

Tutorial on TDDFT: Part 3



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Reduced Density Matrix Functional Theory

One-body reduced density matrix (1-RDM)

- for integer particle number N :

$$\gamma(\vec{r}, \vec{r}') = N \cdot \int \cdots \int \Psi^*(\vec{r}, \vec{x}_2, \dots, \vec{x}_N) \Psi(\vec{r}', \vec{x}_2, \dots, \vec{x}_N) d^3x_2 \cdots d^3x_N$$

Diagonalization yields the natural orbitals $\varphi_j(\vec{r})$ and their occupation numbers n_j :

$$\int \gamma(\vec{r}, \vec{r}') \varphi_j(\vec{r}') d^3r' = n_j \varphi_j(\vec{r})$$

Central Theorem by Gilbert (1975): There is a rigorous 1-1 correspondence $\Psi_{\text{gs}}(r_1, r_2, \dots, r_N) \longleftrightarrow \gamma(\mathbf{r}, \mathbf{r}')$

- Total energy is a unique functional $E[\gamma]$ of the 1-RDM
- Ground-state energy can be calculated by minimizing $E[\gamma]$

Note: For given $\gamma(\vec{r}, \vec{r}')$ the $\{\varphi_j(\vec{r}), n_j\}$ follow from diagonalization, i.e. $n_j = n_j[\gamma]$, $\varphi_j = \varphi_j[\gamma]$

Consequence: Any explicit functional $E[n_j, \varphi_j(\vec{r})]$ is an implicit functional of γ

Functional Minimization

Constraints

- ★ $\sum_i n_i = N$, where N is the number of electrons.
- ★ $\int \phi_i^*(\mathbf{r}) \phi_j(\mathbf{r}) d^3r = \delta_{ij}$, orthonormality constraint.
- ★ $0 \leq n_i \leq 1$, N -representability constraint, guarantees that γ comes from a many-body wavefunction.

Functional Minimization

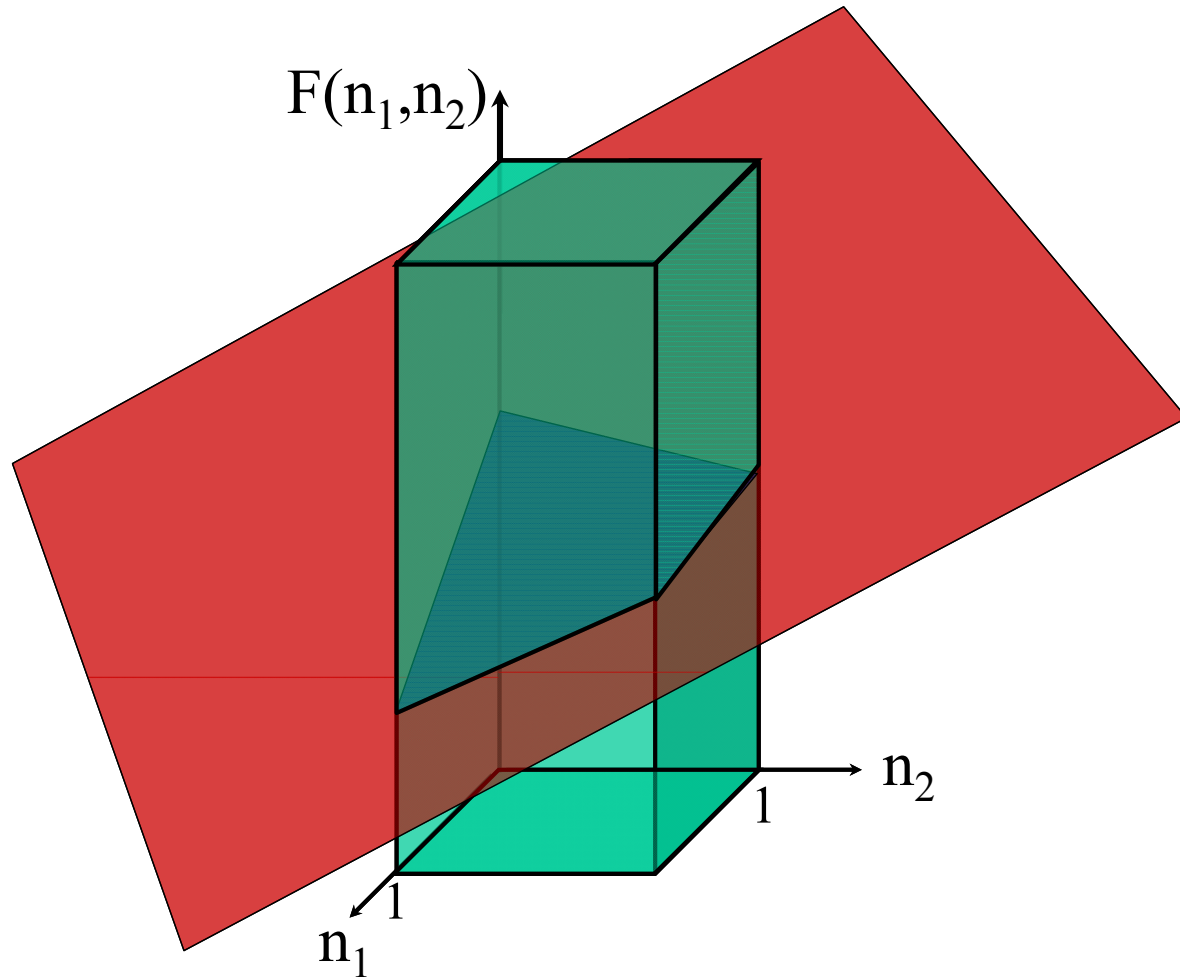
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- The first two are enforced through Lagrange multipliers. The quantity to minimize becomes:

$$\mathcal{F} = E_{\text{tot}} - \mu \left(\sum_i n_i - N \right) - \sum_{ij} \epsilon_{ij} \left(\langle \phi_i | \phi_j \rangle - \delta_{ij} \right)$$

μ : chemical potential.



N-representability condition $0 \leq n_j \leq 1$ generally leads to border minimum.

i.e. one can still minimize but $\frac{\partial F}{\partial n_j} \neq 0$ at minimum

Total-energy functional:

$$E_{\text{tot}}[\gamma] = E_{\text{kin}}[\gamma] + \int v_{\text{ext}}(\vec{r}) \gamma(\vec{r}, \vec{r}) d^3 r + E_{\text{H}}[\gamma] + E_{\text{xc}}[\gamma]$$

Three major differences to DFT

- Kinetic-energy functional is known exactly

$$\begin{aligned} E_{\text{kin}} &= \int d^3 r \int d^3 r' \delta(\vec{r} - \vec{r}') \left(-\frac{\nabla^2}{2} \right) \gamma(\vec{r}, \vec{r}') \\ &= \sum_{j=1}^{\infty} n_j \left\langle \varphi_j \left| -\frac{\nabla^2}{2} \right| \varphi_j \right\rangle \end{aligned}$$

Hence $E_{\text{xc}}[\gamma]$ does not contain any kinetic contributions, and therefore there is no coupling-constant formula.

- There exists no variational equation $\frac{\delta F[\gamma]}{\delta \gamma(\vec{r}, \vec{r}')} = 0$

$$\Rightarrow \frac{\delta F}{\delta \gamma(\vec{r}, \vec{r}')} = \underbrace{\sum_j \int \frac{\delta F}{\delta \varphi_j^*(\vec{x})} \frac{\delta \varphi_j^*(\vec{x})}{\delta \gamma(\vec{r}, \vec{r}')} d^3 \mathbf{x}}_0 + \text{c.c.} + \sum_j \frac{\partial F}{\partial n_j} \frac{\delta n_j}{\delta \gamma(\vec{r}, \vec{r}')}$$

$$= \sum_j \frac{\partial F}{\partial n_j} \varphi_j^*(\vec{r}) \varphi_j(\vec{r}') \neq 0$$

- There exists no Kohn-Sham system reproducing the interacting $\gamma(\vec{r}, \vec{r}')$

Approximations for xc functional

$$E_{xc} = -\frac{1}{2} \sum_{i,j} f(n_i, n_j) \int d^3\mathbf{r} \int d^3\mathbf{r}' \frac{\varphi_i^*(\mathbf{r}) \varphi_j(\mathbf{r}) \varphi_j^*(\mathbf{r}') \varphi_i(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

- Hartree-Fock: $f(n_i, n_j) = n_i n_j$.
- Müller functional [1,2]: $f(n_i, n_j) = \sqrt{n_i n_j}$.
- Gödecker - Umrigar [3]: $f(n_i, n_j) = \sqrt{n_i n_j}$ explicit removal of self-interaction terms.

[1] A. M. K. Müller, *Phys. Lett. A* **105**, 446 (1984).

[2] Buijse, Baerends, *Mol. Phys.* **100**, 401 (2002).

[3] Gödecker, Umrigar, *Phys. Rev. Lett.* **81**, 866 (1998).

The BBC functionals

- **Hierarchy of corrections to the Müller functional**
- **key idea: Distinction between strongly and weakly occupied orbitals**

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- **BBC1:** Sign change of f , if both orbitals are weakly occupied:

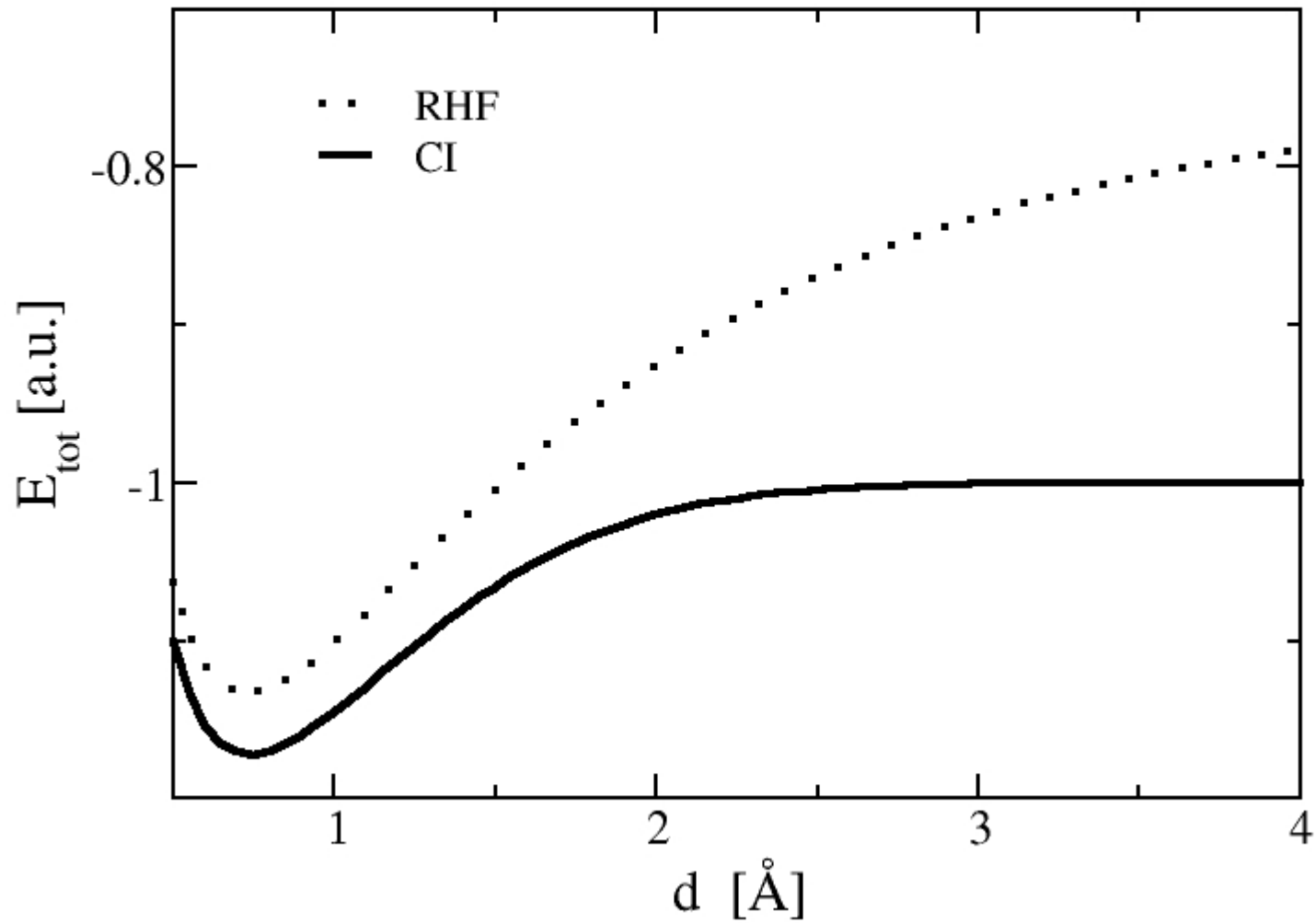
$$f(n_i, n_j) = \begin{cases} -\sqrt{n_i n_j}, & i, j \text{ weakly occupied,} \\ \sqrt{n_i n_j}, & \text{otherwise.} \end{cases}$$

- **BBC2:** Additionally, omission the square root if both orbitals are strongly occupied:

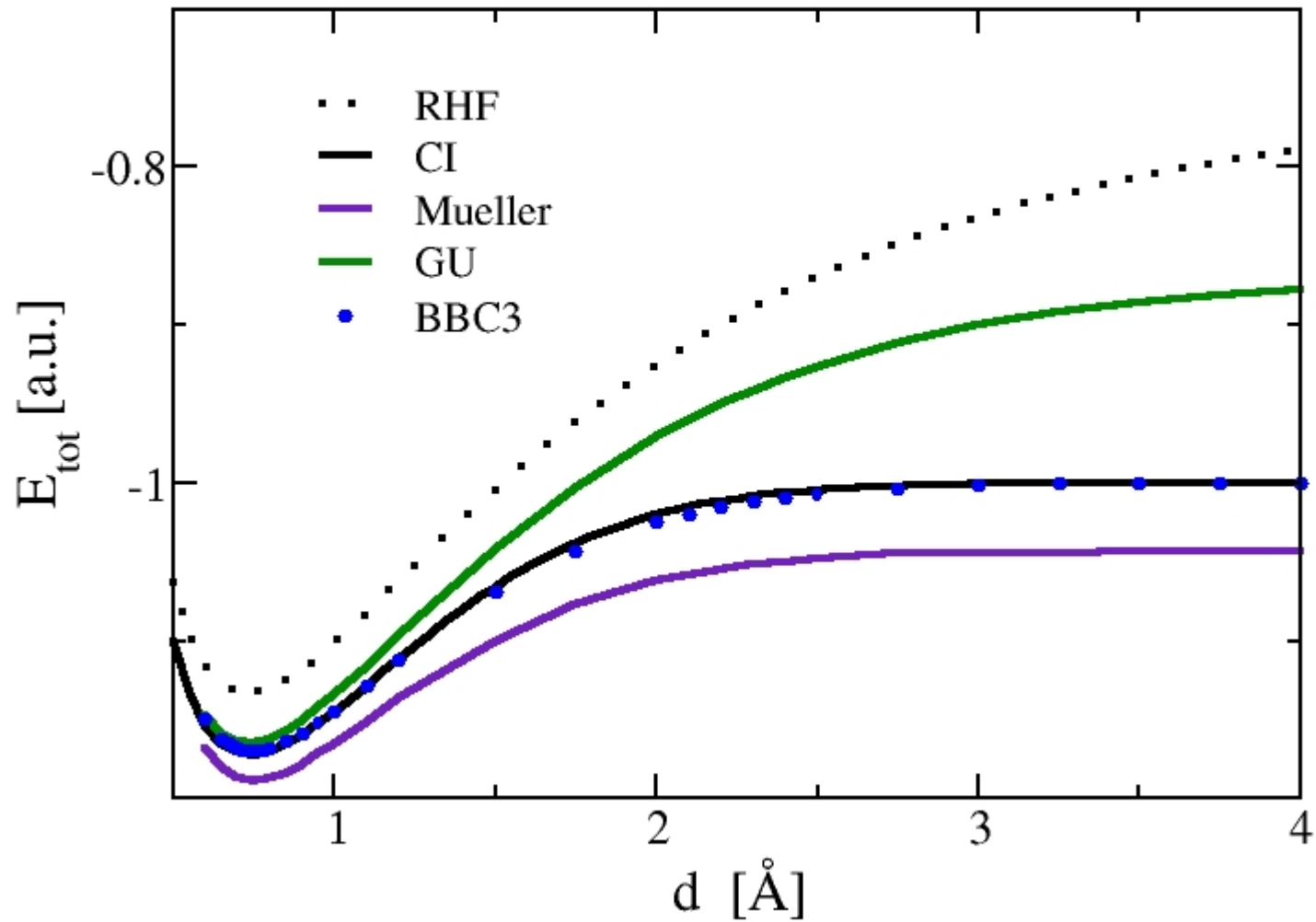
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- **BBC3:** Inclusion of anti-bonding in the list of strongly occupied orbitals, unless it interacts with bonding.
Removal of SI terms.

Application to stretched H_2



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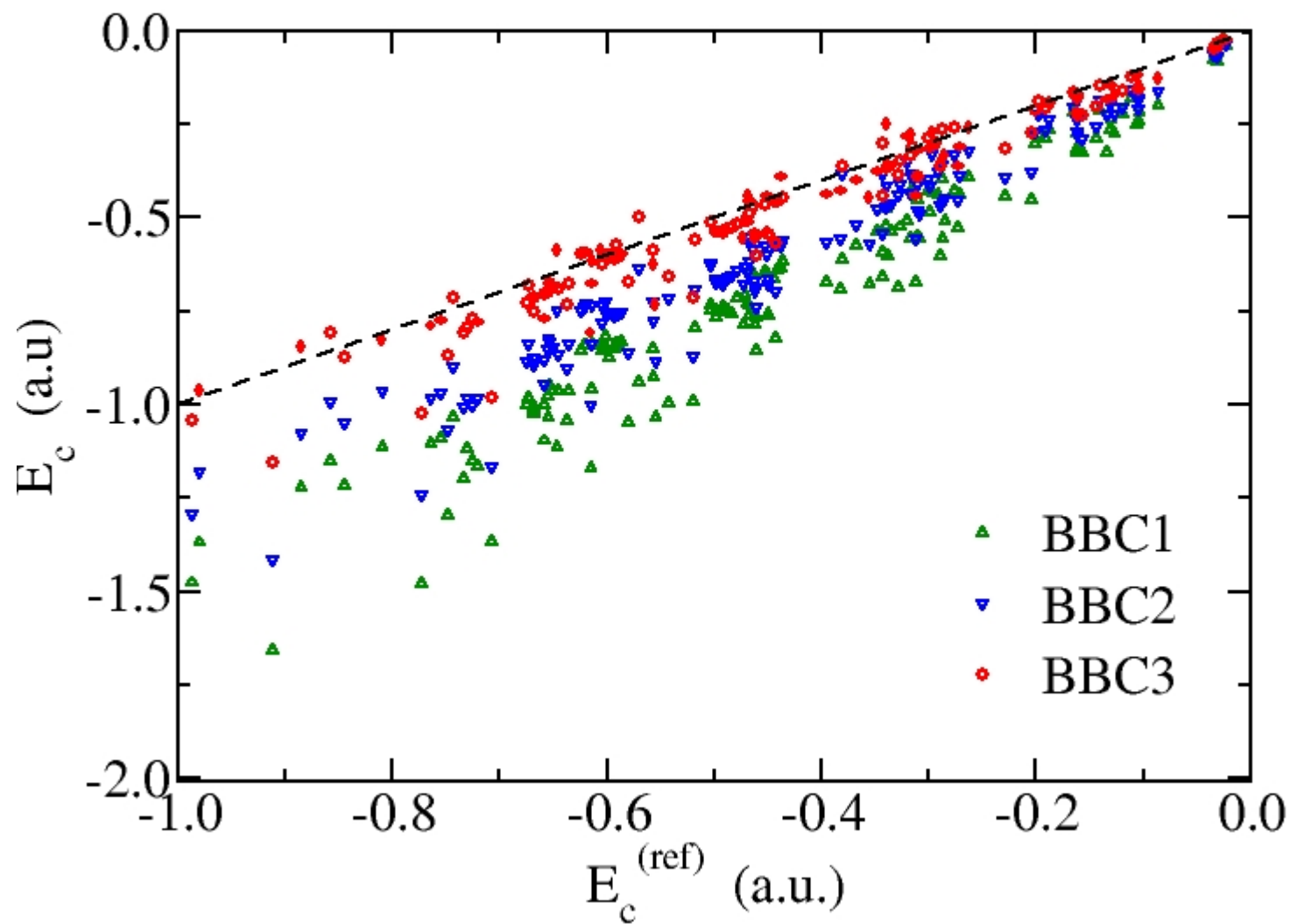


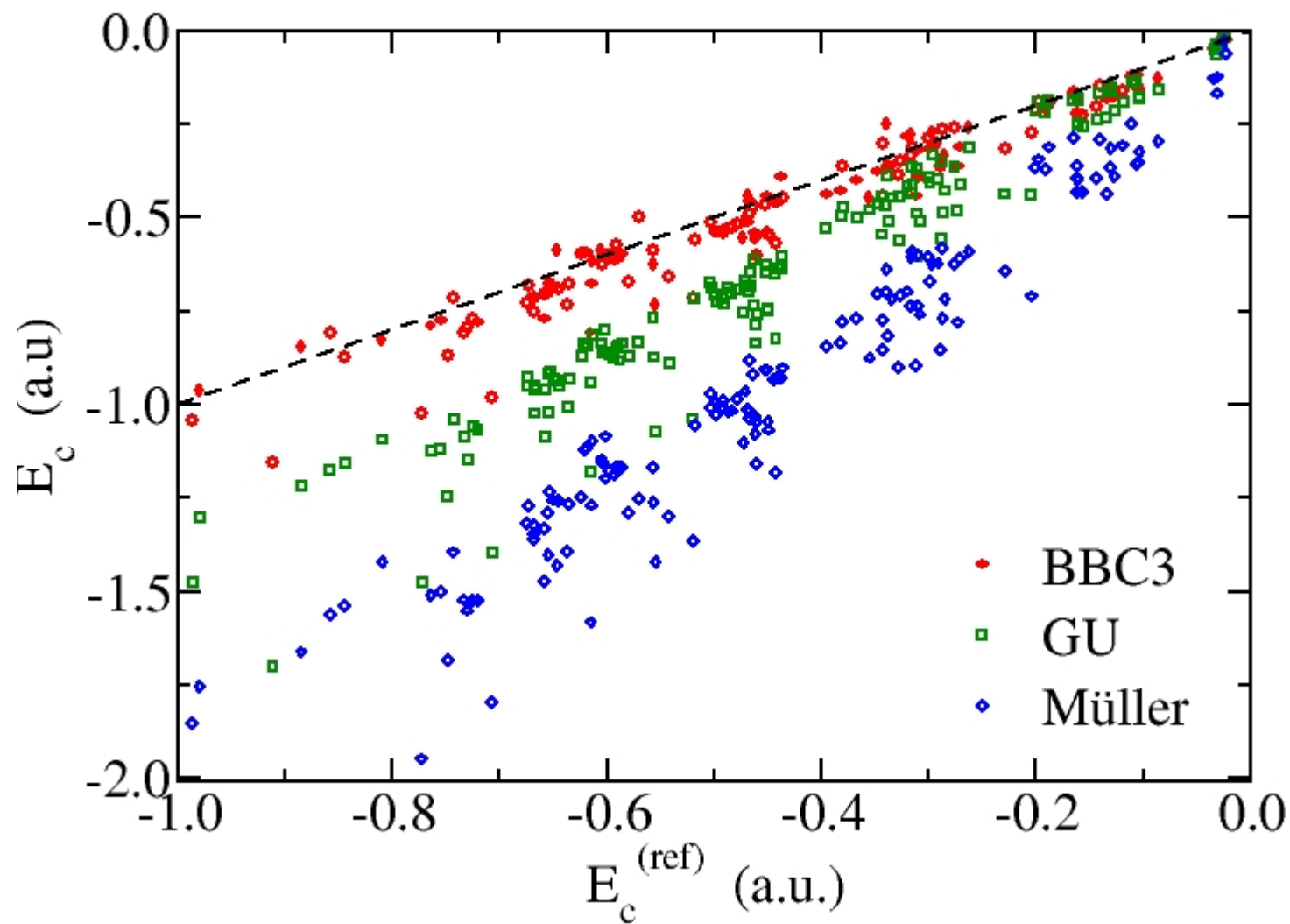
★ **G2/97 test set of molecules [1]:**

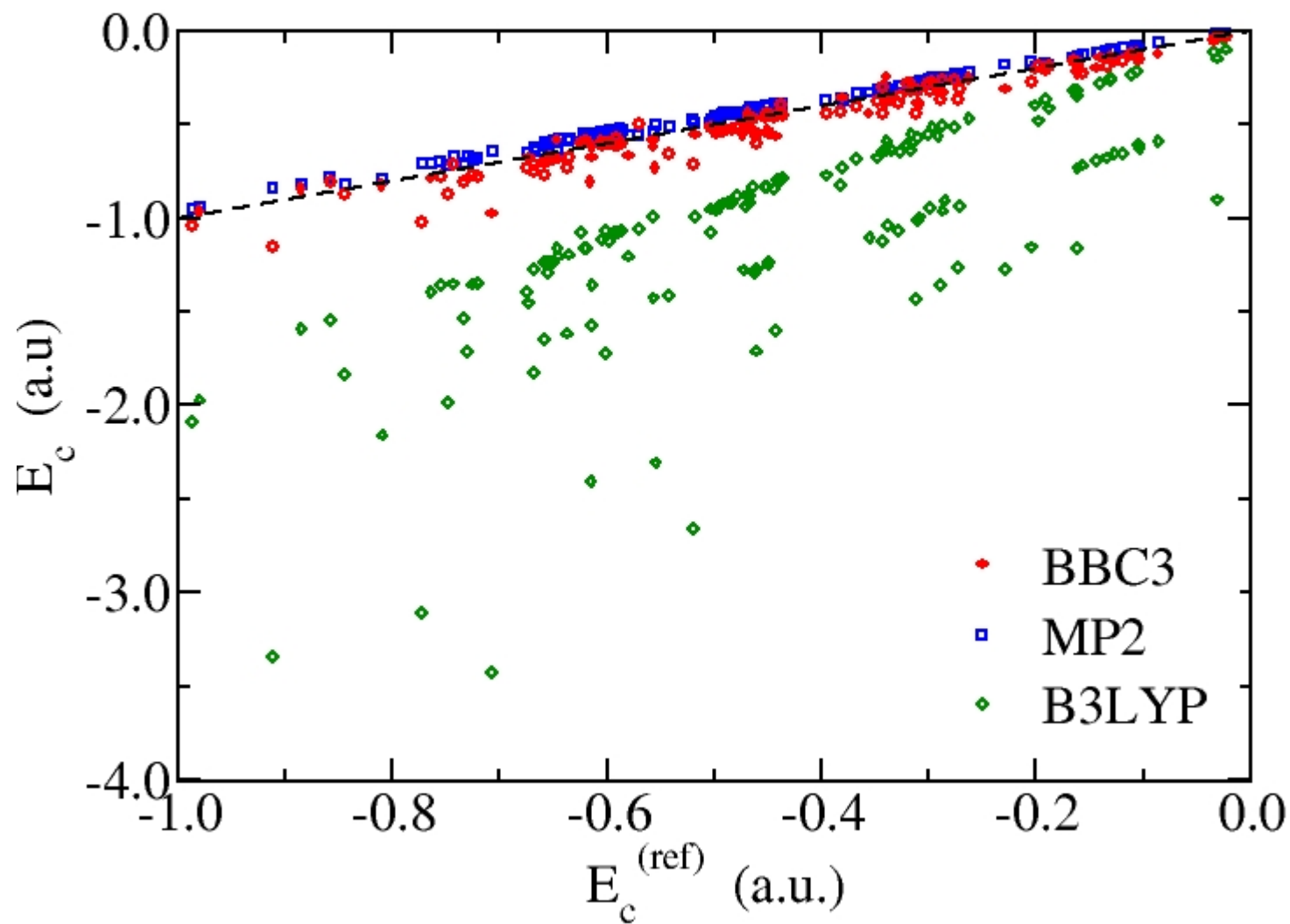
148 neutral molecules including 29 radicals, 35 non-hydrogen systems, 22 hydrocarbons, 47 substituted hydrocarbons and 15 inorganic hydrides.

★ Cartesian 6-31G* Gaussian basis-set









Error in the correlation energies calculated with a variety of methods. Reference energies (E_c^{ref}) were obtained with CCSD(T). The values in the first, second and last column are in a.u.

Method	$\bar{\Delta}$	Δ_{max}	$\bar{\delta}$	δ_{max}	$\bar{\delta}_e$
Müller	0.55	1.23 (C₂Cl₄)	135.7	438.3 (Na₂)	0.019
GU	0.26	0.79 (C₂Cl₄)	51.63	114.2 (Si₂)	0.0072
CGA	0.22	0.55 (C₂Cl₄)	69.11	331.9 (Na₂)	0.0077
BBC1	0.29	0.75 (C₂Cl₄)	69.91	159.1 (Na₂)	0.0098
BBC2	0.18	0.50 (C₂Cl₄)	45.02	125.0 (Na₂)	0.0058
BBC3	0.068	0.27 (C₂Cl₄)	18.37	50.8 (SiH₂)	0.0017
MP2	0.039	0.074 (C₂Cl₄)	11.86	35.7 (Li₂)	0.0015
B3LYP	0.75	2.72 (SiCl₄)	305.0	2803.7 (Li₂)	0.022

The real challenge of Condensed-Matter theory: Ab-initio description Mott insulators

Towards strongly correlated systems

Mott insulators in paramagnetic phase

prototype: 1D chain of hydrogen atoms

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DFT: half-filled band

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⇒ KS system is metallic (independent of xc functional)

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Totally unnatural
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$$E_{\text{gap}} = \underbrace{E_{\text{gap}}^{\text{KS}}}_0 + \Delta_{\text{xc}}$$

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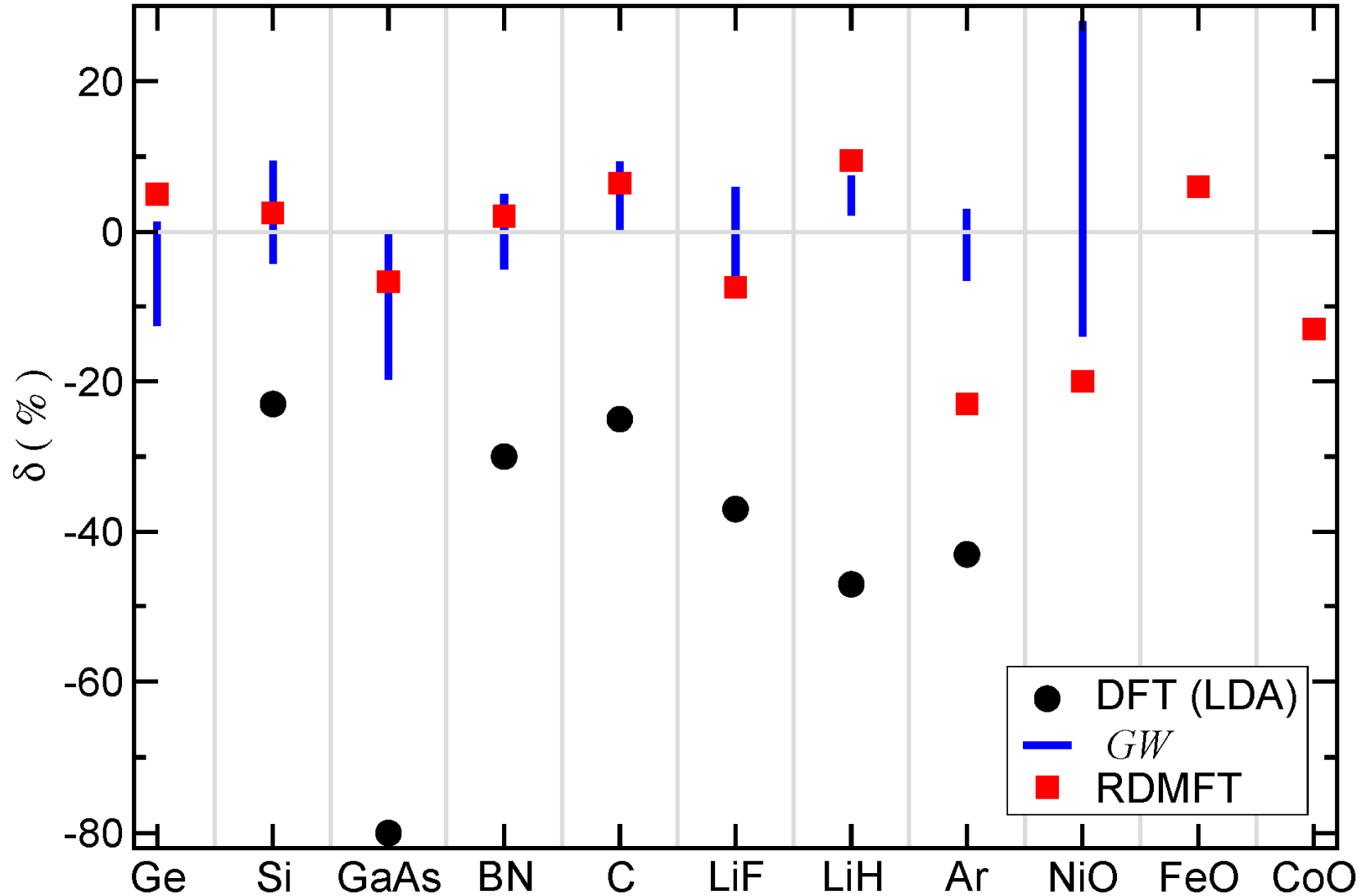
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QP band structure is metallic

To obtain gap: $\Sigma \rightarrow \infty$ for $\omega \rightarrow E_{\text{F}}$

Fundamental gap of semiconductors and insulators

S. Sharma, J.K. Dewhurst, N.N. Lathiotakis and E.K.U.G., Phys. Rev. B **78** (Rapid Comm.), 201103 (2008)



How about time-dependent RDMFT?

$$v(\mathbf{r},t) \xrightarrow{\text{TDSE}} \Psi(\mathbf{r}_1 \dots \mathbf{r}_N, t) \rightarrow \gamma(\mathbf{r}, \mathbf{r}', t)$$

$$\gamma(\mathbf{r}, \mathbf{r}', t) \xrightarrow[\mathbf{r} = \mathbf{r}']{\text{diagonal}} \rho(\mathbf{r}, t) \xrightarrow{\text{TDDFT}} v(\mathbf{r}, t)$$

Hence, for fixed initial state, there is a 1-1 correspondence between $\gamma(\mathbf{r}, \mathbf{r}', t)$ and $v(\mathbf{r}, t)$

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

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Note: There exists no 1-1 correspondence between $\gamma(\mathbf{r}, \mathbf{r}', t)$ and non-local potentials $v(\mathbf{r}, \mathbf{r}', t)$ (integral operators)

How about xc functionals in time-dependent RDMFT?

Use the known functionals of ground-state RDMFT as adiabatic approximation, i.e. make n_k and $\phi_k(\mathbf{r})$ in the Mueller-type expressions time-dependent.

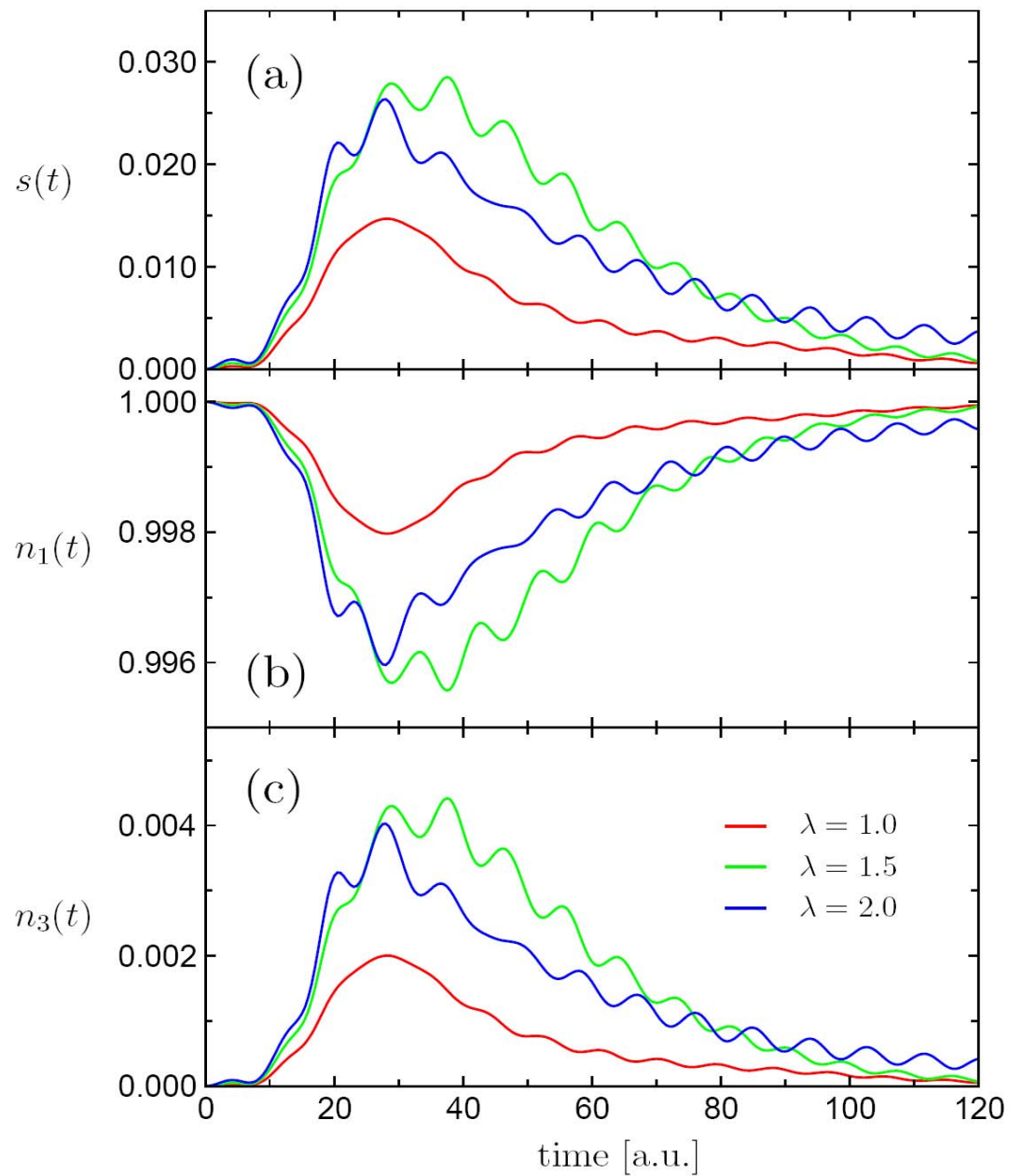
☠ Upon time-propagation, all these adiabatic RDMFT functionals lead to time-independent occupation numbers

H. Appel, E.K.U.G. arXiv:0807.2712

e-He⁺ scattering
(with soft Coulomb
potentials in 1D)

$\lambda =$ coupling constant,
 $k_0 = 0.3$ a.u.

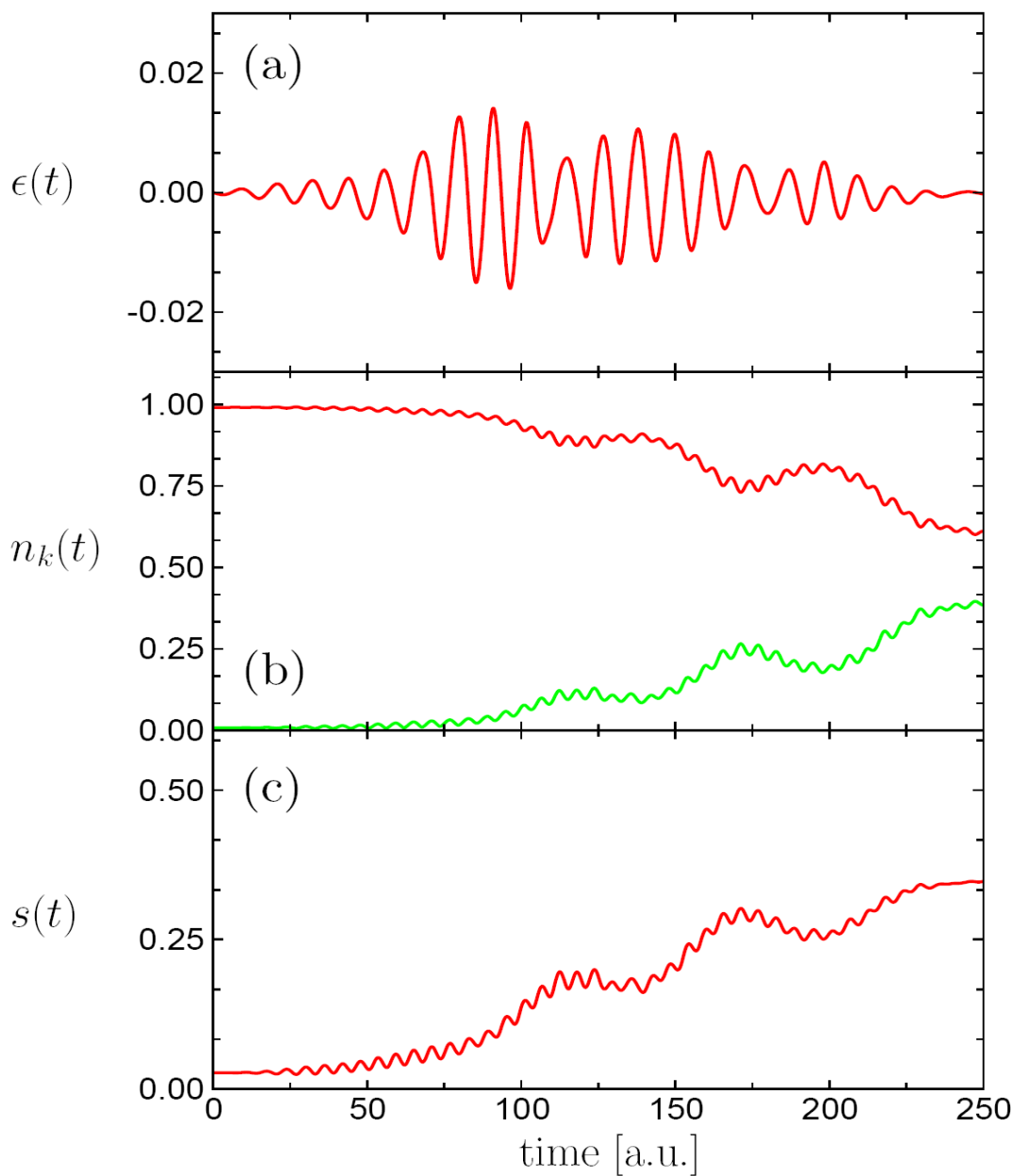
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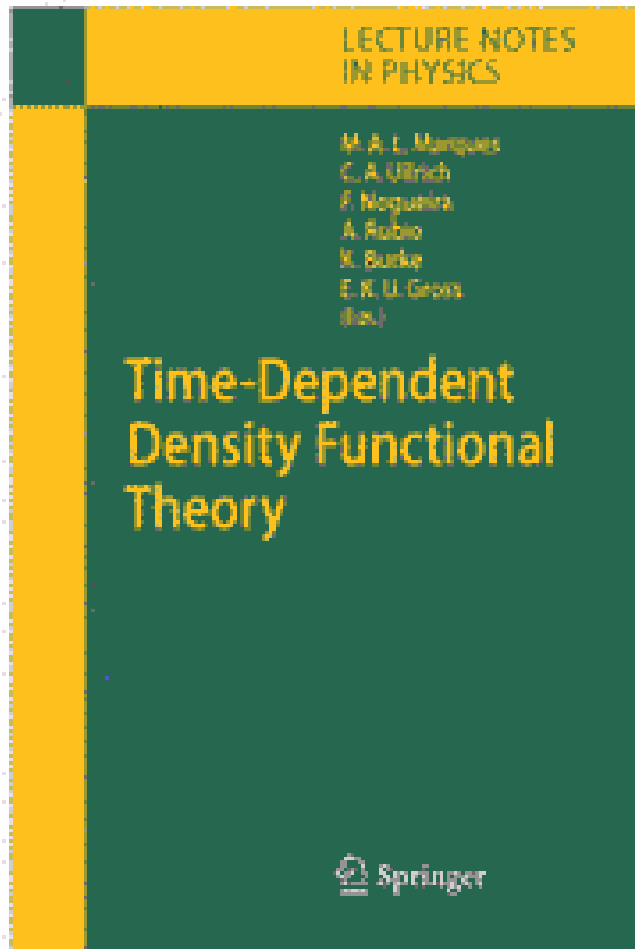
He in 1D with
soft Coulomb potentials,

transition from ground
state to lowest excited
singlet state with
optimized pulse

H. Appel, E.K.U.G.
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Thanks !



**Lecture Notes in Physics 706
(Springer, August 2006)**