



Introduction to QM/MM

Third part

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Outline

Third part

- More on the Exchange Correlation (XC) functionals
- The Grimme dispersion corrections
- Pseudopotentials

Few additional details about the basis sets



Kohn-Sham DFT

Kohn and Sham define a fictitious system of non-interacting particles with a local potential that generates the same density as the density of the real fully-interacting system:

$$\rho(\mathbf{r}) = \sum_{i} |\varphi_{i}(\mathbf{r})|^{2} \qquad \int d\mathbf{r} \, \varphi_{i}^{*}(\mathbf{r}) \, \varphi_{j}(\mathbf{r}) = \delta_{ij}$$

$$E[\rho] = E^{KS}[\{\varphi_{i}\}] =$$

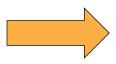
$$= \sum_{i} \int d\mathbf{r} \, \varphi_{i}^{*}(\mathbf{r}) \left(-\frac{\hbar^{2}}{2m_{e}} \nabla^{2} \right) \varphi_{j}(\mathbf{r}) + \int d\mathbf{r} \, V_{\text{ext}}(\mathbf{r}) \rho(\mathbf{r}) + \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \frac{\rho(\mathbf{r}) \rho'(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} + E_{\text{xc}}[\rho] \right)$$

$$E_{\text{KIN}}[\rho] \qquad E_{\text{ext}}[\rho] \qquad E_{\text{H}}[\rho]$$

$$Kohn-Sham equations$$

 $\min_{\rho} E[\rho]$

1 x *N*-electron equation



$$\left\{ -\frac{1}{2} \nabla^2 + V_{\text{ext}}(\mathbf{r}) + \int d\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \underbrace{\left(\frac{\delta E_{\text{xc}}[\rho]}{\delta \rho(\mathbf{r})}\right)}_{\boldsymbol{\sigma}_i(\mathbf{r})} \boldsymbol{\varphi}_i(\mathbf{r}) \neq \boldsymbol{\epsilon}_i \boldsymbol{\varphi}_i(\mathbf{r}) \right\}$$

N x one-electron equations

NOT KNOWN



Exchange-Correlation Functionals

First level of approximation – Local Density Approximation (LDA):

$$E_{\rm xc}^{\rm LDA}[\rho] = \int d\mathbf{r} \; \varepsilon_{\rm xc}^{\rm LDA}(\rho(\mathbf{r})) \, \rho(\mathbf{r})$$

 $\varepsilon_{\rm x}^{\rm LDA}(\rho({\bf r}))$ = Exchange correlation energy per electron of the homogeneous electron gas at density $\rho({\bf r})$:

From quantum Monte Carlo calculations

$$\varepsilon_{\rm xc}^{\rm LDA}(\rho) = \varepsilon_{\rm x}^{\rm LDA}(\rho) + \varepsilon_{\rm c}^{\rm LDA}(\rho) = -\frac{3}{4} \left(\frac{3}{\pi}\rho\right)^{\frac{1}{3}} + \varepsilon_{\rm c}^{\rm LDA}(\rho)$$

Second level of approximation – Generalized Gradient Approximation (GGA):

$$E_{\rm xc}^{\rm GGA}[\rho] = \int d\mathbf{r} \varepsilon_{\rm xc}^{\rm GGA}(\rho(\mathbf{r}), \nabla \rho(\mathbf{r})) \rho(\mathbf{r})$$

Examples: B-LYP, PBE, ...



GGA Functionals

B-LYP (Becke88 + Lee, Yang, and Parr):

$$E_{\mathrm{xc}}^{\mathrm{BLYP}}[\rho] = E_{\mathrm{x}}^{\mathrm{B88}}[\rho] + E_{\mathrm{c}}^{\mathrm{LYP}}[\rho] = \left(E_{\mathrm{x}}^{\mathrm{LDA}}[\rho] - \frac{b}{2^{1/3}}\int d\mathbf{r} \ \rho^{4/3} \frac{x^2}{1 + 6bx \ \mathrm{sinh^{-1}} \ x}\right) + E_{\mathrm{c}}^{\mathrm{LYP}}[\rho]$$
 with $x = 2^{1/3} \frac{|\nabla \rho|}{\rho^{4/3}}$ and $b = 0.0042 \ \mathrm{a.u.}$

PBE (Perdew-Burke-Ernzerhof):

$$E_{\text{xc}}^{\text{PBE}}[\rho] = E_{\text{x}}^{\text{PBE}}[\rho] + E_{\text{c}}^{\text{PBE}}[\rho] = \int \rho(\mathbf{r}) \, \varepsilon_{\text{x}}^{\text{LDA}}(\rho) F_{\text{x}}^{\text{PBE}}(s) d\mathbf{r} + \int \rho(\mathbf{r}) \left[\varepsilon_{\text{c}}^{\text{LDA}}(\rho) + H_{\text{c}}^{\text{PBE}}(s) \right] d\mathbf{r}$$
with
$$F_{\text{x}}^{\text{PBE}}(s) = 1 + \kappa - \frac{\kappa}{1 + \frac{\beta(\pi s)^2}{3\kappa}} \qquad s = \frac{|\nabla \rho|}{(24\pi^2)^{1/3} \rho^{4/3}} \qquad \kappa = 0.804 \qquad \text{from theoretical arguments}$$

$$H_{\text{c}}^{\text{PBE}}(s) = \gamma \phi^3 \ln \left[1 + \frac{\beta}{\gamma} t^2 \left(\frac{1 + At^2}{1 + At^2 + A^2 t^4} \right) \right] \qquad t = \frac{|\nabla \rho|}{\left(\frac{12288}{\pi} \right)^{1/6} \frac{\hbar}{m^{1/2} e} \rho^{7/6}}$$

$$A = \frac{\beta}{\gamma} \frac{1}{e^{-\varepsilon_{\text{c}}^{\text{LDA}}/\gamma \phi^3 - 1}} \qquad \phi = \frac{1}{2} \left[(1 + \eta)^{2/3} + (1 - \eta)^{2/3} \right] \qquad \gamma = \frac{1 - \ln 2}{\pi^2}$$
Relative spin polarization

Hybrid Functionals

$$E_{xc}[\rho] = w_{HF}E_x^{HF}[\rho] + E_{xc}^{other}[\rho]$$

$$E_{x}^{HF}[\rho] = \text{exact exchange} = -\frac{1}{2} \sum_{i,j} \iint \psi_i^*(\mathbf{r}_1) \psi_j^*(\mathbf{r}_2) \frac{1}{r_{12}} \psi_j(\mathbf{r}_1) \psi_j(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2$$

 $w_{HF}[\rho]$ = portion of exact exchange

Examples:

$$E_{xc}^{B3LYP} = E_{x}^{LDA} + a_{0}(E_{x}^{HF} - E_{x}^{LDA}) + a_{x}(E_{x}^{B88} - E_{x}^{LDA}) + E_{c}^{LDA} + a_{c}(E_{c}^{LYP} - E_{c}^{LDA})$$

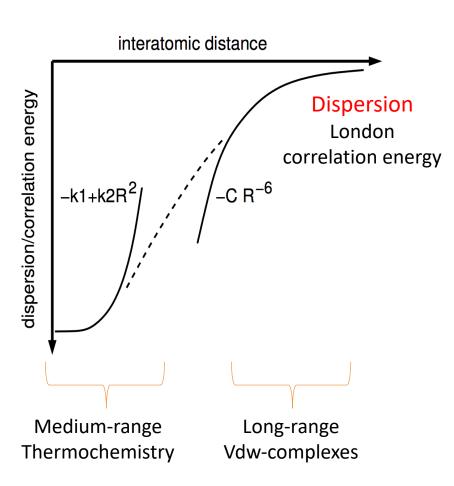
$$a_{0} = 0.20 \qquad a_{x} = 0.72 \qquad a_{c} = 0.81 \qquad \text{Fitted from a set of atomization energies, ionization potentials, proton affinities, and total atomic energies}$$

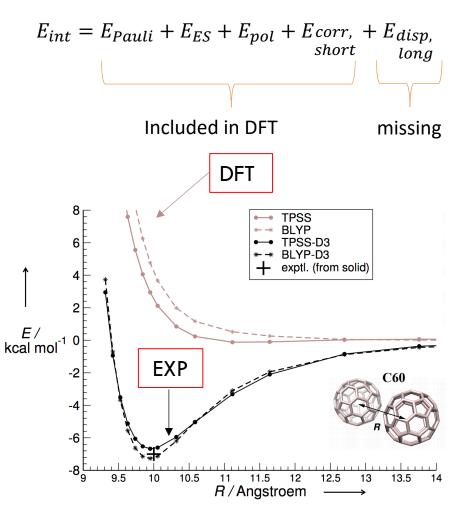
$$E_{xc}^{PBE0} = \frac{1}{4}E_{x}^{HF} + \frac{3}{4}E_{x}^{PBE} + E_{c}^{PBE}$$
$$E_{xc}^{PBE} = E_{x}^{PBE} + E_{c}^{PBE}$$

PBE is a GGA functional



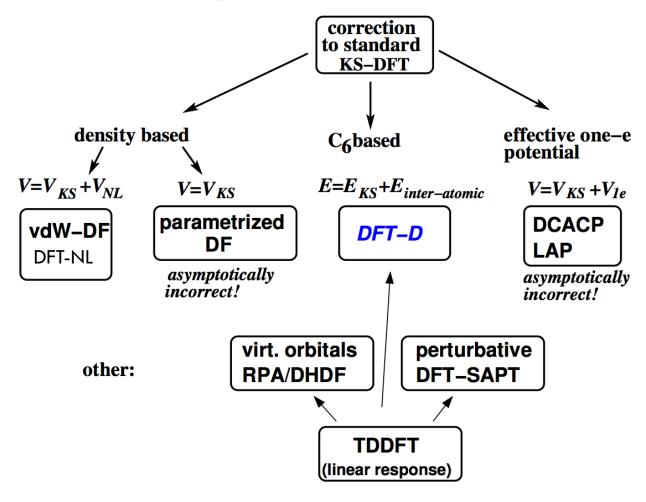
Dispersion problem in DFT







Dispersion corrections



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Grimme dispersion corrections

DFT-D1

S. Grimme, J. Comp. Chem. 25, 1463 (2004).

In CP2K

S. Grimme, J. Comp. Chem. **27**, 1787 (2006).

S. Grimme, J. Antony, S. Ehrlich and H. Krieg,

J. Chem. Phys. **132**, 154104 (2010).

$$E_{\text{DFT-D}} = E_{\text{KS-DFT}} + E_{\text{disp}}$$

$$E_{\rm disp} = E^{(2)} + E^{(3)}$$

DFT-D2:

$$E_{\text{disp}} = -s_6 \sum_{i,j < i}^{N_{\text{atoms}}} f_{damp}(R_{ij}) \frac{C_6^{ij}}{R_{ij}^6}$$

$$s_6 =$$
global scaling parameter depending on the choice of the functional used

$$f_{damp}(R_{ij}) = \frac{1}{1 + \exp\left[-20\left(\frac{R_{ij}}{(R_{vdW}^{i} + R_{vdW}^{j})} - 1\right)\right]}$$

$$C_6^{ij} = \sqrt{C_6^i C_6^j}$$



Basis sets and PW drawback

$$\left\{-\frac{1}{2}\nabla^{2} + V_{\text{ext}}(\mathbf{r}) + \int d\mathbf{r}' \frac{\rho'(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} + \frac{\delta E_{\text{xc}}[\rho]}{\delta \rho(\mathbf{r})}\right\} \varphi_{i}(\mathbf{r}) = \epsilon_{i} \varphi_{i}(\mathbf{r})$$

KS equations

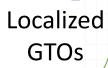
Discretization:

$$\varphi_i(\mathbf{r}) \simeq \sum_{k=1}^M a_k g_k(\mathbf{r})$$

$$\{g_k(\mathbf{r})\}=$$
 Basis set

1s Slater-type function $\approx \exp[-Zr]$

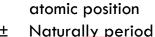
| | GTO | PW |
|----|-----|-----|
| Н | 1 | 1 |
| Li | 4 | 8 |
| С | 9 | 27 |
| Si | 27 | 140 |
| Ge | 76 | 663 |

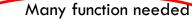


Ortogonal

- Atomic orbital-like
- Few functions needed
- Analytic integration for many operators
- Optimal for regular grids
- Finite extend
- Non-orthogonal
- Linear dependences for large basis set
- Complicated to generate
- Basis set superposition error







Independent from

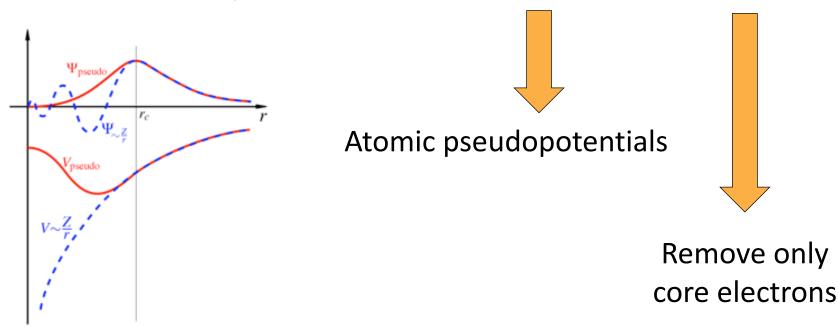


Pseudopotentials

Idea: Replace electronic degrees of freedom in the Hamiltonian by an effective potential

Desirable

properties: The potential should be additive and transferable





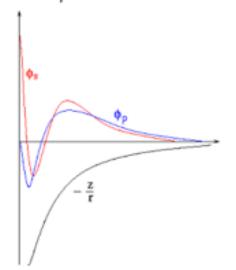
Atomic Pseudopotentials

$$\rho(\mathbf{r}) = \rho^{c}(\mathbf{r}) + \rho^{v}(\mathbf{r})$$

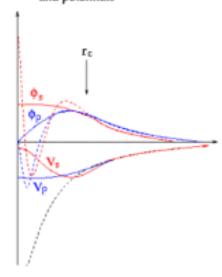


$$\left\{-\frac{1}{2}\nabla^{2} + V_{PP}(\mathbf{r}) + \int d\mathbf{r}' \frac{\rho^{v}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \frac{\delta E_{xc}[\rho^{v}]}{\delta \rho^{v}(\mathbf{r})}\right\} \varphi_{i}^{v}(\mathbf{r}) = \epsilon_{i}\varphi_{i}^{v}(\mathbf{r})$$

Original wavefunctions and potential



The pseudo-wavefunctions and potentials



$$V_{PP}(\mathbf{r}) = \sum_{l} |l\rangle V_{l}^{PP}(\mathbf{r})\langle l|$$

 $|l\rangle$ = Angular momentum projection operator

Pseudopotentials have to be built such that the main properties of the atom are reproduced



Norm-Conserving Pseudopotentials

- 1. Real and pseudo valence eigenvalues agree for a chosen prototype atomic configuration
- 2. Real and pseudo atomic wavefunctions agree beyond a chosen core radius \mathbf{r}_c :

$$\psi_l(\mathbf{r}) = \varphi_l(\mathbf{r}) \qquad \mathbf{r} > \mathbf{r}_c$$

3. The integrals from 0 to \mathbf{R} of the real and pseudo charge densities agree for $R > \mathbf{r}_c$ for each valence state (norm conservation):

$$\langle \psi_l | \psi_l \rangle_R = \langle \varphi_l | \varphi_l \rangle_R \qquad R > \mathbf{r}_c$$

4. The logarithmic derivatives of the real and pseudo wavefunction and their first energy derivatives agree for $\mathbf{r} > \mathbf{r}_c$

G.P. Kerker, J. Phys. C 13, L189 (1980)

G.B. Bachelet et al., Phys. Rev. B, 26, 4199 (1982)

D. Vanderbilt, Phys. Rev. B, 32, 8412 (1985)

A.M. Rappe et al., Phys. Rev. B, 41, 1227 (1990)

N. Troullier and J.L. Martins, Phys. Rev. B, 43, 1993 (1991) J.S. Lin et al., Phys. Rev. B, 47, 4174 (1993)



GTH Pseudopotentials

$$V_{PP}^{GTH}(\mathbf{r}, \mathbf{r}') = V_{LOC}^{GTH}(\mathbf{r}) + V_{NL}^{GTH}(\mathbf{r}, \mathbf{r}')$$

Long-ranged term

Short-ranged term

$$V_{\rm LOC}^{\rm GTH}(\mathbf{r}) = -\frac{Z_{\rm ion}}{|\mathbf{r}|} \operatorname{erf}\left(\frac{|\mathbf{r}|}{\sqrt{2}r_{loc}}\right) + e^{-\frac{1}{2}\left(\frac{|\mathbf{r}|}{r_{loc}}\right)^2} \sum_{i=1}^4 C_i \left(\frac{|\mathbf{r}|}{r_{loc}}\right)^{2i-2} \qquad r_{loc}: \text{ range of Gaussian ionic charge distribution}$$

$$V_{\rm NL}^{\rm GTH}(\mathbf{r},\mathbf{r}') = \sum_{lm} \sum_{ij} \langle \mathbf{r} \big| p_i^{lm} \rangle h_{ij}^l \langle p_{ij}^{lm} \big| \mathbf{r}' \rangle \qquad \langle \mathbf{r} \big| p_i^{lm} \rangle = N_i^l Y^{lm} \left(\frac{\mathbf{r}}{|\mathbf{r}|} \right) |\mathbf{r}|^{l+2i-2} e^{-\frac{1}{2} \left(\frac{|\mathbf{r}|}{r_{loc}} \right)^2}$$
Gaussian-type projector

Optimal decay properties in both real and Fourier space [



 V_{NI}^{GTH} efficiently computed on a grid in real space

Only 7 parameters needed to to specify its analytic form Optimal efficiency in numerical calculations using PW



Separable

Efficient for large systems: quadratic vs cubic scaling!

S. Goedecker, M. Teter, and J. Hutter, Phys. Rev. B **54**, 1703 (1996)

M. Krack, Theor. Chem. Acc., 114, 145 (2005)



GTO-based basis sets

$$\chi^{(k)}_{\zeta,l_x,l_y,l_z}(x,y,z) = N_k x^{l_x} y^{l_y} \ z^{l_z} e^{-\zeta_k r^2} \qquad \text{Gaussian Type Orbital (GTO) } primitive function$$

$$\chi(x,y,z) = \sum_k a_k \chi^{(k)}_{\zeta,l_x,l_y,l_z}(x,y,z) \qquad \text{Contracted function} \qquad \text{Not suitable for production runs}$$

$$\text{SZV} \qquad \text{Single-Zeta Valence} \qquad \text{i.e. 1 contracted function per orbital}$$

$$\text{DZVP} \qquad \text{Double-Zeta Valence} + 1 \text{ set of polarization functions} \qquad \text{i.e. 2 contracted functions per orbital} + 1 \text{ set of polarisation functions with } l = l_{\max} + 1$$

$$\text{TZVP} \qquad \text{Triple-Zeta Valence} + 1 \text{ set of polarization functions} \qquad \text{i.e. 3 contracted functions per orbital} + 1 \text{ set of polarisation functions with } l = l_{\max} + 1$$

$$\text{TZV2P} \qquad \text{Triple-Zeta Valence}, + 2 \text{ sets of polarization functions} \qquad \text{i.e. 3 contracted functions per orbital} + 2 \text{ sets of polarization functions with } l = l_{\max} + 1$$

$$\text{QZV2P} \qquad \text{Quadruple-Zeta Valence}, + 2 \text{ sets of polarization functions} \qquad \text{i.e. 4 contracted functions per orbital} + 2 \text{ sets of polarization functions} \qquad \text{i.e. 4 contracted functions per orbital} + 3 \text{ sets of polarization functions with } l = l_{\max} + 1$$

$$\text{QZV3P} \qquad \text{Quadruple-Zeta Valence}, + 3 \text{ sets of polarization functions} \qquad \text{i.e. 4 contracted functions per orbital} + 3 \text{ sets of polarization functions with } l = l_{\max} + 1$$

MOLOPT basis sets: basis sets optimised for molecular calculations

