Exchange-correlation Functionals in DFT

Lecture 31

CHM 652 / PHY 626
Electronic Structure of Materials

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XC Functionals in DFT

Adapted from Hardy Gross's lecture

https://www.youtube.com/watch?v=dhaI8xXY_fo&t=2619s

Local density approximation (LDA)

$E_{xc}[\rho] =$ smallest part of total energy

simplest approximation : $E_{xc}[\rho] \equiv 0 \;\Rightarrow$ Hartree approach

Result: lattice constants and bonding distances much too large (20%-50%)

$\Rightarrow E_{xc} =$ Nature's glue

LDA (Kohn and Sham, 1965)

$$E_{xc}^{LDA}[\rho] = \int d^3r\, \rho(\vec{r})\, \varepsilon_{xc}^{unif}\left(\rho(\vec{r})\right)$$

$\varepsilon_{xc}^{unif}(\rho)$ xc energy per particle of a uniform electron gas of density ρ
(known from quantum Monte-Carlo and many-body theory)

Result: decent lattice constants, phonons, surface energies of metals

Quantity	Typical deviation (from expt)
• Atomic & molecular ground state energies	< 0.5 %
• Molecular equilibrium distances	< 5 %
• Band structure of metals, Fermi surfaces	few %
• Lattice constants	< 2 %

Systematic error of LDA: Molecular atomisation energies too large and bond lengths and lattice constants too small

One would expect the LDA to be good only for weakly inhomogeneous systems, i.e., systems whose density satisfies:

$$\frac{|\nabla\rho|}{\rho} << k_F = \left(3\pi^2\rho\right)^{1/3} \qquad \text{and} \qquad \frac{|\nabla\rho|}{\rho} << k_{TF} = 4(3\rho/\pi)^{1/6}$$

Why is the LDA good also for strongly inhomogeneous systems?

Answer: Satisfaction of many exact constraints (features of exact xc fctl)

$$E_{xc}^{LDA}[\rho] = \frac{1}{2}\int d^3r\, \rho(\vec{r}) \int d^3r' \frac{\bar{n}_{xc}^{LDA}(\vec{r},\vec{r}\,')}{|\vec{r}\,' - \vec{r}|}$$

$\bar{n}_{xc}(\vec{r},\vec{r}\,')$ coupling-constant-averaged xc hole density $n_{xc} = n_x + n_c$

Important constraints:

$$\int d^3r'\, n_x(\vec{r},\vec{r}\,') = -1 \qquad \int d^3r'\, \bar{n}_c(\vec{r},\vec{r}\,') = 0 \qquad n_x \le 0$$

are satisfied in LDA

Generalized Gradient Approximations (GGA)

$$E_{xc}^{GGA}[\rho] = \int d^3r\ f\left(\rho(\vec{r}), \left|\nabla\rho(\vec{r})\right|\right)$$

Langreth, Mehl (1983), Becke (1986), Perdew, Wang (1988)
PBE: Perdew, Burke, Ernzerhof (1996)

Construction principle: Satisfaction of exact constraints
(important lesson from LDA and from gradient expansion of E_{xc})

Results: GGAs reduce the LDA error in the atomisation energy significantly (but not completely) while LDA bond lengths are over-corrected (i.e. are in GGA too large compared with expt)

Detailed study of molecules (atomization energies)

B. G. Johnson, P. M. W. Gill, J. A. Pople, *J. Chem. Phys.* 97, 7847 (1992)

32 molecules (all neutral diatomics from first-row atoms only and H_2)

Atomization energies (kcal/mol) from:

	$E_x^B + E_c^{VWN}$	$E_x^B + E_c^{LYP}$	HF
mean deviation from experiment	0.1	1.0	-85.8
mean absolute deviation	4.4	5.6	85.8

for comparison:	MP2
	-22.4
	22.4

LIMITATIONS OF LDA/GGA

- Not free from spurious self-interactions: KS potential decays more rapidly than r^{-1} for finite systems

  Consequences:
  - no Rydberg series
  - negative atomic ions not bound
  - ionization potentials (if calculated from highest occupied orbital energy) too small

- Dispersion forces cannot be described

  $W_{int}(R) \longrightarrow e^{-R}$ (rather than R^{-6})

- band gaps too small: G

  $E_{gap}(\mathrm{LDA/GGA}) \approx 0.5\, E_{gap}(\mathrm{expt})$

- Energy-structure dilemma of GGAs

  atomisation energies too large
  bond lengths too large
  (no GGA known that gets both correct!!)

- Wrong ground state for strongly correlated solids, e.g. CoO, La_2CuO_4 predicted as metals

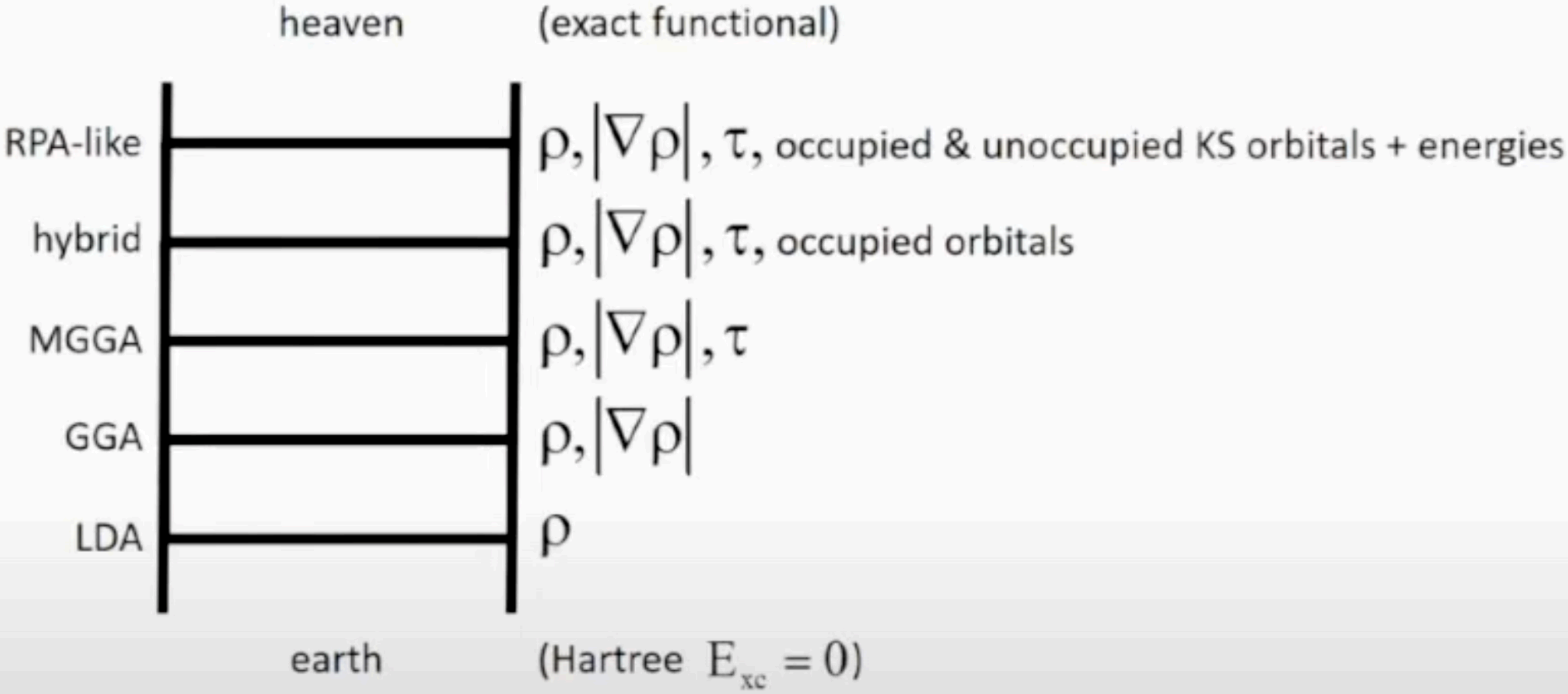
Meta Generalized Gradient Approximations (MGGA)

$$E_{xc}^{MGGA}[\rho] = \int d^3r\, \rho(\vec{r})\, \varepsilon_{xc}^{MGGA}\left(\rho(\vec{r}), |\nabla\rho(\vec{r})|, \tau(\vec{r})\right)$$

$$\tau(\vec{r}) = \frac{1}{2} \sum_{\alpha,\sigma}^{occup} \left|\nabla\psi_{\alpha,\sigma}(\vec{r})\right|^2 \qquad T_s[n] = \int d^3r\, \tau(\vec{r})$$

Result: Solves energy-structure dilemma of GGAs

Jacob's ladder of xc functionals (John Perdew)



heaven (exact functional)

RPA-like $\rho, |\nabla\rho|, \tau,$ occupied & unoccupied KS orbitals + energies

hybrid $\rho, |\nabla\rho|, \tau,$ occupied orbitals

MGGA $\rho, |\nabla\rho|, \tau$

GGA $\rho, |\nabla\rho|$

LDA ρ

earth (Hartree $E_{xc} = 0$)

Adiabatic Connection Formula

$$H(\lambda) = T + \sum_{i=1}^{N} v_{\lambda}(r_i) + \lambda \frac{e^2}{2} \sum_{\substack{i,k=1 \\ i \neq k}}^{N} \frac{1}{|r_i - r_k|} \qquad 0 \leq \lambda \leq 1$$

$$H(\lambda=1) = T + \sum_{i=1}^{N} v_{\text{nuc}}(r_i) + \frac{e^2}{2} \sum_{\substack{i,k=1 \\ i \neq k}}^{N} \frac{1}{|r_i - r_k|}$$

= Hamiltonian of fully interacting system

Choose $v_{\lambda}(r)$ such that for each λ the ground- state density satisfies $\rho_{\lambda}(r) = \rho_{\lambda=1}(r)$

Hence $v_{\lambda=0}(r) = v_{KS}(r)$
$v_{\lambda=1}(r) = v_{\text{nuc}}(r)$

Solve many-body Schroedinger eq for each λ, yielding Ψ_{λ}

Exact representation of $E_{xc}[\rho]$:

$$E_{xc}[\rho] = \int_0^1 d\lambda W_\lambda[\rho] \qquad W_\lambda = \langle \psi_\lambda | V_{ee} | \psi_\lambda \rangle - E_H[\rho]$$

$$\begin{aligned} W_0 &= \langle \psi_0 | V_{ee} | \psi_0 \rangle - E_H[\rho] \\ &= \text{HF exchange} \\ &= E_x^{HF}\left[\{\varphi_i\}\right] \end{aligned}$$

$W_0^{'} = 2E_c^{GL2}$ (Correlation energy in 2nd-order Görling-Levy perturbation theory)

Becke (JCP 1993): $W_\lambda = a + b\lambda$

$$E_{xc}^{BHH} = \frac{1}{2}\left(W_0 + \underset{\underset{\text{GGA}}{\uparrow}}{W_1}\right) \cong \frac{1}{2}E_x^{HF} + \frac{1}{2}W_1^{DFA}$$

$$E_{xc}^{PBE0} = 0.25E_x^{HF} + 0.75E_x^{PBE} + E_c^{PBE}$$

$$E_{xc}^{B3LYP} = 0.2E_x^{HF} + 0.8E_x^{LDA} + 0.72E_x^{B88} + 0.8E_c^{LYP} + 0.15E_c^{VWN}$$

Another way of constructing hybrids: Range separation (Savin, Baer, Kronik)

$$\frac{1}{r_{ij}} = \underbrace{\frac{\mathrm{erf}(\mu r_{ij})}{r_{ij}}}_{\text{long range}} + \underbrace{\frac{\mathrm{erfc}(\mu r_{ij})}{r_{ij}}}_{\text{short range}}$$

- Treat long-range part by wavefunction theory, HF
- Treat short-range part by density functional approximation (GGA)

For solids, it makes sense to do it the other way around
(Heyd, Scuseria, Ernzerhof):

$$E_{xc}^{HSE} = aE_x^{HF,SR}(\mu) + (1-a)E_x^{PBE,SR}(\mu) + E_x^{PBE,LR}(\mu) + E_c^{PBE}$$

5th-rung functionals (using unoccupied KS orbitals)

$$E_c^{MP2} = \frac{1}{2} \sum_{ij}^{\text{occup}} \sum_{ab}^{\text{unoccup}} \frac{\left| \langle ij || ab \rangle \right|^2}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b}$$

$E_c^{RPA}[G_{KS}]$ and beyond RPA-functionals, e.g. E_c^{RPA} plus TDDFT

$$E_{xc} = -\int_0^1 d\lambda \int_0^\infty \frac{du}{2\pi} \int d^3r \int d^3r' \frac{e^2}{|r - r'|} \left\{ \chi^{(\lambda)}(r, r'; iu) + \rho(r)\delta(r - r') \right\}$$

with the response function $\chi^{(\lambda)}(r,r';\omega)$ corresponding to $H(\lambda)$.
$\chi^{(\lambda)}(r,r';\omega)$ can be obtained from linear-response TDDFT

$$\chi^{(\lambda)} = \chi_s + \chi_s \left[\lambda W_{Clb} + f_{xc}^{(\lambda)} \right] \chi^{(\lambda)}$$

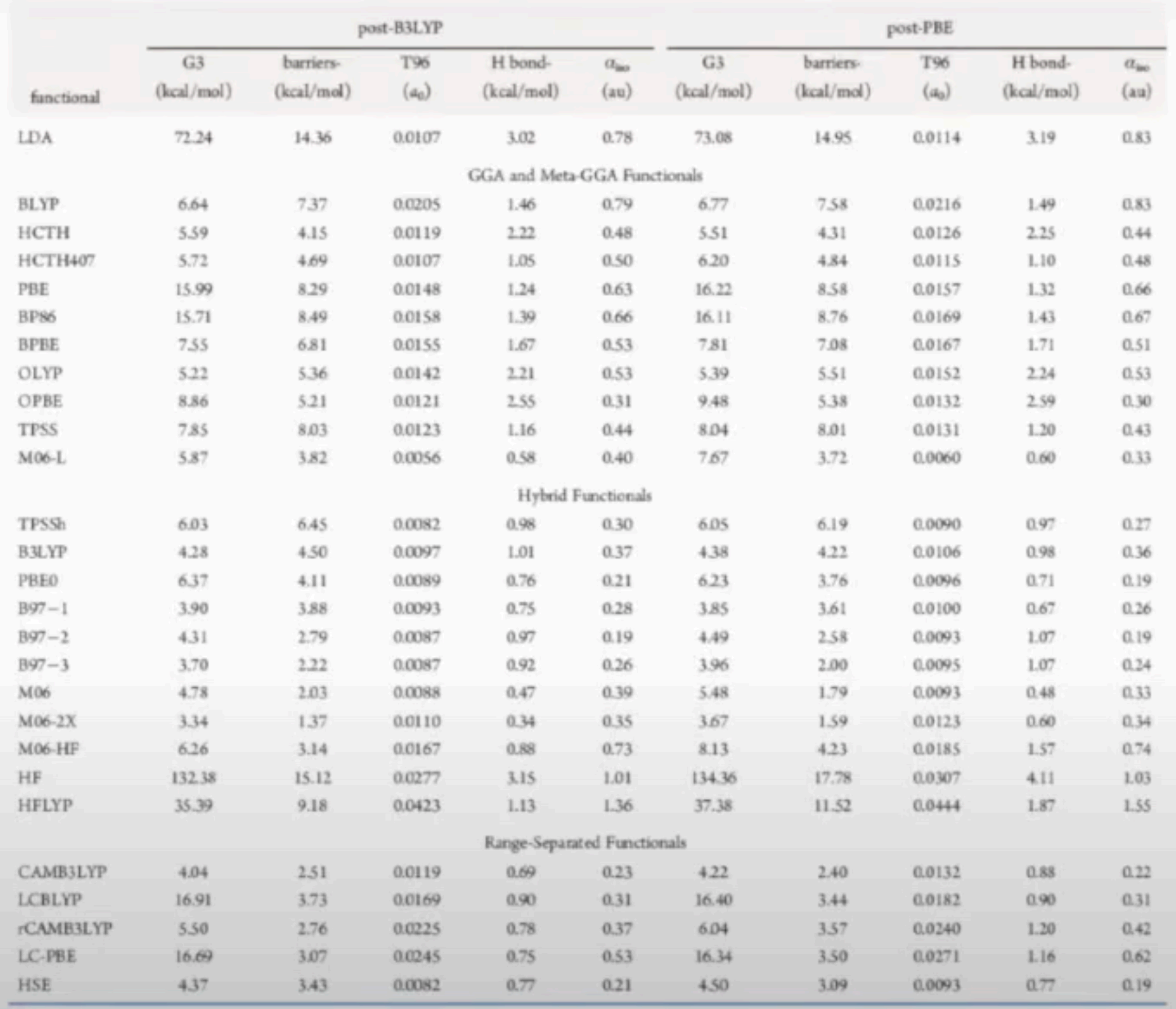
- Non-selfconsistently:
  post-LDA, post-GGA, or post-HF

- Self-consistently, the Kohn-Sham way, yielding the Optimized-Effective Potential (OEP) procedure.
  This determines the variationally best local potential (i.e. the potential whose orbitals minimize the given orbital functional for the total energy)

- Self-consistently, the Generalised Kohn-Sham (GKS) way.
  This determines the variationally best orbitals (not restricted to come from a local potential). The resuting GKS potential can be non-local

- Self-consistently, using the Gidopoulos variational principle.
  This avoids the variational collapse of PT-derived functionals.
  N.I. Gidopoulos, Phys. Rev. A 83, 040502(R), (2011)

- Self-consistently, using the Sham-Schlüter-way (specifically for functionals coming from an approximation of $\Sigma[G_{KS}]$). **This yields that local potential whose density reproduces the density of G**



functional	post-B3LYP G3 (kcal/mol)	barriers (kcal/mol)	T96 (a_0)	H bond (kcal/mol)	α_{iso} (au)	post-PBE G3 (kcal/mol)	barriers (kcal/mol)	T96 (a_0)	H bond (kcal/mol)	α_{iso} (au)
LDA	72.24	14.36	0.0107	3.02	0.78	73.08	14.95	0.0114	3.19	0.83
GGA and Meta-GGA Functionals										
BLYP	6.64	7.37	0.0205	1.46	0.79	6.77	7.58	0.0216	1.49	0.83
HCTH	5.59	4.15	0.0119	2.22	0.48	5.51	4.31	0.0126	2.25	0.44
HCTH407	5.72	4.69	0.0107	1.05	0.50	6.20	4.84	0.0115	1.10	0.48
PBE	15.99	8.29	0.0148	1.24	0.63	16.22	8.58	0.0157	1.32	0.66
BP86	15.71	8.49	0.0158	1.39	0.66	16.11	8.76	0.0169	1.43	0.67
BPBE	7.55	6.81	0.0155	1.67	0.53	7.81	7.08	0.0167	1.71	0.51
OLYP	5.22	5.36	0.0142	2.21	0.53	5.39	5.51	0.0152	2.24	0.53
OPBE	8.86	5.21	0.0121	2.55	0.31	9.48	5.38	0.0132	2.59	0.30
TPSS	7.85	8.03	0.0123	1.16	0.44	8.04	8.01	0.0131	1.20	0.43
M06-L	5.87	3.82	0.0056	0.58	0.40	7.67	3.72	0.0060	0.60	0.33
Hybrid Functionals										
TPSSh	6.03	6.45	0.0082	0.98	0.30	6.05	6.19	0.0090	0.97	0.27
B3LYP	4.28	4.50	0.0097	1.01	0.37	4.38	4.22	0.0106	0.98	0.36
PBE0	6.37	4.11	0.0089	0.76	0.21	6.23	3.76	0.0096	0.71	0.19
B97−1	3.90	3.88	0.0093	0.75	0.28	3.85	3.61	0.0100	0.67	0.26
B97−2	4.31	2.79	0.0087	0.97	0.19	4.49	2.58	0.0093	1.07	0.19
B97−3	3.70	2.22	0.0087	0.92	0.26	3.96	2.00	0.0095	1.07	0.24
M06	4.78	2.03	0.0088	0.47	0.39	5.48	1.79	0.0093	0.48	0.33
M06-2X	3.34	1.37	0.0110	0.34	0.35	3.67	1.59	0.0123	0.60	0.34
M06-HF	6.26	3.14	0.0167	0.88	0.73	8.13	4.23	0.0185	1.57	0.74
HF	132.38	15.12	0.0277	3.15	1.01	134.36	17.78	0.0307	4.11	1.03
HFLYP	35.39	9.18	0.0423	1.13	1.36	37.38	11.52	0.0444	1.87	1.55
Range-Separated Functionals										
CAMB3LYP	4.04	2.51	0.0119	0.69	0.23	4.22	2.40	0.0132	0.88	0.22
LCBLYP	16.91	3.73	0.0169	0.90	0.31	16.40	3.44	0.0182	0.90	0.31
rCAMB3LYP	5.50	2.76	0.0225	0.78	0.37	6.04	3.57	0.0240	1.20	0.42
LC-PBE	16.69	3.07	0.0245	0.75	0.53	16.34	3.50	0.0271	1.16	0.62
HSE	4.37	3.43	0.0082	0.77	0.21	4.50	3.09	0.0093	0.77	0.19