Time-dependent reduced density-matrix-functional theory

Kasia Pernal

pernalk@gmail.com

Institute of Physics, Lodz University of Technology Poland

Outline

- Reduced density matrices
- Equation of motion for the 1-electron reduced density matrix
- Linear response theory
    - adiabatic approximations
    - linear response function
    - excitation energies
    - extended random phase approximation

Note that in the lecture there are two equivalent symbols used for 1-RDM!

$$\Gamma^{(1)} \equiv \Gamma$$

In the literature one often finds lower case gamma for 1-RDM

$$\gamma \equiv \Gamma^{(1)}$$

One-electron reduced density matrix (1-RDM, one-matrix)

$$\Gamma(x,x') \equiv \Gamma^{(1)}(x,x') = N \int \Psi^*(x',\dots,x_N)\Psi(x,\dots,x_N)\, dx_2 \dots dx_N$$

- Definitions of natural spinorbitals and natural occupation numbers

$$\int \Gamma(x,x')\,\varphi_i(x')\,dx' = n_i\,\varphi_i(x)$$

$$\Gamma(x,x') = \sum_i n_i\,\varphi_i(x)\,\varphi_i^*(x')$$

- Properties (sufficient and necessary ensemble N-rep conditions)

$$\forall_{i,j} \quad \int \varphi_i^*(x)\varphi_j(x)\,dx = \delta_{ij}$$

$$\sum_i n_i = N\,, \quad \forall_i \;\; 0 \leq n_i \leq 1$$

where *N* is a number of particles in a system.

p-electron reduced density matrix

- Two-electron reduced density matrix (2-RDM, two-matrix)

$$\Gamma^{(2)}(x_1, x_2; x_1', x_2') = \frac{N(N-1)}{2} \times \int \Psi(x_1', x_2', \ldots, x_N)^* \Psi(x_1, x_2, \ldots, x_N) dx_3 \ldots dx_N$$

p-electron reduced density matrix

- Two-electron reduced density matrix (2-RDM, two-matrix)

$$\Gamma^{(2)}(x_1, x_2; x_1', x_2') = \frac{N(N-1)}{2} \times \int \Psi(x_1', x_2', \ldots, x_N)^* \Psi(x_1, x_2, \ldots, x_N) dx_3 \ldots dx_N$$

- In general one defines a p-particle reduced density matrix as follows

$$\Gamma^{(p)}(x_1, x_2, \ldots, x_p; x_1', x_2' \ldots, x_p') = \left(\begin{array}{c} N \\ p \end{array} \right) \int \Psi(x_1', x_2', \ldots, x_p', x_{p+1}, \ldots, x_N)^* \times \Psi(x_1, x_2, \ldots, x_p, x_{p+1}, \ldots, x_N) dx_{p+1} \ldots dx_N$$

Reduced density matrix functional theory (RDMFT)

- The existence of the functional is assured by the Hohenberg-Kohn theorem extended by Gilbert [*Phys. Rev.* B **12**, 2111 (1975)]

$$\Gamma^{(1)}(x,x') \rightarrow v_{ext} \rightarrow E_0$$

1-RDM is assumed to be v-representable.

- A construction of a functional for ensemble N-representable 1-RDM was provided by S. M. Valone [*J. Chem. Phys*. **73**, 1344, 4653 (1980)]

$$E[\Gamma_e^{(1)}] = \mathrm{Tr}\left[(\hat{t}+\hat{v}_{ext})\hat{\Gamma}_e^{(1)}\right] + \min_{\Gamma^{(N)}\rightarrow\Gamma_e^{(1)}} \mathrm{Tr}\left[\hat{V}_{ee}\hat{\Gamma}^{(N)}\right]$$

$$\hat{\Gamma}^{(N)} = \sum_i \omega_i \left|\Psi_i^N\right\rangle\left\langle\Psi_i^N\right|$$

$$\mathrm{Tr}\left[\hat{V}_{ee}\hat{\Gamma}^{(N)}\right] = \sum_i \omega_i \left\langle \Psi_i | \hat{V}_{ee} | \Psi_i \right\rangle$$

Equation of motion for N-electron density matrix

- Consider a time-dependent Schrödinger equation

$$i\frac{\partial\left|\Psi^N\right\rangle}{\partial t}=\hat{H}\left|\Psi^N\right\rangle$$

- A time-derivative for pure-state (p) N-electron density matrix reads

$$\hat{\Gamma}_p^{(N)}=\left|\Psi^N\right\rangle\left\langle\Psi^N\right|$$

$$\begin{aligned}\frac{\partial\hat{\Gamma}_p^{(N)}}{\partial t}&=\left(\frac{\partial\left|\Psi^N\right\rangle}{\partial t}\right)\left\langle\Psi^N\right|+\left|\Psi^N\right\rangle\left(\frac{\partial\left\langle\Psi^N\right|}{\partial t}\right)\\&=\frac{1}{i}\hat{H}\left|\Psi^N\right\rangle\left\langle\Psi^N\right|-\frac{1}{i}\left|\Psi^N\right\rangle\left\langle\Psi^N\right|\hat{H}\end{aligned}$$

$$i\frac{\partial\hat{\Gamma}_p^{(N)}}{\partial t}=\left[\hat{H},\left|\Psi^N\right\rangle\left\langle\Psi^N\right|\right]=\left[\hat{H},\hat{\Gamma}_p^{(N)}\right]$$

Equation of motion for ensemble N-electron density matrix

- For ensemble-state (e) N-electron density matrix

$$\hat{\Gamma}_e^{(N)} = \sum_j \omega_j \left|\Psi_j^N\right\rangle \left\langle\Psi_j^N\right| = \sum_j \omega_j \hat{\Gamma}_{p,j}^{(N)}$$

a similar equation of motion holds

$$i\frac{\partial\hat{\Gamma}_e^{(N)}}{\partial t} = i\sum_j \omega_j \frac{\partial\hat{\Gamma}_{p,j}^{(N)}}{\partial t}$$

$$= \sum_j \omega_j \left[\hat{H}, \hat{\Gamma}_{p,j}^{(N)}\right] = \left[\hat{H}, \sum_j \omega_j \hat{\Gamma}_{p,j}^{(N)}\right]$$

$$= \left[\hat{H}, \hat{\Gamma}_e^{(N)}\right]$$

Liouville-von Neumann equation

Bogoliubov-Born-Green-Kirkwood-Yvon (BBGKY) hierarchy

- In the first quantization the Liouville-von Neumann equation takes form

$$i\frac{\partial[\Psi(x'_1,\ldots,x'_N)^*\Psi(x_1,\ldots,x_N)]}{\partial t} = \left[\hat{H}_{1\ldots N}\Psi(x_1,\ldots,x_N)\right]\Psi(x'_1,\ldots,x'_N)^* \\ - \Psi(x_1,\ldots,x_N)\left[\hat{H}_{1'\ldots N'}\Psi(x'_1,\ldots,x'_N)^*\right]$$

- Skip primes at the last N-p primed coordinates, integrate over N-p coordinates and multiply both sides by $N!/p!/(N$-$p)!$ to get an equation involving p-RDM and p+1-RDM

$$\begin{aligned} p=1 &: \quad \mathrm{equation}_1[\Gamma^{(1)}(t),\Gamma^{(2)}(t)] \\ p=2 &: \quad \mathrm{equation}_2[\Gamma^{(2)}(t),\Gamma^{(3)}(t)] \\ &\vdots \end{aligned}$$

BBGKY hierarchy

BBGKY hierarchy

- Solving full BBGKY hierarchy is equivalent to solving the time-dependent Schrödinger equation.

BBGKY hierarchy

- Solving full BBGKY hierarchy is equivalent to solving the time-dependent Schrödinger equation.

- One should truncate the hierarchy at some level p and make approximations for the p-RDM.

BBGKY hierarchy

- Solving full BBGKY hierarchy is equivalent to solving the time-dependent Schrödinger equation.

- One should truncate the hierarchy at some level p and make approximations for the p-RDM.

- For example, truncating the hierarchy after the second equation would require approximating 3-RDM by 1- and 2-RDM.

BBGKY hierarchy

- Solving full BBGKY hierarchy is equivalent to solving the time-dependent Schrödinger equation.

- One should truncate the hierarchy at some level p and make approximations for the p-RDM.

- For example, truncating the hierarchy after the second equation would require approximating 3-RDM by 1- and 2-RDM.

- It has been shown that reconstruction schemes giving reasonable results for ground state energy fail when employed in the truncated BBGKY equations [A. Akbari et al., *Phys. Rev.* B **85**, 235121 (2012)]

Equation of motion for 1-RDM

- For the time-dependent Hamiltonian

$$\hat{H}(t) = \sum_{i=1}^{N} \hat{h}(x_i, t) + \frac{1}{2} \sum_{i \neq j}^{N} r_{ij}^{-1}$$

$$\hat{h}(x, t) = -\frac{1}{2} \nabla_r^2 + \upsilon(x, t)$$

the first equation in the BBGKY hierarchy reads

$$\left[i \frac{\partial}{\partial t} - \hat{h}(x_1, t) + \hat{h}(x_1', t) \right] \Gamma^{(1)}(x_1, x_1', t)$$

$$= 2 \int dx_2 \left(r_{12}^{-1} - r_{1'2}^{-1} \right) \Gamma^{(2)}(x_1, x_2; x_1', x_2, t)$$

Equation of motion for 1-RDM

- Due to the Runge-Gross theorem [*Phys. Rev. Lett.* **52**, 997 (1984)]

$$\left\{\Gamma^{(1)}(t), \Psi(t_0)\right\} \rightarrow \Gamma^{(2)}(t)$$

the time-dependent 2-matrix is a functional of the time-dependent 1-matrix

$$\Gamma^{(2)}(t) = \Gamma^{(2)}[\Gamma^{(1)}, \Psi(t_0)](t)$$

Time-dependent 2-RDM is a functional of 1-RDM - proof

- Assume two different (by more than a time-dependent function) time-dependent potentials yielding the same 1-RDM

$$v_1(x,t) - v_2(x,t) \neq c(t)$$

$$v_1(x,t) \rightarrow \Gamma_1^{(1)}(t)$$

$$v_2(x,t) \rightarrow \Gamma_2^{(1)}(t)$$

$$\Gamma_1^{(1)}(t) = \Gamma_2^{(1)}(t) = \Gamma^{(1)}(t)$$

Time-dependent 2-RDM is a functional of 1-RDM - proof

- Assume two different (by more than a time-dependent function) time-dependent potentials yielding the same 1-RDM

$$v_1(x,t) - v_2(x,t) \neq c(t)$$

$$v_1(x,t) \rightarrow \Gamma_1^{(1)}(t)$$

$$v_2(x,t) \rightarrow \Gamma_2^{(1)}(t)$$

$$\Gamma_1^{(1)}(t) = \Gamma_2^{(1)}(t) = \Gamma^{(1)}(t)$$

On one hand

$$\Gamma_1^{(1)}(t) = \Gamma_2^{(1)}(t) \quad \Longrightarrow \quad \rho_1(t) = \rho_2(t)$$

Time-dependent 2-RDM is a functional of 1-RDM - proof

- Assume two different (by more than a time-dependent function) time-dependent potentials yielding the same 1-RDM

$$v_1(x,t) - v_2(x,t) \neq c(t)$$

$$v_1(x,t) \rightarrow \Gamma_1^{(1)}(t)$$

$$v_2(x,t) \rightarrow \Gamma_2^{(1)}(t)$$

$$\Gamma_1^{(1)}(t) = \Gamma_2^{(1)}(t) = \Gamma^{(1)}(t)$$

On one hand

$$\Gamma_1^{(1)}(t) = \Gamma_2^{(1)}(t) \quad \Longrightarrow \quad \rho_1(t) = \rho_2(t)$$

On the other hand, the Runge-Gross theorem states

$$v_1(x,t) - v_2(x,t) \neq c(t) \quad \Longrightarrow \quad \rho_1(t) \neq \rho_2(t)$$

Time-dependent 2-RDM is a functional of 1-RDM - proof

- Assume two different (by more than a time-dependent function) time-dependent potentials yielding the same 1-RDM

$$v_1(x,t) - v_2(x,t) \neq c(t)$$

$$v_1(x,t) \to \Gamma_1^{(1)}(t)$$

$$v_2(x,t) \to \Gamma_2^{(1)}(t)$$

$$\Gamma_1^{(1)}(t) = \Gamma_2^{(1)}(t) = \Gamma^{(1)}(t)$$

On one hand

$$\Gamma_1^{(1)}(t) = \Gamma_2^{(1)}(t) \quad \Longrightarrow \quad \rho_1(t) = \rho_2(t)$$

On the other hand, the Runge-Gross theorem states

$$v_1(x,t) - v_2(x,t) \neq c(t) \quad \Longrightarrow \quad \rho_1(t) \neq \rho_2(t)$$

- Contradictory equations are obtained. Consequently,

$$\left\{\Gamma^{(1)}(t), \Psi(t_0)\right\} \to v(x,t) \to \Psi(t) \to \Gamma^{(2)}(t)$$

Equation of motion for 1-RDM

- Thus, the first equation in the BBGKY hierarchy may be seen as the equation of motion for 1-RDM.

$$\left(i\frac{\partial}{\partial t} - \hat{h}(x_1,t) + \hat{h}(x_1',t)\right)\Gamma^{(1)}(x_1,x_1',t)$$
$$= 2\int dx_2\,(r_{12}^{-1} - r_{1'2}^{-1})\,\Gamma^{(2)}[\Gamma^{(1)}](x_1,x_2;x_1',x_2,t)$$

K. Pernal, O. Gritsenko, and E.J. Baerends, Phys. Rev. A **75**, 012506 (2007)

Equation of motion for 1-RDM

- In the matrix representation in a fixed, time-independent and orthonormal basis set $\{\chi_p(x)\}$

$$\Gamma^{(1)}(x,x') = \sum_{pq} \Gamma^{(1)}_{pq} \chi_p(x)\chi_q(x')^*$$

$$\Gamma^{(2)}(x_1,x_2;x_1',x_2') = \sum_{pqrs} \Gamma^{(2)}_{pqrs}\ \chi_p(x_1)\chi_q(x_2)\chi_r(x_1')^*\chi_s(x_2')^*$$

the equation of motion involving one- and two-electron reduced density matrices reads

$$i\frac{\partial \Gamma_{pq}(t)}{\partial t} = \sum_r \left[h_{qr}(t)\Gamma_{pr}(t) - \Gamma_{rq}(t)h_{rp}(t)\right]$$

$$+2\sum_{rst}[\Gamma^{(2)}_{prst}(t)\left\langle \chi_q\chi_r|\chi_s\chi_t\right\rangle - \left\langle \chi_t\chi_s|\chi_r\chi_p\right\rangle \Gamma^{(2)}_{tsrq}(t)]$$

$$\left\langle \chi_i\chi_k|\chi_j\chi_l\right\rangle = \int\int \chi_i^*(x')\chi_k^*(x)|r-r'|^{-1}\chi_j(x')\chi_l(x)\,dx\,dx'$$

The linear response of the one-matrix

- A linear response of 1-RDM to a perturbation is given by a convolution of the linear response function and the perturbation

$$\delta\Gamma_{ij}(t) = \sum_{kl}\int_{-\infty}^{\infty}\chi_{ij,kl}(t-t')\delta v_{kl}(t')dt'$$

or in terms of the corresponding Fourier transforms

$$\delta\Gamma_{ij}(\omega) = \sum_{kl}\chi_{ij,kl}(\omega)\delta v_{kl}(\omega)$$

- The sum over states (SOS) definition of the response function reads

$$\chi_{ij,kl}(\omega) = \sum_{I\neq 0}\left\{\frac{\left\langle\Psi_0|\hat{a}_j^\dagger\hat{a}_i|\ \Psi_I\right\rangle\left\langle\Psi_I|\hat{a}_k^\dagger\hat{a}_l|\Psi_0\right\rangle}{\omega-E_I+E_0+i\eta} - \frac{\left\langle\Psi_0|\hat{a}_k^\dagger\hat{a}_l|\Psi_I\right\rangle\left\langle\Psi_I|\hat{a}_j^\dagger\hat{a}_i|\Psi_0\right\rangle}{\omega+E_I-E_0+i\eta}\right\}$$

where η is a positive infinitesimal, E_0 is a ground state energy and E_I - excited state energies.

Linear response density matrix functional theory

- Assume the initial conditions at t_0

$$\hat{H} \neq \hat{H}(t)$$

$$\forall_{pq} \quad \Gamma_{pq} = n_p \, \delta_{pq}$$

Linear response density matrix functional theory

- Assume the initial conditions at t_0

$$\hat{H} \neq \hat{H}(t)$$

$$\forall_{pq} \quad \Gamma_{pq} = n_p \, \delta_{pq}$$

- The system is perturbed with a one-electron time-dependent perturbation

$$\hat{H}^{(1)}(t) = \sum_{i=1}^{N} \upsilon(x_i, t)$$

Linear response density matrix functional theory

- Assume the initial conditions at t_0

$$\hat{H} \neq \hat{H}(t)$$

$$\forall_{pq} \quad \Gamma_{pq} = n_p \, \delta_{pq}$$

- The system is perturbed with a one-electron time-dependent perturbation

$$\hat{H}^{(1)}(t) = \sum_{i=1}^{N} v(x_i, t)$$

- The unperturbed (stationary) natural orbitals are used as a basis set, i.e.

$$\varphi_p(x,t) = \sum_q U_{pq}(t) \, \varphi_q(x)$$

Linear response density matrix functional theory

- Assume the initial conditions at t_0

$$\hat{H} \neq \hat{H}(t)$$

$$\forall_{pq} \quad \Gamma_{pq} = n_p\, \delta_{pq}$$

- The system is perturbed with a one-electron time-dependent perturbation

$$\hat{H}^{(1)}(t) = \sum_{i=1}^{N} \upsilon(x_i, t)$$

- The unperturbed (stationary) natural orbitals are used as a basis set, i.e.

$$\varphi_p(x,t) = \sum_q U_{pq}(t)\, \varphi_q(x)$$

- Expand all terms in the equation of motion up to linear terms:

Linear response density matrix functional theory

$$\Gamma_{pq}(t) = n_p\delta_{pq} + \delta\Gamma_{pq}(t)$$
$$h_{pq}(t) = h_{pq} + \upsilon_{pq}(t)$$

$$\sum_{rst}\left[\Gamma^{(2)}_{prst}[\Gamma](t)\left\langle\varphi_q\varphi_r|\varphi_s\varphi_t\right\rangle - \Gamma^{(2)}_{tsrq}[\Gamma](t)\left\langle\varphi_t\varphi_s|\varphi_r\varphi_p\right\rangle\right]$$
$$= \sum_{rst}\left[\Gamma^{(2)}_{prst}[\Gamma]\left\langle\varphi_q\varphi_r|\varphi_s\varphi_t\right\rangle - \Gamma^{(2)}_{tsrq}[\Gamma]\left\langle\varphi_t\varphi_s|\varphi_r\varphi_p\right\rangle\right]$$
$$+ \sum_{rs}\int_{-\infty}^{+\infty} K_{pqrs}(t-t')\delta\Gamma_{rs}(t')dt'$$

where K is called a coupling matrix.

Linear response density matrix functional theory

$$\Gamma_{pq}(t) = n_p \delta_{pq} + \delta\Gamma_{pq}(t)$$
$$h_{pq}(t) = h_{pq} + \upsilon_{pq}(t)$$

$$\sum_{rst} \left[\Gamma^{(2)}_{prst}[\Gamma](t) \left\langle \varphi_q \varphi_r | \varphi_s \varphi_t \right\rangle - \Gamma^{(2)}_{tsrq}[\Gamma](t) \left\langle \varphi_t \varphi_s | \varphi_r \varphi_p \right\rangle \right]$$
$$= \sum_{rst} \left[\Gamma^{(2)}_{prst}[\Gamma] \left\langle \varphi_q \varphi_r | \varphi_s \varphi_t \right\rangle - \Gamma^{(2)}_{tsrq}[\Gamma] \left\langle \varphi_t \varphi_s | \varphi_r \varphi_p \right\rangle \right]$$
$$+ \sum_{rs} \int_{-\infty}^{+\infty} K_{pqrs}(t-t') \delta\Gamma_{rs}(t') dt'$$

where K is called a coupling matrix.

- Zero-order terms drops out (see the stationary equations)

Linear response density matrix functional theory

$$\Gamma_{pq}(t) = n_p \delta_{pq} + \delta\Gamma_{pq}(t)$$
$$h_{pq}(t) = h_{pq} + \upsilon_{pq}(t)$$

$$\sum_{rst} \left[\Gamma^{(2)}_{prst}[\Gamma](t) \left\langle \varphi_q \varphi_r | \varphi_s \varphi_t \right\rangle - \Gamma^{(2)}_{tsrq}[\Gamma](t) \left\langle \varphi_t \varphi_s | \varphi_r \varphi_p \right\rangle \right]$$
$$= \sum_{rst} \left[\Gamma^{(2)}_{prst}[\Gamma] \left\langle \varphi_q \varphi_r | \varphi_s \varphi_t \right\rangle - \Gamma^{(2)}_{tsrq}[\Gamma] \left\langle \varphi_t \varphi_s | \varphi_r \varphi_p \right\rangle \right]$$
$$+ \sum_{rs} \int_{-\infty}^{+\infty} K_{pqrs}(t - t') \delta\Gamma_{rs}(t') dt'$$

where K is called a coupling matrix.

- Zero-order terms drops out (see the stationary equations)
- Fourier transform first-order terms

$$\mathcal{F}[f](\omega) = f(\omega) = \int_{-\infty}^{+\infty} e^{i\omega t} f(t) dt$$

Linear response density matrix functional theory

- Use the convolution theorem

$$h(t) = \int_{-\infty}^{+\infty} g(t-t')f(t')dt' \Longleftrightarrow h(\omega) = g(\omega)f(\omega)$$

and the property

$$\mathcal{F}[\frac{\partial f(t)}{\partial t}](\omega) = i\omega f(\omega)$$

to obtain finally the linear response equation for 1-RDM

$$\forall_{pq} \quad \sum_{rs} \Gamma_{rs}(\omega)[\omega\ \delta_{pr}\delta_{qs} - \delta_{pr}h_{qs} + \delta_{qs}h_{rp} - K_{pqrs}(\omega)] = (n_p - n_q)\, v_{qp}(\omega)$$

where

$$\Gamma_{pq}(\omega) = \mathcal{F}[\delta\Gamma_{pq}(t)](\omega)$$

Coupling matrix

- The ω-dependent coupling matrix *K* is defined as

$$\forall_{pqvw} \quad K_{pqvw}(\omega) = 2 \int e^{-i\omega\,(t-t')}$$

$$\times \left. \frac{\partial \sum_{rst} \left\{ \Gamma^{(2)}_{prst}[\Gamma](t) \langle \varphi_q \varphi_r | \varphi_s \varphi_t \rangle - \Gamma^{(2)}_{tsrq}[\Gamma](t)\ \langle \varphi_t \varphi_s | \varphi_r \varphi_p \rangle \right\}}{\partial \Gamma_{vw}(t')} \right|_{\Gamma=\Gamma^{(0)}} d(t-t')$$

where $\Gamma^{(0)}$ is the stationary one-matrix.

Coupling matrix

- The ω-dependent coupling matrix *K* is defined as

$$\forall_{pqvw} \quad K_{pqvw}(\omega) = 2 \int e^{-i\omega\,(t-t')} \times \left. \frac{\partial \sum_{rst} \left\{ \Gamma^{(2)}_{prst}[\Gamma](t) \langle \varphi_q \varphi_r | \varphi_s \varphi_t \rangle - \Gamma^{(2)}_{tsrq}[\Gamma](t)\ \langle \varphi_t \varphi_s | \varphi_r \varphi_p \rangle \right\}}{\partial \Gamma_{vw}(t')} \right|_{\Gamma=\Gamma^{(0)}} d(t-t')$$

  where $\Gamma^{(0)}$ is the stationary one-matrix.

- We assume the **adiabatic approximation**

$$\left. \frac{\partial \Gamma^{(2)}_{pqrs}[\Gamma](t)}{\partial \Gamma_{vw}(t')} \right|_{\Gamma=\Gamma^{(0)}} \approx \delta(t-t') \left. \frac{\partial \Gamma^{(2)}_{pqrs}[\Gamma]}{\partial \Gamma_{vw}} \right|_{\Gamma=\Gamma^{(0)}}$$

Coupling matrix

- The ω-dependent coupling matrix *K* is defined as

$$\forall_{pqvw} \quad K_{pqvw}(\omega) = 2 \int e^{-i\omega\,(t-t')} \times \left. \frac{\partial \sum_{rst} \left\{ \Gamma^{(2)}_{prst}[\Gamma](t) \langle \varphi_q \varphi_r | \varphi_s \varphi_t \rangle - \Gamma^{(2)}_{tsrq}[\Gamma](t)\ \langle \varphi_t \varphi_s | \varphi_r \varphi_p \rangle \right\}}{\partial \Gamma_{vw}(t')} \right|_{\Gamma=\Gamma^{(0)}} d(t-t')$$

  where $\Gamma^{(0)}$ is the stationary one-matrix.

- We assume the **adiabatic approximation**

$$\left. \frac{\partial \Gamma^{(2)}_{pqrs}[\Gamma](t)}{\partial \Gamma_{vw}(t')} \right|_{\Gamma=\Gamma^{(0)}} \approx \delta(t-t') \left. \frac{\partial \Gamma^{(2)}_{pqrs}[\Gamma]}{\partial \Gamma_{vw}} \right|_{\Gamma=\Gamma^{(0)}}$$

  that results in the ω-free coupling matrix

$$\forall_{pqvw} \ \ K_{pqvw} = 2 \left. \frac{\partial \sum_{rst} \left\{ \Gamma^{(2)}_{prst}[\Gamma] \langle \varphi_q \varphi_r | \varphi_s \varphi_t \rangle - \Gamma^{(2)}_{tsrq}[\Gamma]\ \langle \varphi_t \varphi_s | \varphi_r \varphi_p \rangle \right\}}{\partial \Gamma_{vw}} \right|_{\Gamma=\Gamma^{(0)}}$$

Adiabatic approximation

- Employing the relation

$$2\sum_{rst}\left[\Gamma^{(2)}_{prst}\left\langle\varphi_q\varphi_r|\varphi_s\varphi_t\right\rangle-\Gamma^{(2)}_{tsrq}\left\langle\varphi_t\varphi_s|\varphi_r\varphi_p\right\rangle\right]$$

$$=\int\frac{\delta E_{ee}[\Gamma]}{\delta\varphi_p(x)^*}\varphi_q(x)^*dx-\int\frac{\delta E_{ee}[\Gamma]}{\delta\varphi_q(x)}\varphi_p(x)dx$$

yields

$$\forall_{pqvw}\quad K_{pqvw}=\left.\frac{\partial\left\{\sum_{rs}(W^*_{rs}[\Gamma]-W_{sr}[\Gamma])U^*_{rp}U_{sq}\right\}}{\partial\Gamma_{vw}}\right|_{\Gamma=\Gamma^{(0)}}$$

$$W_{pq}=\left\langle\frac{\delta E_{ee}[\Gamma]}{\delta\varphi_p}\varphi_q\right\rangle$$

- The coupling matrix in the adiabatic approximation is expressed in terms of the derivatives of the energy functional used for ground state calculation.

Consequence of the adiabatic approximation

- No change of the occupation numbers, i.e.

$$\forall_p \;\; \delta n_p(\omega) = 0$$

- Wrong response of the density matrix in the ω→0 limit.

K Pernal, K.J.H. Giesbertz, Reduced density matrix functional theory (RDMFT) and linear response time-dependent RDMFT (TD-RDMFT), Springer (2016)

K. Pernal, O. Gritsenko, and E. J. Baerends, *Phys. Rev. A* **75**, 012506 (2007).

K. Pernal, K. Giesbertz, O. Gritsenko, and E.J. Baerends, *J. Chem. Phys.* **127**, 214101 (2007).

K. Giesbertz, O.V. Gritsenko, and E.J. Baerends, *Phys. Rev. Lett*. **101**, 033004 (2008).

K. J. H. Giesbertz, O. V. Gritsenko, and E. J. Baerends, *Phys. Rev. Lett.* **105**, 013002 (2010).

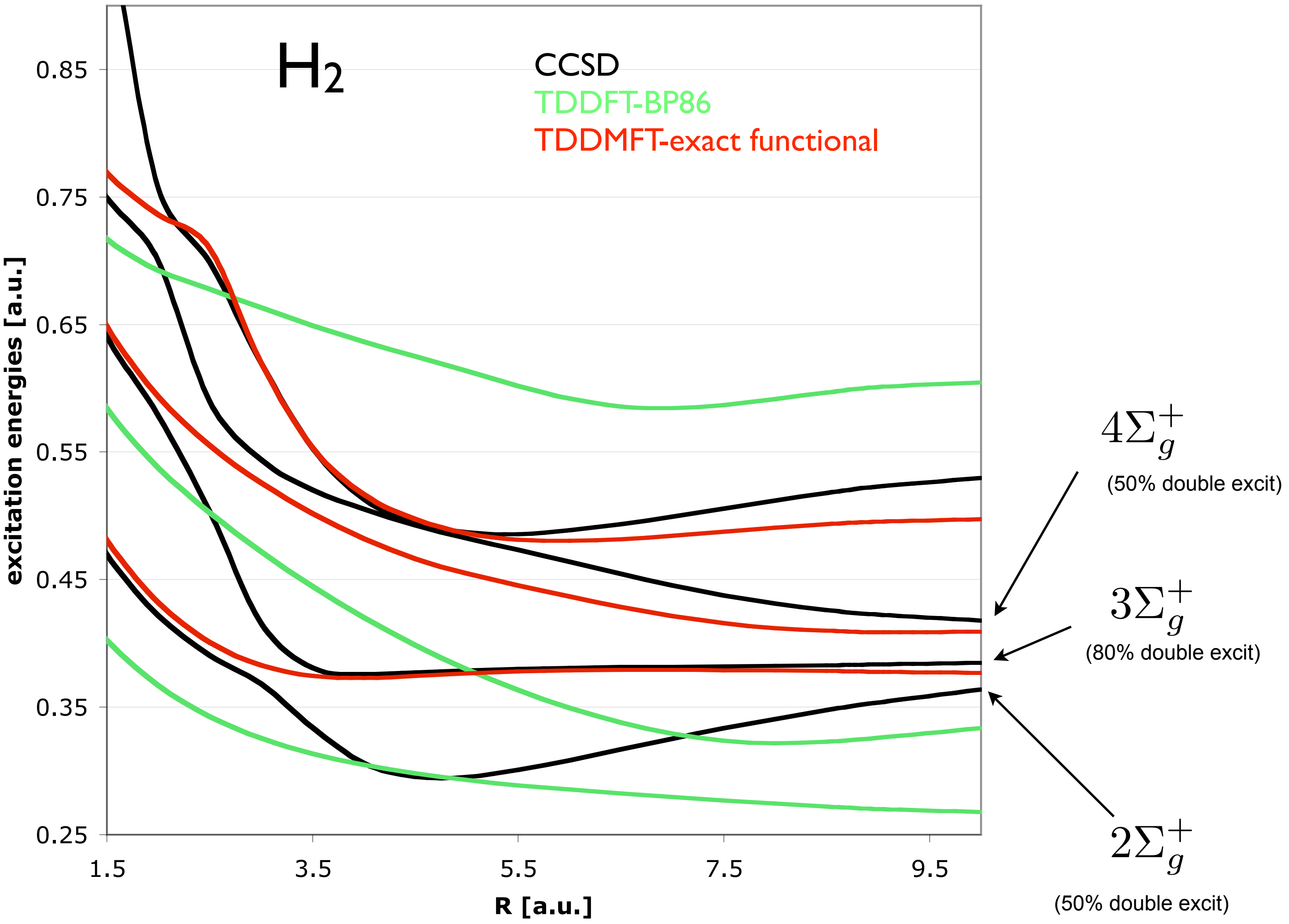
K. J. H. Giesbertz, K. Pernal, O. V. Gritsenko, and E. J. Baerends, *J. Chem. Phys.* **130**, 114104 (2009).

K. J. H. Giesbertz, Ph.D. thesis, Vrije Universiteit, Amsterdam (2010).

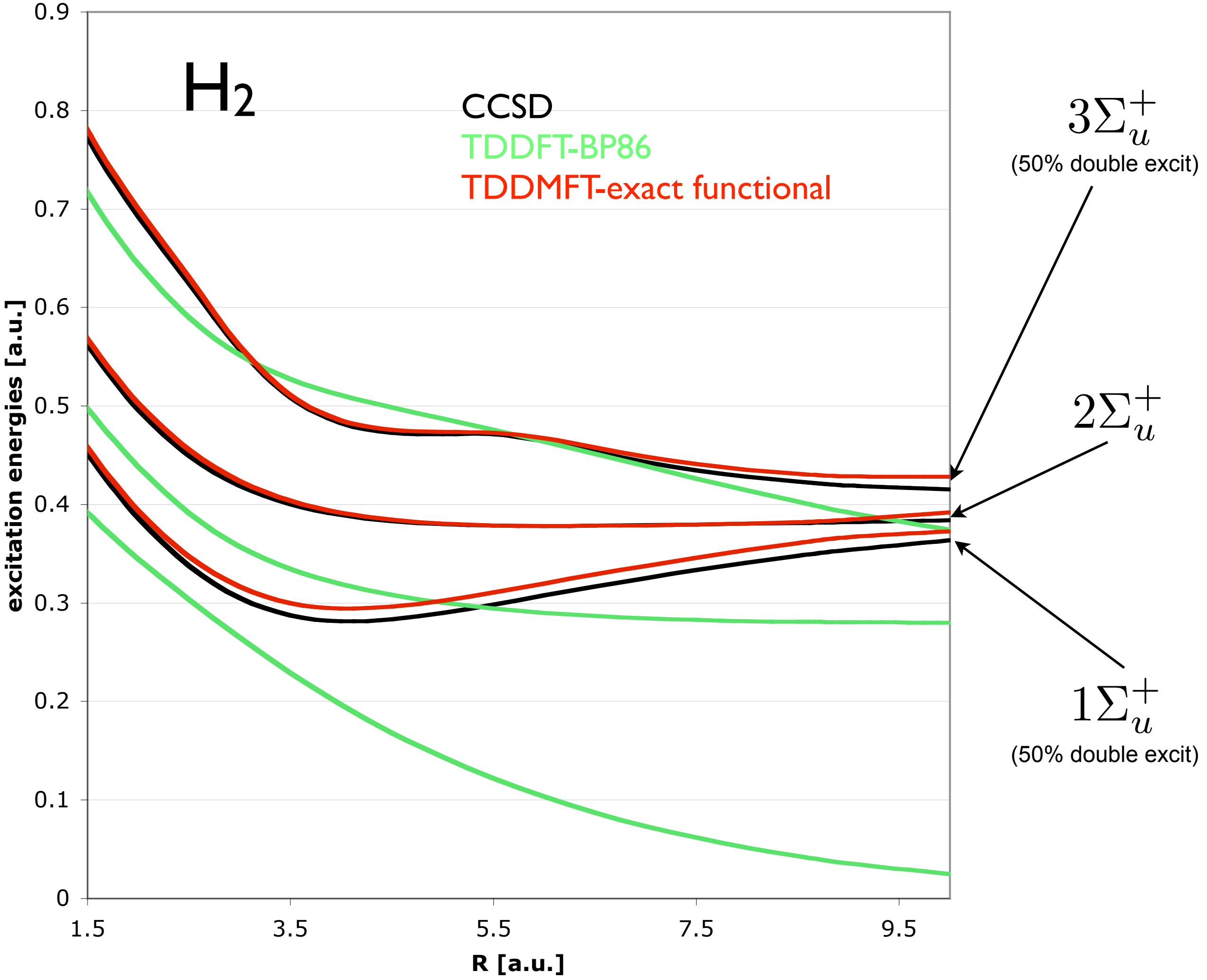
H. Appel and E.K.U. Gross, *Eur. Phys. Lett.* **92**, 23001 (2010).

R. Requist and O. Pankratov, *Phys. Rev. A* **83**, 052510 (2011).

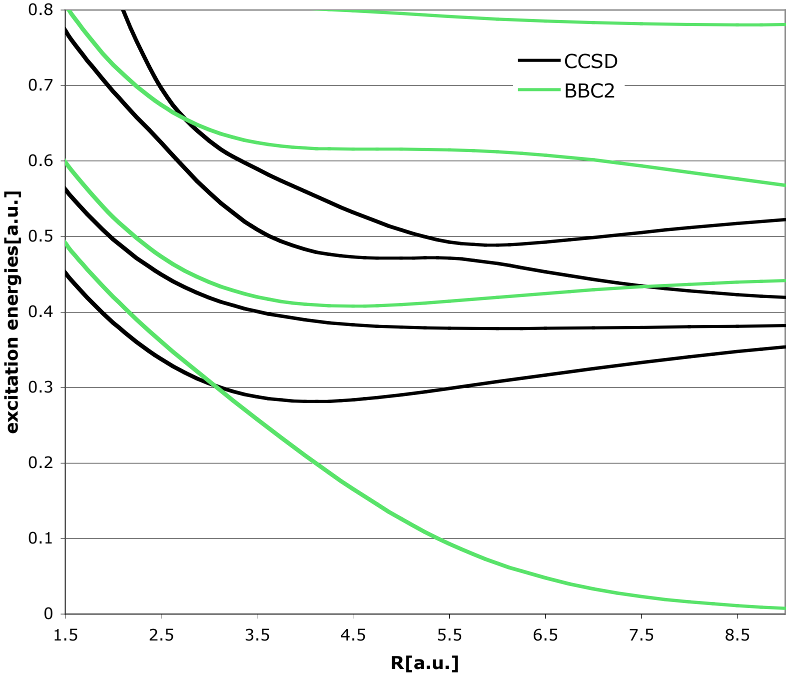
Potential energy curves for the $^1\Sigma_g^+$ excited states for H_2 in aug-cc-pVTZ basis set.



Potential energy curves for the $^1\Sigma_u^+$ excited states for H_2 in aug-cc-pVTZ basis set.

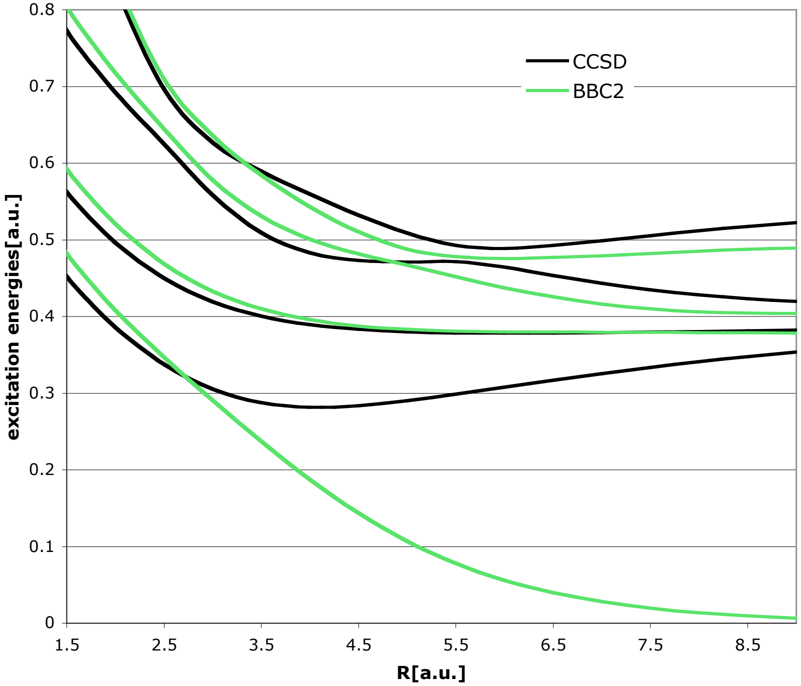


Potential energy curves for the ${}^1\Sigma_u^+$ excited states for H_2 in aug-cc-pVTZ basis set.



$$\delta\Gamma_{pq}(\omega)$$

$$q = 1, \quad p = q+1, \ldots M$$



$$\delta\Gamma_{pq}(\omega)$$

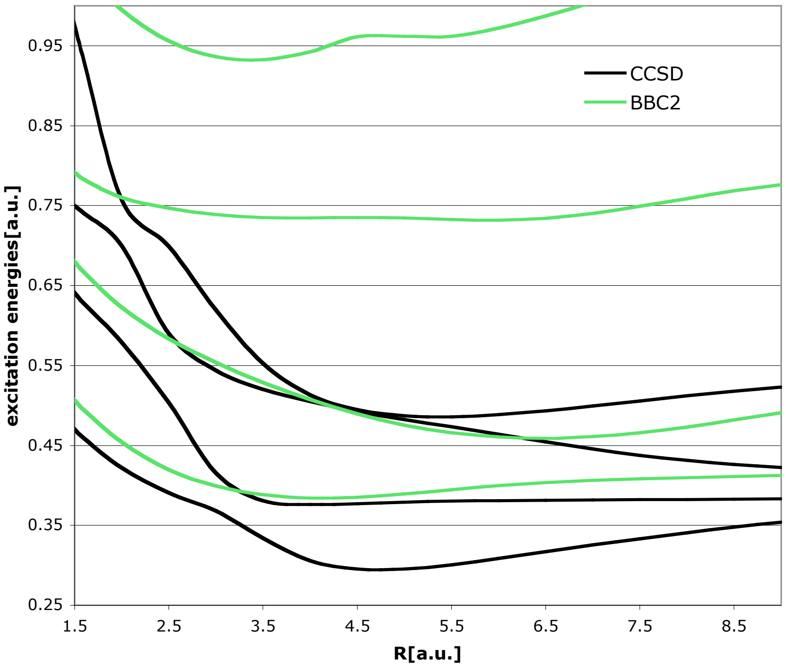
$$q \leq 2, \quad p = q+1, \ldots M$$

Composition of states at R=10 [a.u.]

$$1\,{}^1\Sigma_u^+ \;:\quad 1\sigma_g \rightarrow 1\sigma_u\;,\;(1\sigma_g)^2 \rightarrow 2\sigma_g 1\sigma_u\;(50\%)$$

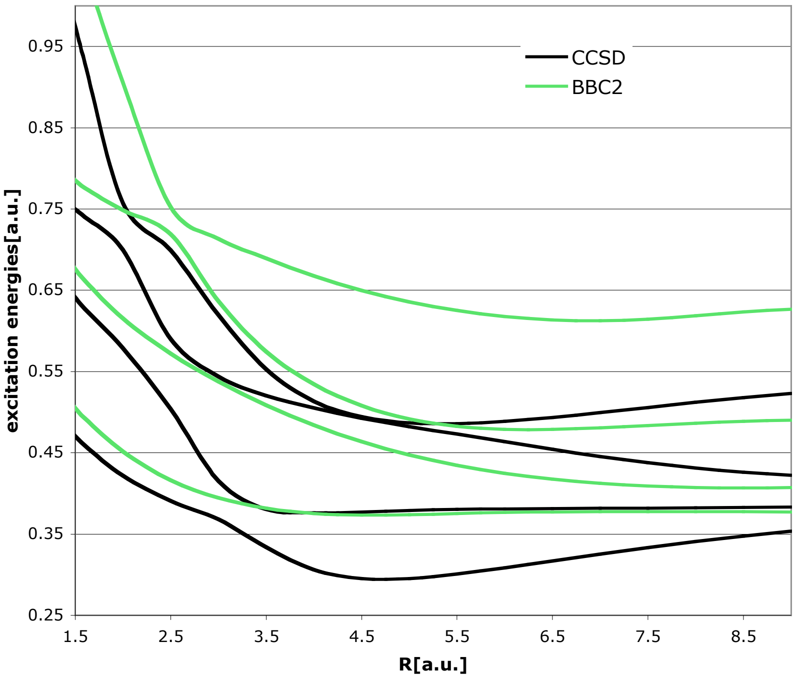
$$3\;{}^1\Sigma_u^+ \;:\quad (1\sigma_g)^2 \rightarrow 2\sigma_g 2\sigma_u\;(50\%)$$

Potential energy curves for the $^1\Sigma_g^+$ excited states for H_2 in aug-cc-pVTZ basis set.



$$\delta\Gamma_{pq}(\omega)$$

$$q = 1, \quad p = q+1, \ldots M$$



$$\delta\Gamma_{pq}(\omega)$$

$$q \leq 2, \quad p = q+1, \ldots M$$

Composition of states at R=10 [a.u.]

$$2\,^1\Sigma_g^+ \;:\quad (1\sigma_g)^2 \rightarrow (1\sigma_u)^2 \;(50\%)$$

$$3\,^1\Sigma_g^+ \;:\quad (1\sigma_g)^2 \rightarrow (1\sigma_u)^2 \;,\; (1\sigma_g)^2 \rightarrow 1\sigma_u 2\sigma_u \;\; (80\%)$$

$$4\,^1\Sigma_g^+ \;:\quad (1\sigma_g)^2 \rightarrow (1\sigma_u)^2 \;,\; (1\sigma_g)^2 \rightarrow 1\sigma_u 3\sigma_u \;\; (50\%)$$

TD-DMFT

- Formulation of time-dependent density matrix functional theory has opened an avenue to calculations of frequency-dependent response properties and excitation energies of atoms and molecules.
- The accuracy of the computed data is limited by both the errors inherent to the adiabatic approximation or its modifications and the quality of the energy functionals.
- Double excitations are in principle within the reach.

A stationary case

- Assume a time-independent Hamiltonian.
- The energy functional

$$E[\{\varphi_p\},\{n_p\}] = \sum_p n_p h_{pp} + E_{ee}[\{\varphi_p\},\{n_p\}]$$

is minimized under N-representability conditions.

- Consider a new functional with the conditions included through Lagrange multipliers

$$\Omega = E[\{\varphi_p\},\{n_p\}] - \sum_{pq} \lambda_{pq} \left(\langle \varphi_p | \varphi_q \rangle - \delta_{pq} \right) - \mu \left(\sum_p n_p - N \right)$$

$$\frac{\delta \Omega}{\delta \varphi_p(x)^*} = \frac{\delta E[\{\varphi_p\},\{n_p\}]}{\delta \varphi_p(x)^*} - \sum_q \lambda_{pq} \varphi_q(x) = 0$$

$$\frac{\partial \Omega}{\partial n_p} = \frac{\partial E[\{\varphi_p\},\{n_p\}]}{\partial n_p} - \mu = 0$$

A stationary case

- The variational equations for the orbitals read

$$n_p h_{qp} + \int \frac{\delta E_{ee}[\{\varphi_p\},\{n_p\}]}{\delta \varphi_p(x)^*} \varphi_q(x)^* dx = \lambda_{pq}$$

or using hermiticity of the Lagrange multiplier matrix $\lambda_{pq}=(\lambda_{qp})^*$

$$\left(n_p - n_q\right) h_{qp} + \int \frac{\delta E_{ee}[\{\varphi_p\},\{n_p\}]}{\delta \varphi_p(x)^*} \varphi_q(x)^* dx - \int \frac{\delta E_{ee}[\{\varphi_p\},\{n_p\}]}{\delta \varphi_q(x)} \varphi_p(x) dx = 0$$

A stationary case

- The variational equations for the orbitals read

$$n_p h_{qp} + \int \frac{\delta E_{ee}[\{\varphi_p\},\{n_p\}]}{\delta \varphi_p(x)^*} \varphi_q(x)^* dx = \lambda_{pq}$$

or using hermiticity of the Lagrange multiplier matrix $\lambda_{pq}=(\lambda_{qp})^*$

$$(n_p - n_q)\, h_{qp} + \int \frac{\delta E_{ee}[\{\varphi_p\},\{n_p\}]}{\delta \varphi_p(x)^*} \varphi_q(x)^* dx - \int \frac{\delta E_{ee}[\{\varphi_p\},\{n_p\}]}{\delta \varphi_q(x)} \varphi_p(x) dx = 0$$

- Equations for the occupation numbers are as follows

$$\frac{\partial E[\{\varphi_p\},\{n_p\}]}{\partial n_p} = \mu$$

A stationary case

- The variational equations for the orbitals read

$$n_p h_{qp} + \int \frac{\delta E_{ee}[\{\varphi_p\},\{n_p\}]}{\delta \varphi_p(x)^*}\varphi_q(x)^* dx = \lambda_{pq}$$

or using hermiticity of the Lagrange multiplier matrix $\lambda_{pq}=(\lambda_{qp})^*$

$$(n_p - n_q)\, h_{qp} + \int \frac{\delta E_{ee}[\{\varphi_p\},\{n_p\}]}{\delta \varphi_p(x)^*}\varphi_q(x)^* dx - \int \frac{\delta E_{ee}[\{\varphi_p\},\{n_p\}]}{\delta \varphi_q(x)}\varphi_p(x) dx = 0$$

- Equations for the occupation numbers are as follows

$$\frac{\partial E[\{\varphi_p\},\{n_p\}]}{\partial n_p} = \mu$$

- Note that the nonnegativity conditions

$$\forall p \quad 0 \le n_p \le 1$$

must be imposed separately.

A stationary case

- For a time-independent Hamiltonian the equation of motion

$$i\frac{\partial \Gamma_{pq}(t)}{\partial t} = \sum_r \left[h_{qr}(t)\Gamma_{pr}(t) - \Gamma_{rq}(t)h_{rp}(t)\right]$$

$$+2\sum_{rst}[\Gamma^{(2)}_{prst}(t)\left\langle \chi_q\chi_r|\chi_s\chi_t\right\rangle - \left\langle \chi_t\chi_s|\chi_r\chi_p\right\rangle \Gamma^{(2)}_{tsrq}(t)]$$

turns into the variational equation for orbitals after

using the natural orbitals as a basis set, i.e. $\{\chi_p(x)\} \equiv \{\varphi_p(x)\}$

$$\forall_{pq} \quad \Gamma_{pq} = n_p\,\delta_{pq}$$

and employing the relation [K. Pernal et al., *Chem. Phys. Lett.* **415**, 71 (2005)]

$$2\sum_{rst}\left[\Gamma^{(2)}_{prst}\left\langle \varphi_q\varphi_r|\varphi_s\varphi_t\right\rangle - \Gamma^{(2)}_{tsrq}\left\langle \varphi_t\varphi_s|\varphi_r\varphi_p\right\rangle\right]$$

$$= \int \frac{\delta E_{ee}[\Gamma]}{\delta \varphi_p(x)^*}\varphi_q(x)^* dx - \int \frac{\delta E_{ee}[\Gamma]}{\delta \varphi_q(x)}\varphi_p(x) dx$$