

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:

$$\rho(\mathbf{r}) = \sum_i |\varphi_i(\mathbf{r})|^2 \quad \int d\mathbf{r} \varphi_i^*(\mathbf{r}) \varphi_j(\mathbf{r}) = \delta_{ij}$$

$$E[\rho] = E^{KS}[\{\varphi_i\}] = \sum_i \int d\mathbf{r} \varphi_i^*(\mathbf{r}) \left(-\frac{\hbar^2}{2m_e} \nabla^2 \right) \varphi_j(\mathbf{r}) + \int d\mathbf{r} V_{\text{ext}}(\mathbf{r}) \rho(\mathbf{r}) + \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \frac{\rho(\mathbf{r}) \rho'(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + E_{\text{xc}}[\rho]$$

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

Kohn-Sham equations

$$\min_{\rho} E[\rho] \quad \longrightarrow \quad \left\{ -\frac{1}{2} \nabla^2 + V_{\text{ext}}(\mathbf{r}) + \int d\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \frac{\delta E_{\text{xc}}[\rho]}{\delta \rho(\mathbf{r})} \right\} \varphi_i(\mathbf{r}) = \epsilon_i \varphi_i(\mathbf{r})$$

1 x N-electron equation



N x one-electron equations

NOT KNOWN

Exchange-Correlation Functionals

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

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

$\varepsilon_x^{LDA}(\rho(\mathbf{r}))$ = Exchange correlation energy per electron of the **homogeneous electron gas** at density $\rho(\mathbf{r})$:

From quantum
Monte Carlo
calculations

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

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

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

Examples: B-LYP, PBE, ...

GGA Functionals

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

$$E_{xc}^{\text{BLYP}}[\rho] = E_x^{\text{B88}}[\rho] + E_c^{\text{LYP}}[\rho] = \left(E_x^{\text{LDA}}[\rho] - \frac{b}{2^{1/3}} \int d\mathbf{r} \rho^{4/3} \frac{x^2}{1+6bx \sinh^{-1} x} \right) + E_c^{\text{LYP}}[\rho]$$

with $x = 2^{1/3} \frac{|\nabla\rho|}{\rho^{4/3}}$ and $b = 0.0042$ a. u.

Fitted from experimental data from noble gases

PBE (Perdew-Burke-Ernzerhof):

$$E_{xc}^{\text{PBE}}[\rho] = E_x^{\text{PBE}}[\rho] + E_c^{\text{PBE}}[\rho] = \int \rho(\mathbf{r}) \varepsilon_x^{\text{LDA}}(\rho) F_x^{\text{PBE}}(s) d\mathbf{r} + \int \rho(\mathbf{r}) [\varepsilon_c^{\text{LDA}}(\rho) + H_c^{\text{PBE}}(s)] d\mathbf{r}$$

with $F_x^{\text{PBE}}(s) = 1 + \kappa - \frac{\kappa}{1 + \frac{\beta(\pi s)^2}{3\kappa}}$ $s = \frac{|\nabla\rho|}{(24\pi^2)^{1/3} \rho^{4/3}}$ $\kappa = 0.804$ $\beta = 0.066725$ From theoretical arguments

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

$$A = \frac{\beta}{\gamma} \frac{1}{e^{-\varepsilon_c^{\text{LDA}}/\gamma\phi^3} - 1} \quad \phi = \frac{1}{2} \left[(1 + \eta)^{2/3} + (1 - \eta)^{2/3} \right] \quad \eta = \frac{1 - \ln 2}{\pi^2}$$

↑ Relative spin polarization ↑

Hybrid Functionals

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

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

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

Examples:

$$E_{xc}^{B3LYP} = E_x^{LDA} + a_0(E_x^{HF} - E_x^{LDA}) + a_x(E_x^{B88} - E_x^{LDA}) + E_c^{LDA} + a_c(E_c^{LYP} - E_c^{LDA})$$

$$a_0 = 0.20$$

$$a_x = 0.72$$

$$a_c = 0.81$$

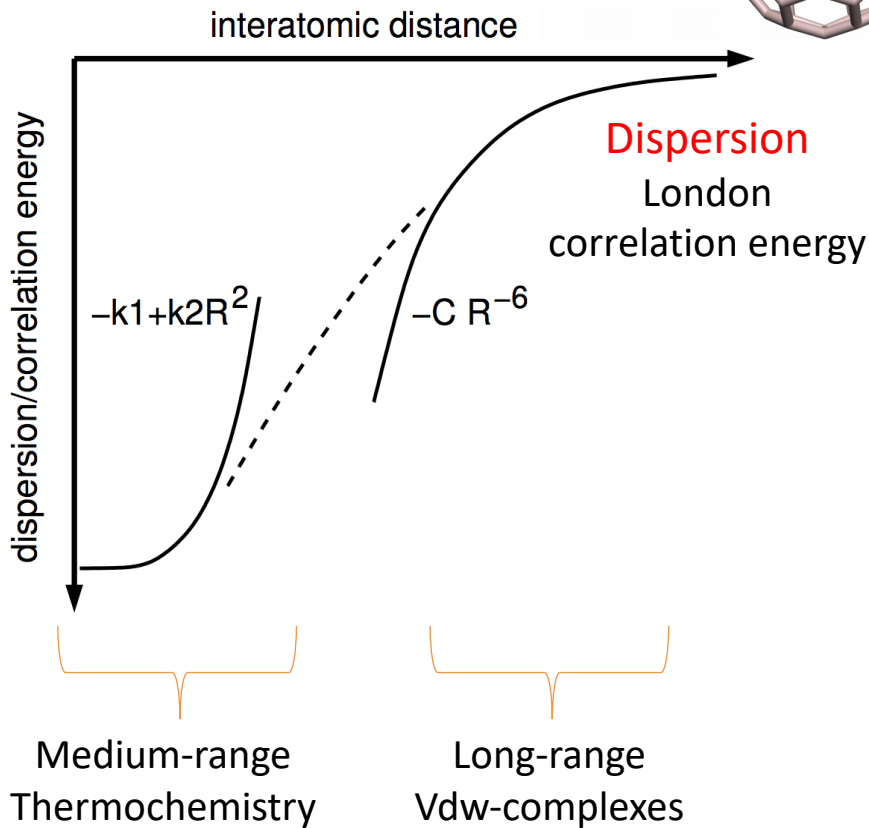
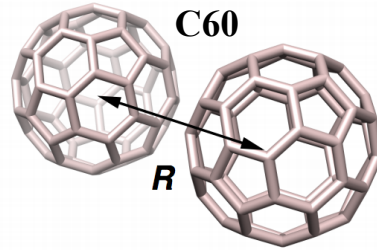
Fitted from a set of atomization energies, ionization potentials, proton affinities, and total atomic energies

$$E_{xc}^{PBEO} = \frac{1}{4} E_x^{HF} + \frac{3}{4} E_x^{PBE} + E_c^{PBE}$$

$$E_{xc}^{PBE} = E_x^{PBE} + E_c^{PBE}$$

PBE is a GGA functional

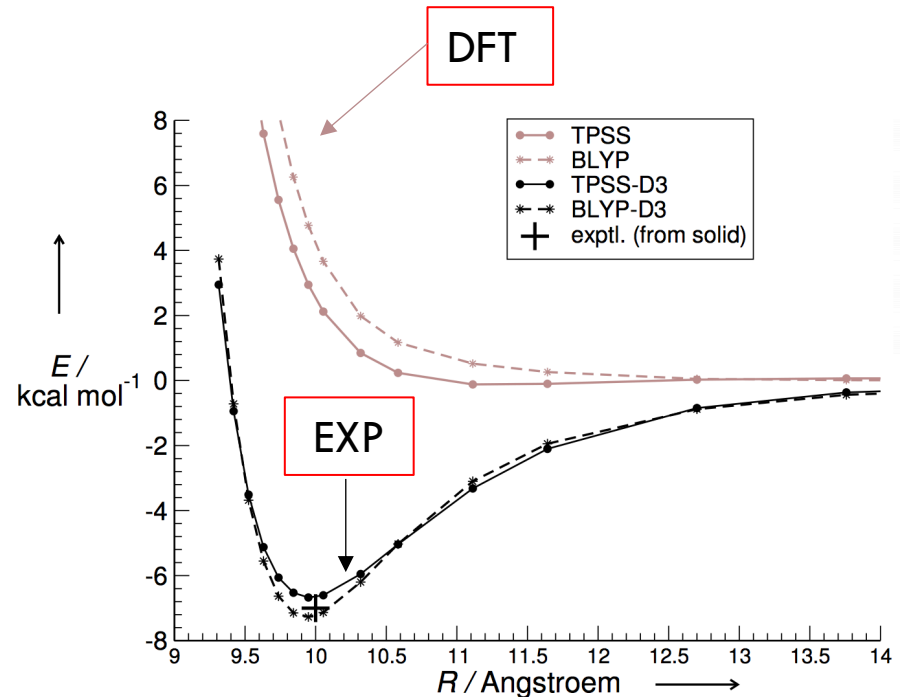
Dispersion problem in DFT



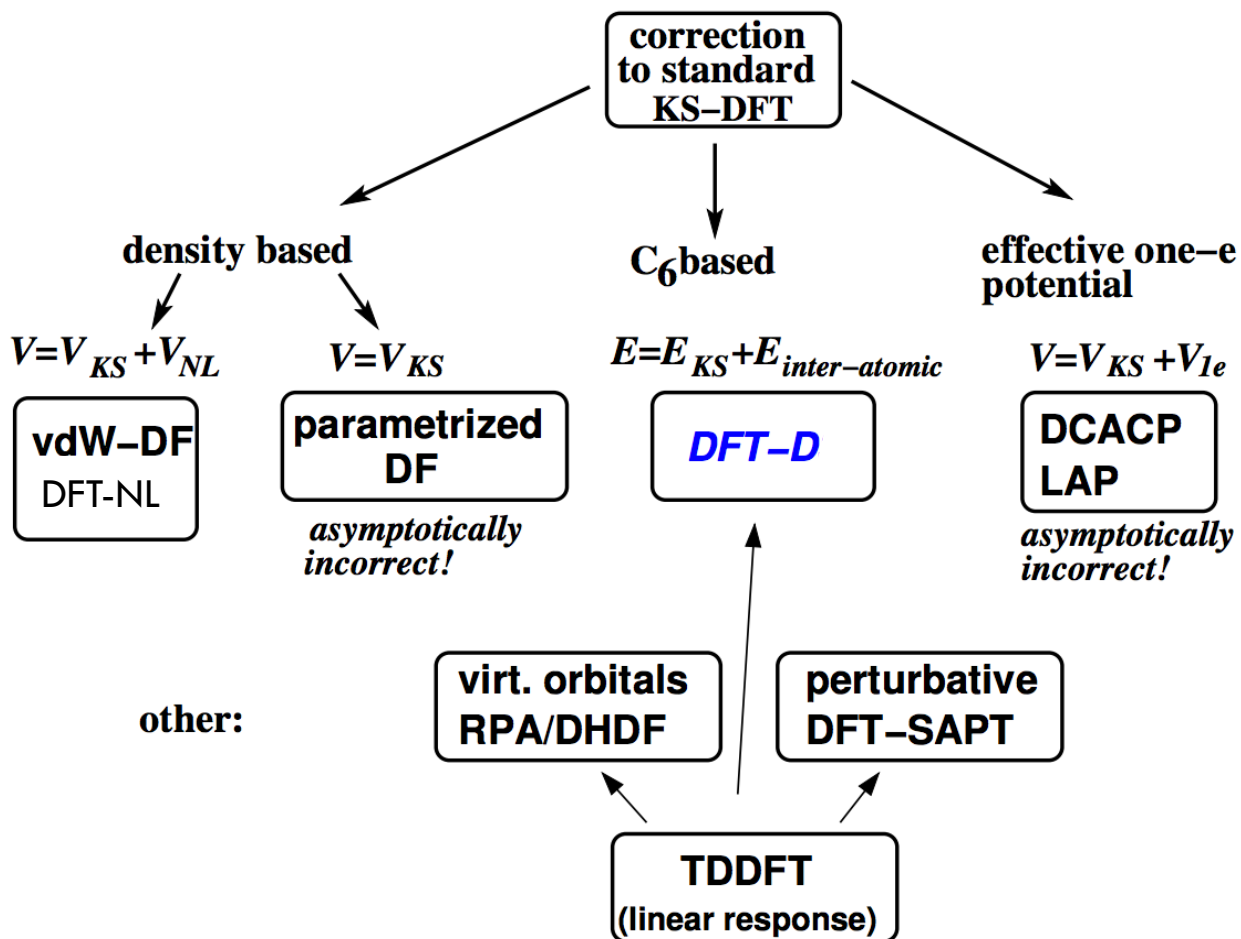
$$E_{int} = E_{Pauli} + E_{ES} + E_{pol} + E_{corr, short} + E_{disp, long}$$

Included in DFT

missing



Dispersion corrections



WIREs Comput. Mol. Sci., 2 (2011) 211

Grimme dispersion corrections

In CP2K	{	DFT-D1	S. Grimme, J. Comp. Chem. 25 , 1463 (2004).
		DFT-D2	S. Grimme, J. Comp. Chem. 27 , 1787 (2006).
		DFT-D3	S. Grimme, J. Antony, S. Ehrlich and H. Krieg, J. Chem. Phys. 132 , 154104 (2010).

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

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

DFT-D2:

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

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

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

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

Basis sets and PW drawback

$$\left\{ -\frac{1}{2} \nabla^2 + V_{\text{ext}}(\mathbf{r}) + \int d\mathbf{r}' \frac{\rho'(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \frac{\delta E_{\text{xc}}[\rho]}{\delta \rho(\mathbf{r})} \right\} \varphi_i(\mathbf{r}) = \epsilon_i \varphi_i(\mathbf{r}) \quad \text{KS equations}$$

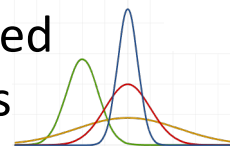
Discretization: $\varphi_i(\mathbf{r}) \approx \sum_{k=1}^M a_k g_k(\mathbf{r})$

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

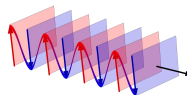
	GTO	PW
H	1	1
Li	4	8
C	9	27
Si	27	140
Ge	76	663

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

Localized
GTOs



Nonlocal
PW



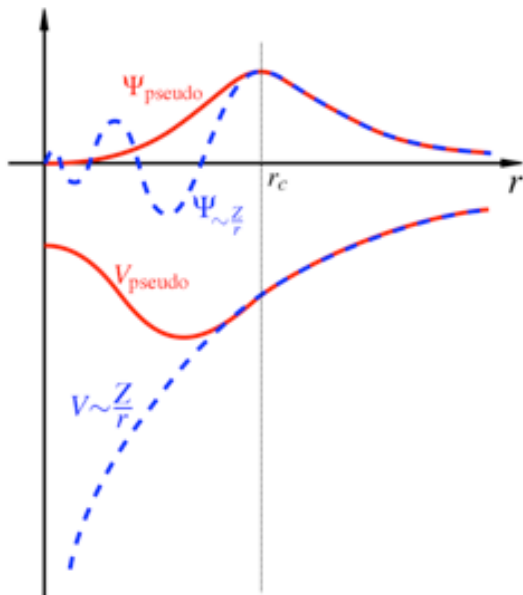
- | | |
|--|--|
| <ul style="list-style-type: none"> + Atomic orbital-like + Few functions needed + Analytic integration for many operators + Optimal for regular grids + Finite extend - Non-orthogonal - Linear dependences for large basis set - Complicated to generate - Basis set superposition error | <ul style="list-style-type: none"> + Orthogonal + Independent from atomic position ± Naturally period - Many function needed |
|--|--|

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

↓
Remove only
core electrons

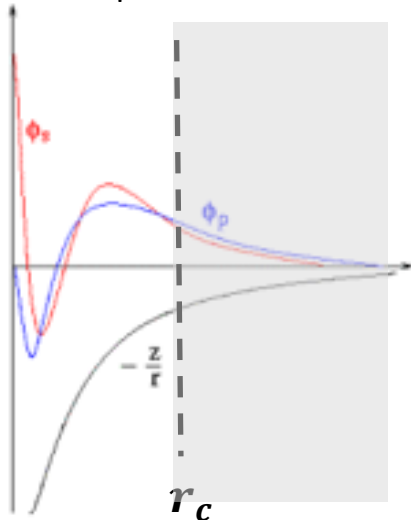
Atomic Pseudopotentials

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

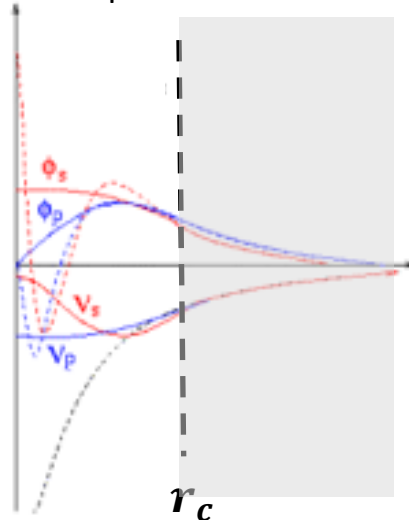


$$\left\{ -\frac{1}{2} \nabla^2 + V_{\text{PP}}(\mathbf{r}) + \int d\mathbf{r}' \frac{\rho^v(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \frac{\delta E_{\text{xc}}[\rho^v]}{\delta \rho^v(\mathbf{r})} \right\} \varphi_i^v(\mathbf{r}) = \epsilon_i \varphi_i^v(\mathbf{r})$$

Original wavefunctions and potential



The **pseudo-wavefunctions** and potentials



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

$|l\rangle =$ 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 :

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

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

$$\langle \psi_l | \psi_l \rangle_{\mathbf{R}} = \langle \varphi_l | \varphi_l \rangle_{\mathbf{R}} \quad \mathbf{R} > \mathbf{r}_c$$

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

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

Long-ranged term

Short-ranged term

$$V_{\text{LOC}}^{\text{GTH}}(\mathbf{r}) = -\frac{Z_{\text{ion}}}{|\mathbf{r}|} \operatorname{erf}\left(\frac{|\mathbf{r}|}{\sqrt{2}r_{\text{loc}}}\right) + e^{-\frac{1}{2}\left(\frac{|\mathbf{r}|}{r_{\text{loc}}}\right)^2} \sum_{i=1}^4 C_i \left(\frac{|\mathbf{r}|}{r_{\text{loc}}}\right)^{2i-2}$$

r_{loc} : range of Gaussian ionic charge distribution

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

Gaussian-type projector

- Optimal decay properties in both real and Fourier space
- Only 7 parameters needed to specify its analytic form
- Optimal efficiency in numerical calculations using PW
- Separable



$V_{\text{NL}}^{\text{GTH}}$ efficiently computed on a grid in real space



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

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

$\chi_i(x, y, z) = \sum_k a_k \chi_{\zeta, l_x, l_y, l_z}^{(k)}(x, y, z)$ *Contracted function*

Not suitable for production runs

Increasing accuracy

Basis set	Composition
SZV	Single-Zeta Valence i.e. 1 contracted function per orbital
DZVP	Double-Zeta Valence + 1 set of polarization functions i.e. 2 contracted functions per orbital + 1 set of polarisation functions with $l = l_{\max} + 1$
TZVP	Triple-Zeta Valence + 1 set of polarization functions i.e. 3 contracted functions per orbital + 1 set of polarisation functions with $l = l_{\max} + 1$
TZV2P	Triple-Zeta Valence, + 2 sets of polarization functions i.e. 3 contracted functions per orbital + 2 sets of polarisation functions with $l = l_{\max} + 1$
QZV2P	Quadruple-Zeta Valence, + 2 sets of polarization functions i.e. 4 contracted functions per orbital + 2 sets of polarisation functions with $l = l_{\max} + 1$
QZV3P	Quadruple-Zeta Valence, + 3 sets of polarization functions i.e. 4 contracted functions per orbital + 3 sets of polarisation functions with $l = l_{\max} + 1$
...	...

MOLOPT basis sets: basis sets optimised for molecular calculations

VandeVondele & Hutter, J. Chem. Phys., 127, 114105 (2007)