

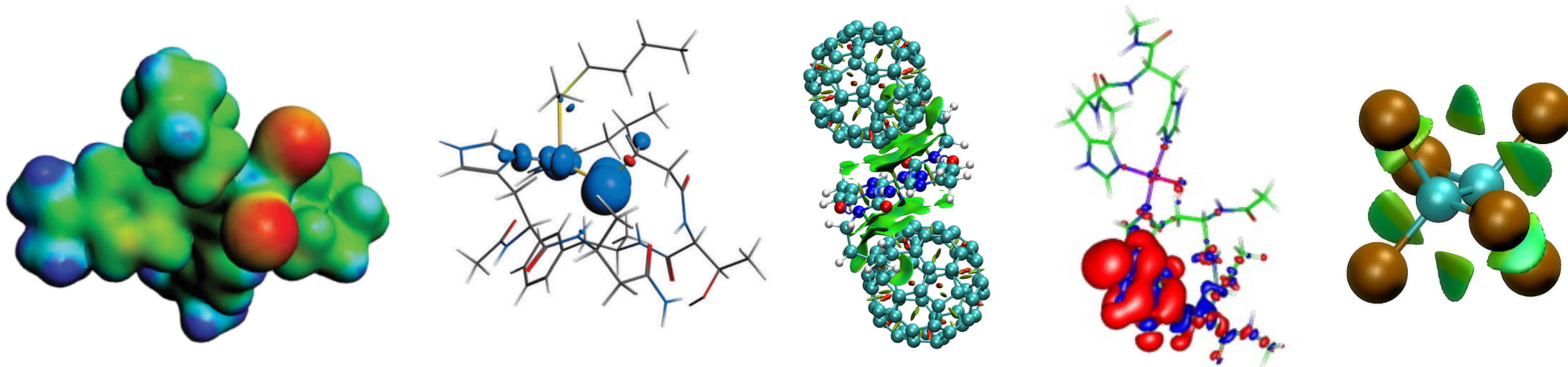
CSC/PRACE Spring School in Computational Chemistry 2019

Introduction to Electronic Structure Theory

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Objective: To get familiarised with the, subjectively chosen, most important concepts of electronic structure theory from a computational chemistry viewpoint. After these lectures, the student will hopefully go for lunch with at least a rudimentary exposure to different approximations to the molecular Schrödinger equation, and the alternative theory of density functionals



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 trivial 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'
 \rightarrow

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

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 proof also indirectly shows that $\rho(\mathbf{r})$ unambiguously defines all properties of the system (that are independent of a magnetic field), even the wave function itself, and all the excited state wave functions

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

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

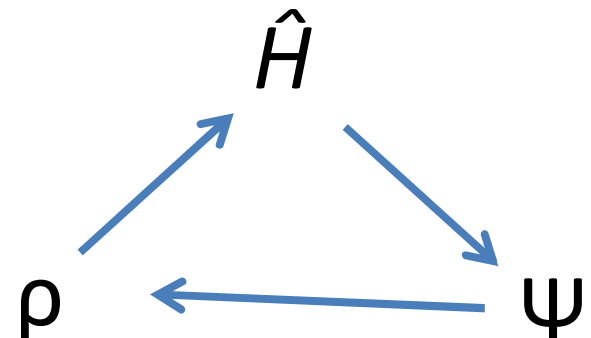
Another way of looking at it:

- 1) The electron density $\rho(r)$ contains **the number of electrons** in the system
- 2) Cusps in $\rho(r)$ 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**

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 $\rho(r)$!**

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

\hat{T}_e , electronic kinetic energy \hat{V}_{ee} , electron-electron repulsion
 \hat{V}_{ne} , electron-nucleus attraction \hat{V}_{nn} , nucleus-nucleus repulsion



Kohn–Sham DFT

- Every specific electron density gives a specific energy (for the GS), the energy is a **functional of ρ**

electronic kinetic energy electron-electron repulsion, $J[\rho]-K[\rho]$

$$E[\rho] = T[\rho] - E_{ne}[\rho] + E_{ee}[\rho]$$

electron-nucleus attraction

- The main problem of early density functionals was a **poor description of the kinetic energy** when modelled by the total density alone
- The exact kinetic energy for a ground state is given by the natural spin orbitals ψ_i and their occupation numbers n_i

$$T = \sum_i^{\infty} n_i \langle \psi_i | -\frac{1}{2} \nabla^2 | \psi_i \rangle$$

- For an interacting system, there's an infinite number of terms, so it cannot be solved exactly
- Kohn and Sham presented a formalism, **based on orbitals**, for treating the kinetic energy

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

$$v_{\text{H}}(\mathbf{r}) = - \sum_a \frac{Z_a}{|\mathbf{R}_a - \mathbf{r}|} + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'$$

- In this approximation, a one-particle Schrödinger equation can be obtained

$$\left[-\frac{1}{2} \nabla^2 + v_{\text{H}}(\mathbf{r}) \right] \psi_i = e_i \psi_i$$

- In **Kohn–Sham DFT**, a system of **independent non-interacting electrons** in a common one-body potential, v_{KS} , is imagined
 - This potential gives **the same electron density as the real, interacting system**
 - **Not always possible**, e.g., Fe and Co atoms! The *v-representability problem*
- 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 correlations energy, but always of opposite sign
- Now, the KS equations can be solved analogously to the SCF Hartree equations by replacing the potential v_H by v_{eff}

$$v_{\text{eff}}(\mathbf{r}) = v(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + v_{xc}(\mathbf{r})$$

Kohn–Sham DFT

- Within KS-DFT, the energy of the ground state is thus given by:

$$E^{\text{DFT}}[\rho] = \sum_i e_i + E_{\text{xc}}[\rho] - \int v_{\text{xc}}(\mathbf{r})\rho(\mathbf{r})dv - \frac{1}{2} \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

or more generally, divided into its components:

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

- 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 different complexity *do* exist also within **DFT**
- The idea is to include **more complex properties** of the electron density into the description
- Most density functionals describe exchange and correlation separately
 - No exchange between α and β spin electrons
 - Correlation energy contains contributions between all electrons
$$E_x(\rho) = E_x^\alpha(\rho_\alpha) + E_x^\beta(\rho_\beta)$$
$$E_c(\rho) = E_c^{\alpha\alpha}(\rho_\alpha) + E_c^{\beta\beta}(\rho_\beta) + E_c^{\alpha\beta}(\rho_\alpha, \rho_\beta)$$
 - Largest contribution from exchange part

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

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

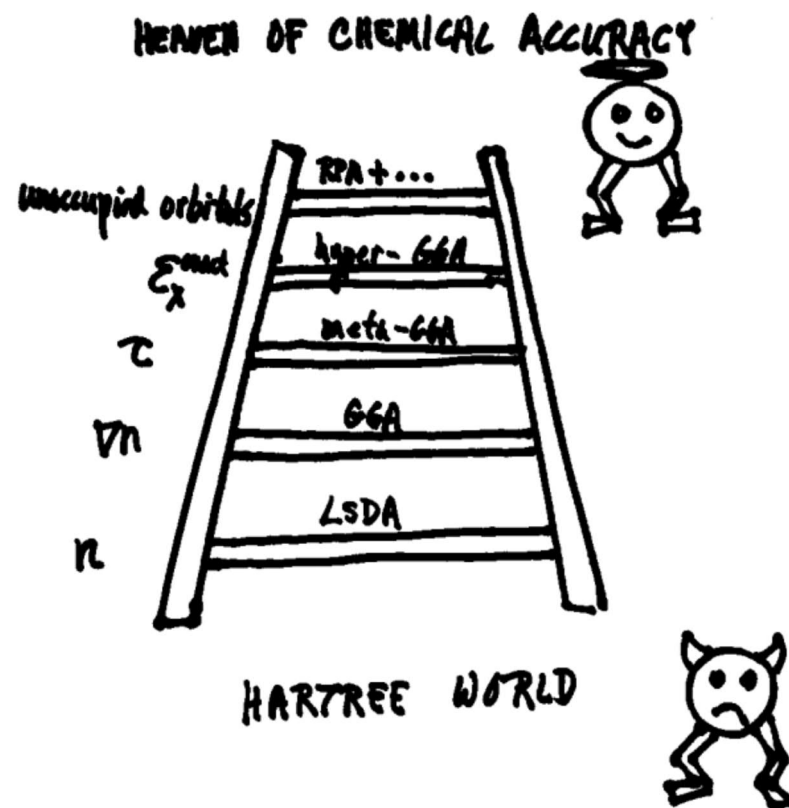
- The exchange energy of a uniform electron gas is analytically known (Slater/Dirac/Bloch exchange)

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

- 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
- A few different LDA correlation functionals are regularly used
 - VWN-3 and VWN-5 by Vosko, Wilk, and Nusair
 - PW92 by Perdew and Wang

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*
- Considering increasing amounts of the information content of the density within the functional form has been described as 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>
- 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** 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 functionals

- 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**
 - Empirical LDAs include those that add some empirical dispersion terms, and Slater's $X\alpha$
- 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>

Generalized Gradient Approximation Made Simple

- John P. Perdew, Kieron Burke,* Matthias Ernzerhof
Department of Physics and Quantum Theory Group, Tulane University, New Orleans, Louisiana 70118
(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]

PBE

- One motivation for the construction was to **simplify the non-empirical PW91 functional**, in which the authors identified the following undesirable features:
 1. The derivation is long, and depends on a mass of detail
 2. The analytic function f is complicated and non-transparent
 3. f is overparametrized
 4. The parameters are not seamlessly joined, leading to spurious wiggles in the XC potential $\delta E_{xc}/\delta\rho$ which comes with some problems
 5. PW91 does not behave correctly under uniform scaling to the high-density limit
 6. It describes linear response of the uniform electron gas *less* satisfactorily than does LDA
- PW91 was constructed to satisfy as many exact conditions as possible
- The semi-local form of a GGA is however *too restrictive*
 - **Fulfilling one exact property can break another!**
- 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**

4. Under uniform scaling, E_X must scale like λ

5. The exact exchange energy obeys the **spin-scaling** relationship

$$E_X[n_\uparrow, n_\downarrow] = (E_X[2n_\uparrow] + E_X[2n_\downarrow])/2$$

6. For the linear response of the spin-unpolarised uniform electron gas, that is, for small density variations around the uniform density, LDA is an excellent approximation to E_{XC} so we want, when $s \rightarrow 0$

$$F_X(s) \rightarrow 1 + \mu s^2 \quad \mu = \beta(\pi^2/3) \simeq 0.21951$$

7. *The Lieb–Oxford bound* will be satisfied if the spin-polarised enhancement factor grows gradually to a maximum value of 2.273

$$E_X[n_\uparrow, n_\downarrow] \geq E_{XC}[n_\uparrow, n_\downarrow]$$

$$\geq -1.679e^2 \int d^3r n^{4/3}$$

- **Satisfied by the simple** $F^{\text{PBE}}(s) = 1 + 0.804 - \frac{0.804}{1 + \frac{0.21951}{0.804}s^2}$

PBE exchange

- Again, quite much simpler than PW91:

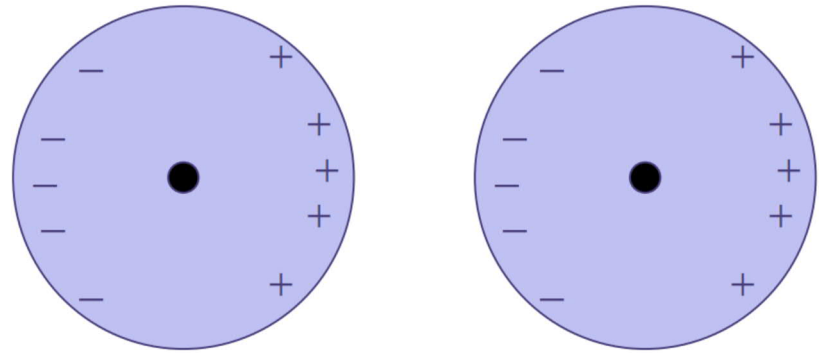
$$F^{\text{PW91}}(s) = \frac{1 + 0.19645s \operatorname{arcsinh}(7.7956s) + \left(0.2743 - 0.1508e^{-100s^2}\right) s^2}{1 + 0.19645s \operatorname{arcsinh}(7.7956s) + 0.004s^4}$$

The GGA proposed here retains correct features of LSD, and combines them with the most energetically important features of gradient-corrected nonlocality. The correct but less important features of PW91 which have been sacrificed are (1) correct second-order gradient coefficients for E_X and E_C in the slowly varying limit, and (2) correct nonuniform scaling of E_X in limits where the reduced gradient s tends to ∞ .

Calculations of atomization energies for small molecules (Table I) also show that our simple new E_{XC}^{GGA} yields essentially the same results as the more Byzantine PW91. Except for its additional satisfaction of conditions (c) and (f) and its smoother potential, the new GGA is close to PW91. However, its simpler form and derivation make it easier to understand, apply, and perhaps improve.

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

- Attempts to modify (reparametrize) existing functionals
- **X3LYP**, Xu and Goddard, *PNAS* **101** (2004) 2673.
 - Was designed for non-covalent interactions
 - But doesn't work that well...
 - ...it shouldn't
- Truhlar *et al* have designed several Minnesota functionals
 - **MPW1B95, MPWB1K, MPWKICIS, MPWKICIS1K, MPW3LYP, MPWLYP1M, X1B95, XB1K, BB1K, PW6B95, PWB6K, M05, M05-2X, M06, M06-L, M06-HF, M06-2X, M08-HX, M08-SO, ...**
 - Some of them seem to **work well also for non-covalent interactions**, at least some of the time, but none are really that well tested (yet)
 - *Very highly parameterised*, very difficult to predict *when* they fail, but they *do* fail!

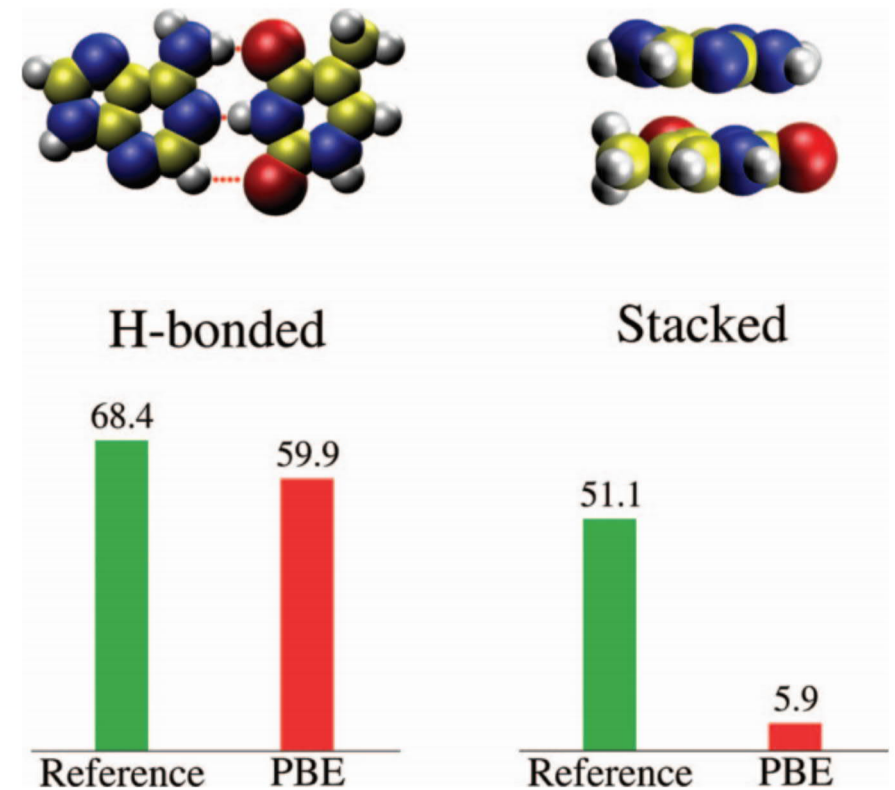


FIG. 3. Two binding configurations of the DNA base pairs adenine and thymine. A hydrogen bonded structure is shown on the left (hydrogen bonds indicated by red dots) and a “stacked” geometry on the right. For the hy-

DFT for dispersion–B2PLYP

- Also incorporation of **correlated WF methods (MP2)** has been used

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

Semiempirical hybrid density functional with perturbative second-order correlation

Stefan Grimme^{a)}

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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

- Can also be considered to be 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

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

where (in spin-orbital form)

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

One can note from the expression that when

- $a_x = 0; b=1; c=0$, B2-PLYP = BLYP
- $a_x = 1; b=0; c=1$, B2-PLYP = MP2

Final fitted parameters:

$$a_x = 0.57; c = 0.27; b = 1 - c = 0.73$$

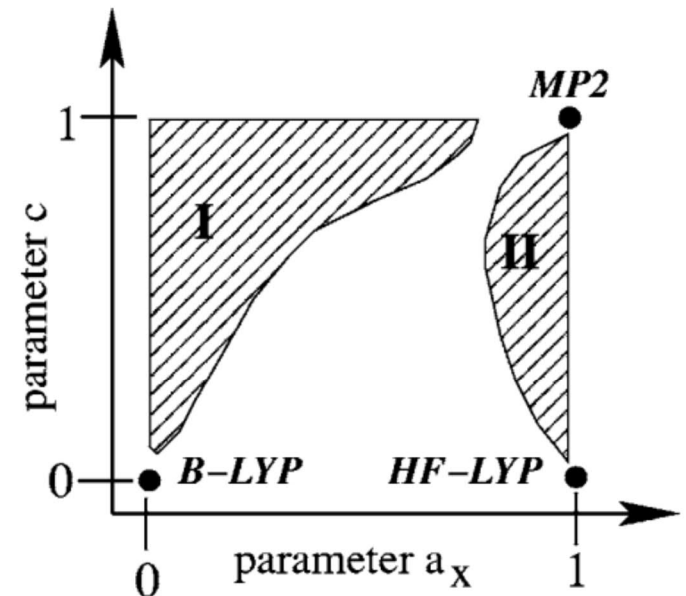


FIG. 1. Schematic description of possible methods arising from different combinations of HF exchange end PT2 mixing parameters. The dashed areas I and II can be excluded by physical reasoning (see text).

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

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

- These are computed from atomic ionisation potentials and static dipole polarisabilities $C_6^a = 0.05 N I_p^a \alpha^a$
- $N = 2, 10, 18, 36, 54$ for rows 1–5, respectively
- Assumed to be constant for all molecules
 - a somewhat crude assumption

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

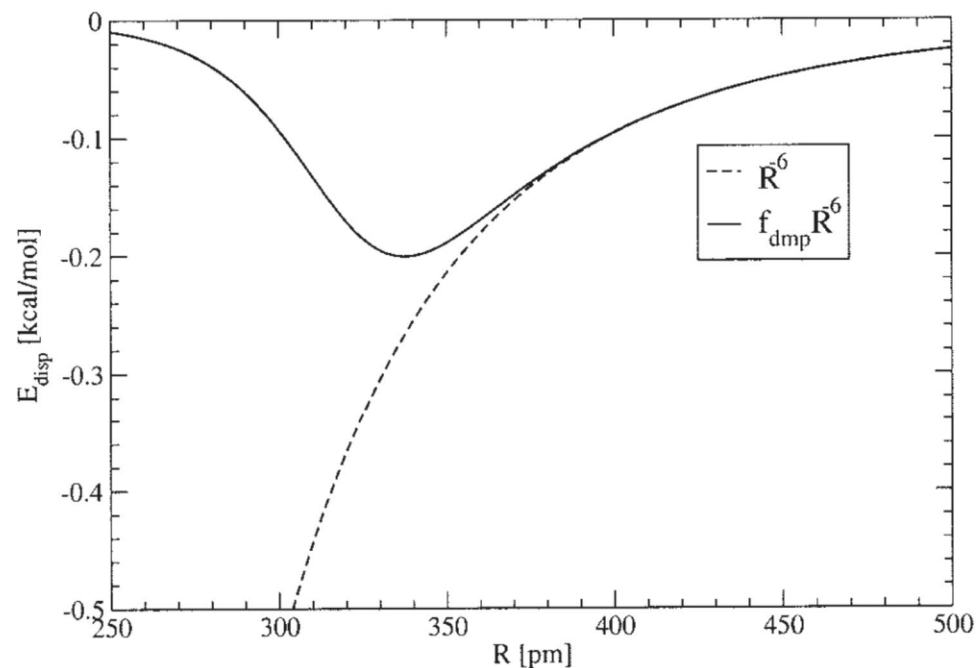


Figure 1. Dispersion contributions to the interaction potentials for two carbon atoms ($s_6 = 1.0$) separated by a distance R . The dashed line shows the undamped potential for comparison.

DFT-D

- The damping function has the form:
$$f_{\text{dmp}}(R_{ij}) = \frac{1}{1 + e^{-d(R_{ij}/R_r - 1)}}$$
- R_r is the sum of the atomic van der Waals radii
 - These need to be fitted/computed. Assumed to be constant for all molecules
 - Not as bad as for C_6
- d is a “sufficiently large” (=20) damping parameter, which switches off the correction at small distances
 - No correction at small distances
 - Some correction at intermediate distances
 - Full correction at large distances
- 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!

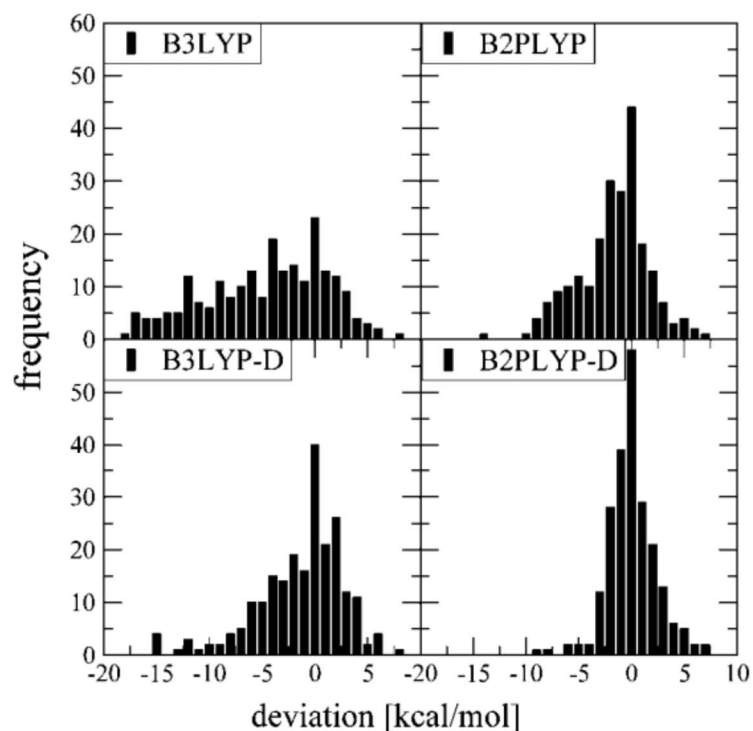


FIGURE 3. Histogram of deviations with respect to experimental data for the G3/99 set of heats of formation. The corresponding MAD values are 5.6 kcal mol⁻¹ (B3LYP), 3.1 kcal mol⁻¹ (B3LYP-D), 2.4 kcal mol⁻¹ (B2PLYP), and 1.7 kcal mol⁻¹ (B2PLYP-D).

Average signed errors for H-bonded, dispersion bonded, and “mixed” interaction energies from the S22 set; BSSE corrected TZVP, 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
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(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

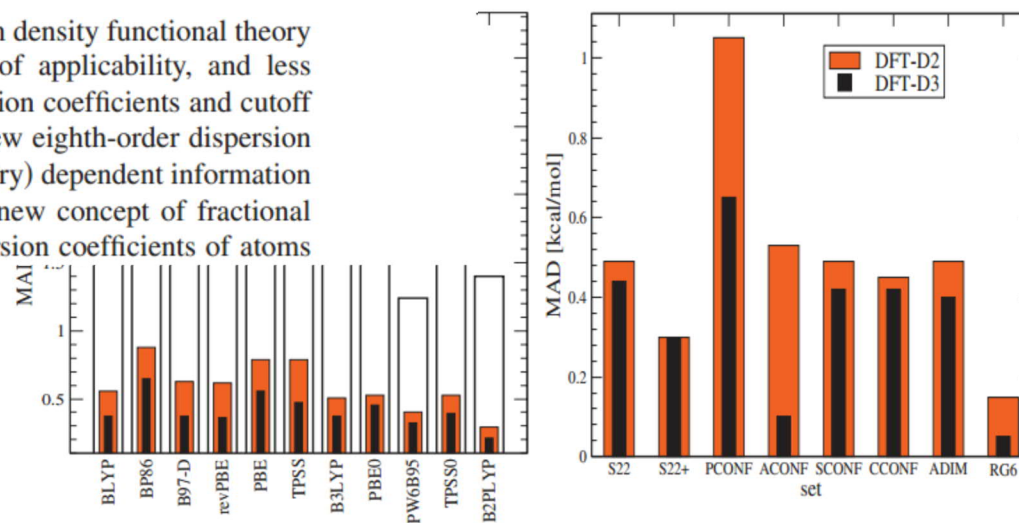



FIG. 7. Left: Comparison of MAD values for different functionals without dispersion correction (DFT), with the old (DFT-D2), and new (DFT-D3) versions. Right: MAD values averaged over nine DFs (excluding BP86 and PBE) for the different subsets.

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 softwares 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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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**

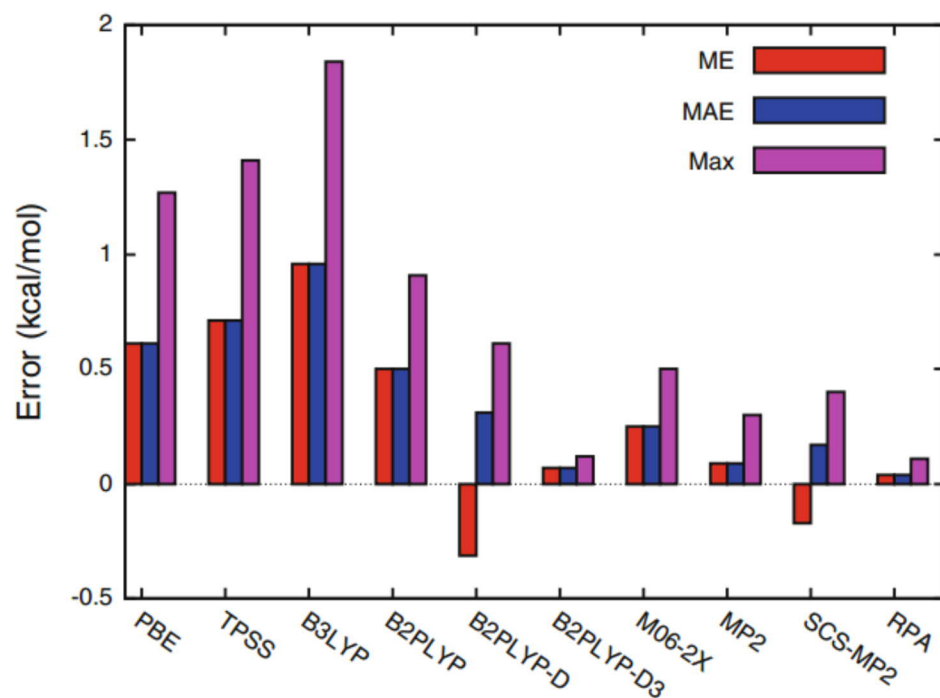


Fig. 5 RPA mean errors (ME), mean absolute errors (MAE), and maximum absolute errors (Max) (kcal/mol) in the relative energies of *n*-alkane conformers compared to other methods. Geometries and

Electron correlation methods based on the random phase approximation

Henk Eshuis · Jefferson E. Bates · Filipp Furche

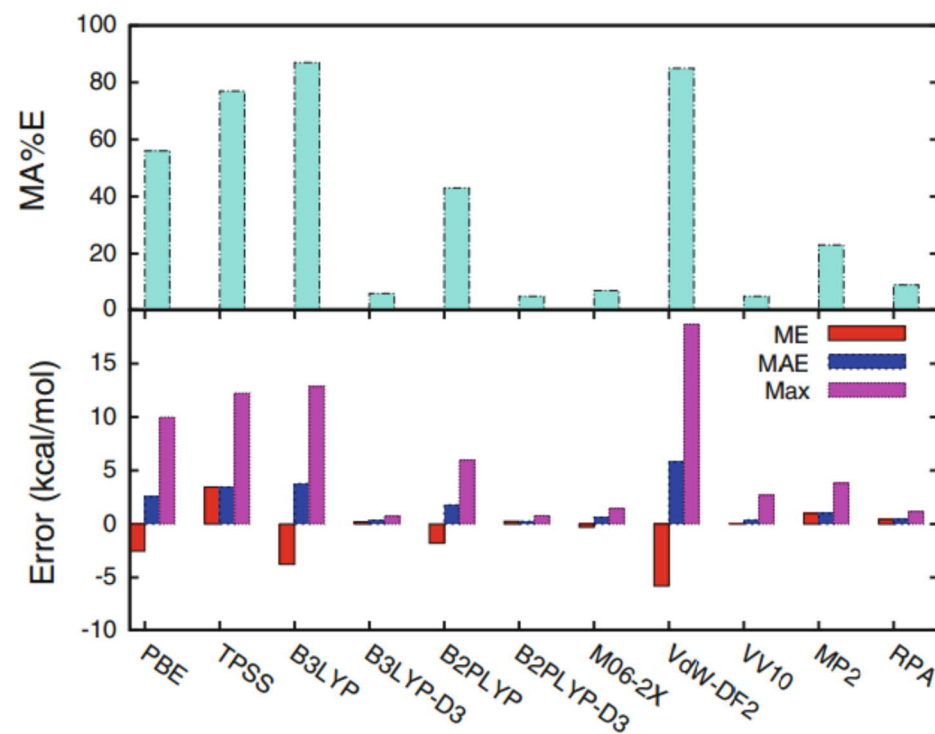



Fig. 6 RPA mean absolute percentage errors (MA%E), mean errors (ME), mean absolute errors (MAE), and maximum absolute errors (Max) (kcal/mol) for the S22 test set compared to other methods.

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

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!