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Kohn-Sham equations beyond the single-determinant approximation

14.03.2013 | N.N. Lathiotakis, N. Helbig, N.I. Gidopoulos, A. Rubio

Outline

1. Reduced Density-Matrix Functional Theory (RDMFT)
2. Local effective potential
3. Results
4. Conclusions

Reduced density-matrix functional theory

Reduced density matrix functional theory

$$\Psi(\mathbf{r}_1 ... \mathbf{r}_N) \leftrightarrow \gamma(\mathbf{r}, \mathbf{r}')$$

$$\gamma(\mathbf{r}, \mathbf{r}') = N \int d^3r_2 ... d^3r_N \Psi^*(\mathbf{r}' ... \mathbf{r}_N)\Psi(\mathbf{r} ... \mathbf{r}_N)$$

- Every ground-state observable is a functional of $\gamma(\mathbf{r}, \mathbf{r}')$

Ground-state energy

$$E[\gamma] = E_{\rm kin}[\gamma] + E_{\rm ext}[\gamma] + E_H[\gamma] + E_{xc}[\gamma]$$

Reduced density-matrix functional theory

Natural orbitals and occupation numbers

$$\gamma(\mathbf{r},\mathbf{r}') = \sum_{j=1}^{\infty} n_j \varphi_j^*(\mathbf{r}')\varphi_j(\mathbf{r})$$

- No non-interacting system due to idempotency
- Minimize total energy with respect to occupation numbers and natural orbitals

$$F^{(j)}\varphi_j = \sum_k \epsilon_{jk}\varphi_k$$

Local potential I

Idea: replace expensive minimization wrt. natural orbitals by a single-particle equation with a local potential

$$\left[-\frac{\nabla^2}{2} + v_{eff}(\mathbf{r})\right] \varphi_j(\mathbf{r}) = \epsilon_j \varphi_j(\mathbf{r})$$

- Orbitals will be an approximation to the true natural orbitals
- Find the best effective potential v_{eff} by minimizing the energy

OEP type equations to determine the orbitals

Local potential II

- Occupation numbers are still determined via direct minimization
- Local potential is an additional constraint in the minimization of the orbitals
- Computational cost for determining the natural orbitals is the same as for orbital functionals in DFT
- Energy eigenvalues can be used as an approximation for ionization potentials

Results - correlation energies

		Müller	BBC3	Power	ML
H_2O	loc. pot.	-0.35	-0.13	-0.09	-0.19
	dir. min.	-0.51	-0.26	-0.17	-0.29
CO	loc. pot.	-0.54	-0.17	-0.18	-0.30
	dir. min.	-0.76	-0.33	-0.28	-0.39
CO_2	loc. pot.	-0.97	-0.36	-0.34	-0.51
	dir. min.	-1.29	-0.59	-0.48	-0.66
C_2H_2	loc. pot.	-0.55	-0.20	-0.16	-0.25
	dir. min.	-0.75	-0.34	-0.25	-0.35

Table: Correlation energies (in Ha) from local potential and direct minimization

Results - H_2 dissociation

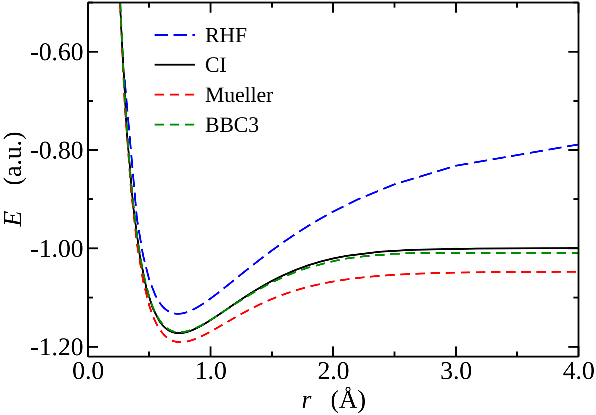

Figure: Dissociation of H_2

Results - H_2 dissociation

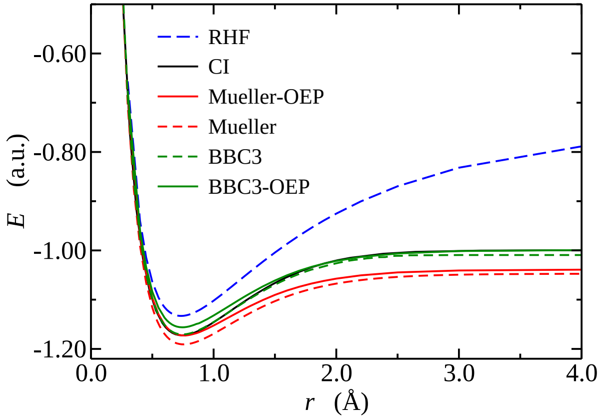

Figure: Dissociation of H_2

Results - local potential

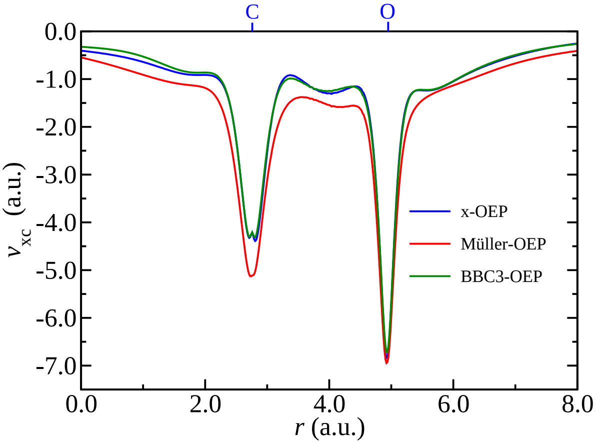

Figure: Local effective potential for CO

Results - energy eigenvalues I

		HF	Müller	BBC3	Power	ML	Exp. IP
H_2O	ϵ_N	13.73	21.22	12.78	17.77	14.06	12.78
	ϵ_{N-1}	15.71	22.78	14.86	19.75	16.16	14.83
	ϵ_{N-2}	19.15	26.36	18.38	23.31	19.70	18.72
CO	ϵ_N	15.14	20.85	12.51	18.53	15.94	14.01
CO_2	ϵ_N	14.74	25.89	18.08	22.57	17.54	13.78
	ϵ_{N-1}	19.22	28.79	21.49	25.70	20.77	18.30
C_2H_2	ϵ_N	11.07	20.17	12.58	16.35	14.01	11.49
	ϵ_{N-1}	18.47	24.12	17.46	21.09	19.06	16.70
	ϵ_{N-2}	20.88	25.54	19.11	22.69	20.75	18.70
Av. Error %		8.09	40.39	8.43	36.56	8.99	

Table: Energy eigenvalues and ionization potentials (all numbers in eV)

Results - energy eigenvalues II

		HF	Müller	BBC3	Power	ML	Exp. IP
H_2O	ϵ_N	13.73	13.32	12.82	12.60	13.03	12.78
	ϵ_{N-1}	15.71	14.93	14.90	14.56	15.14	14.83
	ϵ_{N-2}	19.15	18.21	18.42	17.99	18.70	18.72
CO	ϵ_N	15.14	14.87	12.51	14.70	14.29	14.01
CO_2	ϵ_N	14.74	15.87	14.51	15.30	14.57	13.78
	ϵ_{N-1}	19.22	18.74	17.91	18.41	17.79	18.30
C_2H_2	ϵ_N	11.07	12.85	11.15	11.54	11.42	11.49
	ϵ_{N-1}	18.47	16.83	16.08	16.27	16.52	16.70
	ϵ_{N-2}	20.88	18.38	17.80	17.90	18.28	18.70
Av. Error %		8.09	4.94	3.16	4.2	3.53	

Table: Energy eigenvalues and ionization potentials (all numbers in eV) without weakly-weakly terms in OEP equation

Conclusions

- Efficient method to calculate approximate natural orbitals - computational costs on the level of OEP
- Recovers more than half of the correlation energy of direct minimization
- Energy eigenvalues compare well with ionization potentials

Allows for the use of RDMFT methodology
at the cost of a DFT calculation

Work done together with...

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