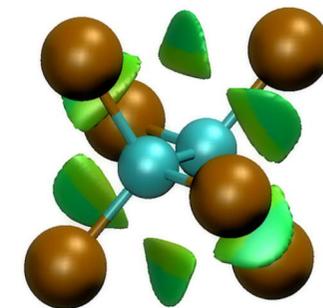
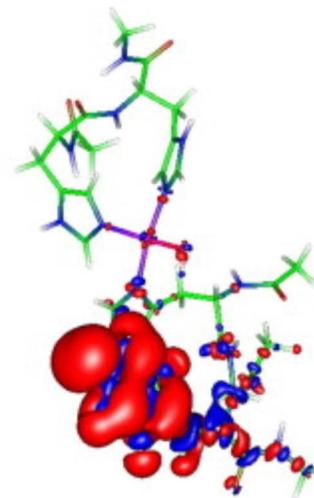
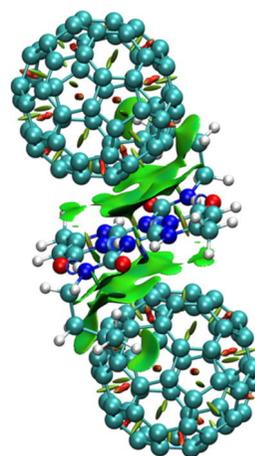
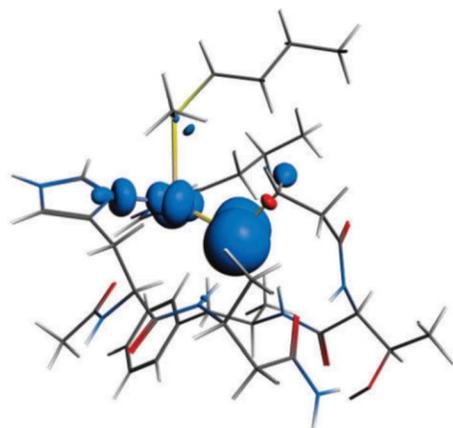
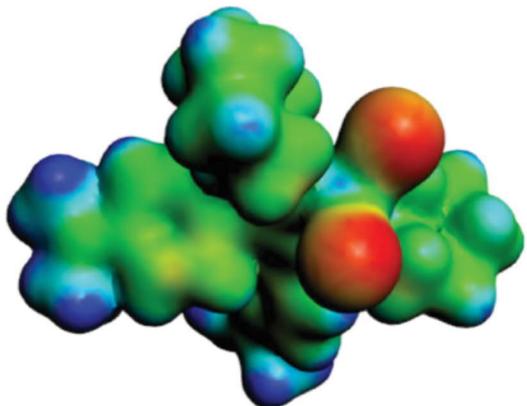


CSC/PRACE Spring School in Computational Chemistry 2020

Introduction to Electronic Structure Theory

Mikael Johansson

Part II: Density Functional Theory



The basic ideas of DFT

- The foundation for contemporary DFT is the Hohenberg–Kohn theorem (1964)
 - *The energy of a molecular system, as well as all other observables are unambiguously defined by the electron density of the system*
- Implication: No direct knowledge of the wave function is necessary, and thus, **no need to solve the Schrödinger equation**
- An exact solution of the SE requires, in principle, a computational effort scaling **exponentially** with the number of electrons
 - The dimensionality of FCI is approximately $[N!/(n/2)! \cdot (N-n/2)!]^2$ $N =$ number of orbitals,
 $n =$ number of electrons
- In contrast, the equations of the perfect density functionals should require an effort **independent of the number of electrons**; the dimensionality would be 3.
 - The development of functionals are nowhere near this nirvana
- Next, we will have a quick look at different density functional types in use today
 - pre-HK DFT (Thomas–Fermi, Dirac) will be left for self-study

The Hohenberg–Kohn theorem

The potential for the ground state of a finite system is directly (up to a constant) defined by the electron density

Proof: let $v(r)$ be the potential and $\rho(r)$ the electron density. If the HK theorem would *not* be true, another potential $v'(r)$, where $\mathbf{v}'(\mathbf{r}) \neq \mathbf{v}(\mathbf{r}) + \text{constant}$, giving the same $\rho(r)$ should exist. Thus, also two different wave functions, Ψ and Ψ' , corresponding to the external potential v and v' would exist

The variational principle: $E_0 = \langle \Psi | H | \Psi \rangle < \langle \Phi | H | \Phi \rangle$, Ψ is the exact wf, Φ not

Now, with $\rho(r)$ and $\rho'(r)$ identical, identical kinetic energies and electron-electron interaction for H and H'

→

$$\begin{aligned} E_0 = \langle \Psi | H | \Psi \rangle &< \langle \Psi' | H | \Psi' \rangle = \langle \Psi' | H - H' + H' | \Psi' \rangle \\ &= \langle \Psi' | H' | \Psi' \rangle + \langle \Psi' | H - H' | \Psi' \rangle = E'_0 + \langle \Psi' | H - H' | \Psi' \rangle \end{aligned}$$

but also:

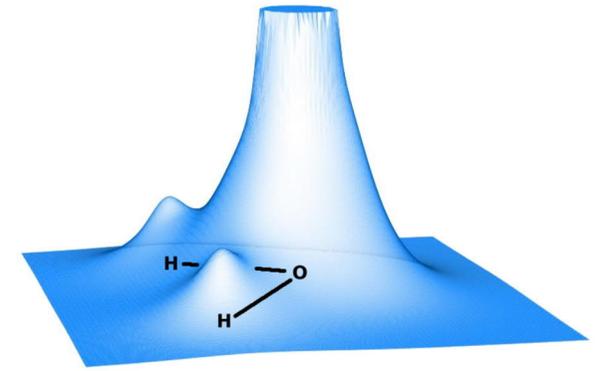
$$E'_0 = \langle \Psi' | H' | \Psi' \rangle < \langle \Psi | H' | \Psi \rangle = \langle \Psi | H | \Psi \rangle + \langle \Psi | H' - H | \Psi \rangle = E_0 + \langle \Psi | H' - H | \Psi \rangle$$

- The above *cannot be true*, as it implies $E_0 > E'_0 > E_0$

The Hohenberg–Kohn theorem according to E.B. Wilson

Another way of looking at it:

- 1) The electron density $\rho(\mathbf{r})$ contains **the number of electrons** in the system
- 2) Cusps in $\rho(\mathbf{r})$ appear at atomic nuclei, defining **the position of atoms**
- 3) The forms of the cusps define the number of protons, that is, **the atom types**



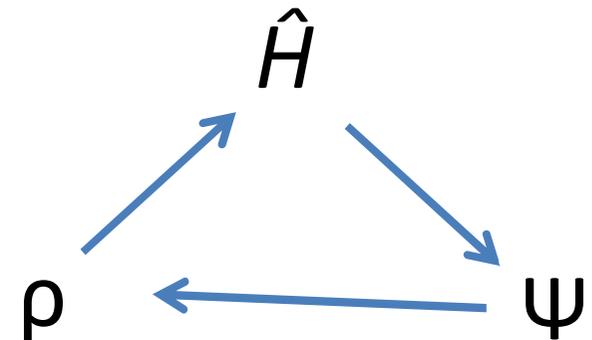
$$Z_k = -\frac{a_0}{2n(\mathbf{r})} \left. \frac{dn(\mathbf{r})}{dr} \right|_{r \rightarrow \mathbf{R}_k}$$

We note that in order to define the molecular electronic Hamiltonian, only the number of electrons and the atomic coordinates, which make up the external potential, are needed;

we have everything in $\rho(\mathbf{r})$!

$$\hat{H} = -\frac{1}{2} \sum_i^n \nabla_i^2 - \sum_i^n \sum_I^N \frac{Z_I}{r_{Ii}} + \sum_{i < j}^n \frac{1}{r_{ij}} + V^{\text{nuc}}$$

\hat{T}_e , electronic kinetic energy (points to $-\frac{1}{2} \sum_i^n \nabla_i^2$)
 \hat{V}_{ee} , electron-electron repulsion (points to $\sum_{i < j}^n \frac{1}{r_{ij}}$)
 \hat{V}_{ne} , electron-nucleus attraction (points to $-\sum_i^n \sum_I^N \frac{Z_I}{r_{Ii}}$)
 \hat{V}_{nn} , nucleus-nucleus repulsion (points to V^{nuc})



Kohn–Sham DFT

- Idea based on **Hartree’s model** where the electrons move in an effective potential created by the nuclei and the *mean field* created by the other electrons

$$v_{\text{H}}(\mathbf{r}) = - \sum_a \frac{Z_a}{|\mathbf{R}_a - \mathbf{r}|} + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \quad \left[-\frac{1}{2} \nabla^2 + v_{\text{H}}(\mathbf{r}) \right] \psi_i = e_i \psi_i$$

- In **Kohn–Sham DFT**, a system of **independent non-interacting electrons** in a common one-body potential, v_{KS} , is imagined
- KS also introduced orbitals into DFT, originally *assumed* to be independent reference orbitals fulfilling the Schrödinger equation for independent particles:

$$\left[-\frac{1}{2} \nabla^2 + v_{\text{KS}} \right] \psi_i = e_i \psi_i$$

Kohn–Sham DFT

- The introduction of orbitals **increases the dimensionality of DFT** from 3 to **3N**
- This is more than compensated for by a **much-improved** description of the **kinetic energy**
 - Still, dimensionality the same as for the simplest wave function methods!
- The KE for the **non-interacting** electrons is then (lower index *s* denotes *single*-electron equations):

$$T_s[\rho] = \sum_{i=1}^N \langle \psi_i | -\frac{1}{2} \nabla^2 | \psi_i \rangle$$

- Electrons of course *do* interact, and the missing part is denoted the correlation kinetic energy

$$T_c[\rho] = T[\rho] - T_s[\rho] \geq 0$$

- T_c is usually included in an **exchange/correlation** term E_{xc}
 - The amount of kinetic correlation energy is of the same order of magnitude as the total correlation energy, but always of opposite sign
- Now, the KS equations can be solved analogously to the SCF Hartree equations

Kohn–Sham DFT

- Within KS-DFT, the energy of the ground state, divided into its components, is then given by:

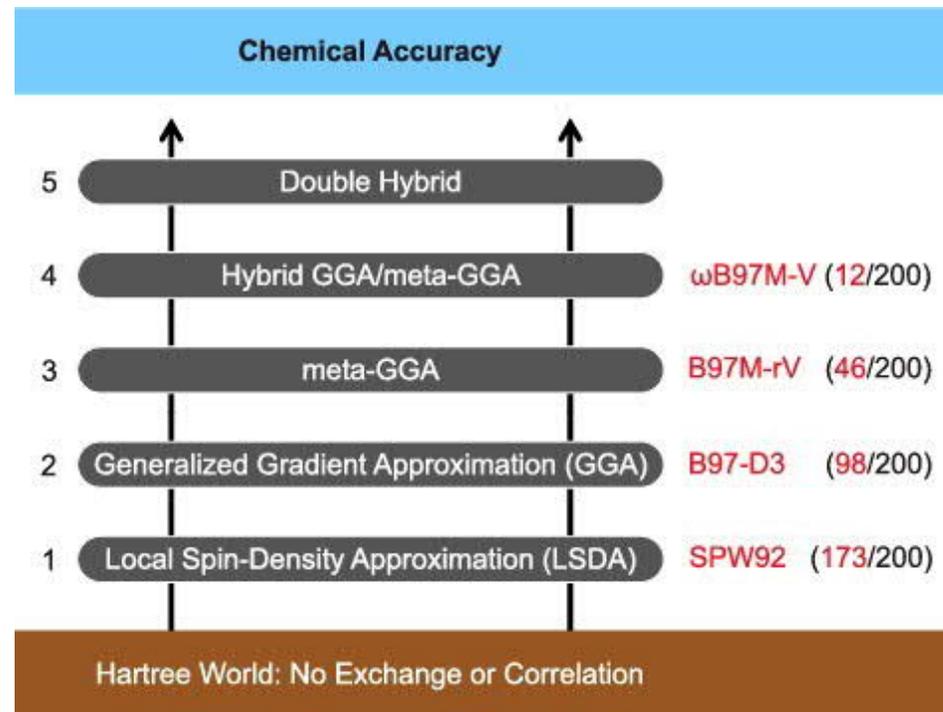
$$E^{\text{DFT}}[\rho] = T_s[\rho] + E_{\text{ne}}[\rho] + J[\rho] + E_{\text{xc}}[\rho]$$

- We now have an **exact energy expression**
- Further, of the terms, all but the last, the exchange/correlation energy, *can* be solved exactly
- Kohn and Sham paved the way for a renaissance for DFT
 - The problem of the kinetic energy was largely solved
- **New challenge:** Find a solution for E_{xc}

Different DFT models

- In wave function theory, there is a **systematic way of improving the quality of the model**
 - Not much joy if the systems are so large that nothing proper can be performed...
- Within DFT, **the exact functional really is unknown**
 - Some **constraints** on properties the functional should fulfil *are* known

- Hierarchies of complexity *do* exist also within **DFT**
- The idea is to include **more complex properties** of the electron density into the description
- Climbing **Jacob's ladder of DFT**: each rung bringing the functional closer to perfection
 - Perdew *et al.*, "Some Fundamental Issues in Ground-State Density Functional Theory: A Guide for the Perplexed", *J. Chem. Theory Comput.* **5** (2009) 902, <http://dx.doi.org/10.1021/ct800531s>
 - Mardirossian & Head-Gordon (2017) "Thirty years of density functional theory in computational chemistry: an overview and extensive assessment of 200 density functionals" <https://doi.org/10.1080/00268976.2017.1333644>



The Local Density Approximation (LDA)

- Takes only the electron density in specific points in space into account $\varepsilon^{\text{LSDA}} = \varepsilon^{\text{LSDA}}(\rho_\alpha, \rho_\beta)$
- In LDA, the electron density is assumed to vary slowly in space

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

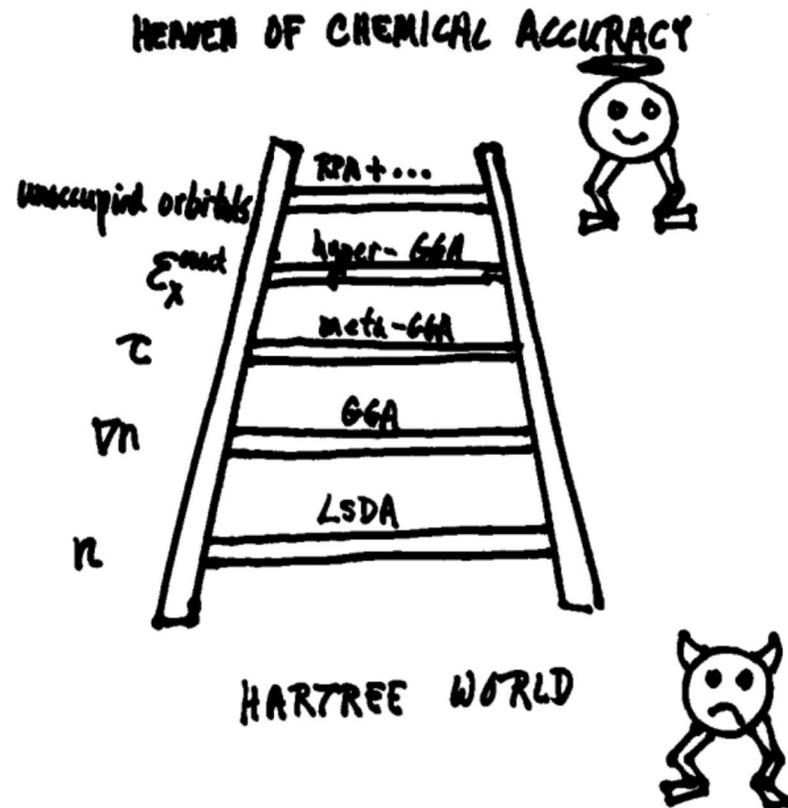
- The exchange energy of a uniform electron gas is analytically known (Slater/Dirac/Bloch exchange)

$$E_{\text{x}}^{\text{LDA}}[\rho] = -C_{\text{x}} \int \rho^{4/3}(\mathbf{r}) d\mathbf{r}, \quad C_{\text{x}} = \frac{3}{4} \left(\frac{3}{\pi} \right)^{1/3}$$

- This is where the train stops for analytically derived DFT
- There is no known equation for the correlation energy for even such a simple model system as the uniform electron gas!
 - It can, however, be computed very accurately using quantum Monte Carlo, and numerical fits to the results can be formulated
- The fact remains that already the LDA correlation functionals are nothing but *ad hoc* functionals with no real physical meaning except that they provide good results

Chemically useful approximations

- LDA is not accurate enough for chemistry
 - On rare occasions, it *seems* to be, but only due to heavy error cancellation
- In order to construct more accurate functionals, one notes that $\rho(\mathbf{r})$ contains *much more information than just the electron density at specific points*
- Increased accuracy (usually) comes at a price: Climbing the ladder makes the calculations more expensive!



The Generalised Gradient Approximation

- The electron density is *not* uniform
- GGAs account for this by also considering the **gradient of the density** $\nabla\rho$ into account
 - Introduced in 1986 by Perdew and Wang; before, gradients had only been considered to second order, $|\nabla\rho|^2$
 - Term generalised comes from the GGAs considering higher powers of $|\nabla\rho|$ into account; *generally*, any power
- A general GGA thus has the form $\varepsilon^{\text{GGA}} = \varepsilon^{\text{GGA}}(\rho_\alpha, \rho_\beta, \nabla\rho_\alpha, \nabla\rho_\beta)$
- GGAs are **semi-local**
- Usually build upon the LDA expressions:

$$E_x^{\text{B88}} = E_x^{\text{LSDA}} - \beta \sum_\sigma \int \rho_\sigma^{4/3} \frac{x_\sigma^2}{1 + 6\beta x_\sigma \sinh^{-1} x_\sigma} d\mathbf{r}$$

$$\varepsilon_c^{\text{PBE}}(r_s, \zeta, t) = \varepsilon_c^{\text{PW92}}(r_s, \zeta) + H(r_s, \zeta, t)$$

Meta-GGAs

- In addition to ρ and $\nabla\rho$, also the **Laplacian** $\nabla^2\rho$ and/or **the kinetic energy density** τ considered

$$\varepsilon^{\text{mGGA}} = \varepsilon^{\text{mGGA}}(\rho_\alpha, \rho_\beta, \nabla\rho_\alpha, \nabla\rho_\beta, \nabla^2\rho_\alpha, \nabla^2\rho_\beta, \tau_\alpha, \tau_\beta) \quad \tau_\sigma(\mathbf{r}) = \frac{1}{2} \sum_i^{\text{occ}} |\nabla\psi_{i\sigma}(\mathbf{r})|^2$$

- τ depends on the KS orbitals, meta-GGAs that use τ are thus **non-local**

Hybrid functionals

- Hartree–Fock can in principle provide the **exact exchange** energy via the orbitals

$$E_x^{\text{HF}} = -\frac{1}{2} \sum_i^n \sum_j^n \int \int \frac{\psi_i(\mathbf{r}_1)\psi_j(\mathbf{r}_1)\psi_i(\mathbf{r}_2)\psi_j(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2$$

- A **hybrid method** combines HF-like exchange energy with a DFT description of E_{xc}
- The simplest hybrid would just take HF exchange and DFT correlation $E_{xc} = E_x^{\text{HF}} + E_c^{\text{DFT}}$
 - Too simple, doesn't work well
- Combining **a fraction** of HF-like exchange improves thermochemical results **dramatically**
- **B3LYP** (1993!) made many chemists true believers in the power of DFT

$$E_{xc}^{\text{B3LYP}} = a_0 E_x^{\text{HF}} + (1 - a_0) E_x^{\text{LSDA}} + a_x \Delta E_x^{\text{B88}} + (1 - a_c) E_c^{\text{VWN}} + a_c E_c^{\text{LYP}}$$

- Others found the fraction Frankensteinian:
 - P. Gill, "Obituary: Density Functional Theory (1927-1993)", *Aust. J. Chem.* **54** (2001) 661, <http://dx.doi.org/10.1071/CH02049>

Functional development philosophies

- Even with the **ingredients** of different levels of DFT in place, the actual **recipe** on how to use them is completely open
- Different approaches exist
 - Invent a functional form that reproduces wanted data: **empirical**
 - Invent a functional form that fulfils known properties of the true functional: **non-empirical**
 - Use both approaches; often starting from a non-empirical formulation and slightly adjusting it for pragmatic reasons
- Empirical functionals usually work well **for systems similar to those parameterised for**
 - Can fail spectacularly when outside their comfort region
- Non-empirical functionals usually perform less well
 - But without parameters for specific systems, can be hoped to perform equally well for “everything”

Non-empirical functionals

- **LDA is usually non-empirical**
- GGAs and meta-GGAs come in many forms, most of which have at least some parameters fitted to experimental data
- The typical non-empirical GGA is **PBE**, for solids **PBEsol** is better
- The typical non-empirical meta-GGA is **TPSS**, an even better one is **revTPSS**:
 - Perdew *et al*, “Workhorse Semilocal Density Functional for Condensed Matter Physics and Quantum Chemistry”, *PRL* **103** 026403, <http://dx.doi.org/10.1103/PhysRevLett.103.026403>
- **A closer look at PBE**, *Phys. Rev. Lett.* **77** (1996) 3865, <http://dx.doi.org/10.1103/PhysRevLett.77.3865>

PBE

Generalized Gradient Approximation Made Simple

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(Received 21 May 1996)

Generalized gradient approximations (GGA's) for the exchange-correlation energy improve upon the local spin density (LSD) description of atoms, molecules, and solids. We present a simple derivation of a simple GGA, in which all parameters (other than those in LSD) are fundamental constants. Only general features of the detailed construction underlying the Perdew-Wang 1991 (PW91) GGA are invoked. Improvements over PW91 include an accurate description of the linear response of the uniform electron gas, correct behavior under uniform scaling, and a smoother potential. [S0031-9007(96)01479-2]

- One motivation for the construction was to **simplify the non-empirical PW91 functional**
- For PBE, only conditions that were considered energetically important are satisfied
 - Less important conditions are ignored

Next up, a **quick non-detailed overview of the “derivation”**

PBE correlation

$$\varepsilon_c^{\text{PBE}}(r_s, \zeta, t) = \varepsilon_c^{\text{PW92}}(r_s, \zeta) + H(r_s, \zeta, t)$$

$$t = |\nabla\rho| / (2gk_s\rho) \quad \text{dimensionless density gradient}$$

$$r_s = (3 / (4\pi\rho))^{1/3} \quad \text{Wigner-Seitz radius (avg. radius containing one electron)}$$

$$\zeta = (\rho_\uparrow - \rho_\downarrow) / \rho \quad \text{relative spin polarisation}$$

- Builds upon LDA (specified as PW92 LDA)

PBE correlation

- Three exact conditions are satisfied

1. In the slowly varying limit ($t \rightarrow 0$), H should go to

$$H \rightarrow (e^2/a_0)\beta\phi^3t^2$$

2. In the rapidly varying limit ($t \rightarrow \infty$)

$$H \rightarrow -\epsilon_C^{\text{unif}}$$

This makes correlation vanish

3. Under uniform scaling, the correlation energy must scale to a constant

$$\rho_\lambda(x, y, z) = \lambda^3 \rho(\lambda x, \lambda y, \lambda z)$$

$$\lim_{\lambda \rightarrow \infty} E_c[\rho_\lambda] = \text{const} > -\infty$$

To achieve this, H must cancel the logarithmic singularity of ϵ_C^{LDA}

PBE correlation

- All the above three conditions are satisfied by the following form for H :

$$H = (e^2/a_0)\gamma\phi^3 \times \ln\left\{1 + \frac{\beta}{\gamma} t^2 \left[\frac{1 + At^2}{1 + At^2 + A^2t^4} \right] \right\},$$

where

$$A = \frac{\beta}{\gamma} [\exp\{-\epsilon_C^{\text{unif}}/(\gamma\phi^3 e^2/a_0)\} - 1]^{-1}.$$

- When $t=0$, H is exactly condition 1, when $t \rightarrow \infty$, H grows monotonically to the limit of condition 2
- Thus, $E_C^{\text{GGA}} \leq 0$

PBE correlation

- Compared to PW91, quite much simpler:

$$\varepsilon_c^{\text{PW91}}(r_s, \zeta, t) = \varepsilon_c^{\text{PW92}}(r_s, \zeta) + H_0(r_s, \zeta, t) + H_1(r_s, \zeta, t)$$

$$H_0(r_s, \zeta, t) = \frac{g^3 \beta^2}{2\alpha} \ln \left(1 + \frac{2\alpha}{\beta} \frac{t^2 + At^4}{1 + At^2 + A^2 t^4} \right)$$

$$A = \frac{2\alpha}{\beta} \frac{1}{e^{-2\alpha\varepsilon_c^{\text{PW92}}/(g^3\beta^2)} - 1}$$

$$H_1(r_s, \zeta, t) = \nu \left(C_c(r_s) - C_c(0) - \frac{3}{7}c_x \right) g^3 t^2 e^{-100g^4(k_s^2/k_F^2)t^2}$$

$$C_c(r_s) = \frac{0.002568 + 0.023266r_s + 7.389 \cdot 10^{-6}r_s^2}{1 + 8.723r_s + 0.472r_s^2 + 0.07389r_s^3} + 0.001667$$

PBE exchange

$$E_x^{\text{GGA}}[\rho] = \int f(\rho(\mathbf{r}), |\nabla\rho(\mathbf{r})|) d^3r = -C_x \int \rho^{4/3}(\mathbf{r}) F(s(\mathbf{r})) d^3r$$
$$s = |\nabla\rho| / (2\rho k_F) \text{ with } k_F = (3\pi^2\rho)^{1/3}$$

- Based on four additional conditions

Satisfied by the simple

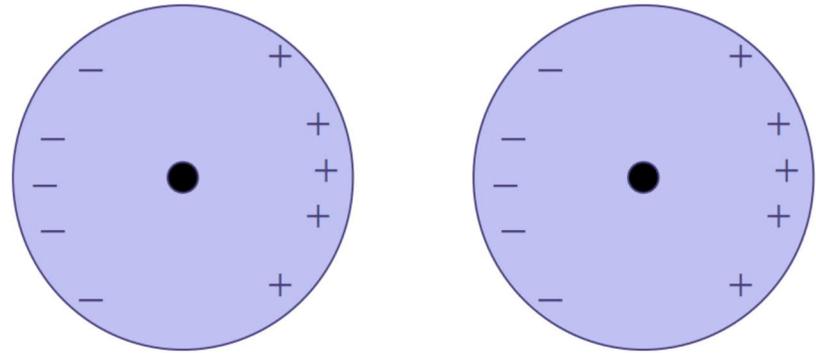
$$F^{\text{PBE}}(s) = 1 + 0.804 - \frac{0.804}{1 + \frac{0.21951}{0.804}s^2}$$

Again, quite much simpler than PW91:

$$F^{\text{PW91}}(s) = \frac{1 + 0.19645s \operatorname{arcsinh}(7.7956s) + (0.2743 - 0.1508e^{-100s^2}) s^2}{1 + 0.19645s \operatorname{arcsinh}(7.7956s) + 0.004s^4}$$

DFT for dispersion

- **What is dispersion interaction?**
- **Attraction** between neutral fragments due to polarisation caused by quantum fluctuations



- Also known as **van der Waals** and **London** forces
- Decays as R^{-6} , strength depends on the IP and polarisability of the fragments (London, 1930):

$$U_{\text{London}} = -\frac{2}{3} \frac{I_1 I_2}{I_1 + I_2} \alpha'_1 \alpha'_2 \frac{1}{r^6}$$

- **Nonlocal** phenomenon, no overlap of electron densities needed
- The functionals we have seen so far are (semi)local, at least up to GGA level
 - $E[\text{LDA}] = E[\rho]$
 - $E[\text{GGA}] = E[\rho, |\nabla\rho|^n]$
 - $E[\text{m-GGA}] = E[\rho, |\nabla\rho|^n, |\nabla^2\rho|, \tau]$ (**τ orbital dependent, though!**)
 - hybrids don't help, **vdW is correlation**

- Therefore, **there is no reason, even possibility** for vdW forces to be described well by semi-local functionals

DFT for dispersion

Some attempts to modify (reparametrize) existing functionals

- Cannot really work if the necessary physical information is missing!

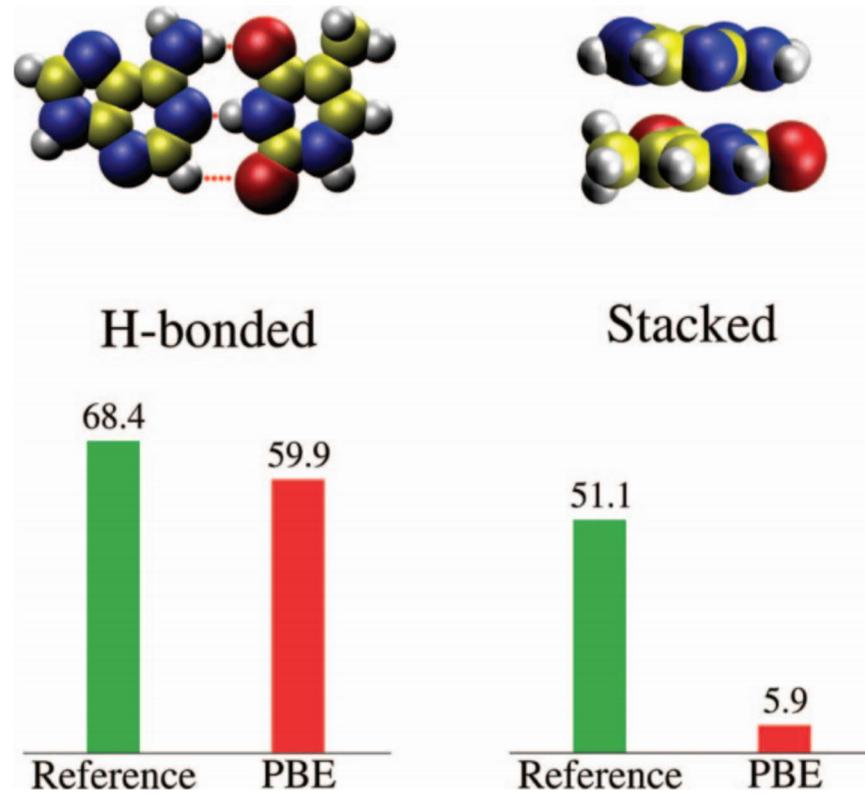


FIG. 3. Two binding configurations of the DNA base pairs adenine and thymine. A hydrogen bonded structure is shown on the left (hydrogen bonds indicated by red dots) and a “stacked” geometry on the right. For the hy-

DFT for dispersion – double hybrids

Incorporation of **correlated WF methods (MP2)** has also been used

THE JOURNAL OF CHEMICAL PHYSICS **124**, 034108 (2006)

Semiempirical hybrid density functional with perturbative second-order correlation

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The uniformity with which B2-PLYP improves for a wide range of chemical systems emphasizes the need of (virtual) orbital-dependent terms that describe nonlocal electron correlation in accurate exchange-correlation functionals. From a practical point of view, the new functional seems to be very robust and it is thus suggested as an efficient quantum chemical method of general purpose. © 2006 American Institute of Physics. [DOI: [10.1063/1.2148954](https://doi.org/10.1063/1.2148954)]

- **B2-PLYP**, Grimme *J. Chem. Phys.* **124** (2006) 034108
 - Based on the B88 exchange functional and the LYP correlation functional (BLYP)
- HF exact exchange added
- Second order perturbation (PT2/MP2) added: It is thus a **double-hybrid functional**

DFT for dispersion – B2PLYP

- On the **fifth rung of Jacob's ladder**, as it takes virtual orbitals into account

Our much simpler ansatz for a combination of KS-DFT and PT is based on the following expression for the exchange-correlation energy E_{xc} and is given by

$$E_{xc} = (1 - a_x)E_x^{GGA} + a_x E_x^{HF} + bE_c^{GGA} + cE_c^{PT2}, \quad (1)$$

where (in spin-orbital form)

$$E_c^{PT2} = \frac{1}{4} \sum_{ia} \sum_{jb} \frac{[(ia|jb) - (ib|ja)]^2}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b}. \quad (2)$$

DFT for dispersion – B2PLYP

- **“Drawbacks” of B2-PLYP compared to “normal” DFT**
- Higher basis set demand
 - The virtual space in the PT2 treatment requires larger basis sets, just as normal WF MP2
 - Minimum recommended: TZVPP
 - “I would consider an B2PLYP/6-31g* type calculation as almost useless”, Grimme, CCL 16 Oct 2009
- Somewhat larger computational cost
 - Compared to other hybrids, not that bad, as the MP2 term can be computed quite efficiently with RI (RI-B2-PLYP)
- **Still not that good for long-range dispersion!**
 - PT2 part relatively small compared to the poorly performing LYP correlation
- Overall, **seems to work quite well**, however
- Newer double hybrids among the best for thermochemistry *for molecules made from main-group elements*

Empirical force-field type dispersion on top of DFT: DFT-D

- MM force fields can perform much better for dispersion than DFT, at least for dispersion
- The R^{-6} term is simply one of the force field parameters
- As dispersion is long-range, it usually has a very **small effect on the total density**
- This motivates the general form of DFT-D

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

- The dispersion correction is just **added on top** of the normal DFT calculation
- The potential energy surface is thus modified, and better geometries and binding energies should then be obtained

DFT-D

- The form of E_{disp} is relatively simple (Grimme, *J. Comput. Chem.* 27 (2006) 1787 (actually, the second incarnation, DFT-D2):

$$E_{\text{disp}} = -s_6 \sum_{i=1}^{N_{\text{at}}-1} \sum_{j=i+1}^{N_{\text{at}}} \frac{C_6^{ij}}{R_{ij}^6} f_{\text{dmp}}(R_{ij})$$

N_{at} is the number of atoms

C_6 are atomic dispersion coefficients, and $C_6^{ij} = \sqrt{C_6^i C_6^j}$

s_6 is a functional dependent **global scaling factor**

DFT-D

$$E_{\text{disp}} = -s_6 \sum_{i=1}^{N_{\text{at}}-1} \sum_{j=i+1}^{N_{\text{at}}} \frac{C_{6}^{ij}}{R_{ij}^6} f_{\text{dmp}}(R_{ij})$$

The **damping function** f_{dmp} is compulsory to avoid near-singularities for small R

- This would lead to infinite attraction...
- It also ensures that vdW correction takes place at the distances which are relevant **and neglected by normal DFT**, that is, long-range interaction where e-density overlap is small

At short distances, the R^{-6} behaviour is not valid anymore, either

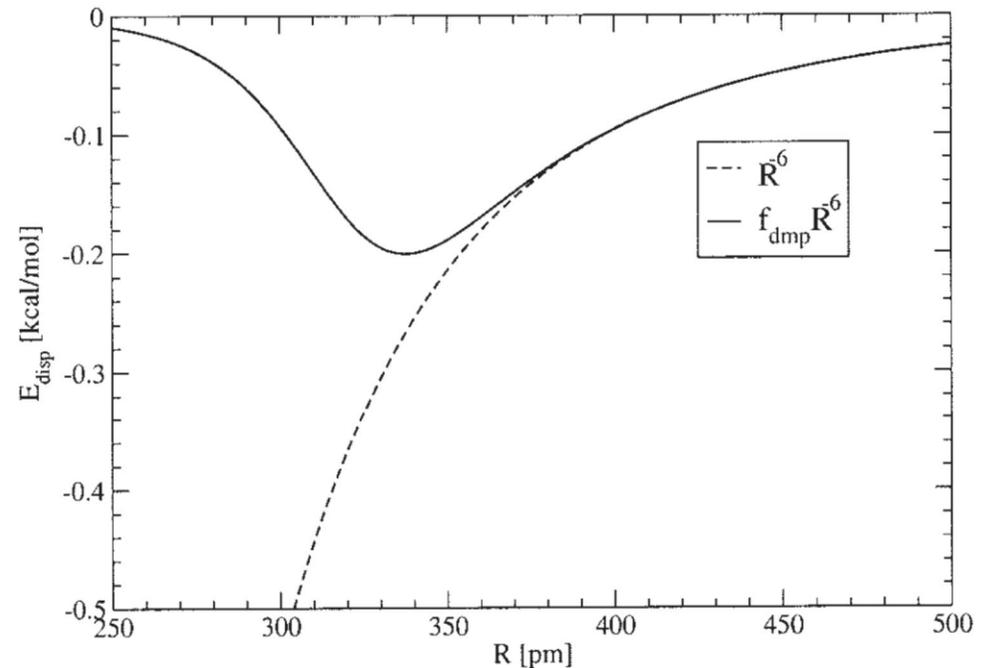


Figure 1. Dispersion contributions to the interaction potentials for two carbon atoms ($s_6 = 1.0$) separated by a distance R . The dashed line shows the undamped potential for comparison.

DFT-D

- The damping function has the form:
$$f_{\text{dmp}}(R_{ij}) = \frac{1}{1 + e^{-d(R_{ij}/R_r - 1)}}$$
- The problem of **double-counting correlation** is still real, even after damping!
 - “Fixed” by the scaling parameter s_6
 - s_6 is fitted to 40 non-covalently bound complexes
 - PBE: 0.75
 - BLYP: 1.2
 - BP86: 1.05
 - TPSS: 1.0
 - B3LYP: 1.05
 - B97-D: 1.25
 - B2PLYP: 0.55 ← dispersion already in via PT2 (note: *triple-counting* of correlation...)

Performance of DFT-D

- DFT-D usually works quite well!

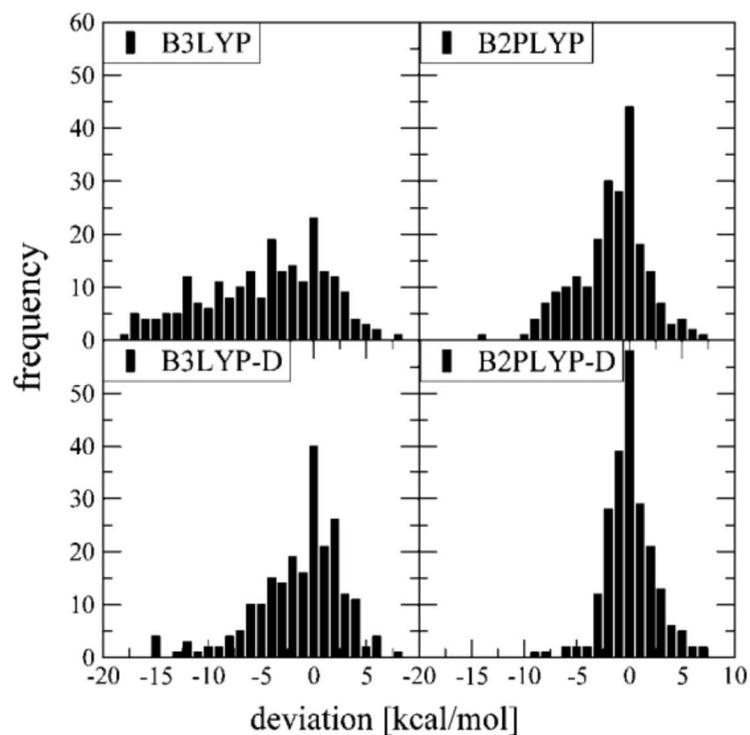


FIGURE 3. Histogram of deviations with respect to experimental data for the G3/99 set of heats of formation. The corresponding MAD values are 5.6 kcal mol⁻¹ (B3LYP), 3.1 kcal mol⁻¹ (B3LYP-D), 2.4 kcal mol⁻¹ (B2PLYP), and 1.7 kcal mol⁻¹ (B2PLYP-D).

Average signed errors for H-bonded, dispersion bonded, and “mixed” interaction energies from the S22 set; kcal/mol, DFT / **DFT-D** (*J. Comput. Chem.* **28** (2007) 555)

	H-bonded	dispersion	mixed
PBE	0.77 / -0.70	4.90 / 0.52	1.88 / 0.08
TPSS	1.45 / -0.23	5.81 / 0.74	2.46 / 0.47
B3LYP	1.70 / -0.31	6.56 / 0.87	2.86 / 0.58

BUT: DFT-D is not the final solution!

- Just as with force fields, it works well for the types of systems it was designed for
- The possible double counting of correlation is ever present
- **There is no way to know exactly what is missing in DFT,** and thus adding “something” on top can (*will*) fail

DFT-D3

- Latest *commonly available* version (2010) of Grimme's scheme with less empiricism and more geometry dependence
- **Recommended.** <http://dx.doi.org/10.1063/1.3382344>

THE JOURNAL OF CHEMICAL PHYSICS **132**, 154104 (2010)

A consistent and accurate *ab initio* parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu

Stefan Grimme,^{a)} Jens Antony, Stephan Ehrlich, and Helge Krieg
Theoretische Organische Chemie, Organisch-Chemisches Institut, Universität Münster, Corrensstrasse 40, D-48149 Münster, Germany

(Received 18 January 2010; accepted 16 March 2010; published online 16 April 2010)

The method of dispersion correction as an add-on to standard Kohn–Sham density functional theory (DFT-D) has been refined regarding higher accuracy, broader range of applicability, and less empiricism. The main new ingredients are atom-pairwise specific dispersion coefficients and cutoff radii that are both computed from first principles. The coefficients for new eighth-order dispersion terms are computed using established recursion relations. System (geometry) dependent information is used for the first time in a DFT-D type approach by employing the new concept of fractional coordination numbers (CN). They are used to interpolate between dispersion coefficients of atoms

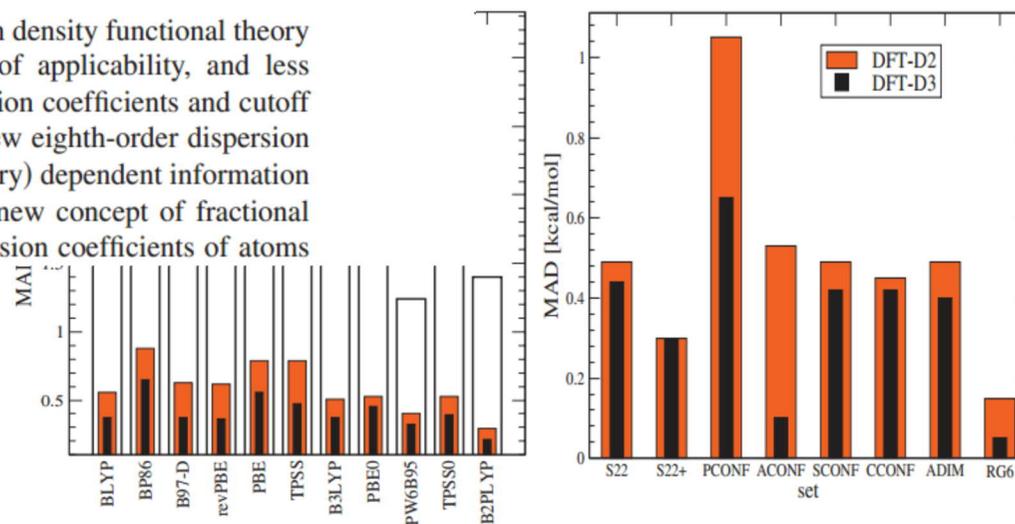


FIG. 7. Left: Comparison of MAD values for different functionals without dispersion correction (DFT), with the old (DFT-D2), and new (DFT-D3) versions. Right: MAD values averaged over nine DFs (excluding BP86 and PBE) for the different subsets.

DFT-D4

- Latest version (2019) of Grimme's scheme
- Adds dependence on atomic charge for the dipole polarizabilities in the DFT-D3 model
- Will find its way to the major QC packages soon enough

A Generally Applicable Atomic-Charge Dependent London Dispersion Correction Scheme

Version 2  Preprint revised on 25.01.2019, 17:50 and posted on 25.01.2019, 17:57 by [Eike Caldeweyher](#), [Sebastian Ehlert](#), [Andreas Hansen](#), [Hagen Neugebauer](#), [Sebastian Spicher](#), [Christoph Bannwarth](#), [Stefan Grimme](#)

The D4 model is presented for the accurate computation of London dispersion interactions in density functional theory approximations (DFT-D4) and generally for atomistic modeling methods. In this successor to the DFT-D3 model, the atomic coordination-dependent dipole polarizabilities are scaled based on atomic partial charges which can be taken from various sources. For this purpose, a new charge-dependent parameter-economic scaling function is designed. Classical charges are obtained from an atomic electronegativity equilibration procedure for which efficient

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- [Computational Chemistry and Modeling](#)
- [Bonding](#)

The Random Phase Approximation (RPA)

- The RPA idea is old, from the 1950's
- Used to be much too expensive
- In 2008, Furche reformulated the RPA into a useably efficient form
 - “Developing the random phase approximation into a practical post-Kohn–Sham correlation model”, *J. Chem. Phys.* **129** (2008) 114105, <http://dx.doi.org/10.1063/1.2977789>
- **Non-empirical**

Electron correlation methods based on the random phase approximation

Henk Eshuis · Jefferson E. Bates · Filipp Furche

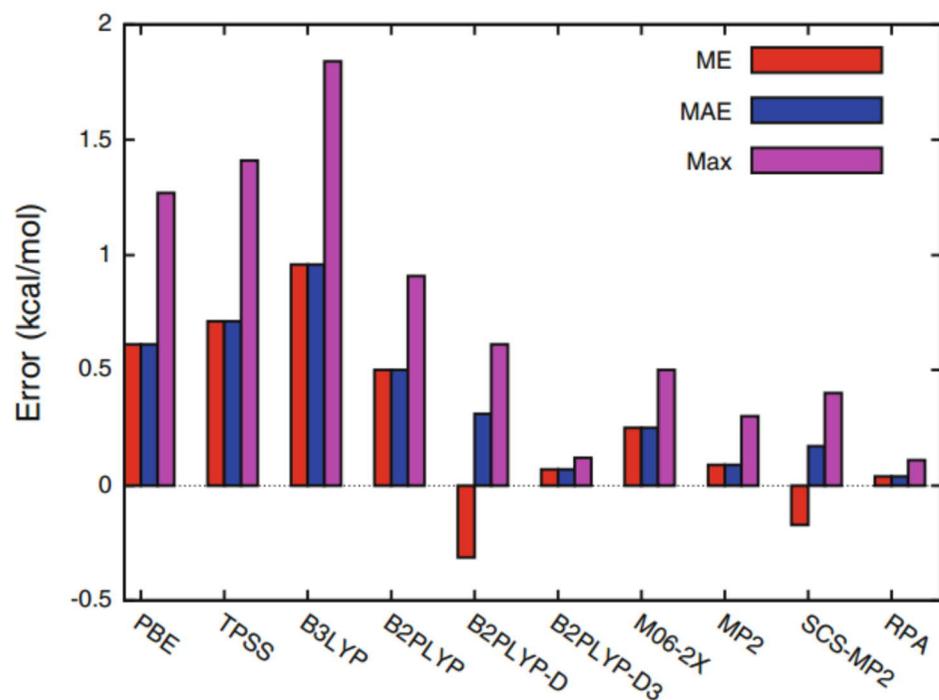


Fig. 5 RPA mean errors (ME), mean absolute errors (MAE), and maximum absolute errors (Max) (kcal/mol) in the relative energies of *n*-alkane conformers compared to other methods. Geometries and

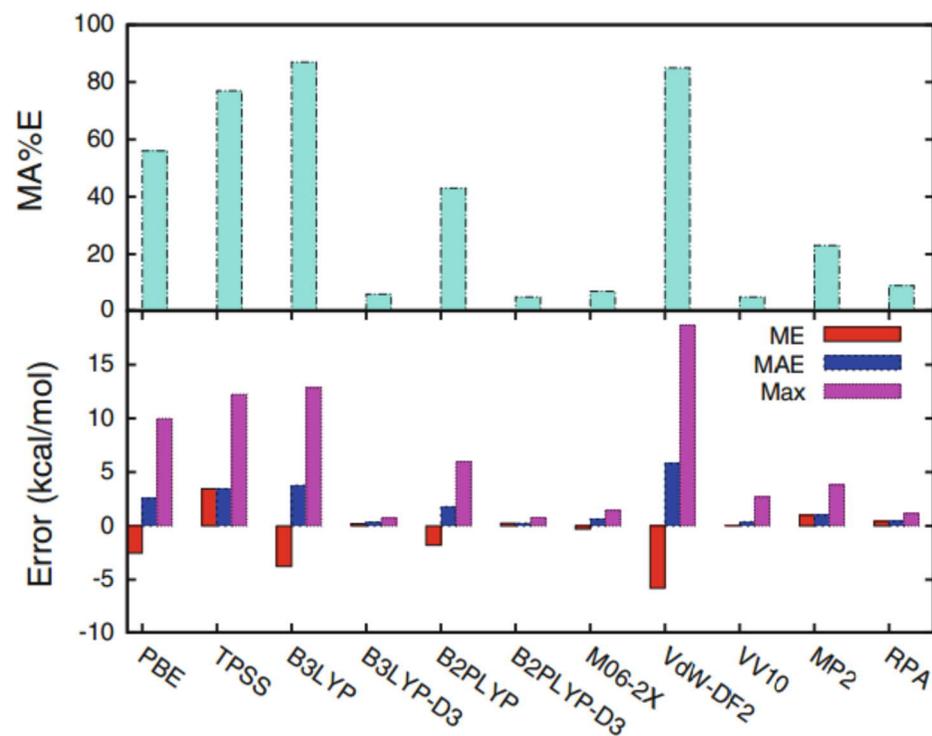


Fig. 6 RPA mean absolute percentage errors (MA%E), mean errors (ME), mean absolute errors (MAE), and maximum absolute errors (Max) (kcal/mol) for the S22 test set compared to other methods.

Bypassing the Kohn-Sham equations with machine learning

Felix Brockherde, Leslie Vogt, Li Li, Mark E. Tuckerman , Kieron Burke  & Klaus-Robert Müller 

Nature Communications 8, Article number: 872 (2017) | [Download Citation](#) 

Abstract

Last year, at least 30,000 scientific papers used the Kohn–Sham scheme of density functional theory to solve electronic structure problems in a wide variety of scientific fields. Machine learning holds the promise of learning the energy functional via examples, bypassing the need to solve the Kohn–Sham equations. This should yield substantial savings in computer time, allowing larger systems and/or longer time-scales to be tackled, but attempts to machine-learn this functional have been limited by the need to find its derivative. The present work overcomes

Semi-local machine-learned kinetic energy density functional with third-order gradients of electron density

J. Chem. Phys. 148, 241705 (2018); <https://doi.org/10.1063/1.5007230>

Junji Seino¹, Ryo Kageyama², Mikito Fujinami²,  Yasuhiro Ikabata¹, and  Hiromi Nakai^{1,2,3,4,a)}

[View Affiliations](#)



Topics ▾

Correction: [J. Chem. Phys. 149, 079901 \(2018\)](#)

ABSTRACT

A semi-local kinetic energy density functional (KEDF) was constructed based on machine learning (ML). The present scheme adopts electron densities and their gradients up to third-order as the explanatory variables for ML and the Kohn-Sham (KS) kinetic energy density as the response variable in atoms and

What density functional to choose?

- **Search the literature for benchmark studies** of similar systems!
- If you are looking at something new, you **really need to do some benchmarking** yourself



Cite this: *Phys. Chem. Chem. Phys.*,
2017, 19, 32184

A look at the density functional theory zoo with the advanced GMTKN55 database for general main group thermochemistry, kinetics and noncovalent interactions†

Lars Goerigk, *^a Andreas Hansen, ^b Christoph Bauer, ^b Stephan Ehrlich, ^{‡b}
Asim Najibi ^a and Stefan Grimme *^b

<https://doi.org/10.1039/C7CP04913G>

<http://www.thch.uni-bonn.de/GMTKN55>

We present the GMTKN55 benchmark database for general main group thermochemistry, kinetics and noncovalent interactions. Compared to its popular predecessor GMTKN30 [Goerigk and Grimme J. Chem. Theory Comput., 2011, 7, 291], it allows assessment across a larger variety of chemical problems—with 13 new benchmark sets being presented for the first time—and it also provides reference values of significantly higher quality for most sets. **GMTKN55 comprises 1505 relative energies based on 2462 single-point calculations** and it is accessible to the user community via a dedicated website. Herein, we demonstrate the importance of better reference values, and we re-emphasise the need for London-dispersion corrections in density functional theory (DFT) treatments of thermochemical problems, including Minnesota methods. We assessed 217 variations of dispersion-corrected and -uncorrected density functional approximations, and carried out a detailed analysis of 83 of them to identify robust and reliable approaches. Double-hybrid functionals are the most reliable approaches for thermochemistry and noncovalent interactions, and they should be used whenever technically feasible. These are, in particular, DSD-BLYP-D3(BJ), DSD-PBEP86-D3(BJ), and B2GPPLYP-D3(BJ). The best hybrids are ω B97X-V, M052X-D3(0), and ω B97X-D3, but we also recommend PW6B95-D3(BJ) as the best conventional global hybrid. At the meta-generalised-gradient (meta-GGA) level, the SCAN-D3(BJ) method can be recommended. Other meta-GGAs are outperformed by the GGA functionals revPBE-D3(BJ), B97-D3(BJ), and OLYP-D3(BJ). We note that many popular methods, such as B3LYP, are not part of our recommendations. In fact, with our results we hope to inspire a change in the user community's perception of common DFT methods. We also encourage method developers to use GMTKN55 for cross-validation studies of new methodologies.

We present the GMTKN55 benchmark database for general main group thermochemistry, kinetics and noncovalent interactions. Compared to its popular predecessor GMTKN30 [Goerigk and Grimme J. Chem. Theory Comput., 2011, 7, 291], it allows assessment across a larger variety of chemical problems—with 13 new benchmark sets being presented for the first time—and it also provides reference values of significantly higher quality for most sets. **GMTKN55 comprises 1505 relative energies based on 2462 single-point calculations** and it is accessible to the user community via a dedicated website. Herein, we demonstrate the importance of better reference values, and **we re-emphasise the need for London-dispersion corrections** in density functional theory (DFT) treatments of thermochemical problems, including Minnesota methods. We assessed 217 variations of dispersion-corrected and -uncorrected density functional approximations, and carried out a detailed analysis of 83 of them to identify robust and reliable approaches. Double-hybrid functionals are the most reliable approaches for thermochemistry and noncovalent interactions, and they should be used whenever technically feasible. These are, in particular, DSD-BLYP-D3(BJ), DSD-PBEP86-D3(BJ), and B2GPPLYP-D3(BJ). The best hybrids are ω B97X-V, M052X-D3(0), and ω B97X-D3, but we also recommend PW6B95-D3(BJ) as the best conventional global hybrid. At the meta-generalised-gradient (meta-GGA) level, the SCAN-D3(BJ) method can be recommended. Other meta-GGAs are outperformed by the GGA functionals revPBE-D3(BJ), B97-D3(BJ), and OLYP-D3(BJ). We note that many popular methods, such as B3LYP, are not part of our recommendations. In fact, with our results we hope to inspire a change in the user community's perception of common DFT methods. We also encourage method developers to use GMTKN55 for cross-validation studies of new methodologies.

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GMTKN55 benchmark continued

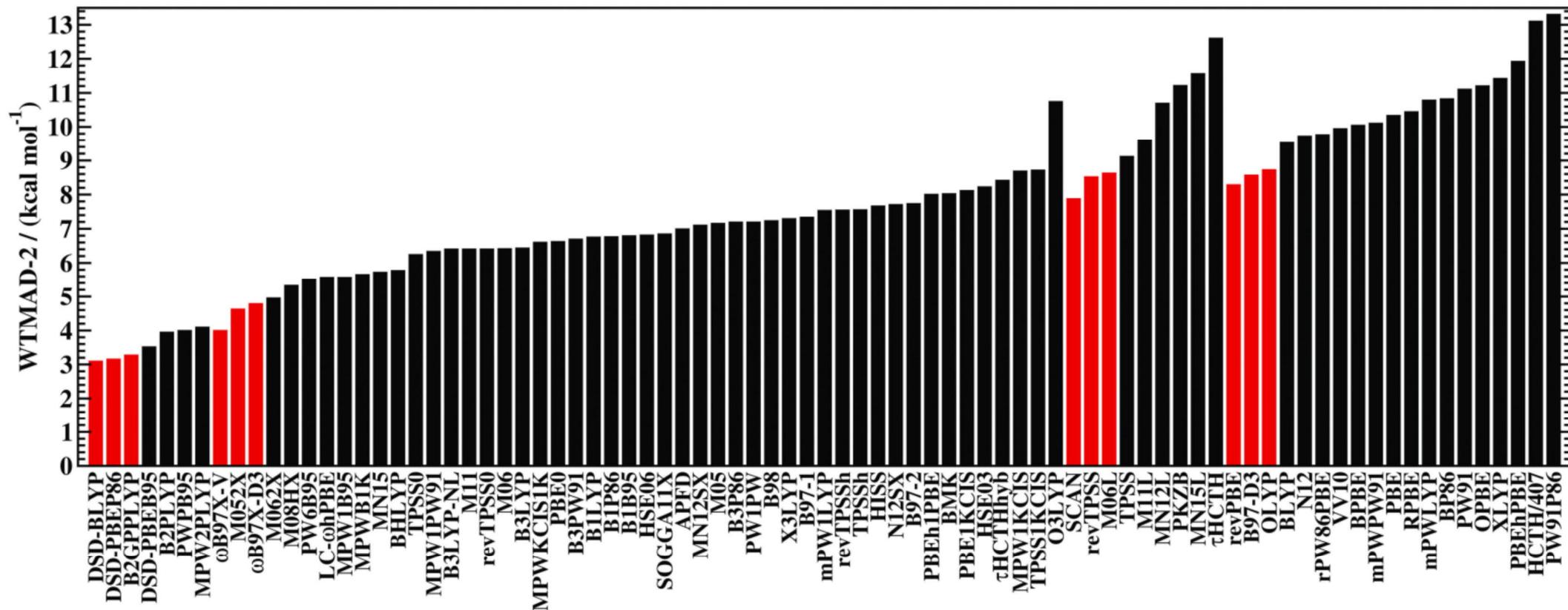


Fig. 8 Final WTMAD-2 values over the entire GMTKN55 for all assessed 83 dispersion-corrected DFAs (kcal mol⁻¹). The red bars indicate the three best approaches on their respective rung of Jacob's Ladder. The suffix "D3" was omitted in all cases, unless it is needed to avoid ambiguity.

GMTKN55 benchmark continued

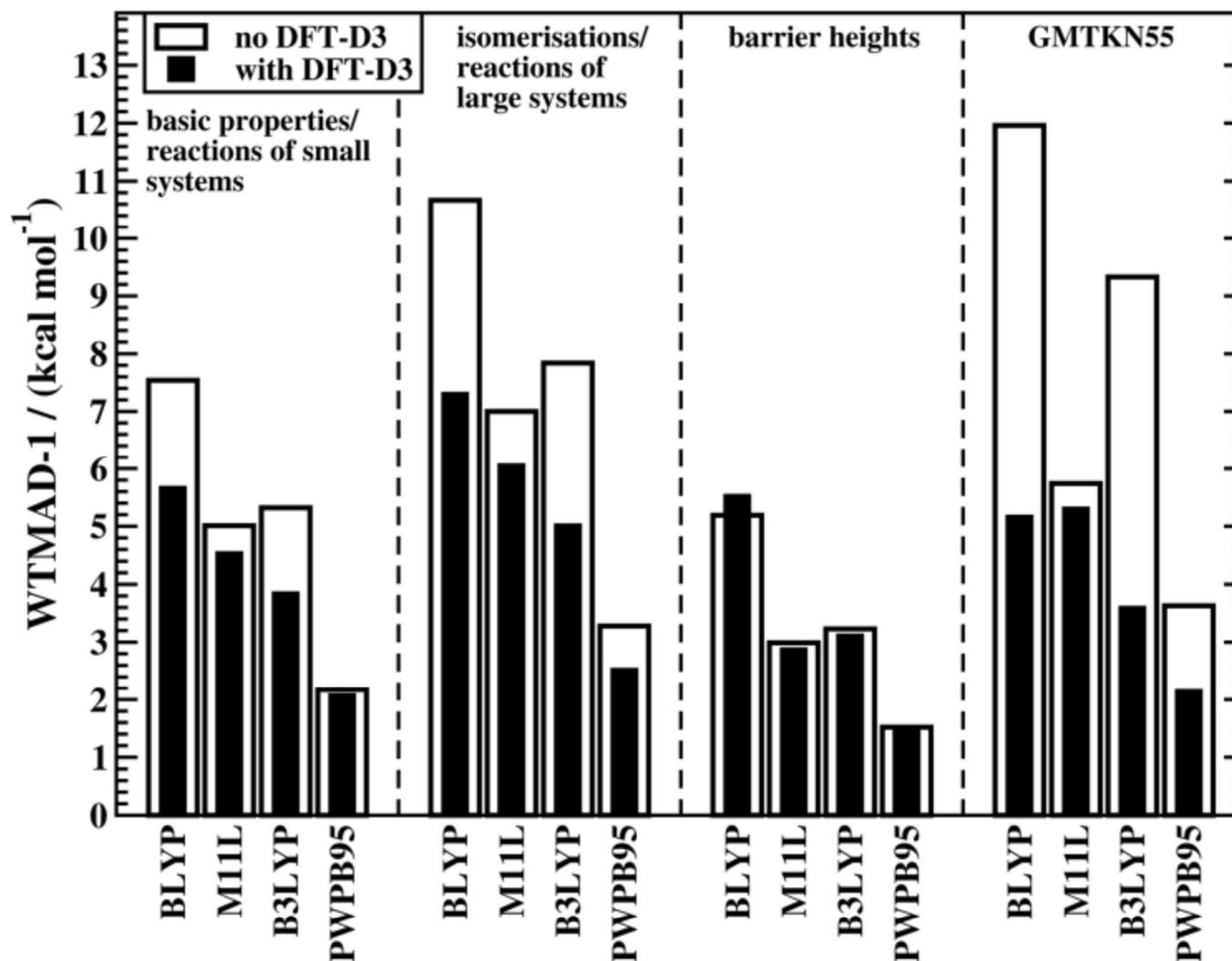


Fig. 2 The effect of dispersion corrections on WTMAD-1 values (kcal mol⁻¹) for the thermochemistry and kinetics categories of GMTKN55 and for the entire database.

Table 1 Description of the subsets within the GMTKN55 database and changes com

Set	Description		
		C60ISO ⁸⁰	Relative energies between C ₆₀ isomers
		PArel	Relative energies in protonated isomers
		Reaction barrier heights	
		BH76 ^{10,11,23}	Barrier heights of hydrogen transfer, heavy atom transfer, nucleophilic substitution, unimolecular and association reactions
		BHPERI ^{23,81-83}	Barrier heights of pericyclic reactions
		BHDIV10	Diverse reaction barrier heights
		INV24 ⁸⁴	Inversion/racemisation barrier heights
		BHROT27	Barrier heights for rotation around single bonds
		PX13 ⁸⁵	Proton-exchange barriers in H ₂ O, NH ₃ , and HF clusters
		WCPT18 ⁸⁶	Proton-transfer barriers in uncatalysed and water-catalysed reactions
		Intermolecular noncovalent interactions	
		RG18	Interaction energies in rare-gas complexes
		ADIM6 ³³	Interaction energies of <i>n</i> -alkane dimers
		S22 ¹³	Binding energies of noncovalently bound dimers
		S66 ⁸⁸	Binding energies of noncovalently bound dimers
		HEAVY28 ³³	Noncovalent interaction energies between heavy element hydrides
		WATER27 ⁸⁹	Binding energies in (H ₂ O) _{<i>n</i>} , H ⁺ (H ₂ O) _{<i>n</i>} and OH ⁻ (H ₂ O) _{<i>n</i>}
		CARBHB12	Hydrogen-bonded complexes between carbene analogues and H ₂ O, NH ₃ , or HCl
		PNICO23 ⁹¹	Interaction energies in pnictogen-containing dimers
		HAL59 ^{92,93}	Binding energies in halogenated dimers (incl. halogen bonds)
		AHB21 ⁹⁴	Interaction energies in anion-neutral dimers
		CHB6 ⁹⁴	Interaction energies in cation-neutral dimers
		IL16 ⁹⁴	Interaction energies in anion-cation dimers
		Intramolecular noncovalent interactions	
		IDISP ^{12,23,24,95,96}	Intramolecular dispersion interactions
		ICONF	Relative energies in conformers of inorganic systems
		ACONF ⁹⁷	Relative energies of alkane conformers
		AMINO20x4 ⁹⁸	Relative energies in amino acid conformers
		PCONF21 ^{100,101}	Relative energies in tri- and tetrapeptide conformers
		MCONF ¹⁰²	Relative energies in melatonin conformers
		SCONF ^{2,3,103}	Relative energies of sugar conformers
		UPU23 ¹⁰⁴	Relative energies between RNA-backbone conformers
		BUT14DIOL ¹⁰⁵	Relative energies in butane-1,4-diol conformers
Basic properties and reaction energies for small systems			
W4-11 ⁸	Total atomisation energies		
G21EA ^{3,23}	Adiabatic electron affinities		
G21IP ^{3,23}	Adiabatic ionisation potentials		
DIPCS10	Double-ionisation potentials of closed-shell systems		
PA26	Adiabatic proton affinities (incl. of amino acids)		
SIE4x4 ^c	Self-interaction-error related problems		
ALKBDE10 ⁵⁹	Dissociation energies in group-1 and -2 diatomics		
YBDE18 ⁶⁰	Bond-dissociation energies in ylides		
AL2x6	Dimerisation energies of AlX ₃ compounds		
HEAVYSB11	Dissociation energies in heavy-element compounds		
NBPRC ^{23,24,61}	Oligomerisations and H ₂ fragmentations of NH ₃ /BH ₃ systems H ₂ activation reactions with PH ₃ /BH ₃ systems		
ALK8	Dissociation and other reactions of alkaline compounds		
RC21	Fragmentations and rearrangements in radical cations		
G2RC ^{4,23}	Reaction energies of selected G2/97 systems		
BH76RC ²³	Reaction energies of the BH76 ^{10,11,23} set		
FH51 ^{63,64}	Reaction energies in various (in-)organic systems		
TAUT15	Relative energies in tautomers		
DC13 ^{18,23,28,65-73}	13 difficult cases for DFT methods		
Reaction energies for large systems and isomerisation reactions			
MB16-43	Decomposition energies of artificial molecules		
DARC ^{23,74}	Reaction energies of Diels-Alder reactions		
RSE43 ⁷⁵	Radical-stabilisation energies		
BSR36 ^{76,77}	Bond-separation reactions of saturated hydrocarbons		
CDIE20 ⁷⁸	Double-bond isomerisation energies in cyclic systems		
ISO34 ¹²	Isomerisation energies of small and medium-sized organic molecules		
ISOL24 ⁷⁹	Isomerisation energies of large organic molecules		

Thirty years of density functional theory in computational chemistry: an overview and extensive assessment of 200 density functionals

Narbe Mardirossian^a and Martin Head-Gordon^{a,b}

<https://doi.org/10.1080/00268976.2017.1333644>

- Another **very good benchmark** for main-group thermochemistry
- **Includes a comprehensive discussion about DFT**, *e.g.*, on functional ingredients
- From abstract:
 - “Ultimately, today’s state-of-the-art functionals are close to achieving the level of accuracy desired for a broad range of chemical applications, and **the principal remaining limitations are associated with systems that exhibit significant self-interaction/delocalisation errors and/or strong correlation effects.**”

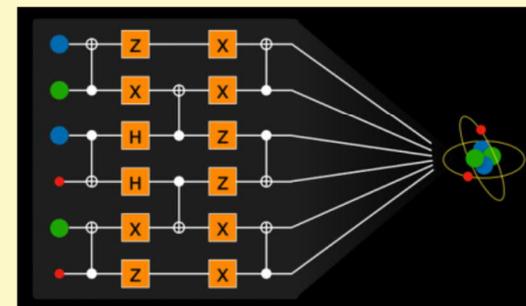
Functional	NCED	NCEC	NCD	IE	ID	TCE	TCD	BH	EBL	EBE
SPW92	2.14	37.77	7.60	2.22	6.76	42.23	65.35	19.55	0.195	2.81
PBE	1.96	4.08	3.26	1.15	6.53	9.22	15.58	9.17	0.327	2.16
TPSS	2.58	8.90	2.63	1.39	8.44	5.94	10.45	8.03	0.398	2.80
B3LYP	2.86	8.91	1.77	1.49	11.10	5.24	11.97	5.96	0.643	3.04
PBE-D3(BJ)	0.46	5.78	3.67	0.71	5.19	9.67	17.20	9.99	0.049	0.42
revPBE-D3(BJ)	0.49	6.60	2.54	0.77	5.21	6.60	9.91	8.30	0.053	0.44
BLYP-D3(BJ)	0.34	2.18	2.82	0.68	11.40	6.63	11.11	9.91	0.031	0.25
B97-D3(BJ)	0.47	4.82	2.52	0.78	9.15	4.66	7.92	8.32	0.045	0.42
TPSS-D3(BJ)	0.38	2.28	3.06	0.69	6.47	5.88	8.86	8.72	0.070	0.33
SCAN-D3(BJ)	0.54	9.18	3.41	0.55	4.46	5.25	6.39	7.83	0.037	0.60
M06-L	0.55	2.20	1.87	0.71	10.16	5.44	12.97	6.85	0.043	0.60
B97M-rV	0.22	0.67	2.04	0.28	6.45	3.57	4.78	4.36	0.025	0.17
PBE0-D3(BJ)	0.44	4.45	2.28	0.58	3.47	4.76	8.72	4.91	0.043	0.46
B3LYP-D3(BJ)	0.31	3.02	1.88	0.49	8.51	3.72	5.97	5.65	0.022	0.37
ω B97X-D	0.37	1.01	1.46	0.67	3.11	3.44	5.79	2.34	0.038	0.42
ω B97X-V	0.24	0.64	1.23	0.27	2.72	3.41	5.01	2.44	0.042	0.15
TPSSh-D3(BJ)	0.36	1.73	2.49	0.62	5.29	5.55	5.92	6.63	0.068	0.33
M06-2X	0.43	2.52	0.99	0.50	5.56	3.29	7.23	2.57	0.077	0.33
MN15	0.47	1.83	0.96	0.71	4.06	3.76	6.44	1.98	0.042	0.60
ω B97M-V	0.18	0.48	1.13	0.28	2.05	2.48	4.30	1.68	0.014	0.15
Minimum	0.18	0.48	0.91	0.27	2.05	2.48	4.30	1.68	0.014	0.15
Best	ω B97M-V	ω B97M-V	M08-SO	B97M-V	ω B97X-V					

Figure 17. RMSDs in kcal/mol [...] for the 20 density functionals featured in this review, along with the minimum RMSD from across all 200 benchmarked functionals [...] NCED stands for non-covalent dimers (easy), NCEC stands for non-covalent clusters (easy), NCD stands for non-covalent dimers (difficult), IE stands for isomerisation energies (easy), ID stands for isomerisation energies (difficult), TCE stands for thermochemistry (easy), TCD stands for thermochemistry (difficult), and BH stands for barrier heights.

Quantum Chemistry in the Age of Quantum Computing

Yudong Cao,^{†,‡} Jonathan Romero,^{†,‡} Jonathan P. Olson,^{†,‡} Matthias Degroote,^{†,¶,§} ID
Peter D. Johnson,^{†,‡} Mária Kieferová,^{¶,⊥,‡} Ian D. Kivlichan,^{#,†} Tim Menke,^{#,⊗,△} Borja Peropadre,[‡]
Nicolas P. D. Sawaya,[▽] ID Sukin Sim,^{†,‡} Libor Veis,[◆] ID and Alán Aspuru-Guzik^{*,†,‡,¶,§,○,□} ID

ABSTRACT: Practical challenges in simulating quantum systems on classical computers have been widely recognized in the quantum physics and quantum chemistry communities over the past century. Although many approximation methods have been introduced, the complexity of quantum mechanics remains hard to appease. The advent of quantum computation brings new pathways to navigate this challenging and complex landscape. By manipulating quantum states of matter and taking advantage of their unique features such as superposition and entanglement, quantum computers promise to efficiently deliver accurate results for many important problems in quantum chemistry, such as the electronic structure of molecules. In the past two decades, significant advances have been made in developing algorithms and physical hardware for quantum computing, heralding a revolution in simulation of quantum systems. This Review provides an overview of the algorithms and results that are relevant for quantum chemistry. The intended audience is both quantum chemists who seek to learn more about quantum computing and quantum computing researchers who would like to explore applications in quantum chemistry.



Helsinki Winter School in Theoretical Chemistry 2020

This is the 36th Winter School

QC-4C: Quantum Computers for Chemistry

Helsinki, 14-17 December 2020

Organised by the University of Helsinki and CSC

Summary

Computational methods and simulations can be *immensely useful* for explaining, predicting, and designing chemistry and chemical phenomena

One has to know the methods well, however!

- What are the strengths *and limitations* of a specific methodology?

The computer will almost always give you a number, it is up to you as a scientist to assess the reliability of the result!

Further reading

- The surface was barely scratched; **For more detail, the following text books are excellent**
- Frank Jensen, “Introduction to Computational Chemistry”
 - Great overview of QC methods, as well as the basics of MM
- Wolfram Koch, Max C. Holthausen, “A Chemist’s Guide to Density Functional Theory”
 - Fundamentals of DFT from a chemical viewpoint
- Kieron Burke *et al*, “The ABC of DFT”, <http://dft.uci.edu/research.php>
 - A more in-depth treatment of DFT. Preliminary version but already good
- Trygve Helgaker, Poul Jørgensen, Jeppe Olsen, “Molecular Electronic-Structure Theory”
 - Very detailed account of correlated wave-function methods
- Steven M. Bachrach, “Computational Organic Chemistry”
 - Brief intro of methods, followed by examples relevant for organic chemistry

Three recent overviews of different density functionals:

- Mardirossian & Head-Gordon (2017) “Thirty years of density functional theory in computational chemistry: an overview and extensive assessment of 200 density functionals” <https://doi.org/10.1080/00268976.2017.1333644>
- Goerigk *et al.* (2017) “A look at the density functional theory zoo with the advanced GMTKN55 database for general main group thermochemistry, kinetics and noncovalent interactions” <https://doi.org/10.1039/C7CP04913G>
- Dohm *et al.* (2018) “Comprehensive Thermochemical Benchmark Set of Realistic Closed-Shell Metal Organic Reactions” <https://doi.org/10.1021/acs.jctc.7b01183>

Good luck!