DFT in depth
the exchange-correlation term

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Outline

- exchange and correlation in DFT

- local density and local spin density approximation

- generalised gradient approximation

- semilocal functionals beyond GGA

- VASP input and output

- nonlocal and hybrid functionals

- applications

DFT energy functional:

$$E[n] = T[n] + \int d\mathbf{r}\, V_{\text{ext}}(\mathbf{r})n(\mathbf{r}) + \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + E_{\text{xc}}[n] \qquad (1)$$

Hohenberg-Kohn theorems [1]:

HK1 The full many-particle ground state is a unique functional of $n(\mathbf{r})$.

HK2 $E[n]$ assumes its minimum value for the ground state density w.r.t. all densities fullfilling $\int n(\mathbf{r})d\mathbf{r} = N$.

Finding the minimum energy

- Minimizing the energy functional (1) directly

$$\frac{\partial T[n]}{\partial n(\mathbf{r})} + V_{\text{ext}}(\mathbf{r}) + \int d\mathbf{r}' n(\mathbf{r}') \frac{1}{|\mathbf{r} - \mathbf{r}'|} + \frac{\partial E_{\text{xc}}[n]}{\partial n(\mathbf{r})} = \lambda n(\mathbf{r}). \qquad (2)$$

- Solving the Kohn-Sham equations [2]

$$\left(-\frac{1}{2}\nabla^2 + V_{\text{ext}}(\mathbf{r}) + V_{\text{xc}}(\mathbf{r}) + \int d\mathbf{r}' n(\mathbf{r}') \frac{1}{|\mathbf{r} - \mathbf{r}'|} \right) \psi_k(\mathbf{r}) = \varepsilon_k \psi_k(\mathbf{r}), \qquad (3)$$

leading to

$$E = \sum_{k=1}^{N} \varepsilon_k - \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + E_{\text{xc}}[n] - \int d\mathbf{r}\, V_{\text{xc}}[n(\mathbf{r})]n(\mathbf{r}). \qquad (4)$$

only $E_{\text{xc}}[n]$ and $V_{\text{xc}}[n(\mathbf{r})] = \frac{\partial E_{\text{xc}}[n]}{\partial n(\mathbf{r})}$ are to be approximated!

Exchange-correlation energy

$$E_{\text{xc}}[n] = T[n] - T_0[n] + U_{\text{xc}}[n], \tag{5}$$

$T[n] - T_0[n] \ldots$ kinetic energy difference of interacting and non-interacting system

$U_{\text{xc}}[n] \ldots$ Coulomb interaction of electrons with exchange correlation hole n_{xc}

Adiabatic connection formula:

$$E_{\text{xc}}[n] = \frac{1}{2} \int d\mathbf{r}\, n(\mathbf{r}) \int d\mathbf{r}' \int_0^1 d\lambda\, \frac{n_{\text{xc},\lambda}(\mathbf{r},\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}, \tag{6}$$

$\lambda \ldots$ interaction parameter.

Coulomb interaction is isotropic:

$$E_{\text{xc}}[n] = \frac{1}{2} \int d\mathbf{r}\, n(\mathbf{r}) \int_0^\infty dR R^2 \frac{1}{R} \int d\Omega \int_0^1 d\lambda n_{\text{xc},\lambda}(\mathbf{r},\mathbf{R}). \tag{7}$$

Exchange-correlation hole $n_{xc}(\mathbf{r}\sigma, \mathbf{r}'\sigma')$

Definition from two-electron density matrix,

$$\rho_2(\mathbf{r}\sigma, \mathbf{r}'\sigma') \equiv n_\sigma(\mathbf{r}) \left(n_{\sigma'}(\mathbf{r}') + n_{xc}(\mathbf{r}\sigma, \mathbf{r}'\sigma') \right), \tag{8}$$

n_{xc} is local,

$$\lim_{|\mathbf{r}-\mathbf{r}'|\to\infty} n_{xc}(\mathbf{r}\sigma, \mathbf{r}'\sigma') = 0, \tag{9}$$

from the Pauli exclusion principle follows

$$n_{xc}(\mathbf{r}\sigma, \mathbf{r}\sigma) = -n_\sigma(\mathbf{r}). \tag{10}$$

Dividing n_{xc} in exchange and correlation part,
$n_{xc}(\mathbf{r}\sigma, \mathbf{r}'\sigma') = n_x(\mathbf{r}\sigma, \mathbf{r}'\sigma') + n_c(\mathbf{r}\sigma, \mathbf{r}'\sigma')$, yields

$$n_x(\mathbf{r}\sigma, \mathbf{r}'\sigma') \leq 0, \qquad \int d\mathbf{r}' \, n_x(\mathbf{r}\sigma, \mathbf{r}'\sigma') = -\delta_{\sigma,\sigma'}, \tag{11}$$

and

$$\int d\mathbf{r}' \, n_c(\mathbf{r}\sigma, \mathbf{r}'\sigma') = 0. \tag{12}$$

Lieb-Oxford bound,

$$E_{\text{xc}}[n] \geq -D \int d\mathbf{r}\, n^{4/3}(\mathbf{r}), \qquad 1.44 \leq D \leq 1.68. \tag{13}$$

Uniform scaling, e.g.,

$$E_{\text{x}}[\gamma^3 n(\gamma\mathbf{r})] = \gamma E_{\text{x}}[n(\mathbf{r})], \qquad E_{\text{c}}[\gamma^3 n(\gamma\mathbf{r})] > \gamma E_{\text{c}}[n(\mathbf{r})] \quad (\gamma > 1), \tag{14}$$

$$\lim_{\gamma \to 0} \frac{1}{\gamma} E_{\text{xc}}[\gamma^3 n(\gamma\mathbf{r})] \equiv B[n(\mathbf{r})] < E_{\text{xc}}[n(\mathbf{r})]. \tag{15}$$

non-uniform scalin, e.g.,

$$\lim_{\gamma \to 0} \frac{1}{\gamma} E_{\text{xc}}[\gamma^2 n(\gamma x, \gamma y, z)] > -\infty \tag{16}$$

$$\lim_{\gamma \to \infty} E_{\text{xc}}[\gamma n(\gamma x, y, z)] > -\infty, \tag{17}$$

... and many more.

$$E_{\mathrm{xc}} = \int d\mathbf{r}\, n(\mathbf{r})\, \varepsilon_{\mathrm{xc}}(n(\mathbf{r})). \qquad (18)$$

$\varepsilon_{\mathrm{xc}}(n(\mathbf{r}))\ldots$ exchange correlation energy of a uniform electron gas.

Exchange:

$$E_{\mathrm{x}} = \sum_{\sigma} -k \int d\mathbf{r}\, n_{\sigma}^{\frac{4}{3}}(\mathbf{r}), \qquad (19)$$

with $k = \frac{2}{2^{4/3}} \frac{3}{2} \left(\frac{3}{4\pi}\right)^{\frac{1}{3}}$ in LDA and $k = \frac{3}{2} \left(\frac{3}{4\pi}\right)^{\frac{1}{3}}$ in LSDA.

Correlation:

Parametrised from quantum Monte Carlo Simulations.

Local Density Approximation (LDA) II

- fully local

- exchange and correlation of a *physical system*

- obeys uniform scaling relations (e.g. 14,15)

- does **not** obey non-uniform scaling relations (e.g. 16,17)

- although qualitatively wrong exchange-correlation hole, good approximation for the spherical average

Overall, LDA performs remarkably well!
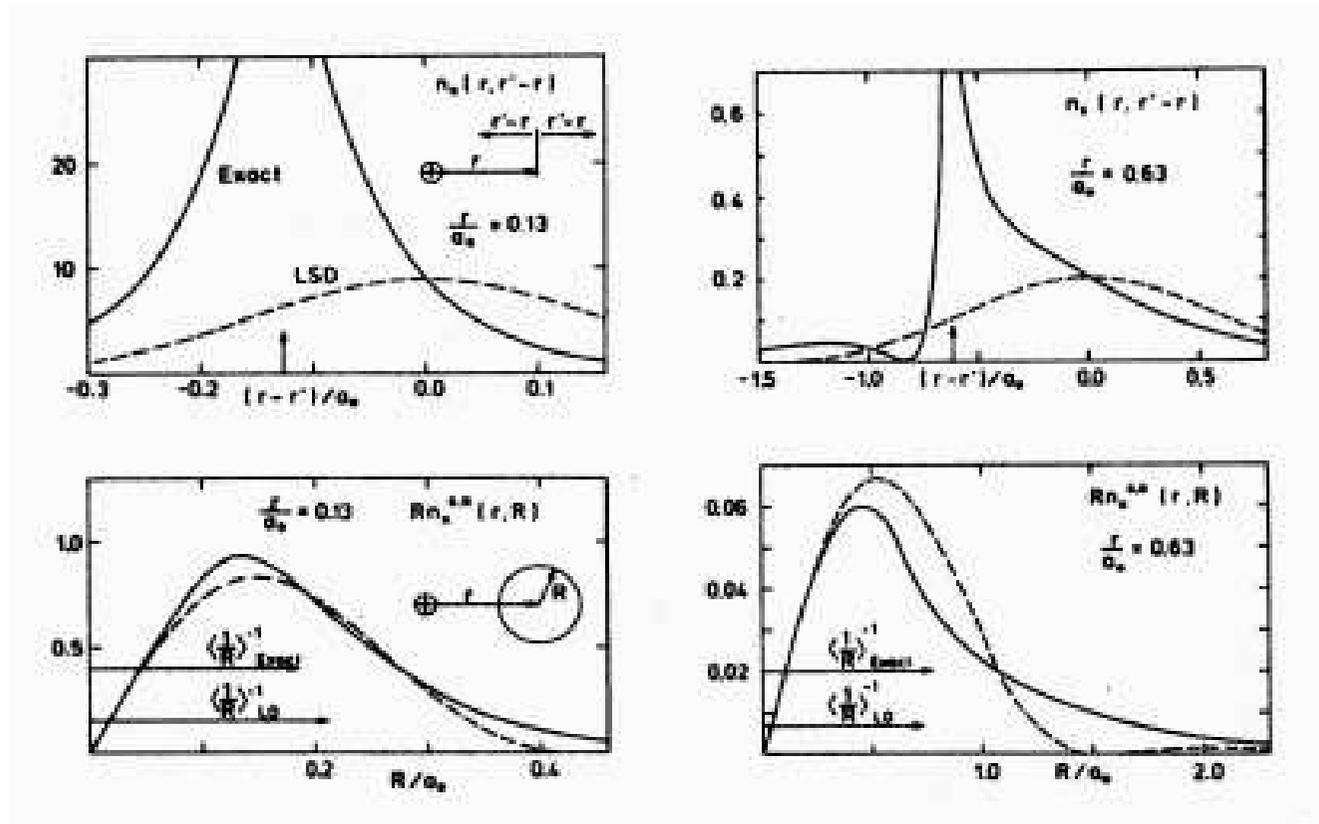
Figure 1: Exact and LSDA local (top) and integrated (bottom) exchange hole in a nitrogen atom (from [4]).

Spin-polarised exchange-correlation

Replacing scalar potentials and densities by spin-matrices [5]

$$V(\mathbf{r}) \to V_{\alpha\beta}(\mathbf{r}) \qquad n(\mathbf{r}) \to n_{\alpha\beta}(\mathbf{r}), \tag{20}$$

HK1 is lost (class of potentials leads to same density matrix).

BUT: ground-states and derived quantities of the classes are equal
$$\to \text{DFT still valid.}$$

Exchange energy treated seperatly for both spins

Correlation energy Commonly written as functionals of $r_s \propto \rho^{-1/3}$ and $\zeta = \frac{n_\uparrow - n_\downarrow}{n}$

- von Barth and Hedin: correlation potential and energy from RPA

- Vosko, Wilk, and Nusair: included interpolations from quantom Monto Carlo
  results for $\zeta = 0$ and $\zeta = 1$.

Gradient Expansion Approximation (GEA)

Already suggested by Kohn and Sham [2],

$$
\begin{aligned}
E_{\text{xc}}^{\text{GEA}}[n_\uparrow, n_\downarrow] \;=\; & \int d\mathbf{r}\, n(\mathbf{r})\, \varepsilon_{\text{xc}}(n_\uparrow(\mathbf{r}), n_\downarrow(\mathbf{r})) + \\[2mm]
+ \; & \sum_{\sigma, \sigma'} C_{\sigma, \sigma'}(n_\uparrow(\mathbf{r}), n_\downarrow(\mathbf{r})) \frac{\nabla n_\sigma}{n_\sigma^{2/3}} \frac{\nabla n_{\sigma'}}{n_{\sigma'}^{2/3}}.
\end{aligned}
\tag{21}
$$

- n_{xc} not the exchange-correlation hole of *any* physical system

- improvement over LSDA for slowly varying systems

Typically GEA performs **worse** than LSDA for real electronic systems.

Generalised Gradient Approximation (GGA)

General *semi*local approximation to the exchange-correlation energy as a functional of the density and its gradient to fullfill a maximum number of exact relations,

$$E_{\text{xc}}^{\text{GGA}}[n_{\uparrow}, n_{\downarrow}] = \int d\mathbf{r} \, f(n_{\uparrow}(\mathbf{r}), n_{\downarrow}(\mathbf{r}), \nabla n_{\uparrow}(\mathbf{r}), \nabla n_{\downarrow}(\mathbf{r})), \qquad (22)$$

Exchange correlation potential:

$$V_{\text{xc}}[n(\mathbf{r})] = \frac{\partial E_{\text{xc}}[n]}{\partial n(\mathbf{r})} - \nabla \cdot \frac{\partial E_{\text{xc}}[n]}{\partial(\nabla n(\mathbf{r}))}. \qquad (23)$$

The gradient of the density is usually determined *numerically*.

GGA Examples I

- Langreth-Mehl 1983 (LM)

  - Construction from wave-vector analysis of E_{xc}

  - Correlation term for small k set to zero

  - Correction in right direction but major shortcomings, e.g. uniform gas limit is not correct

- Perdew-Wang 1986 (PW86)

  - real space cutoff to E_x of GEA

  - reciprocal space cutoff to E_c of GEA

- Becke-Perdew 1988 (BP)

  - Improved exchange functional with a single adjustable parameter

- Lee-Yang-Parr 1988 (LYP)

  - correlation functional derived from the Cole-Salvetti formula

- Perdew-Wang 1991 (PW91) [6]

  – purely ab-initio

  – fullfills almost all scaling relations except high density limit of uniform scaling

Exchange energy:

$$E_{\text{x}}^{\text{PW91}}[n] = -\int d\mathbf{r}\, n \frac{3k_F}{4\pi} \frac{1 + 0.1965 s \sinh^{-1}(7.796s) + (0.274 - 0.151 e^{-100s^2}) s^2}{1 + 0.1964 s \sinh^{-1}(7.796s) + 0.004 s^4}$$

Correlation energy:

$$E_{\text{c}}^{\text{PW91}}[n] = \int d\mathbf{r}\, n \left(\varepsilon_{\text{c}}(\mathbf{r}_s, \zeta) + H(t, r_s, \zeta) \right)$$

with $k_F = (3\pi^2 n)^{1/3}$, $s = |\nabla n|/2k_F n$, $t = |\nabla n|/2g k_s n$, $g = [(1+\zeta)^{2/3} + (1-\zeta)^{2/3}]/2$, and $k_s = (4k_F/\pi)^{1/2}$.

GGA Examples III

- Perdew-Burke-Ernzerhof 1996 (PBE)

  – simplification of the derivation of PW91

  – only minor changes to PW91

- Revised Perdew-Burke-Ernzerhof 1999 (RPBE)

  – semi-empirical change of PBE to improve atomisation energies of small molecules and chemisorption energies of atoms and molecules on transition metal surfaces

Many GGAs are tailored for specific classes of problems and have therefore a limited general applicability.

Extending the GGA

Problem:

- GGA cannot describe the $r \to \infty$ limit of the xc-energy density and the xc-potential *simultaneously* correctly.

Solution:

- include further semilocal information of the density, e.g. $\Delta n(\mathbf{r})$

- include semilocal information of the orbitals, e.g. the kinetic energy density,

$$\tau(\mathbf{r}) = \frac{1}{2} \sum_{k=1}^{N} |\nabla \psi_k(\mathbf{r})|^2 \,, \tag{24}$$

Laplacian of the density

Advantage:

- straight forward exchange-correlation potential

$$V_{\mathrm{xc}}[n(\mathbf{r})] = \frac{\partial E_{\mathrm{xc}}[n]}{\partial n(\mathbf{r})} - \nabla \cdot \frac{\partial E_{\mathrm{xc}}[n]}{\partial(\nabla n(\mathbf{r}))} + \Delta \cdot \frac{\partial E_{\mathrm{xc}}[n]}{\partial(\Delta n(\mathbf{r}))} \tag{25}$$

Disadvantage:

- numerically unstable

Examples:

- Jemmer and Knowles (1995)

- Filatov and Thiel (1998) (FT98)

Kinetic energy density

modifications of the LDA which do not consider the nature of the orbitals involved are unlikely to be satisfactory in all systems

Jones and Gunarsson 1985

Problem:

- Determination of the exchange-correlation potential

Solution:

- Optimised effective potential method

$$\sum_i \int d\mathbf{r}' \left(V_{\mathrm{xc}}^{\mathrm{OEP}}(\mathbf{r}') - \frac{1}{\psi_i(\mathbf{r}')} \frac{\partial E_{\mathrm{xc}}[\{\psi_i\}]}{\partial \psi_i^*(\mathbf{r}')} \right) \psi_i^*(\mathbf{r}') G_i(\mathbf{r}',\mathbf{r}) \psi_i(\mathbf{r}) + c.c. = 0$$

- Neumann-Nobes-Handy method

$$\int \psi_i V_{\mathrm{xc}} \psi_k d\mathbf{r} = \ldots + \int \nabla \psi_i \, 2 \frac{\partial \varepsilon_{\mathrm{xc}}(n, \nabla n, \tau)}{\partial \tau} \nabla \psi_k d\mathbf{r}$$

$$\boxed{\textit{VASP Input}}$$

- Choose the exchange correlation functional

  - via the `POTCAR` file

  - by setting `GGA = __|CA|91|PE|RP` in the `INCAR` file

    * `__` (two blanks) ...LDA exchange only
    * `CA` ...LDA exchange and correlation

- Switch on *non-selfconsistent* PKZB meta-GGA energy

  - based on PBE potentials (only those include the kinetic energy density)

  - set `LMETAGGA=.TRUE.` in the `INCAR` file

- *non-selfconsistent* aspherical contributions to the on-site GGA energy (PAW potentials only)

  - set `LASPH=.TRUE.` in the `INCAR` file

VASP output

- OSZICAR and stdout:

```
1 F= -.35333292E+01 E0= -.35333292E+01 d E =-.748238E-17

1 F(ASPHER.)= -.35567321E+01 E0(ASPHER.)= -.35567321E+01

1 F(METAGGA)= 0.32195711E+01 E0(METAGGA)= 0.32195711E+01
```

- OUTCAR:

```
ASPHERICAL CONTRIBUTION TO EXCH AND CORRELATION IN SPHERES (eV)

----------------------------------------------------

standard PAW PS : AE= 135.083574 -166.260165

Aspheric PAW PS : AE= 135.115379 -166.315373

core xc AE= -1334.998410

----------------------------------------------------

Aspherical result:

free energy TOTEN = -3.556732 eV

energy without entropy= -3.556732 energy(sigma->0) = -3.556732
```

- OUTCAR cont'd:

```
METAGGA EXCHANGE AND CORRELATION (eV)

---------------------------------------------------

LDA+GGA E(xc) EXCG = -164.793059

LDA+GGA PAW PS : AE= 135.115379 -166.315373

core xc AE= -1334.998410

metaGGA E(xc) EXCM = -164.476006

metaGGA PAW PS : AE= 134.494206 -159.234950

metaGGA core xc AE= -1378.140708

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METAGGA result:

free energy TOTEN = 3.219571 eV


energy without entropy= 3.219571 energy(sigma->0) = 3.219571
```

Motivation:

Adiabatic connection formula (6)

$$E_{xc}[n] = \int_0^1 U_{xc,\lambda}[n] d\lambda \approx \frac{1}{2} U_{xc,0}[n] + \frac{1}{2} U_{xc,1}[n] \tag{26}$$

$U_{xc,0}[n]$ ... nonlocal exchange energy of KS-orbitals
$U_{xc,1}[n]$ ... *potential* energy of exchange-correlation

Common hybrid functional B3LYP:

$$E_{xc} = (1 - a_0)E_x^{LSDA} + a_0 E_x^{exact} + a_x \Delta E_x^{B88} + a_c E_c^{LYP} + (1 - a_c)E_c^{VWN}, \tag{27}$$

$a_0 = 0.20$, $a_x = 0.72$, and $a_c = 0.81$.

Implementation of exact exchange

$E_{\mathrm{x}}^{\mathrm{exact}}$ is a sum of four-center integrals,

$$E_{\mathrm{x}}^{\mathrm{exact}} = -\frac{1}{2} \sum_{m,n}^{N} f_n f_m \int \frac{d\mathbf{r}d\mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|} \phi_m^*(\mathbf{r})\phi_m(\mathbf{r}')\phi_n(\mathbf{r})\phi_n^*(\mathbf{r}'), \qquad (28)$$

Scaling problem:

- DFT scaling (VASP): $O(N^2)$

- E_{x} scaling (plane waves): $O(N^3 \log N)$

Periodic boundary conditions (PBC):

- Integrable divergence in reciprocal space for $\mathbf{G} = \mathbf{0}$.

- Remove the singulartiy due to PBC by "localising" the orbitals.
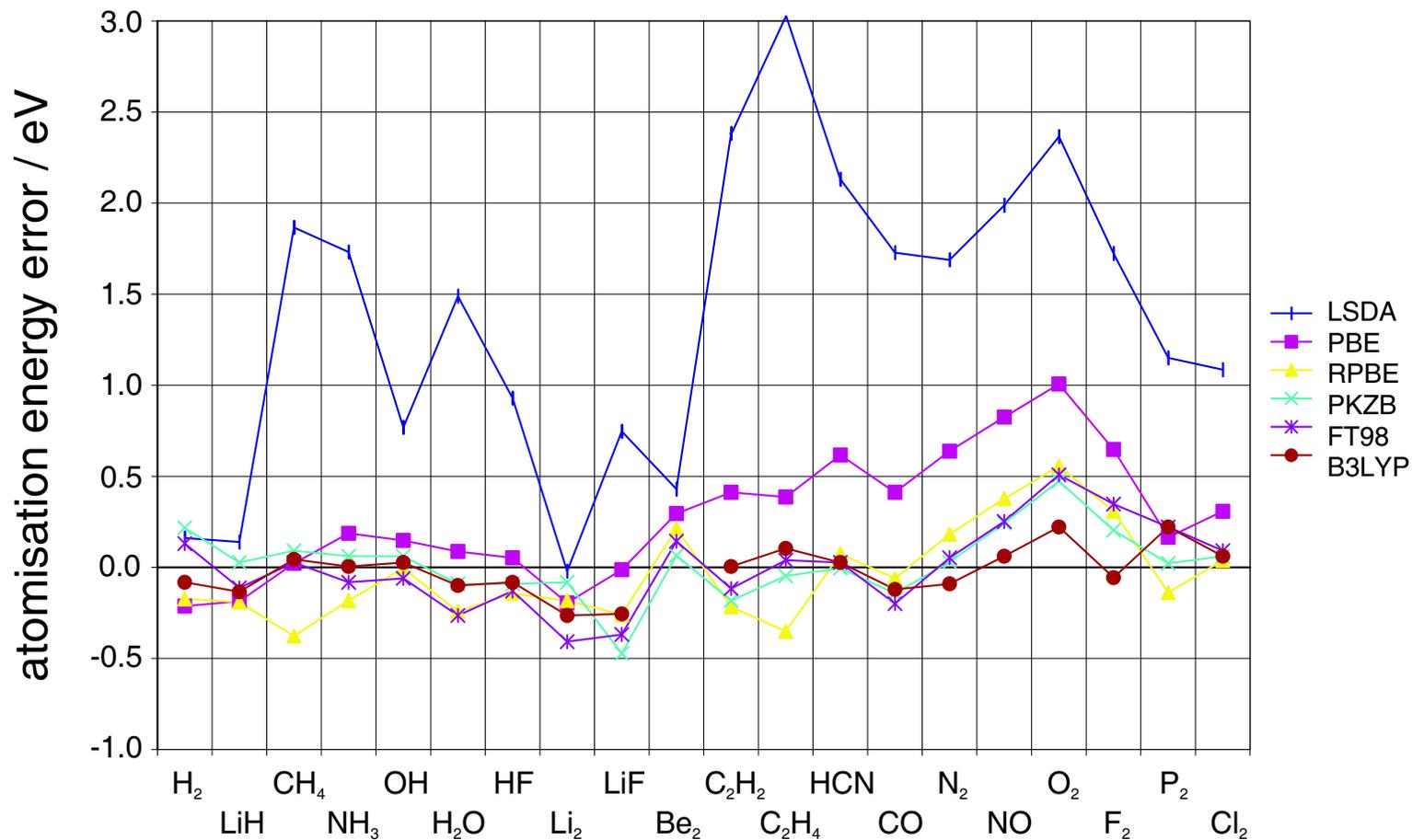
Figure 2: Atomisation energy errors ($E_{calc} - E_{exp}$) of small molecules (results from [7] (B3PW91) and [8])
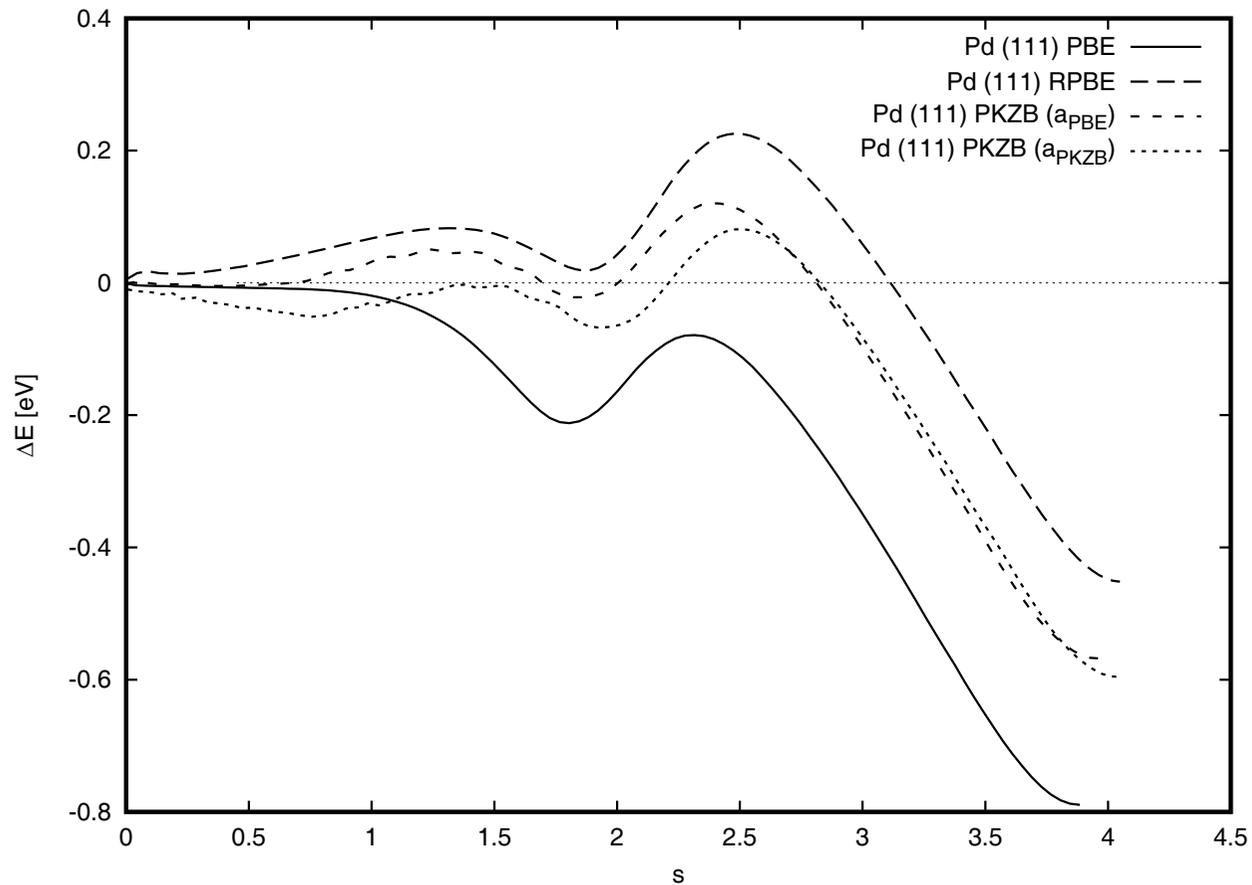
Figure 3: Minimum energy path (MEP) of the H_2 approach over the Pd(111) surface (RH, thesis)

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