

Orbital-dependent functionals in DFT

A new generation of density-functional methods employs exchange-correlation functionals $E_{xc}\{\{\phi_i\}\}$ that exhibit explicit dependence on orbitals; density dependence only implicit through orbitals $\phi_i[\rho]$.

Taking the functional derivative with respect to density to obtain exchange-correlation potential not straightforward but via optimized effective potential v_{xc} method

Numerical stability of resulting integral equation for v_{xc} problematic

Development of DFT

Ground state energy of an electronic system
 $E_0 = T_s + U + E_x + E_c + \int dr v_{nuc}(\mathbf{r})\rho(\mathbf{r})$

Thomas-Fermi-Dirac

$$E_0 = T_s[\rho] + U[\rho] + E_x[\rho] + E_c[\rho] + \int dr v_{nuc}(\mathbf{r})\rho(\mathbf{r})$$

$$\delta E / \delta \rho(\mathbf{r}) = \mu$$

Conventional Kohn-Sham

$$E_0 = T_s\{\{\phi_i\}\} + U[\rho] + E_x[\rho] + E_c[\rho] + \int dr v_{nuc}(\mathbf{r})\rho(\mathbf{r})$$

$$[\hat{T} + \hat{v}_{nuc} + \hat{u} + \hat{v}_x + \hat{v}_c]\phi_i = \varepsilon_i \phi_i$$

Kohn-Sham with orbital dependent functionals

$$E_0 = T_s\{\{\phi_i\}\} + U[\rho] + E_x\{\{\phi_i\}\} + E_c\{\{\phi_i\}\} + \int dr v_{nuc}(\mathbf{r})\rho(\mathbf{r})$$

$$[\hat{T} + \hat{v}_{nuc} + \hat{u} + \hat{v}_x + \hat{v}_c]\phi_i = \varepsilon_i \phi_i$$

Shortcomings of LDA/GGA methods

DFT (ground states)

- Unphysical Coulomb self-interactions
- Static correlation not treated correctly
- Dispersion interactions (VdW bonding) not described

TDDFT (excited states)

- Excitations with Rydberg character inaccurate
- Excitations in long conjugate systems of π -electrons systematically underestimated
- Description of 2e-excitations and excitonic effects problematic
- Charge-transfer excitations qualitatively incorrect

KS methods with orbital-dependent functionals

$$\hat{v}_{ext} \rightarrow \hat{T} + \hat{v}_{ext} + \hat{u}[\rho_0] + \hat{v}_{xc}\{\{\phi_i\}\} \rightarrow \phi_i \rightarrow \rho_0 \rightarrow U[\rho_0], \int dr v_{ext}(\mathbf{r})\rho_0(\mathbf{r})$$

Examples for orbital-dependent functionals
Exchange energy

$$E_x = - \sum_{i,j}^{occ} \int dr dr' \frac{\phi_i(\mathbf{r}')\phi_j(\mathbf{r}')\phi_j(\mathbf{r})\phi_i(\mathbf{r})}{|\mathbf{r}' - \mathbf{r}|}$$

meta-GGA functionals

$$E_{xc} = \int dr \epsilon_{xc}([\rho, \nabla\rho, \nabla^2\rho, \tau]; \mathbf{r}) \rho(\mathbf{r}) \quad \text{with} \quad \tau(\mathbf{r}) = \frac{1}{2} \sum_i^{occ} [\nabla\phi_i(\mathbf{r})]^2$$

Orbital-dependent functionals $F\{\{\phi_i\}\}$ are implicit density functionals $F\{\{\phi_i[\rho]\}\}$

Derivatives of orbital-dependent functionals, the OEP equation

$$\text{Exchange-correlation potential} \quad v_{xc}(\mathbf{r}) = \frac{\delta E_{xc}\{\{\phi_i\}\}}{\delta \rho(\mathbf{r})}$$

Integral equation for v_{xc} by taking derivative $\frac{\delta E_{xc}}{\delta v_s(\mathbf{r})}$ in two ways

$$\int dr' \frac{\delta E_{xc}}{\delta \rho(\mathbf{r}')} \frac{\delta \rho(\mathbf{r}')}{\delta v_s(\mathbf{r})} = \int dr' \sum_i^{occ} \frac{\delta E_{xc}}{\delta \phi_i(\mathbf{r}')} \frac{\delta \phi_i(\mathbf{r}')}{\delta v_s(\mathbf{r})}$$

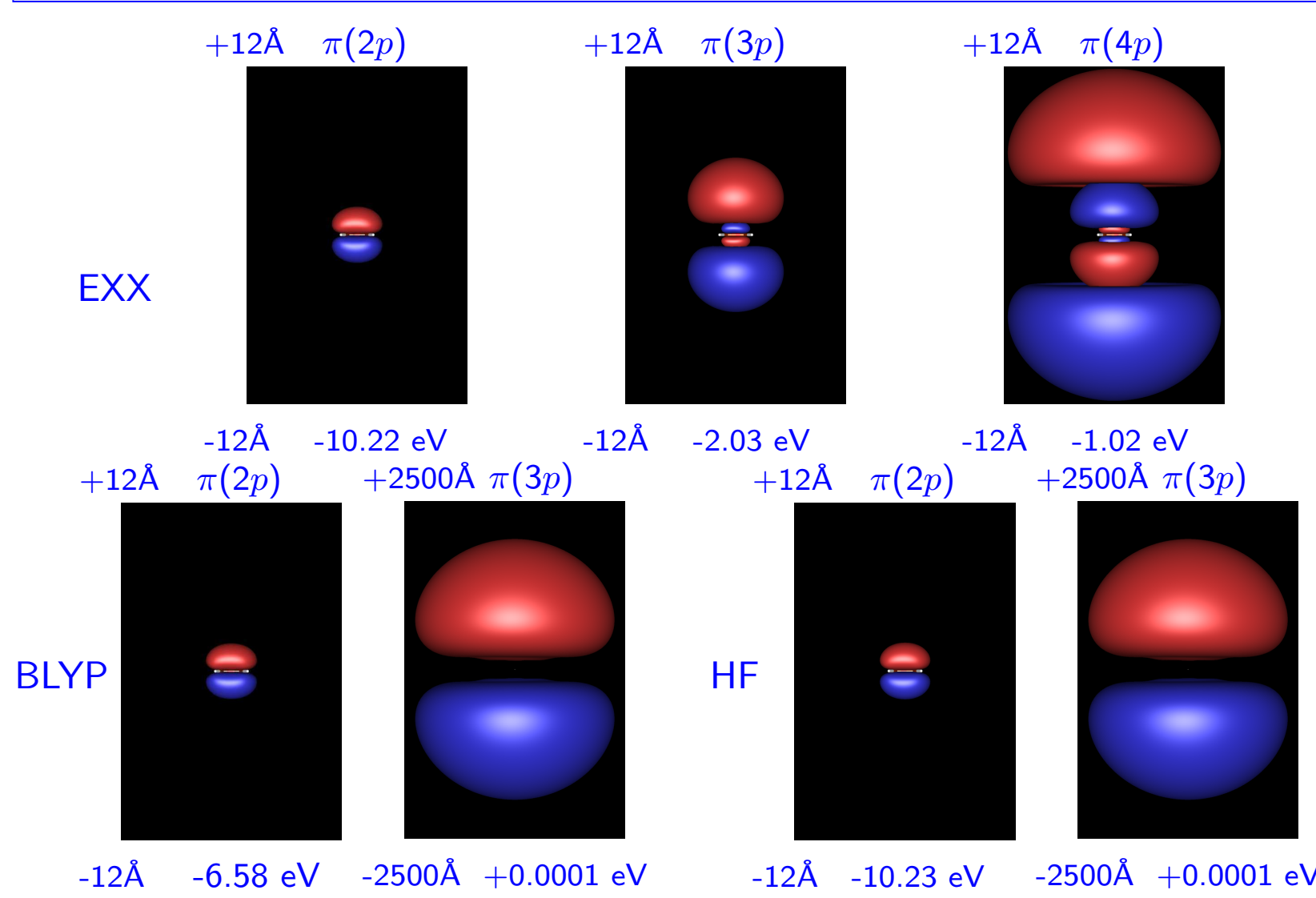
$$\int dr' X_s(\mathbf{r}, \mathbf{r}') v_{xc}(\mathbf{r}') = t(\mathbf{r})$$

$$\text{KS response function} \quad X_s(\mathbf{r}, \mathbf{r}') = 4 \sum_i^{occ} \sum_a^{unocc} \frac{\phi_i(\mathbf{r})\phi_a(\mathbf{r})\phi_a(\mathbf{r}')\phi_i(\mathbf{r}')}{\varepsilon_i - \varepsilon_a}$$

$$\text{Perturbation theory yields} \quad \frac{\delta \phi_i(\mathbf{r}')}{\delta v_s(\mathbf{r})} = \sum_{s \neq i} \phi_s(\mathbf{r}') \frac{\phi_s(\mathbf{r})\phi_i(\mathbf{r})}{\varepsilon_i - \varepsilon_s}$$

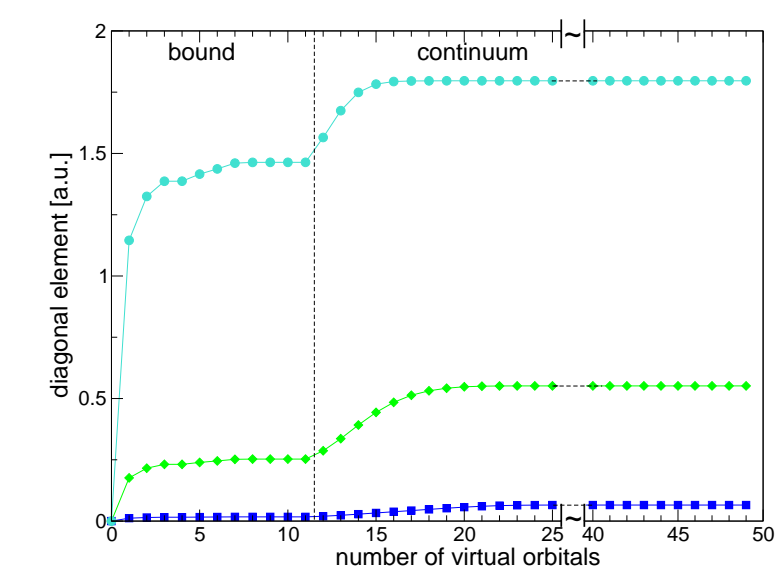
$$\text{Derivative of } E_{xc}\{\{\phi_i\}\} \text{ yields} \quad \frac{\delta E_{xc}}{\delta \phi_i(\mathbf{r}')}$$

Rydberg orbitals of ethene



Convergence of KS response matrix of Be

$$X_{s,kl} = 4 \sum_i^{occ} \sum_a^{unocc} \frac{\langle \phi_i | f_k | \phi_a \rangle \langle \phi_a | f_l | \phi_i \rangle}{\varepsilon_i - \varepsilon_a}$$



Continuum contributes strongly to elements of X_s

Basisset OEP methods

$$\int dr' X_s(\mathbf{r}, \mathbf{r}') v_x(\mathbf{r}') = 4 \sum_i^{occ} \sum_a^{unocc} \frac{\phi_i(\mathbf{r})\phi_a(\mathbf{r}) \langle \phi_a | \hat{v}_x^{NL} | \phi_i \rangle}{\varepsilon_i - \varepsilon_a}$$

Representation of v_x within auxiliary basisset $\{f_k\}$

$$v_x(\mathbf{r}) = \sum_k v_{x,k} f_k(\mathbf{r})$$

OEP equation
 $X_s v_x = t$

with

$$X_{s,kl} = 4 \sum_i^{occ} \sum_a^{unocc} \frac{\langle \phi_i | f_k | \phi_a \rangle \langle \phi_a | f_l | \phi_i \rangle}{\varepsilon_i - \varepsilon_a}$$

and

$$t_k = 4 \sum_i^{occ} \sum_a^{unocc} \frac{\langle \phi_i | f_k | \phi_a \rangle \langle \phi_a | \hat{v}_x^{NL} | \phi_i \rangle}{\varepsilon_i - \varepsilon_a}$$

Representation of orbitals in second basis set $\{\chi_\mu\}$ (orbital basis set)

Numerical stable exact exchange gaussian basissets KS method

Auxiliary basisset $f_k(\mathbf{r}) = \int dr' g_k(\mathbf{r}') / |\mathbf{r} - \mathbf{r}'|$

Gaussian functions $g_k(\mathbf{r}')$ derived from orbital basis set

Incorporation of exact conditions to treat asymptotic of $v_x(\mathbf{r})$

$$\int dr \rho_x(\mathbf{r}) = -1$$

$$\langle \phi_{HOMO} | v_x | \phi_{HOMO} \rangle = \langle \phi_{HOMO} | \hat{v}_x^{NL} | \phi_{HOMO} \rangle$$

Construction and balancing scheme for auxiliary and orbital basis sets

efficient, purely analytical, numerical stable method that can easily be implemented.

Possible auxiliary basisset $\{f_k\}$

$$v_x(\mathbf{r}) = \sum_k v_{x,k} f_k(\mathbf{r})$$

- Plane Waves (periodic systems)
- Gaussian functions
- Electrostatic potential of Gaussian functions $f_k(\mathbf{r}) = \int dr' g_k(\mathbf{r}') / |\mathbf{r} - \mathbf{r}'|$

$$v_x(\mathbf{r}) = \int dr' \frac{\rho_x(\mathbf{r}')}{|\mathbf{r}' - \mathbf{r}|}$$

with

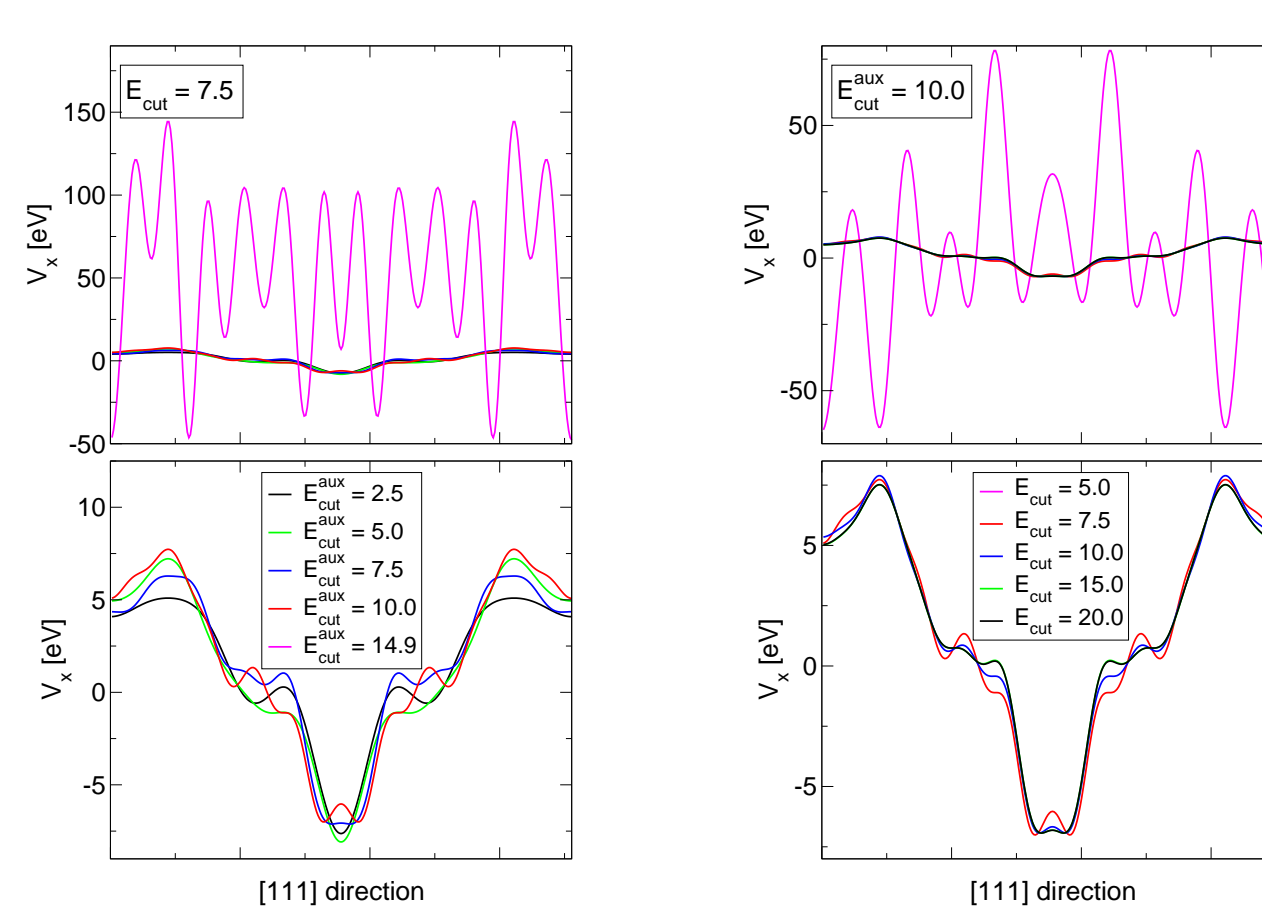
$$\rho_x(\mathbf{r}) = \sum_k \rho_{x,k} g_k(\mathbf{r})$$

- Products of orbital basis functions $f_k(\mathbf{r}) = \chi_\mu(\mathbf{r})\chi_\nu(\mathbf{r})$
- Products of occupied times unoccupied orbitals $f_k(\mathbf{r}) = \phi_i(\mathbf{r})\phi_s(\mathbf{r})$

Results for Be

| orbital bas. | VDZ $N_{aux} = 7$ | VTZ $N_{aux} = 8$ | VQZ $N_{aux} = 9$ | Partridge3 $N_{aux} = 11$ | even(1.5) $N_{aux} = 38$ | OEP(num) |
|--------------|----------------------|----------------------|----------------------|------------------------------|-----------------------------|----------|
| cVDZ | 0.000(3) | 0.000(4) | 0.000(5) | 0.000(7) | 0.000(34) | 0.115 |
| cVTZ | 0.000(1) | 0.000(2) | 0.000(3) | 0.000(5) | 0.000(28) | 0.197 |
| cVTZ+d | 0.001 | 0.000 | 0.000 | 0.000(3) | 0.000(28) | 0.217 |
| cVQZ | 0.016 | 0.000 | 0.000 | 0.000(3) | 0.000(30) | 0.347 |
| VDZ | 0.624 | 0.608 | 0.603 | 0.538 | 0.525(23) | 0.572 |
| VTZ | 0.629 | 0.608 | 0.604 | 0.584 | 0.552(22) | 0.579 |
| VTZ+d | 0.629 | 0.608 | 0.604 | 0.584 | 0.546(20) | 0.579 |
| VQZ | 0.628 | 0.609 | 0.607 | 0.588 | 0.565(21) | 0.584 |
| Partridge3 | 0.629 | 0.609 | 0.607 | 0.595 | 0.582(17) | 0.589 |
| even(1.5) | 0.630 | 0.610 | 0.607 | 0.595 | 0.591(2) | 0.591 |

Balancing of basis sets, example of bulk silicon



Numerical stable results for $E_{cut}^{aux} \approx \frac{2}{3} E_{cut}$

TDDFT with exact exchange kernel

Time-dependent density-functional theory requires exchange-correlation kernels, i.e., the frequency-dependent functional derivatives of exchange-correlation potentials

Integral equation for exact frequency-dependent exchange kernel $f_x(\omega, \mathbf{r}_1, \mathbf{r}_2)$

$$\int dr_3 dr_4 X_s(\omega, \mathbf{r}_1, \mathbf{r}_3) f_x(\omega, \mathbf{r}_3, \mathbf{r}_4) X_s(\omega, \mathbf{r}_4, \mathbf{r}_2) = h_x(\omega, \mathbf{r}_1, \mathbf{r}_2)$$

The function $h_x(\omega, \mathbf{r}_1, \mathbf{r}_2)$ depends on KS orbitals and eigenvalue differences

OEP-like equation with two KS response functions

OEP versus exact exchange-only KS

Unphysical oscillations if orbital basis set too small for auxiliary basis set

Critical point: Convergence of response matrix elements with orbital basis

$$X_{s,kl} = 4 \sum_i^{occ} \sum_a^{unocc} \frac{\langle \phi_i | f_k | \phi_a \rangle \langle \phi_a | f_l | \phi_i \rangle}{\varepsilon_i - \varepsilon_a}$$

For unbalanced basis sets

- Eigenvalues of X_s with too small magnitude (oscillations in $v_x(\mathbf{r})$)
- OEP procedure still works but no longer corresponds to exact exchange-only KS method and leads to unphysical exchange potentials

Summary and literature

Density-functional methods with orbital-dependent functionals are very promising and may represent future of DFT

Numerical stable OEP methods required for further development of DFT

Literature

- Orbital-dependent functionals in general: J. Chem. Phys. **123**, 062203 (2005); references therein.
- Numerical stable EXX: J. Chem. Phys.; **127**, 054102 (2007).
- OEP versus KS: J. Chem. Phys. **128**, 104104 (2008).
- OEP versus HF: Chem. Phys. Lett. **455**, 110 (2008).
- Multiconfiguration OEP: J. Chem. Phys. **128**, 144109 (2008).