sum_{i<j}^n \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}\end{aligned}$$

Hartree Atomic Units

. . . are used throughtout

$$\begin{aligned} e &\equiv 1 \\ m_{\mathrm{el}} &\equiv 1 \\ \hbar &\equiv 1 \\ 4\pi\varepsilon_0 &\equiv 1 \end{aligned}$$

Hartree Atomic Units

. . . are used throughtout

$$\begin{aligned} e &\equiv 1 \text{ a.u. of charge} \\ m_{\mathrm{el}} &\equiv 1 \text{ a.u. of mass} \\ \hbar &\equiv 1 \text{ a.u. of action} \\ 4\pi\varepsilon_0 &\equiv 1 \text{ a.u. of permittivity} \end{aligned}$$

Simplification of the Electronic Wavefunction

- Hartree product:

$$\Pi_{\mathrm{H}}(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_n) = \phi_1(\mathbf{x}_1) \cdot \phi_2(\mathbf{x}_2) \cdot \ldots \cdot \phi_n(\mathbf{x}_n)$$

  - electrons have individuality (can be labeled)
  - in line with intuitive chemical concepts
  - violates Pauli principle
- Hartree–Fock wavefunction: antisymmetrized Hartree product

$$\Phi_{\mathrm{HF}}(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_n) = \tilde{N}\hat{A}\phi_1(\mathbf{x}_1) \cdot \phi_2(\mathbf{x}_2) \cdot \ldots \cdot \phi_n(\mathbf{x}_n)$$

  - electrons have no individuality (indistinguishable)
  - in line with Pauli principle
  - introduces difficulties for “intuitive” concepts

Hartree–Fock Equations

- canonical Hartree–Fock equations:

$$\left[\hat{h} + \sum_j (\hat{J}_j - \hat{K}_j)\right] \phi_i \quad = \quad \epsilon_i \phi_i$$

with

$$\begin{aligned} \hat{h} &= -\frac{\nabla^2}{2} - \sum_I^n \frac{Z_I}{|\mathbf{r} - \mathbf{R}_I|} \\ \hat{J}_j &= \langle \phi_j | 1/r_{12} | \phi_j \rangle \\ \hat{K}_j \phi_i &= \langle \phi_j | 1/r_{12} | \phi_i \rangle \phi_j \end{aligned}$$

- solution: basis set expansion

$$\phi_i = \sum_\mu c_{\mu i} \chi_\mu$$

Solution of the Hartree–Fock Equations

- insert ansatz into Hartree–Fock equations,

$$\hat{f} \sum_\mu c_{\mu i} \chi_\mu = \epsilon_i \sum_\mu c_{\mu i} \chi_\mu$$

  where

$$\hat{f} = \hat{h} + \sum_j (\hat{J}_j - \hat{K}_j)$$

- multiply from the left with $\langle \chi_\nu |$

$$\sum_\mu \underbrace{\langle \chi_\nu | \hat{f} | \chi_\mu \rangle}_{f_{\nu\mu}} c_{\mu i} = \epsilon_i \sum_\mu c_{\mu i} \underbrace{\langle \chi_\nu | \chi_\mu \rangle}_{S_{\nu\mu}}$$

  or

$$\mathbf{f}\mathbf{c}_i = \epsilon_i \mathbf{S}\mathbf{c}_i$$

Population Analysis: Are There Atoms in Molecules?

Integral over sum of orbital densities:

$$\begin{aligned}\sum_i^n \int |\phi_i|^2 \mathrm{d}\mathbf{r} &= \sum_i^n \sum_{\alpha\beta}^m c_{\alpha i} c_{\beta i} \int \chi_\alpha \chi_\beta \mathrm{d}\mathbf{r} \\ &= \sum_{\alpha\beta}^m \left(\sum_i^n c_{\alpha i} c_{\beta i} \right) S_{\alpha\beta} = \sum_{\alpha\beta}^m P_{\alpha\beta} S_{\alpha\beta} = n\end{aligned}$$

- atoms are no “elementary units” in quantum chemistry
- but: we can use several partitioning schemes to assign effective charges to atomic centers
- Mulliken electron population of atom A:

$$n_A = \sum_{\alpha \in A} \sum_\beta P_{\alpha\beta} S_{\alpha\beta}$$

gross charges: $Q_A = Z_A - n_A$

Population Analysis

Density-based schemes avoid basis set problems:

- Bader charges:

$$Q_A = Z_A - \int_{\text{atomic basin}} \rho(\mathbf{r}) d\mathbf{r}$$

  (defined through $\nabla \rho(\mathbf{r}) \cdot n(\mathbf{r}) = 0$)

- Hirshfeld charges:

$$Q_A = Z_A - \int p_A(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r}$$

  with

$$\begin{aligned} p_A(\mathbf{r}) &= \frac{\rho_A^{\text{free atom}}(\mathbf{r})}{\rho^{\text{promolecule}}(\mathbf{r})} \\ \rho^{\text{promolecule}}(\mathbf{r}) &= \sum_A \rho_A^{\text{free atom}}(\mathbf{r}) \end{aligned}$$

- similar: Voronoi charges (hard boundaries)

Orbitals in Hartree–Fock Theory

- canonical HF orbitals are often delocalized
- energy and properties remain unchanged under unitary transformation among occupied orbitals

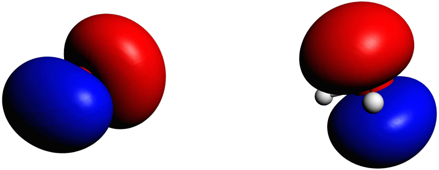
$$\tilde{\phi}_i(\mathbf{x}) = \sum_{k=1}^{n} U_{ik}\phi_k \quad \text{or} \quad \tilde{\boldsymbol{\phi}} = \mathbf{U} \cdot \boldsymbol{\phi}$$

- localized orbitals: often more useful for chemical concepts
- Boys–Foster localization:
  find $\mathbf{U}$ that minimizes distance between electrons in a spatial orbital

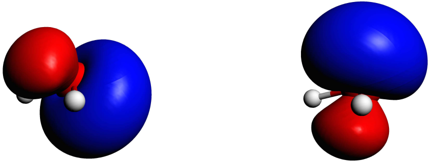
$$\sum_i \langle \tilde{\phi}_i \langle \tilde{\phi}_i | (r_{12})^2 | \tilde{\phi}_i \rangle \tilde{\phi}_i \rangle.$$

- Pipek–Mezey localization: maximize sum of Mulliken charges

Canonical vs. Localized Orbitals



canonical orbitals



localized orbitals (Boys−Foster)

Quasi-Electrons

- Edminston–Ruedenberg (ER) localization:
  find $\mathbf{U}$ such that exchange is minimized,

$$\sum_{i<j} \int \int \tilde{\phi}_i^*(\mathbf{x}_1)\tilde{\phi}_j(\mathbf{x}_1)\frac{1}{r_{12}}\tilde{\phi}_j^*(\mathbf{x}_2)\tilde{\phi}_i(\mathbf{x}_2)\mathrm{d}\mathbf{x}_1\mathrm{d}\mathbf{x}_2 = \text{min}$$

(alternative formulation: maximize self-energy)

- ER orbitals: often similar to Hartree orbitals (exchange completely missing)

$\Rightarrow$ "Hartree orbitals describe the quasi-electrons of chemists"

H. Primas, U. Müller–Herold, Elementare Quantenchemie

II. Subsystem Approaches in Quantum Chemistry

Group Functions

- subsystems A and B will be distinct if each is described by “its own wavefunction”,

$$\Psi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_{n_A+n_B}) = \Psi_A(\mathbf{x}_1, \ldots, \mathbf{x}_{n_A})\Psi_B(\mathbf{x}_{n_A+1}, \ldots, \mathbf{x}_{n_A+n_B})$$

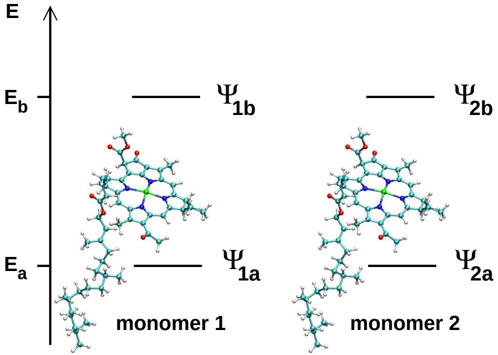
- Pauli principle requires:

$$\Psi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_{n_A+n_B}) = \tilde{N}\hat{A}\left[\Psi_A(\mathbf{x}_1, \ldots, \mathbf{x}_{n_A})\Psi_B(\mathbf{x}_{n_A+1}, \ldots, \mathbf{x}_{n_A+n_B})\right],$$

(unless separation $A - B$ becomes very large; exact for non-interacting subsystems)

- can be starting point for accurate calculations
  (if Ψ_A, Ψ_B are highly accurate)
- note: Slater determinant is included as a special case

Group Functions



- example for group functions:
  discussion of energy-transfer phenomena: $|DA\rangle$, $|D^{*}A\rangle$, $|DA^{*}\rangle$
- basis for exciton models

Hybrid Methods

General idea:

- calculate energy of active subsystem (1) with accurate method (M_1)
- add correction for interaction with environment (2) based on less accurate method (M_2)

$$
\begin{aligned}
E_{\text{tot}} &= E_1^{M_1} + E_2^{M_2} + E_{1\leftrightarrow 2}^{M_2} \quad \text{(additive scheme)} \\
E_{\text{tot}} &= E_1^{M_1} + E_{(1+2)}^{M_2} - E_1^{M_2} \quad \text{(subtractive scheme)}
\end{aligned}
$$

since $E_{(1+2)}^{M_2} = E_1^{M_2} + E_2^{M_2} + E_{1\leftrightarrow 2}^{M_2}$

- can be extended to several layers
- examples: QM/MM, WF/DFT, ONIOM, QM/PCM

Hybrid Methods

- simple hybrid methods only partition the energy (mechanical embedding; wavefunction/density (1) unchanged)
- electronic/Hamiltonian embedding:
  wavefunction (1) polarized by environment

$$\left[-\frac{1}{2}\nabla^2 + v_{\mathrm{HF/KS}}(\mathbf{r}) + v_{\mathrm{emb}}(\mathbf{r})\right]\phi_i(\mathbf{r}) = \epsilon_i\phi_i(\mathbf{r})$$

  e.g.

$$v_{\mathrm{emb}}(\mathbf{r}) = -\sum_{A\in\mathrm{MM}} \frac{q_A}{|\mathbf{r}-\mathbf{R}_A|}$$

- more advanced schemes consider back-polarization of the environment by the active system

Increment Methods

General idea:

- largest part of total energy is due to energies of (isolated) subsystems
- interaction energy: mainly due to pair interactions
- general energy expression:

$$\begin{aligned}
E_{\text{tot}} &= \sum_{I} E_I + \sum_{I<J} E_{I\leftrightarrow J} + \sum_{I<J<K} E_{I\leftrightarrow J\leftrightarrow K} + \ldots \\
E_{I\leftrightarrow J} &= E_{IJ} - E_I - E_J \\
E_{I\leftrightarrow J\leftrightarrow K} &= E_{IJK} - E_I - E_J \\
&\quad -(E_{IJ} - E_I - E_J) - (E_{IK} - E_I - E_K) - (E_{JK} - E_J - E_K)
\end{aligned}$$

- nth-order increment method: exact for n subsystems

Other Subsystem Methods

- methods that partition the correlation energy
  (⇒ increment methods for E_{corr})
- correlation methods based on localized orbitals
  - conventional methods (e.g., CI-type):

$$\Psi = c_{\mathrm{HF}}\Phi_{\mathrm{HF}} + \sum_{ia} c_i^a \Phi_i^a + \sum_{ijab} c_{ij}^{ab} \Phi_{ij}^{ab} + \ldots,$$

  - local methods:
    create a domain $[i]$ of virtual orbitals spatially close to $\tilde{\phi}_i(\mathbf{r})$
  - include all excitations from $\tilde{\phi}_i$ to $[i]$
  - include all double excitations from $\phi_{i,j}$ to pair domain $[i,j]$
  - group pair domains into strong, weak, and distant pairs
- methods that partition the density matrix
- What about density-based schemes?

III. Subsystem Density-Functional Theory

Some Basics of DFT

General Idea:

- calculate energy based on observable real-space quantity $\rho(\mathbf{r})$

Formal basis:

- 1st HK theorem:
  The ground-state electron density determines the external potential (and thus $\hat{H}$, Ψ_i, E_i, and all properties).
- 2nd HK theorem:
  We can obtain the electronic ground-state energy E_0 from a variational procedure:

$$E_0 = \min_{\rho \in \{\rho\}_v} E[\rho]$$

Minimization of the Energy Functional

- minimize energy subject to constraint:

$$\int \rho(\mathbf{r})\mathrm{d}\mathbf{r} = n$$

⇒ construct Lagrange functional:

$$L[\rho] = E[\rho] - \mu \left[\int \rho(\mathbf{r})\mathrm{d}\mathbf{r} - n \right]$$

and minimize unconstrained

- minimization condition:

$$\delta L[\rho] \quad = \quad \int \frac{\delta L[\rho]}{\delta \rho(\mathbf{r})} \delta\rho(\mathbf{r})\mathrm{d}\mathbf{r} = 0$$

or

$$\frac{\delta L[\rho]}{\delta \rho(\mathbf{r})} = 0 \quad \Leftrightarrow \quad \frac{\delta E[\rho]}{\delta \rho(\mathbf{r})} - \mu = 0 \quad \Leftrightarrow \quad \mu = \frac{\delta E[\rho]}{\delta \rho(\mathbf{r})}$$

(Euler–Lagrange equation)

Some Basics of DFT

Partitioning of the energy:

$$E[\rho] = V_{\text{ext}}[\rho] + V_{\text{ee}}[\rho] + T[\rho]$$

where

$$V_{\text{ext}}[\rho] = \int \rho(\mathbf{r}) v_{\text{ext}}(\mathbf{r}) \mathrm{d}\mathbf{r}$$

$$v_{\text{ext}}(\mathbf{r}) = -\sum_{A} \frac{Z_A}{|\mathbf{r} - \mathbf{R}_A|} \qquad \text{(most often)}$$

$$V_{ee}[\rho] = \left\langle \Psi \left| \sum_{i<j} \frac{1}{r_{ij}} \right| \Psi \right\rangle = \underbrace{\frac{1}{2} \int \int \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{r_{12}} \mathrm{d}\mathbf{r}_1 \mathrm{d}\mathbf{r}_2}_{J[\rho]} + \underbrace{V_{ee,\text{nc}}[\rho]}_{???}$$

$$T[\rho] = \left\langle \Psi \left| \sum_{i} \frac{-\nabla_i^2}{2} \right| \Psi \right\rangle = ???$$

Some Basics of DFT

Partitioning of the energy:

$$E[\rho] = V_{\mathrm{ext}}[\rho] + V_{\mathrm{ee}}[\rho] + T[\rho]$$

where

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

$$v_{\mathrm{ext}}(\mathbf{r}) = -\sum_A \frac{Z_A}{|\mathbf{r} - \mathbf{R}_A|} \qquad \text{(most often)}$$

$$V_{ee}[\rho] = \left\langle \Psi \middle| \sum_{i<j} \frac{1}{r_{ij}} \middle| \Psi \right\rangle = \underbrace{\frac{1}{2} \int \int \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{r_{12}} \mathrm{d}\mathbf{r}_1 \mathrm{d}\mathbf{r}_2}_{J[\rho]} + \underbrace{V_{ee,\mathrm{nc}}[\rho]}_{???}$$

$$T[\rho] = \left\langle \Psi \middle| \sum_i \frac{-\nabla_i^2}{2} \middle| \Psi \right\rangle \approx \underbrace{C_F \int \rho^{5/3}(\mathbf{r}) \mathrm{d}\mathbf{r}}_{T_{\mathrm{TF}}[\rho]} \qquad \text{(very crude)}$$

Functional Derivatives

- functional derivative:

$$s(x) = \frac{\delta F[f]}{\delta f(x)}$$

  is defined through:

$$F[f(x) + \delta f(x)] = F[f(x)] + \int s(x)\delta f(x)dx + \mathcal{O}(\delta f^2)$$

- simple example:

$$\begin{aligned} V_{\text{ext}}[\rho(\mathbf{r}) + \delta\rho(\mathbf{r})] &= \int v_{\text{ext}}(\mathbf{r})[\rho(\mathbf{r}) + \delta\rho(\mathbf{r})]\mathrm{d}\mathbf{r} \\ &= \underbrace{\int v_{\text{ext}}(\mathbf{r})\rho(\mathbf{r})\mathrm{d}\mathbf{r}}_{V_{\text{ext}}[\rho]} + \int \underbrace{v_{\text{ext}}(\mathbf{r})}_{\frac{\delta V_{\text{ext}}[\rho]}{\delta\rho(\mathbf{r})}} \delta\rho(\mathbf{r})\mathrm{d}\mathbf{r} \end{aligned}$$

Functional Derivatives

Coulomb energy

$$\begin{aligned}
J[\rho+\delta\rho] &= \frac{1}{2}\int\int \frac{(\rho(\mathbf{r}_1)+\delta\rho(\mathbf{r}_1))(\rho(\mathbf{r}_2)+\delta\rho(\mathbf{r}_2))}{|\mathbf{r}_1-\mathbf{r}_2|}\mathrm{d}\mathbf{r}_1\mathrm{d}\mathbf{r}_2 \\
&= \frac{1}{2}\int\int \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{|\mathbf{r}_1-\mathbf{r}_2|}\mathrm{d}\mathbf{r}_1\mathrm{d}\mathbf{r}_2 + \frac{1}{2}\int\int \frac{\rho(\mathbf{r}_1)\delta\rho(\mathbf{r}_2)}{|\mathbf{r}_1-\mathbf{r}_2|}\mathrm{d}\mathbf{r}_1\mathrm{d}\mathbf{r}_2 \\
&\quad + \frac{1}{2}\int\int \frac{\delta\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{|\mathbf{r}_1-\mathbf{r}_2|}\mathrm{d}\mathbf{r}_1\mathrm{d}\mathbf{r}_2 + \frac{1}{2}\int\int \frac{\delta\rho(\mathbf{r}_1)\delta\rho(\mathbf{r}_2)}{|\mathbf{r}_1-\mathbf{r}_2|}\mathrm{d}\mathbf{r}_1\mathrm{d}\mathbf{r}_2 \\
&= J[\rho] + \int \underbrace{\left(\int \frac{\rho(\mathbf{r}_2)}{|\mathbf{r}_1-\mathbf{r}_2|}\mathrm{d}\mathbf{r}_2\right)}_{v_{\mathrm{Coul}}(\mathbf{r}_1)} \delta\rho(\mathbf{r}_1)\mathrm{d}\mathbf{r}_1 + \mathcal{O}[(\delta\rho(\mathbf{r}))^2]
\end{aligned}$$

$$\frac{\delta J[\rho]}{\delta\rho(\mathbf{r})} = v_{\mathrm{Coul}}(\mathbf{r})$$

Thomas–Fermi Theory

- $T_{\mathrm{TF}}[\rho]$: exact kinetic energy for homogeneous electron gas
- energy functional and Lagrangian:

$$\begin{aligned} E_{\mathrm{TF}}[\rho] &= V_{\mathrm{ext}}[\rho] + J[\rho] + T_{\mathrm{TF}}[\rho] \\ L_{\mathrm{TF}}[\rho] &= E_{\mathrm{TF}} - \mu \left[\int \rho(\mathbf{r}) \mathrm{d}\mathbf{r} - n \right] \end{aligned}$$

- minimization condition:

$$\mu = \frac{\delta E_{\mathrm{TF}}[\rho]}{\delta \rho(\mathbf{r})} = \frac{5}{3} C_F \rho^{2/3}(\mathbf{r}) + v_{\mathrm{ext}}(\mathbf{r}) + v_{\mathrm{Coul}}(\mathbf{r})$$

- very simple DFT model
- extension: Dirac exchange $E_x^{\mathrm{Dirac}}[\rho] = -C_x \int \rho^{4/3}(\mathbf{r}) \mathrm{d}\mathbf{r}$

Kinetic-Energy Functionals: Another Example

- assume one-electron system, $\rho(\mathbf{r}) = |\phi(\mathbf{r})|^2$

$$
\begin{aligned}
T = T[\phi] &= -\frac{1}{2}\int \phi(\mathbf{r})\nabla^2\phi(\mathbf{r})\mathrm{d}\mathbf{r} \\
&= \frac{1}{2}\int (\nabla\phi(\mathbf{r}))(\nabla\phi(\mathbf{r}))\mathrm{d}\mathbf{r} \\
&= \frac{1}{2}\int \left(\nabla\sqrt{\rho(\mathbf{r})}\right)\left(\nabla\sqrt{\rho(\mathbf{r})}\right)\mathrm{d}\mathbf{r} \\
&= \frac{1}{2}\int \left(\frac{1}{2\sqrt{\rho(\mathbf{r})}}\nabla\rho(\mathbf{r})\right)\left(\frac{1}{2\sqrt{\rho(\mathbf{r})}}\nabla\rho(\mathbf{r})\right)\mathrm{d}\mathbf{r} \\
&= \frac{1}{8}\int \frac{|\nabla\rho(\mathbf{r})|^2}{\rho(\mathbf{r})}\mathrm{d}\mathbf{r}
\end{aligned}
$$

⇒ von Weizsäcker functional $T_{\mathrm{vW}}[\rho]$

Kohn–Sham DFT

Non-interacting System

- consider system of non-interacting “electrons”:

$$\hat{H}_s = \hat{T}_s + \hat{V}_s = \sum_{i=1}^{n} \left[-\frac{1}{2}\nabla_i^2 + v_s(\mathbf{r}_i) \right]$$

- *exact* wavefunction for this system:
  antisymmetrized product (Slater determinant) of orbitals ϕ_i,

$$\left[-\frac{1}{2}\nabla^2 + v_s(\mathbf{r}) \right] \phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r})$$

- *exact* kinetic energy of this system:

$$T_s[\{\phi_i\}] = \sum_i \left\langle \phi_i \middle| \frac{-\nabla^2}{2} \middle| \phi_i \right\rangle$$

Kohn–Sham DFT

Non-interacting System

- ground-state density of this system:

$$\rho(\mathbf{r}) = \sum_i^{\text{occ}} |\phi_i(\mathbf{r})|^2$$

- this density fulfills (2nd HK theorem):

$$\begin{aligned} \mu &= \frac{\delta E_s[\rho]}{\delta \rho(\mathbf{r})} \\ &= \frac{\delta T_s[\{\phi_i\}]}{\delta \rho(\mathbf{r})} + v_s(\mathbf{r}) \end{aligned}$$

(Euler–Lagrange eq.)

Kohn–Sham DFT

Central assertion in Kohn–Sham theory:

For any interacting system of electrons, there is a potential $v_s(\mathbf{r})$, so that the ground-state density of the interacting system equals that of a non-interacting system with external potential $v_s(\mathbf{r})$.

$\Rightarrow$ ρ_0 is v_s-representable

- use $T_s[\{\phi_i\}]$ as approximation for $T[\rho]$

$$\begin{aligned} E[\rho] &= T_s[\{\phi_i\}] + V_{\text{ext}}[\rho] + J[\rho] + (V_{ee}[\rho] - J[\rho] + T[\rho] - T_s[\{\phi_i\}]) \\ &= T_s[\{\phi_i\}] + V_{\text{ext}}[\rho] + J[\rho] + E_{xc}[\rho] \end{aligned}$$

Kohn–Sham DFT

Euler–Lagrange equation for the interacting system:

$$\mu = \frac{\delta E[\rho]}{\delta \rho(\mathbf{r})}$$

Kohn–Sham DFT

Euler–Lagrange equation for the interacting system:

$$\begin{aligned}\mu &= \frac{\delta E[\rho]}{\delta \rho(\mathbf{r})} \\ &= \frac{\delta T[\{\phi_i\}]}{\delta \rho(\mathbf{r})} + \frac{\delta J[\rho]}{\delta \rho(\mathbf{r})} + \frac{\delta V_{\mathrm{ext}}[\rho]}{\delta \rho(\mathbf{r})} + \frac{\delta E_{xc}[\rho]}{\delta \rho(\mathbf{r})}\end{aligned}$$

Kohn–Sham DFT

Euler–Lagrange equation for the interacting system:

$$\begin{aligned}
\mu &= \frac{\delta E[\rho]}{\delta \rho(\mathbf{r})} \\
&= \frac{\delta T[\{\phi_i\}]}{\delta \rho(\mathbf{r})} + \frac{\delta J[\rho]}{\delta \rho(\mathbf{r})} + \frac{\delta V_{\mathrm{ext}}[\rho]}{\delta \rho(\mathbf{r})} + \frac{\delta E_{xc}[\rho]}{\delta \rho(\mathbf{r})} \\
&= \frac{\delta T[\{\phi_i\}]}{\delta \rho(\mathbf{r})} + v_{\mathrm{Coul}}(\mathbf{r}) + v_{\mathrm{ext}}(\mathbf{r}) + v_{\mathrm{xc}}(\mathbf{r})
\end{aligned}$$

Kohn–Sham DFT

Euler–Lagrange equation for the interacting system:

$$
\begin{aligned}
\mu &= \frac{\delta E[\rho]}{\delta \rho(\mathbf{r})} \\
&= \frac{\delta T[\{\phi_i\}]}{\delta \rho(\mathbf{r})} + \frac{\delta J[\rho]}{\delta \rho(\mathbf{r})} + \frac{\delta V_{\mathrm{ext}}[\rho]}{\delta \rho(\mathbf{r})} + \frac{\delta E_{xc}[\rho]}{\delta \rho(\mathbf{r})} \\
&= \frac{\delta T[\{\phi_i\}]}{\delta \rho(\mathbf{r})} + v_{\mathrm{Coul}}(\mathbf{r}) + v_{\mathrm{ext}}(\mathbf{r}) + v_{\mathrm{xc}}(\mathbf{r}) \\
&= \frac{\delta T[\{\phi_i\}]}{\delta \rho(\mathbf{r})} + v_{\mathrm{eff}}(\mathbf{r})
\end{aligned}
$$

Kohn–Sham DFT

Euler–Lagrange equation for the interacting system:

$$\begin{aligned}
\mu &= \frac{\delta E[\rho]}{\delta \rho(\mathbf{r})} \\
&= \frac{\delta T[\{\phi_i\}]}{\delta \rho(\mathbf{r})} + \frac{\delta J[\rho]}{\delta \rho(\mathbf{r})} + \frac{\delta V_{\text{ext}}[\rho]}{\delta \rho(\mathbf{r})} + \frac{\delta E_{xc}[\rho]}{\delta \rho(\mathbf{r})} \\
&= \frac{\delta T[\{\phi_i\}]}{\delta \rho(\mathbf{r})} + v_{\text{Coul}}(\mathbf{r}) + v_{\text{ext}}(\mathbf{r}) + v_{\text{xc}}(\mathbf{r}) \\
&= \frac{\delta T[\{\phi_i\}]}{\delta \rho(\mathbf{r})} + v_{\text{eff}}(\mathbf{r})
\end{aligned}$$

⇒ is fulfilled by the density of the non-interacting system

⇒ choose $v_s(\mathbf{r}) = v_{\text{eff}}(\mathbf{r})$ and solve

$$\left[-\frac{1}{2}\nabla^2 + v_{\text{eff}}(\mathbf{r})\right]\phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r})$$

(Kohn–Sham equations)

Kohn–Sham DFT

Euler–Lagrange equation for the interacting system:

$$\begin{aligned} \mu &= \frac{\delta E[\rho]}{\delta \rho(\mathbf{r})} \\ &= \frac{\delta T[\{\phi_i\}]}{\delta \rho(\mathbf{r})} + \frac{\delta J[\rho]}{\delta \rho(\mathbf{r})} + \frac{\delta V_{\text{ext}}[\rho]}{\delta \rho(\mathbf{r})} + \frac{\delta E_{xc}[\rho]}{\delta \rho(\mathbf{r})} \\ &= \frac{\delta T[\{\phi_i\}]}{\delta \rho(\mathbf{r})} + v_{\text{Coul}}(\mathbf{r}) + v_{\text{ext}}(\mathbf{r}) + v_{\text{xc}}(\mathbf{r}) \\ &= \frac{\delta T[\{\phi_i\}]}{\delta \rho(\mathbf{r})} + v_{\text{eff}}(\mathbf{r}) \end{aligned}$$

- ⇒ is fulfilled by the density of the non-interacting system
- ⇒ choose $v_s(\mathbf{r}) = v_{\text{eff}}(\mathbf{r})$ and solve

$$\left[-\frac{1}{2}\nabla^2 + v_{\text{eff}}[\rho](\mathbf{r})\right]\phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r})$$

(Kohn–Sham equations)

Kohn–Sham DFT

Remaining problem: $E_{xc}[\rho]$

- often partitioned into

$$E_{xc}[\rho] = E_x[\rho] + E_c[\rho]$$

- several strategies for the development of approximations
  - exactly solvable models (local density approximation, LDA)
  - generalized gradient approximation (GGA; may involve exact constraints)
  - Meta-GGAs
  - empirical fits
  - Hybrid functionals
  - generalized random phase approximation (RPA)

G.E. Scuseria, V.N. Staroverov, in: C.E. Dykstra, G.Frenking, K.S. Kim, G.E. Scuseria (Eds.) *Theory and Applications of Computational Chemistry: The First Forty Years*, Elsevier, Amsterdam 2005, pp. 669–724.

Density-Partitioning Schemes

General idea:

- HK theorems: $E_0 = E[\rho_0] = \min_\rho E[\rho]$
- electron density is a real-space quantity
- additive for different subsystems,

$$\rho_{\text{tot}}(\mathbf{r}) = \sum_I p_I(\mathbf{r})\rho_{\text{tot}}(\mathbf{r}) = \sum_I \rho_I(\mathbf{r})$$

- problems:
  - how can we obtain the (optimum) $\rho_I(\mathbf{r})$?
  - how can we approximate the energy functional?

Density Partitioning: Early Attempts

Zeroth-order approximation:

- start from unperturbed densities (Gombas, 1949)

$$\rho_{\text{tot}}(\mathbf{r}) = \sum_I \rho_I^0(\mathbf{r})$$

- Gordon–Kim model (1972):
  - Hartree–Fock monomer densities,

$$\rho(\mathbf{r}) = \rho_{\text{tot}}(\mathbf{r}) = \rho_A^{\text{HF}}(\mathbf{r}) + \rho_B^{\text{HF}}(\mathbf{r})$$

  - Thomas–Fermi kinetic energy functional,

$$E_{\text{GK}}[\rho] = T_{\text{TF}}[\rho] + E_{\text{Coul}}[\rho] + E_x^{\text{Dirac}}[\rho] + E_c^{\text{LDA}}[\rho] + \int \rho(\mathbf{r}) v_{\text{ext}}(\mathbf{r}) \mathrm{d}\mathbf{r}$$

Gordon–Kim Model

Equilibrium distances of rare gas dimers:
(in units of Å)

	calc.	exp.
Ne–Ne	3.0	∼3.1
Ar–Ar	3.6	∼3.8
Kr–Kr	3.8	∼3.9

interaction energies: quite good, better than KS-DFT

R.G. Gordon, Y.S. Kim, *J. Chem. Phys.* **56** (1972), 3122.

Gordon–Kim Model

Equilibrium distances of rare gas dimers:
(in units of Å)

	calc.	exp.
Ne–Ne	3.0	∼3.1
Ar–Ar	3.6	∼3.8
Kr–Kr	3.8	∼3.9

interaction energies: quite good, better than KS-DFT

R.G. Gordon, Y.S. Kim, *J. Chem. Phys.* **56** (1972), 3122.

Why did this work?

The Gordon–Kim Model

- was mainly applied to rare gas dimers

⇒ very weak density perturbations

- was not used self-consistently

⇒ avoids problems of kinetic-energy *potentials* to reproduce shell-structure in atomic densities

- was applied to study interaction energies only,

$$E_{\mathrm{GK}}^{\mathrm{int}} = V_{nn} + E_{\mathrm{GK}}[\rho] - (E_{\mathrm{GK}}[\rho_a] + E_{\mathrm{GK}}[\rho_b])$$

- atomic densities taken from Hartree–Fock calculations
- both kinetic-energy and exchange–correlation energy have wrong distance dependence

⇒ cancellation of several error sources

Energy Functional without $T[\rho]$

KS orbital energies:

$$\begin{aligned}
\sum_{i}^{\text{occ}} \epsilon_i &= \sum_{i}^{\text{occ}} \langle \phi_i | -\nabla^2/2 | \phi_i \rangle + \int d\mathbf{r} \left[\sum_{i}^{\text{occ}} |\phi_i(\mathbf{r})|^2 (v_{\text{Coul}}(\mathbf{r}) + v_{xc}(\mathbf{r}) + v_{\text{ext}}(\mathbf{r})) \right] \\
&= \sum_{i}^{\text{occ}} \langle \phi_i | -\nabla^2/2 | \phi_i \rangle + \int d\mathbf{r} \left[\rho(\mathbf{r}) (v_{\text{Coul}}(\mathbf{r}) + v_{xc}(\mathbf{r}) + v_{\text{ext}}(\mathbf{r})) \right]
\end{aligned}$$

Energy Functional without $T[\rho]$

KS orbital energies:

$$\begin{aligned}\sum_i^{\text{occ}} \epsilon_i &= \sum_i^{\text{occ}} \langle \phi_i | -\nabla^2/2 | \phi_i \rangle + \int d\mathbf{r} \left[\sum_i^{\text{occ}} |\phi_i(\mathbf{r})|^2 (v_{\text{Coul}}(\mathbf{r}) + v_{xc}(\mathbf{r}) + v_{\text{ext}}(\mathbf{r})) \right] \\ &= \sum_i^{\text{occ}} \langle \phi_i | -\nabla^2/2 | \phi_i \rangle + \int d\mathbf{r} \left[\rho(\mathbf{r}) (v_{\text{Coul}}(\mathbf{r}) + v_{xc}(\mathbf{r}) + v_{\text{ext}}(\mathbf{r})) \right]\end{aligned}$$

total electronic energy:

$$\begin{aligned}E[\rho] &= \sum_i^{\text{occ}} \langle \phi_i | -\nabla^2/2 | \phi_i \rangle + \frac{1}{2} \int \rho(\mathbf{r}) v_{\text{Coul}}(\mathbf{r}) d\mathbf{r} + E_{xc}[\rho] + \int \rho(\mathbf{r}) v_{\text{ext}}(\mathbf{r}) d\mathbf{r} \\ &= \sum_i^{\text{occ}} \epsilon_i - \frac{1}{2} \int \rho(\mathbf{r}) v_{\text{Coul}}(\mathbf{r}) d\mathbf{r} - \int \rho(\mathbf{r}) v_{xc}(\mathbf{r}) d\mathbf{r} + E_{xc}[\rho]\end{aligned}$$

Energy Functional without $T[\rho]$

KS orbital energies:

$$\begin{aligned}
\sum_i^{\mathrm{occ}} \epsilon_i &= \sum_i^{\mathrm{occ}} \langle \phi_i | -\nabla^2/2 | \phi_i \rangle + \int d\mathbf{r} \left[\sum_i^{\mathrm{occ}} |\phi_i(\mathbf{r})|^2 (v_{\mathrm{Coul}}(\mathbf{r}) + v_{xc}(\mathbf{r}) + v_{\mathrm{ext}}(\mathbf{r})) \right] \\
&= \sum_i^{\mathrm{occ}} \langle \phi_i | -\nabla^2/2 | \phi_i \rangle + \int d\mathbf{r} \left[\rho(\mathbf{r}) (v_{\mathrm{Coul}}(\mathbf{r}) + v_{xc}(\mathbf{r}) + v_{\mathrm{ext}}(\mathbf{r})) \right]
\end{aligned}$$

total electronic energy:

$$\begin{aligned}
E[\rho] &= \sum_i^{\mathrm{occ}} \langle \phi_i | -\nabla^2/2 | \phi_i \rangle + \frac{1}{2} \int \rho(\mathbf{r}) v_{\mathrm{Coul}}(\mathbf{r}) d\mathbf{r} + E_{xc}[\rho] + \int \rho(\mathbf{r}) v_{\mathrm{ext}}(\mathbf{r}) d\mathbf{r} \\
&= \sum_i^{\mathrm{occ}} \epsilon_i - \frac{1}{2} \int \rho(\mathbf{r}) v_{\mathrm{Coul}}(\mathbf{r}) d\mathbf{r} - \int \rho(\mathbf{r}) v_{xc}(\mathbf{r}) d\mathbf{r} + E_{xc}[\rho]
\end{aligned}$$

kinetic energy is implicitly contained in orbital energies

The Harris Functional

- assume density change is small:

$$\rho(\mathbf{r}) = \rho^0(\mathbf{r}) + \delta\rho(\mathbf{r})$$

- define change in effective potential

$$\begin{aligned}\delta v_{\text{eff}}(\mathbf{r}) &= v_{\text{eff}}[\rho](\mathbf{r}) - v_{\text{eff}}[\rho^0](\mathbf{r}) \\ &= \left[v_{\text{Coul}}[\rho](\mathbf{r}) - v_{\text{Coul}}[\rho^0](\mathbf{r})\right] + \left[v_{xc}[\rho](\mathbf{r}) - v_{xc}[\rho^0](\mathbf{r})\right]\end{aligned}$$

- determine orbitals for fixed potential (no SCF)

$$\left(-\frac{1}{2}\nabla^2 + v_{\text{eff}}[\rho^0](\mathbf{r})\right)\tilde{\phi}_i(\mathbf{r}) = \tilde{\epsilon}_i\tilde{\phi}_i(\mathbf{r})$$

- 1st order approximation for true orbital energies:

$$\sum_i^{\text{occ}} \epsilon_j \approx \sum_i^{\text{occ}} \tilde{\epsilon}_i + \int \rho(\mathbf{r})\delta v_{\text{eff}}(\mathbf{r})\mathrm{d}\mathbf{r}$$

The Harris Functional

- approximation for total energy:

$$\begin{aligned} E[\rho] &\approx \sum_{j}^{\mathrm{occ}} \tilde{\epsilon}_j + E_{xc}[\rho] + \int \rho(\mathbf{r}) \left[\delta v_{\mathrm{eff}}(\mathbf{r}) - \frac{1}{2} v_{\mathrm{Coul}}[\rho](\mathbf{r}) - v_{xc}[\rho](\mathbf{r}) \right] \mathrm{d}\mathbf{r} \\ &= \sum_{j}^{\mathrm{occ}} \tilde{\epsilon}_j + E_{xc}[\rho] + \int \rho(\mathbf{r}) \left[\frac{1}{2} v_{\mathrm{Coul}}[\rho](\mathbf{r}) - v_{\mathrm{Coul}}[\rho^0](\mathbf{r}) - v_{xc}[\rho^0](\mathbf{r}) \right] \mathrm{d}\mathbf{r}. \end{aligned}$$

- XC term:

$$E_{xc}[\rho] - \int \rho(\mathbf{r}) v_{xc}[\rho^0](\mathbf{r}) \mathrm{d}\mathbf{r}$$

$$\approx E_{xc}[\rho^0] + \int \frac{\delta E_{xc}[\rho^0]}{\delta \rho(\mathbf{r})} \delta\rho(\mathbf{r}) \mathrm{d}\mathbf{r} - \int \rho^0(\mathbf{r}) v_{xc}[\rho^0](\mathbf{r}) \mathrm{d}\mathbf{r} - \int \delta\rho(\mathbf{r}) v_{xc}[\rho^0](\mathbf{r}) \mathrm{d}\mathbf{r}$$

$$= E_{xc}[\rho^0] - \int \rho^0(\mathbf{r}) v_{xc}[\rho^0](\mathbf{r}) \mathrm{d}\mathbf{r}$$

The Harris Functional

- Coulomb term:

$$\int \rho(\mathbf{r}) \left[\frac{1}{2} v_{\text{Coul}}[\rho](\mathbf{r}) - v_{\text{Coul}}[\rho^0](\mathbf{r})\right] \mathbf{dr}$$

$$= \int\int (\rho^0(\mathbf{r}) + \delta\rho(\mathbf{r})) \left[\frac{1}{2} \cdot \frac{(\rho^0(\mathbf{r}') + \delta\rho(\mathbf{r}'))}{|\mathbf{r} - \mathbf{r}'|} - \frac{\rho^0(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}\right] \mathbf{dr}'\mathbf{dr}$$

$$\approx -\frac{1}{2} \int \rho^0(\mathbf{r}) v_{\text{Coul}}[\rho^0](\mathbf{r})\mathbf{dr}$$

- energy (to first order in $\delta\rho$):

$$E[\rho] \approx \sum_i^{\text{occ}} \tilde{\epsilon}_i - \int \rho^0(\mathbf{r}) \left[\frac{1}{2} v_{\text{Coul}}[\rho^0](\mathbf{r}) + v_{xc}[\rho^0](\mathbf{r})\right] \mathbf{dr} + E_{xc}[\rho^0].$$

⇒ only density ρ^0 appears!

J. Harris, *Phys. Rev. B* **31** (1985), 1770.

Harris Functional: Results

	E_b (eV)			R_e (bohr)			ω_e (meV)		
	Harris	KS	exp.	Harris	KS	exp.	Harris	KS	exp.
Be_2	0.49	0.50	0.1	4.50	4.63	4.66	45	45	28
N_2	10.7	11.34	9.91	2.03	2.08	2.07	346	296	292
F_2	3.7	3.32	1.65	2.71	2.62	2.68	120	133	111
Cu_2	2.9	2.65	2.03	4.10	4.10	4.20	35	41	33

J. Harris, *Phys. Rev. B* **31** (1985), 1770.

Subsystem DFT

- total density:

$$\rho(\mathbf{r}) = \sum_i |\phi_i^{\text{super}}(\mathbf{r})|^2$$

- partition into subsystem contributions:

$$\rho(\mathbf{r}) = \sum_I \rho_I(\mathbf{r})$$

- write each ρ_I in terms of subsystem orbitals

$$\rho_I(\mathbf{r}) = \sum_i |\phi_{i_I}(\mathbf{r})|^2$$

- assume all ϕ_{i_I} are known (but not ϕ_i^{super})

Subsystem DFT

- problem for calculations of KS energy: $T_s[\{\phi_i^{\text{super}}\}]$
- write formally exactly as

$$T_s[\{\phi_i^{\text{super}}\}] = \sum_I T_s[\{\phi_{i_I}\}] + \left[T_s[\{\phi_i^{\text{super}}\}] - \sum_I T_s[\{\phi_{i_I}\}] \right]$$

or

$$T_s[\{\phi_i^{\text{super}}\}, \{\{\phi_{i_J}\}\}] = \sum_I T_s[\{\phi_{i_I}\}] + T_s^{\text{nadd}}[\{\phi_i^{\text{super}}\}, \{\{\phi_{i_J}\}\}]$$

- introduce density-dependent approximation,

$$T_s^{\text{nadd}}[\{\phi_i^{\text{super}}\}, \{\{\phi_{i_J}\}\}] \approx T_s^{\text{nadd}}[\{\rho_J\}] = T_s[\rho] - \sum_I T_s[\rho_I]$$

One-Particle Equations in Subsystem DFT

- energy functional:

$$E[\{\rho_J\}] \quad = \quad E_{\text{ext}}[\rho] + E_{\text{Coul}}[\rho] + E_{xc}[\rho] + \sum_I T_s[\{\phi_{i_I}\}] + T_s^{\text{nadd}}[\{\rho_J\}],$$

- choose no. of electrons per subsystem (N_J)
- construct Lagrangian

$$L[\{\rho_J\}] = E[\{\rho_J\}] + \sum_I \mu_I \left(\int \mathrm{d}^3 r \rho_I(\mathbf{r}) - N_I \right)$$

and minimize w.r.t. all ρ_K

⇒ Euler–Lagrange equations:

$$0 = v_{\text{ext}}(\mathbf{r}) + v_{\text{Coul}}[\rho](\mathbf{r}) + v_{xc}[\rho](\mathbf{r}) + \frac{\delta T_s[\{\phi_{i_K}\}]}{\delta \rho_K(\mathbf{r})} + \frac{\delta T_s^{\text{nadd}}[\{\rho_K\}]}{\delta \rho_K(\mathbf{r})} + \mu_K$$

Frozen-Density Embedding

- assume all subsystem densities are v_s-representable

⇒ subsystem orbitals can be obtained from

$$\left(-\frac{1}{2}\nabla^2 + v_{\text{eff}}^{\text{sub}}[\rho, \rho_I](\mathbf{r})\right)\phi_{i_I} = \epsilon_{i_I}\phi_{i_I},$$

⇒ if we choose

$$v_{\text{eff}}^{\text{sub}}[\rho, \rho_I](\mathbf{r}) = v_{\text{eff}}[\rho](\mathbf{r}) + \frac{\delta T_s[\rho]}{\delta\rho(\mathbf{r})} - \frac{\delta T_s[\rho_I]}{\delta\rho_I(\mathbf{r})},$$

the systems of non-interacting particles fulfill

$$v_{\text{eff}}^{\text{sub}}[\rho, \rho_I](\mathbf{r}) + \frac{\delta T_s[\{\phi_{i_I}\}]}{\delta\rho_I(\mathbf{r})} + \mu_I = 0$$

⇒ these are the sought-for densities

Some References on Subsystem (TD)DFT

- Subsystem DFT:

  P. Cortona, Phys. Rev. B **44** (1991), 8454

- Frozen density embedding (FDE):

  T.A. Wesolowski, A. Warshel, J. Phys. Chem. **97** (1993), 8050.

- FDE-TDDFT:

  M.E. Casida, T.A. Wesolowski, Int. J. Quant. Chem. **96** (2004), 577; T.A. Wesolowski, J. Am. Chem. Soc. **126** (2004), 11444.

- Subsystem TDDFT:

  JN, J. Chem. Phys. **126** (2007), 134116.

- 3-FDE:

  C.R. Jacob, L. Visscher, J. Chem. Phys. **128** (2008), 155102.

- ADF implementation:

  JN, C.R. Jacob, T.A. Wesolowski, E.J. Baerends, *J. Phys. Chem. A* **109** (2005), 7805;

  C.R. Jacob, JN, L. Visscher, *J. Comput. Chem.* **29** (2008), 1011.

- overview over subsystem methods for spectroscopy:

  JN, *ChemPhysChem* (2009), DOI: 10.1002/cphc.200900538.

Embedding Potential

- define complementary density to $\rho_I(\mathbf{r})$

$$\rho_I^{\text{compl.}}(\mathbf{r}) = \sum_{J,J\neq I} \rho_J(\mathbf{r}) = \rho(\mathbf{r}) - \rho_I(\mathbf{r})$$

- one-particle equations become

$$\left(-\frac{1}{2}\nabla^2 + v_{\text{eff}}[\rho_I](\mathbf{r}) + v_{\text{emb}}[\rho_I, \rho_I^{\text{compl.}}]\right)\phi_{i_I} = \epsilon_{i_I}\phi_{i_I}$$

(Kohn–Sham equations with constrained electron density, KSCED)

- embedding potential

$$\begin{aligned} v_{\text{emb}}[\rho_I, \rho_I^{\text{compl.}}](\mathbf{r}) &= \sum_{J,J\neq I} v_{\text{ext}}^J(\mathbf{r}) + \sum_{J,J\neq I} v_{\text{Coul}}[\rho_J](\mathbf{r}) \\ &\quad + \{v_{xc}[\rho](\mathbf{r}) - v_{xc}[\rho_I](\mathbf{r})\} + \frac{\delta T_s[\rho]}{\delta\rho(\mathbf{r})} - \frac{\delta T_s[\rho_I]}{\delta\rho_I(\mathbf{r})} \end{aligned}$$

Solution of the KSCED equations

1. define subsystems ($\mathbf{R}_A$, Z_A, $A \in I$, and N_I)
2. provide density guess for each subsystem; most common: solve KS equations for all isolated subsystems
3. loop over all subsystems:
    - calculate embedding potential due to all other subsystems
    - solve KSCED equations for currently active subsystem I
    - update density ρ_I
    - if density change in system I is negligible: stop
    - otherwise: next cycle in loop

Note: step 2 is crucial for the definition of the subsystems

Frozen-Density Embedding

- common type of partitioning:
  "active subsystem" and "environment"
- environment has small (though non-negligible) influence on properties of active part

⇒ construct density guess of the environment ($\rho_2(\mathbf{r})$)

- determine embedding potential due to $\rho_2(\mathbf{r})$
- calculate density of active part (ρ_1)
- "orbital-free embedding", "frozen DFT", "FDE"

Monomer vs. Supermolecular Expansion

of subsystem densities

- main computational advantage with monomer basis sets:

$$\phi_{i_1} = \sum_{\nu_1} c_{i_1\nu_1}\chi_{\nu_1}, \qquad \phi_{i_2} = \sum_{\nu_2} c_{i_1\nu_2}\chi_{\nu_2}$$

$$\rho = \sum_{i_1}^{\mathrm{occ}_1} \left| \sum_{\nu_1} c_{i_1\nu_1}\chi_{\nu_1} \right|^2 + \sum_{i_2}^{\mathrm{occ}_2} \left| \sum_{\nu_2} c_{i_2\nu_2}\chi_{\nu_2} \right|^2$$

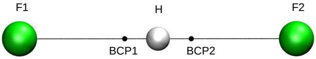
- properties often converge faster with supermolecular basis:

$$\phi_{i_{1/2}} = \sum_{\nu_1} c_{i_{1/2}\nu_1}\chi_{\nu_1} + \sum_{\nu_2} c_{i_{1/2}\nu_2}\chi_{\nu_2}$$

$$\rho = \sum_{i_1}^{\mathrm{occ}_1} \left| \sum_{\nu_1} c_{i_1\nu_1}\chi_{\nu_1} + \sum_{\nu_2} c_{i_1\nu_2}\chi_{\nu_2} \right|^2 + \sum_{i_2}^{\mathrm{occ}_2} \left| \sum_{\nu_1} c_{i_2\nu_1}\chi_{\nu_1} + \sum_{\nu_2} c_{i_2\nu_2}\chi_{\nu_2} \right|^2$$

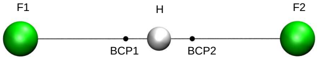
(computationally [much] more demanding)

Electron Densities from FDE: F$-$H$-$F$^-$



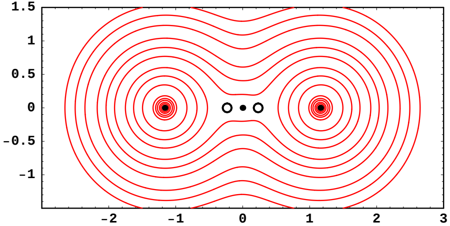
- strong, symmetric hydrogen bonds
- ρ_1: H$-$F2, ρ_2: F1$^-$ $\Rightarrow$ asymmetric fragments

Electron Densities from FDE: $F{-}H{-}F^-$



- strong, symmetric hydrogen bonds
- ρ_1: H–F2, ρ_2: $F1^-$ $\Rightarrow$ asymmetric fragments

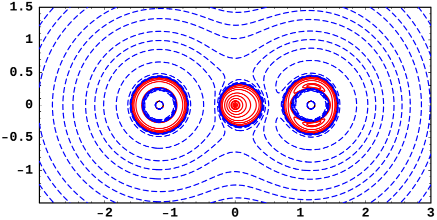
Density from FDE:



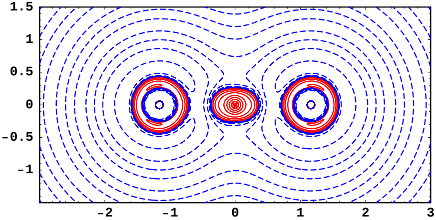
K. Kiewisch, G. Eickerling, M. Reiher, JN, *J. Chem. Phys.* **128** (2008), 044114.

F−H−F$^-$: negative Laplacian L

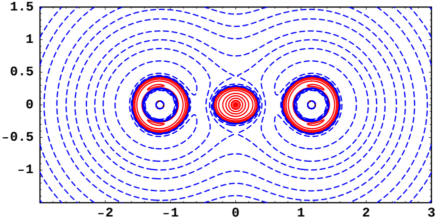
L_{frag}



L_{emb}

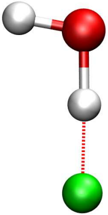


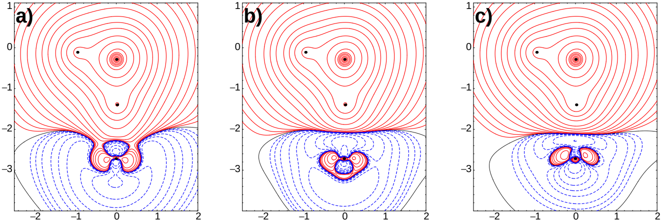
L_{super}



K. Kiewisch, G. Eickerling, M. Reiher, JN, *J. Chem. Phys.* **128** (2008), 044114.

v_s-Representability Conditions





a) initial F^- fragment, b) fully relaxed, c) fully relaxed, ghost basis

- all ρ_J must be v_s-representable
- test case: $\rho_{\text{water}}^{\text{emb,exact}} := \rho_{\text{tot}} - \rho_{\text{F}^-}$ for $H_2O \cdots F^-$
- negative areas in target density reduced upon relaxation

K. Kiewisch, G. Eickerling, M. Reiher, JN, *J. Chem. Phys.* **128** (2008), 044114.

IV. (Subsystem) TDDFT

Time-Dependent DFT

Formal Basis:

- Runge–Gross theorem (1984):
  one-to-one correspondence between $v_{\text{ext}}(\mathbf{r}, t)$ and $\rho(\mathbf{r}, t)$
- Runge and Gross also developed an effective one-electron equation

$$\left(-\frac{1}{2}\nabla^2 + v_{\text{eff}}(\mathbf{r}, t)\right)\psi_i(\mathbf{r}, t) = \mathrm{i}\frac{\partial}{\partial t}\psi_i(\mathbf{r}, t)$$

$\Rightarrow$ TDKS equations, where

$$v_{\text{eff}}(\mathbf{r}, t) = v_{\text{ext}}(\mathbf{r}, t) + v_{\text{Coul}}(\mathbf{r}, t) + v_{\text{xc}}(\mathbf{r}, t)$$

- solutions (unperturbed system):

$$\psi_i^{(0)}(\mathbf{r}, t) = e^{-\mathrm{i}\epsilon_i t}\phi_i(\mathbf{r}),$$

Linear Response TDDFT

- apply small perturbation

$$\delta v_{\mathrm{eff}}(\mathbf{r},t) = \delta v^{\mathrm{pert}}\left[e^{\mathrm{i}\omega t} + e^{-\mathrm{i}\omega t}\right] = 2\delta v^{\mathrm{pert}}\cos(\omega t),$$

- write perturbed wavefunction as

$$\psi_i(\mathbf{r},t) = \psi_i^{(0)}(\mathbf{r},t) + \delta\psi_i(\mathbf{r},t)$$

- insert into TDKS equation, subtract unperturbed TDKS equations

$$\left[-\frac{1}{2}\nabla^2 + v_{\mathrm{eff}}(\mathbf{r}) + \delta v_{\mathrm{eff}}(\mathbf{r},t)\right]\delta\psi_i(\mathbf{r},t) + \delta v_{\mathrm{eff}}(\mathbf{r},t)\psi_i^{(0)}(\mathbf{r},t) \quad = \quad \mathrm{i}\frac{\partial}{\partial t}\delta\psi_i(\mathbf{r},t)$$

- expand $\delta\psi_i(\mathbf{r},t)$ into unperturbed functions

$$\delta\psi_i(\mathbf{r},t) = \sum_r c_{ir}(t)\psi_r^{(0)}(\mathbf{r},t)$$

Linear Response TDDFT

- solve for c_{is} (to first order)

$$c_{is}(t) = -\frac{1}{2}\left(\frac{e^{[\mathrm{i}(\omega_{si}+\omega)]t}}{(\omega_{si}+\omega)} + \frac{e^{[\mathrm{i}(\omega_{si}-\omega)]t}}{(\omega_{si}-\omega)}\right)\langle\phi_s|\delta v^{\mathrm{pert}}|\phi_i\rangle$$

  with $\omega_{si} = \epsilon_s - \epsilon_i$

- first-order change in the density

$$\begin{aligned}\delta\rho(\mathbf{r},t) &= \rho(\mathbf{r},t) - \rho^{(0)}(\mathbf{r},t) \\ &= \sum_r n_r \left[\psi_r^{(0)*}(\mathbf{r},t)\delta\psi_r(\mathbf{r},t) + \psi_r^{(0)}(\mathbf{r},t)\delta\psi_r^*(\mathbf{r},t)\right]\end{aligned}$$

  (n_r = occupation number of orbital r)

Frequency-Dependent Response

- insert expression for c_{rs} into ansatz for $\delta\psi_r(\mathbf{r}, t)$
- insert ansatz for $\delta\psi_r(\mathbf{r}, t)$ into $\delta\rho(\mathbf{r}, t)$
- identify Fourier components of $\delta\rho$

$$\delta\rho(\mathbf{r}, \omega) = \sum_{rs} n_r \left[\frac{\langle\phi_r|\delta v^{\mathrm{pert}}|\phi_s\rangle \phi_s^*(\mathbf{r})\phi_r(\mathbf{r})}{\omega - \omega_{sr}} - \frac{\langle\phi_s|\delta v^{\mathrm{pert}}|\phi_r\rangle \phi_r^*(\mathbf{r})\phi_s(\mathbf{r})}{\omega + \omega_{sr}} \right]$$

- $\phi_r(\mathbf{r})$ can always be chosen real
- for real perturbations (electric fields):

$$\langle\phi_s|\delta v^{\mathrm{pert}}|\phi_r\rangle = \delta v_{sr}^{\mathrm{pert}} = \delta v_{rs}^{\mathrm{pert}}$$

- occ–occ and virt–virt pairs do not contribute to $\delta\rho(\mathbf{r}, \omega)$

The Perturbed Density Matrix

- rewrite $\delta\rho$ as

$$\begin{aligned}
\delta\rho(\mathbf{r},\omega) &= \sum_{ia}\left[\frac{1}{\omega-\omega_{ai}}-\frac{1}{\omega+\omega_{ai}}\right]\delta v_{ia}^{\text{pert}}\phi_i(\mathbf{r})\phi_a(\mathbf{r}) \\
&= \sum_{ia}\left[\frac{\omega+\omega_{ai}}{\omega^2-\omega_{ai}^2}-\frac{\omega-\omega_{ai}}{\omega^2-\omega_{ai}^2}\right]\delta v_{ia}^{\text{pert}}\phi_i(\mathbf{r})\phi_a(\mathbf{r}) \\
&= \sum_{ia}2\left[\frac{\omega_{ai}}{\omega^2-\omega_{ai}^2}\right]\delta v_{ia}^{\text{pert}}\phi_i(\mathbf{r})\phi_a(\mathbf{r}) \\
&= \sum_{ia}2P_{ia}(\omega)\phi_i(\mathbf{r})\phi_a(\mathbf{r})
\end{aligned}$$

where

$$\begin{aligned}
P_{ia}(\omega) &= \chi_{ia}^s(\omega)\delta v_{ia}^{\text{pert}} \\
\chi_{ia}^s(\omega) &= \frac{\omega_{ia}}{\omega_{ia}^2-\omega^2}=\frac{\omega_{ai}}{\omega^2-\omega_{ai}^2}
\end{aligned}$$

Linear Response in the Potential

- external perturbation δv_{ext} induces $\delta\rho$
- $\delta\rho$ induces change in potential, $\delta v_{\mathrm{eff}} \delta v_{\mathrm{ind}}$

$$\delta v_{ia}^{\mathrm{pert}} = \delta v_{ia}^{\mathrm{ext}} + \delta v_{ia}^{\mathrm{ind}},$$

$$\begin{aligned}
\delta v_{ia}^{\mathrm{ind}} &= \langle \phi_i | \delta v^{\mathrm{ind}} | \phi_a \rangle \\
&= \int \mathrm{d}^3 r_1 \, \{ \phi_i(\mathbf{r}_1) \delta v_{\mathrm{ind}} \phi_a(\mathbf{r}_1) \} \\
&= \int \mathrm{d}^3 r_1 \left\{ \phi_i(\mathbf{r}_1) \left[\int \mathrm{d}^3 r_2 \frac{\delta v_{\mathrm{eff}}(\mathbf{r}_1)}{\delta\rho(\mathbf{r}_2)} \delta\rho(\mathbf{r}_2) \right] \phi_a(\mathbf{r}_1) \right\} \\
&= \int \mathrm{d}^3 r_1 \left\{ \phi_i(\mathbf{r}_1) \left[\int \mathrm{d}^3 r_2 \left(\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} + f_{xc}(\mathbf{r}_1, \mathbf{r}_2) \right) \delta\rho(\mathbf{r}_2) \right] \phi_a(\mathbf{r}_1) \right\}
\end{aligned}$$

Exchange–Correlation Kernel

- $f_{xc}(\mathbf{r}_1, \mathbf{r}_2)$ = Fourier transform of

$$f_{xc}(\mathbf{r}, \mathbf{r}', t, t') = \frac{\delta v_{\mathrm{xc}}(\mathbf{r}, t)}{\delta \rho(\mathbf{r}', t')}$$

- . . . gives rise to causality problems
- typical approximation

$$f_{xc}(\mathbf{r}, \mathbf{r}') = \frac{\delta v_{\mathrm{xc}}(\mathbf{r})}{\delta \rho(\mathbf{r}')}$$

- exchange part

$$f_x(\mathbf{r}, \mathbf{r}') \approx -\frac{4}{9} C_x \rho^{-2/3}(\mathbf{r}') \delta(\mathbf{r} - \mathbf{r}')$$

Linear Response in the Potential

- matrix elements of the induced potential:

$$\delta v_{ia}^{\text{ind}} = \sum_{jb} 2K_{ia,jb} P_{jb}(\omega)$$

- coupling matrix

$$K_{ia,jb} = \int \mathrm{d}^3 r_1 \left\{ \phi_i(\mathbf{r}_1) \left[\int \mathrm{d}^3 r_2 \left(\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} + f_{xc} \right) \phi_j(\mathbf{r}_2) \phi_b(\mathbf{r}_2) \right] \phi_a(\mathbf{r}_1) \right\}$$

- combine results for $\delta v_{ia}^{\text{ind}}$ and $\delta v_{ia}^{\text{ext}}$

$$P_{ia}(\omega) = \frac{\omega_{ia}}{\omega_{ia}^2 - \omega^2} \underbrace{\left[\delta v_{ia}^{\text{ext}} + \sum_{jb} 2K_{ia,jb} P_{jb}(\omega) \right]}_{\delta v_{ia}^{\text{pert}}}$$

Response Equations in Matrix Form

- solve for $\delta v_{ia}^{\text{ext}}$

$$\sum_{jb} \left[\underbrace{\omega_{jb}\delta_{ij}\delta_{ab} - 2K_{ia,jb}}_{\mathbf{M}_{ia,jb}} - \frac{\omega^2}{\omega_{jb}}\delta_{ij}\delta_{ab} \right] P_{jb}(\omega) \quad = \quad \delta v_{ia}^{\text{ext}}$$

- introduce matrix $\mathbf{S}$

$$S_{ia,jb} = \frac{1}{(\epsilon_b - \epsilon_j)}\delta_{ij}\delta_{ab},$$

- re-write equation in matrix–vector form:

$$\begin{aligned} \left[\mathbf{M} + \omega^2\mathbf{S}\right] \mathbf{P}(\omega) \quad &= \quad \delta\mathbf{v}^{\text{ext}}, \\ \mathbf{S}^{-1/2}\left[\mathbf{M} + \omega^2\mathbf{S}\right] \underbrace{\mathbf{S}^{-1/2}\mathbf{S}^{1/2}}_{\mathbf{1}} \mathbf{P}(\omega) \quad &= \quad \mathbf{S}^{-1/2}\delta\mathbf{v}^{\text{ext}} \end{aligned}$$

Response Equations in Matrix Form

- formal solution for $\mathbf{P}$:

$$\mathbf{P}(\omega) = \mathbf{S}^{-1/2}\left[\underbrace{\mathbf{S}^{-1/2}\mathbf{M}\mathbf{S}^{-1/2}}_{-\mathbf{\Omega}} + \omega^2\mathbf{1}\right]^{-1}\mathbf{S}^{-1/2}\delta\mathbf{v}^{\text{ext}},$$

$$\mathbf{P}(\omega) = \mathbf{S}^{-1/2}\left[\omega^2\mathbf{1} - \mathbf{\Omega}\right]^{-1}\mathbf{S}^{-1/2}\delta\mathbf{v}^{\text{ext}}$$

where

$$\Omega_{ia,jb*} = (\epsilon_a - \epsilon_i)^2\delta_{ij}\delta_{ab} + 2\sqrt{(\epsilon_a - \epsilon_i)}K_{ia,jb}\sqrt{(\epsilon_b - \epsilon_j)}$$

Casida's Equation for Excitation Energies

- re-write matrix equation as

$$\left[\mathbf{\Omega} - \omega^2 \mathbf{1}\right] \underbrace{\mathbf{S}^{1/2}\mathbf{P}(\omega)}_{\mathbf{F}} \quad = \quad -\mathbf{S}^{-1/2}\delta\mathbf{v}^{\text{ext}}$$

- consider $\delta v^{\text{ext}} \rightarrow 0$:

$$\left[\mathbf{\Omega} - \omega_k^2 \mathbf{1}\right] \mathbf{F}_k \quad = \quad \mathbf{0}$$

- identical to constrained variational treatment (Ziegler et al.)

Subsystem TDDFT

- partition density response

$$\delta\rho(\mathbf{r}) = \sum_I \delta\rho_I(\mathbf{r})$$

- expand response density in products of subsystem orbitals

$$\delta\rho_I(\mathbf{r}) \quad = \quad \sum_{(ia)_I} 2\delta P_{(ia)_I}\phi_{i_I}(\mathbf{r})\phi_{a_I}(\mathbf{r}),$$

- perturbed density matrix

$$\begin{aligned} P_{(ia)_I}(\omega) &= \chi^s_{(ia)_I}(\omega)\delta v^{\text{pert}}_{(ia)_I} \\ \delta v^{\text{pert}}_{(ia)_I} &= \delta v^{\text{ext}}_{(ia)_I} + \delta v^{\text{ind}}_{(ia)_I} \end{aligned}$$

Local Response Approximation

- total induced potential:

$$\delta v_I^{\mathrm{ind}}(\mathbf{r}_1) = \int d\mathbf{r}_2 \left[\left(f_{Cxck}^{\mathrm{tot}} - \left.\frac{\delta^2 T_s[\rho]}{\delta\rho^2}\right|_{\rho_I} \right) \delta\rho_I(\mathbf{r}_2) + f_{Cxck}^{\mathrm{tot}} \sum_{J,J\neq I} \delta\rho_J(\mathbf{r}_2) \right]$$

Local Response Approximation

- total induced potential:

$$\delta v_I^{\mathrm{ind}}(\mathbf{r}_1) = \int d\mathbf{r}_2 \left[\left(f_{Cxck}^{\mathrm{tot}} - \left. \frac{\delta^2 T_s[\rho]}{\delta \rho^2} \right|_{\rho_I} \right) \delta\rho_I(\mathbf{r}_2) + f_{Cxck}^{\mathrm{tot}} \sum_{J, J \neq I} \delta\rho_J(\mathbf{r}_2) \right]$$

- approximation for local excitations

Effective Kernel in Subsystem TDDFT

- matrix elements of the induced potential

$$\delta v^{\mathrm{ind}}_{(jb)_I} \quad = \quad 2 \sum_{(ia)_J} K^{\mathrm{eff}}_{(jb)_I,(ia)_J} \delta P_{(ia)_J}$$

where

$$\begin{aligned} K^{\mathrm{eff}}_{(jb)_I,(ia)_J} \quad = \quad & \int \mathrm{d}^3 r_1 \left\{ \quad \phi_{j_I}(\mathbf{r}_1)\phi_{b_I}(\mathbf{r}_1) \times \right. \\ & \left. \int \mathrm{d}^3 r_2 \left(f^{\mathrm{tot}}_{Cxck}(\mathbf{r}_1,\mathbf{r}_2) - \frac{\delta^2 T_s[\rho_I]}{\delta\rho(\mathbf{r}_2)\delta\rho(\mathbf{r}_1)} \delta_{IJ} \right) \phi_{i_J}(\mathbf{r}_2)\phi_{a_J}(\mathbf{r}_2) \right\} \end{aligned}$$

- total effective response kernel:

$$f^{\mathrm{tot}}_{Cxck}(\mathbf{r}_1,\mathbf{r}_2) = \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} + \frac{\delta^2 E_{xc}[\rho]}{\delta\rho(\mathbf{r}_2)\delta\rho(\mathbf{r}_1)} + \frac{\delta^2 T_s[\rho]}{\delta\rho(\mathbf{r}_2)\delta\rho(\mathbf{r}_1)}$$

Subsystem TDDFT in Matrix Form

- perturbed density matrix

$$\delta P_{(jb)_I} \quad = \quad \chi^s_{(jb)_I} \left[\delta v^{\text{ext}}_{(jb)_I} + 2 \sum_{(ia)_J} K^{\text{eff}}_{(jb)_I,(ia)_J} \delta P_{(ia)_J} \right]$$

- matrix equation for excitation energies

$$\left[\mathbf{\Omega}^{\text{s}} - \omega_k^2 \right] \mathbf{F}^{\text{s}}_k = 0$$

Approximate Solutions

full problem:

$$\left[\begin{pmatrix} \mathbf{\Omega}_{AA} & \mathbf{\Omega}_{AB} & \cdots & \mathbf{\Omega}_{AZ} \\ \mathbf{\Omega}_{BA} & \mathbf{\Omega}_{BB} & \cdots & \mathbf{\Omega}_{BZ} \\ \vdots & \vdots & \ddots & \vdots \\ \mathbf{\Omega}_{ZA} & \mathbf{\Omega}_{ZB} & \cdots & \mathbf{\Omega}_{ZZ} \end{pmatrix} - \omega_k^2\right] \begin{pmatrix} \mathbf{F}_k^A \\ \mathbf{F}_k^B \\ \vdots \\ \mathbf{F}_k^Z \end{pmatrix} = \begin{pmatrix} \mathbf{0}_A \\ \mathbf{0}_B \\ \vdots \\ \mathbf{0}_Z \end{pmatrix}$$

1. diagonalize subsystem problems $\Rightarrow$ yields $\mathbf{U}_A, \mathbf{U}_B, \ldots$ (solution factor matrices) within “local response approximation”
2. construct supermatrix $\mathbf{U}$ containing $\mathbf{U}_A, \mathbf{U}_B$ blocks on the diagonal
3. transform equation by $\mathbf{U}$

but: that still requires all couplings

JN, J. Chem. Phys. **126** (2007), 134116.

Approximate Solutions

full problem:

$$\left[\begin{pmatrix} \mathbf{\Omega}_{AA} & & & \\ & \mathbf{\Omega}_{BB} & & \\ & & \ddots & \\ & & & \mathbf{\Omega}_{ZZ} \end{pmatrix} - \omega_k^2\right]\begin{pmatrix} \mathbf{F}_k^A \\ \mathbf{F}_k^B \\ \vdots \\ \mathbf{F}_k^Z \end{pmatrix} = \begin{pmatrix} \mathbf{0}_A \\ \mathbf{0}_B \\ \vdots \\ \mathbf{0}_Z \end{pmatrix}$$

1. diagonalize subsystem problems ⇒ yields $\mathbf{U}_A, \mathbf{U}_B, \ldots$ (solution factor matrices) within “local response approximation”
2. construct supermatrix $\mathbf{U}$ containing $\mathbf{U}_A, \mathbf{U}_B$ blocks on the diagonal
3. transform equation by $\mathbf{U}$

but: that still requires all couplings

JN, J. Chem. Phys. **126** (2007), 134116.

Approximate Solutions

full problem:

$$\left[\begin{pmatrix} \boldsymbol{\Omega}_{AA} & \boldsymbol{\Omega}_{AB} & \cdots & \boldsymbol{\Omega}_{AZ} \\ \boldsymbol{\Omega}_{BA} & \boldsymbol{\Omega}_{BB} & \cdots & \boldsymbol{\Omega}_{BZ} \\ \vdots & \vdots & \ddots & \vdots \\ \boldsymbol{\Omega}_{ZA} & \boldsymbol{\Omega}_{ZB} & \cdots & \boldsymbol{\Omega}_{ZZ} \end{pmatrix} - \omega_k^2\right] \begin{pmatrix} \mathbf{F}_k^A \\ \mathbf{F}_k^B \\ \vdots \\ \mathbf{F}_k^Z \end{pmatrix} = \begin{pmatrix} \mathbf{0}_A \\ \mathbf{0}_B \\ \vdots \\ \mathbf{0}_Z \end{pmatrix}$$

1. diagonalize subsystem problems $\Rightarrow$ yields $\mathbf{U}_A, \mathbf{U}_B, \ldots$ (solution factor matrices) within “local response approximation”
2. construct supermatrix $\mathbf{U}$ containing $\mathbf{U}_A, \mathbf{U}_B$ blocks on the diagonal
3. transform equation by $\mathbf{U}$

but: that still requires all couplings

JN, J. Chem. Phys. **126** (2007), 134116.

Approximate Solutions

full problem:

$$\left[\begin{pmatrix} \omega_{A,0}^2 & \tilde{\boldsymbol{\Omega}}_{AB} & \cdots & \tilde{\boldsymbol{\Omega}}_{AZ} \\ \tilde{\boldsymbol{\Omega}}_{BA} & \omega_{B,0}^2 & \cdots & \tilde{\boldsymbol{\Omega}}_{BZ} \\ \vdots & \vdots & \ddots & \vdots \\ \tilde{\boldsymbol{\Omega}}_{ZA} & \tilde{\boldsymbol{\Omega}}_{ZB} & \cdots & \omega_{Z,0}^2 \end{pmatrix} - \omega_k^2\right] \begin{pmatrix} \tilde{\mathbf{F}}_k^A \\ \tilde{\mathbf{F}}_k^B \\ \vdots \\ \tilde{\mathbf{F}}_k^Z \end{pmatrix} = \begin{pmatrix} \mathbf{0}_A \\ \mathbf{0}_B \\ \vdots \\ \mathbf{0}_Z \end{pmatrix}$$

1. diagonalize subsystem problems ⇒ yields $\mathbf{U}_A, \mathbf{U}_B, \ldots$ (solution factor matrices) within “local response approximation”
2. construct supermatrix $\mathbf{U}$ containing $\mathbf{U}_A, \mathbf{U}_B$ blocks on the diagonal
3. transform equation by $\mathbf{U}$

but: that still requires all couplings

JN, J. Chem. Phys. **126** (2007), 134116.

Approximate Solutions

full problem:

$$\left[\begin{pmatrix} \omega_{A,0}^2 & \tilde{\Omega}_{AB} & \cdots & \tilde{\Omega}_{AZ} \\ \tilde{\Omega}_{BA} & \omega_{B,0}^2 & \cdots & \tilde{\Omega}_{BZ} \\ \vdots & \vdots & \ddots & \vdots \\ \tilde{\Omega}_{ZA} & \tilde{\Omega}_{ZB} & \cdots & \omega_{Z,0}^2 \end{pmatrix} - \omega_k^2 \right] \begin{pmatrix} \tilde{\mathbf{F}}_k^A \\ \tilde{\mathbf{F}}_k^B \\ \vdots \\ \tilde{\mathbf{F}}_k^Z \end{pmatrix} = \begin{pmatrix} \mathbf{0}_A \\ \mathbf{0}_B \\ \vdots \\ \mathbf{0}_Z \end{pmatrix}$$

1. diagonalize subsystem problems ⇒ yields $\mathbf{U}_A, \mathbf{U}_B, \ldots$ (solution factor matrices) within "local response approximation"
2. construct supermatrix $\mathbf{U}$ containing $\mathbf{U}_A, \mathbf{U}_B$ blocks on the diagonal
3. transform equation by $\mathbf{U}$

but: that still requires all couplings

JN, J. Chem. Phys. **126** (2007), 134116.

Selective Inclusion of Couplings

- FDE often works fine without intersystem couplings

Selective Inclusion of Couplings

- FDE often works fine without intersystem couplings
- critical cases: identical chromophores, degenerate excitations

Selective Inclusion of Couplings

- FDE often works fine without intersystem couplings
- critical cases: identical chromophores, degenerate excitations

new protocol:

1. calculate most important eigenvectors for subsystems to be coupled

Selective Inclusion of Couplings

- FDE often works fine without intersystem couplings
- critical cases: identical chromophores, degenerate excitations

new protocol:

1. calculate most important eigenvectors for subsystems to be coupled
2. calculate intersystem couplings only for these states
   (or a subset of them)

Selective Inclusion of Couplings

- FDE often works fine without intersystem couplings
- critical cases: identical chromophores, degenerate excitations

new protocol:

1. calculate most important eigenvectors for subsystems to be coupled
2. calculate intersystem couplings only for these states
(or a subset of them)
3. diagonalize the corresponding subblock of $\tilde{\boldsymbol{\Omega}}^{\mathrm{sub}}$

Selective Inclusion of Couplings

- FDE often works fine without intersystem couplings
- critical cases: identical chromophores, degenerate excitations

new protocol:

1. calculate most important eigenvectors for subsystems to be coupled
2. calculate intersystem couplings only for these states
   (or a subset of them)
3. diagonalize the corresponding subblock of $\tilde{\mathbf{\Omega}}^{\mathrm{sub}}$

requires matrix elements between subsystem excitations μ_A, ν_B:

$$\tilde{\Omega}_{\mu_A \nu_B} = \sum_{(ia)_A} \sum_{(jb)_B} U_{(ia)_A \mu_A} \Omega_{(ia)_A (jb)_B} U_{(jb)_B \nu_B}$$

A Closer Look at the Coupling Matrix Elements

- explicit expression for $\tilde{\Omega}_{\mu_A \nu_B}$:

$$\begin{aligned}
\tilde{\Omega}_{\mu_A \nu_B} &= \int d\mathbf{r}_1 2 \sum_{(ia)_A} U_{(ia)_A \mu_A} \sqrt{\omega_{(ia)_A}} \phi_{i_A} \phi_{a_A} \int d\mathbf{r}_2 f^{\text{tot}}_{Cxck} \sum_{(jb)_B} U_{(jb)_B \nu_B} \sqrt{\omega_{(jb)_B}} \phi_{j_B} \phi_{b_B} \\
&= \int d\mathbf{r}_1 \int d\mathbf{r}_2 2 \rho^t_{\mu_A}(\mathbf{r}_1) f^{\text{tot}}_{Cxck} \rho^t_{\nu_B}(\mathbf{r}_2)
\end{aligned}$$

A Closer Look at the Coupling Matrix Elements

- explicit expression for $\tilde{\Omega}_{\mu_A \nu_B}$:

$$\begin{aligned}
\tilde{\Omega}_{\mu_A \nu_B} &= \int d\mathbf{r}_1 2 \sum_{(ia)_A} U_{(ia)_A \mu_A} \sqrt{\omega_{(ia)_A}} \phi_{i_A} \phi_{a_A} \int d\mathbf{r}_2 f^{\text{tot}}_{Cxck} \sum_{(jb)_B} U_{(jb)_B \nu_B} \sqrt{\omega_{(jb)_B}} \phi_{j_B} \phi_{b_B} \\
&= \int d\mathbf{r}_1 \int d\mathbf{r}_2 2 \rho^t_{\mu_A}(\mathbf{r}_1) f^{\text{tot}}_{Cxck} \rho^t_{\nu_B}(\mathbf{r}_2)
\end{aligned}$$

⇒ interaction between “transition densities” of local excitations

A Closer Look at the Coupling Matrix Elements

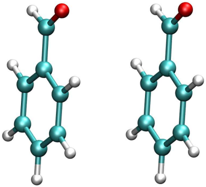
- explicit expression for $\tilde{\Omega}_{\mu_A \nu_B}$:

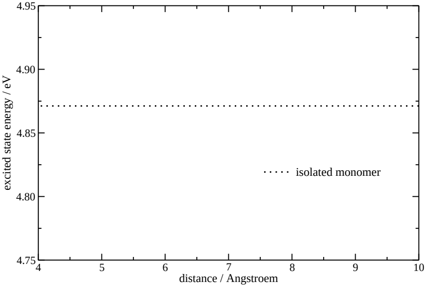
$$\begin{aligned}\tilde{\Omega}_{\mu_A \nu_B} &= \int d\mathbf{r}_1 2 \sum_{(ia)_A} U_{(ia)_A \mu_A} \sqrt{\omega_{(ia)_A}} \phi_{i_A} \phi_{a_A} \int d\mathbf{r}_2 f^{\text{tot}}_{Cxck} \sum_{(jb)_B} U_{(jb)_B \nu_B} \sqrt{\omega_{(jb)_B}} \phi_{j_B} \phi_{b_B} \\ &= \int d\mathbf{r}_1 \int d\mathbf{r}_2 2 \rho^t_{\mu_A}(\mathbf{r}_1) f^{\text{tot}}_{Cxck} \rho^t_{\nu_B}(\mathbf{r}_2)\end{aligned}$$

$\Rightarrow$ interaction between “transition densities” of local excitations

$\Rightarrow$ $k_{\text{EET}} \propto \left| \tilde{\Omega}_{\mu_A \nu_B} \right|^2$

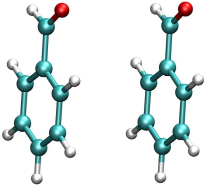
Coupled FDE: Interacting Dimers

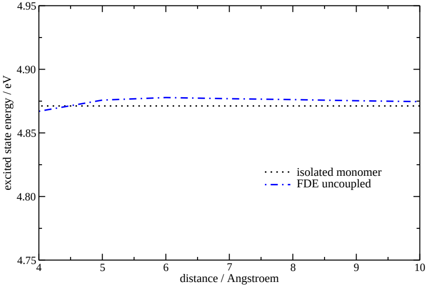




$\pi \rightarrow \pi^*$ in benzaldehyde (BP86/TZP, 20 monomer states):

Coupled FDE: Interacting Dimers

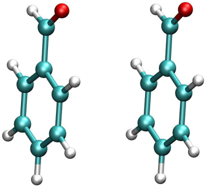


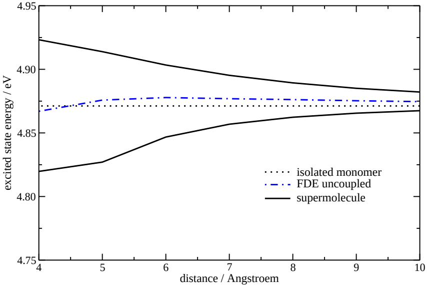


$\pi \rightarrow \pi^*$ in benzaldehyde (BP86/TZP, 20 monomer states):

- uncoupled FDE: slight shift in monomer excitation

Coupled FDE: Interacting Dimers

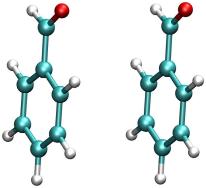


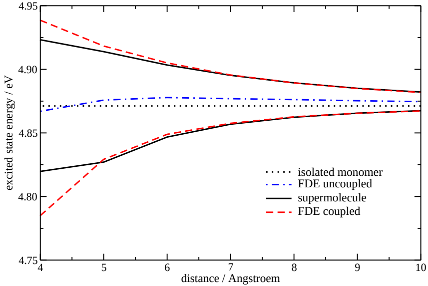


$\pi \rightarrow \pi^*$ in benzaldehyde (BP86/TZP, 20 monomer states):

- uncoupled FDE: slight shift in monomer excitation
- supermolecular TDDFT: splitting between monomer excitations

Coupled FDE: Interacting Dimers





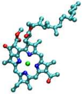
$\pi \rightarrow \pi^*$ in benzaldehyde (BP86/TZP, 20 monomer states):

- uncoupled FDE: slight shift in monomer excitation
- supermolecular TDDFT: splitting between monomer excitations
- coupled FDE: splitting is reproduced

JN, J. Chem. Phys. **126** (2007), 134116.

Natural Light-Harvesting Complexes

Structure of LH2 of *Rhodopseudomonas acidophila*

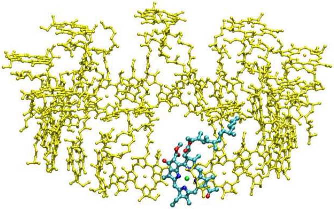


- main pigments: Bchl a

G. McDermott *et. al*, *Nature* **374** (1995), 517.

Natural Light-Harvesting Complexes

Structure of LH2 of *Rhodopseudomonas acidophila*

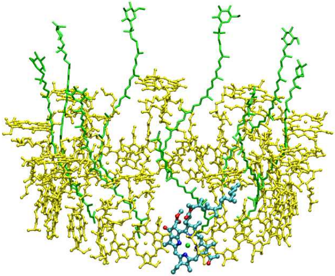


- main pigments: Bchl a
- 9 pairs of $\{\alpha, \beta\}$-Bchl a in B850 unit, 9 Bchl a in B800 unit

G. McDermott *et. al*, *Nature* **374** (1995), 517.

Natural Light-Harvesting Complexes

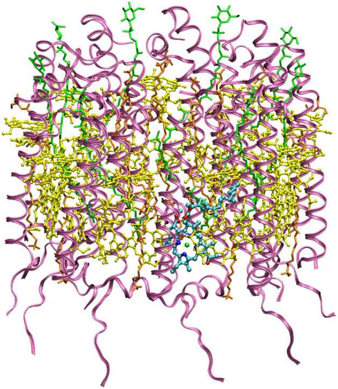
Structure of LH2 of *Rhodopseudomonas acidophila*



- main pigments: Bchl a
- 9 pairs of $\{\alpha, \beta\}$-Bchl a in B850 unit, 9 Bchl a in B800 unit
- 9 carotenoid pigments (rhodopin glucoside)

G. McDermott *et. al*, *Nature* **374** (1995), 517.

Natural Light-Harvesting Complexes
Structure of LH2 of *Rhodopseudomonas acidophila*



- main pigments: Bchl a
- 9 pairs of $\{\alpha, \beta\}$-Bchl a in B850 unit, 9 Bchl a in B800 unit
- 9 carotenoid pigments (rhodopin glucoside)
- 9 α- and β-apoproteins

G. McDermott *et. al*, *Nature* **374** (1995), 517.

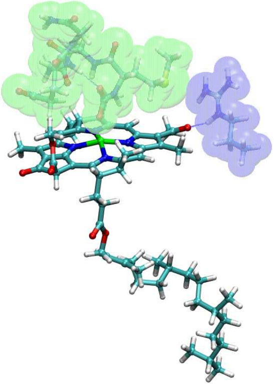
Protein–Pigment Interactions in LH2

Rhodopseudomonas acidophila

excitation energies (eV; SAOP/TZP/FDE) for B800 Bchl a:

environment	Q_y	Q_x
exp.[1]	1.60	2.15
—	1.61	1.95
α-Met1	1.61	1.90
β-Arg20	1.55	1.85

[1] *in vitro*, R.E. Blankenship, *Molecular Mechanisms of Photosynthesis* Blackwell Science, Oxford, 2002.

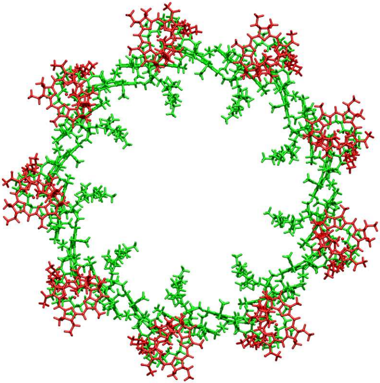


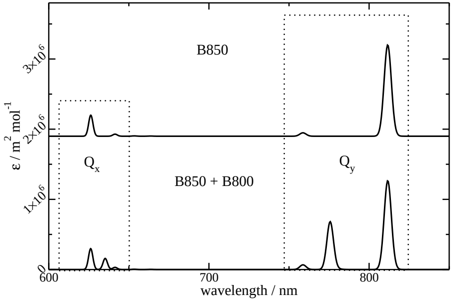
- shifts from FDE agree with conventional TDDFT results

  Z. He, V. Sundström, T. Pullerits, *J. Phys. Chem. B* **106** (2002), 11606.

⇒ protein environment can be described by FDE

Photosynthetic Light-Harvesting Complexes





(SAOP/TZP/FDEc; ca. 3800 atoms)

- strong excitonic coupling in B850
- B850 and B800 spectra do not interact strongly

JN, *J. Phys. Chem. B*, **112** (2008), 2207.