Hybrid functionals
Theory and applications

Leeor Kronik

Department of Materials and Interfaces,

Weizmann Institute of Science, Rehovoth, Israel

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Global hybrid functionals

$$E_{xc}^{\mathrm{hyb}}[n] = aE_x^{\mathrm{exact}}[n] + (1-a)E_x^{\mathrm{app}}[n] + E_c^{\mathrm{app}}[n]$$

a - Fraction of exact (Fock) exchange
app = usually GGA, sometimes meta-GGA

Becke, J. Chem. Phys. 98, 5648 (1993)

Can be solved using OEP, but practically almost never is. Instead:

$$\left(-\frac{1}{2}\nabla^2 + V_{ion}(r) + V_H([n];r) + a\hat{V}_F + (1-a)v_x^{sl}([n];r) + v_c^{sl}([n];r)\right)\varphi_i(r) = \varepsilon_i\varphi_i(r)$$

- Hence the name “hybrid”…
- Just “mix and match” of Hartree-Fock and Kohn-Sham?
- Uncontrolled approximation to Kohn-Sham theory?

The adiabatic connection theorem

Harris & Jones, J. Phys. F 4, 1170 (1974); Gunnarson & Lundqvist, Phys. Rev. B 13, 4274 (1976); Langreth & Perdew, Phys. Reb. B 15, 2884 (1977).

Transition adiabatically *from the many-electron system to the Kohn-Sham system, while retaining the density throughout*

$$\hat{H}_\lambda = \hat{T} + \hat{V}_{\mathrm{ext},\lambda} + \lambda \hat{V}_{\mathrm{ee}}$$

$$E_{\mathrm{tot},\lambda} = \int v_{\mathrm{ext},\lambda}(\vec{r}) n(\vec{r}) d^3 r + F_\lambda[n]$$

$$F_\lambda[n] = \langle \Psi_\lambda | \hat{T} + \lambda \hat{V}_{\mathrm{ee}} | \Psi_\lambda \rangle$$

$$0 \leqslant \lambda \leqslant 1$$

The adiabatic connection theorem (2)

$$E_{\mathrm{xc}}[n] = F_1[n] - F_0[n] - E_H[n]$$
$$= \int_0^1 \frac{\partial F_\lambda[n]}{\partial \lambda} d\lambda - E_H[n]$$
$$\equiv \int_0^1 E_{\mathrm{xc},\lambda}[n] d\lambda,$$

$$E_{\mathrm{xc},\lambda}[n] = \langle \Psi_\lambda | \hat{V}_{\mathrm{ee}} | \Psi_\lambda \rangle - E_H[n].$$

E_{xc} as the area under the $E_{xc,\lambda}$ curve!

$$E_x[n] = E_{\mathrm{xc},0}[n] = \langle \Psi_0 | \hat{V}_{\mathrm{ee}} | \Psi_0 \rangle - E_H[n]$$

A new mixing of Hartree–Fock and local density-functional theories

Axel D. Becke
Department of Chemistry, Queen's University, Kingston, Ontario, Canada K7L 3N6

(Received 12 August 1992; accepted 8 October 1992)

***J. Chem. Phys.* 98, 1372 (1993).**

Previous attempts to combine Hartree–Fock theory with local density-functional theory have been unsuccessful in applications to molecular bonding. We derive a new coupling of these two theories that maintains their simplicity and computational efficiency, and yet greatly improves their predictive power. Very encouraging results of tests on atomization energies, ionization potentials, and proton affinities are reported, and the potential for future development is discussed.

A bad idea: $E_{\mathrm{XC}} = E_X + E_C^{\mathrm{LSDA}}$

A better idea: $E_{\mathrm{XC}} \simeq \frac{1}{2} E_X + \frac{1}{2} U_{\mathrm{XC}}^{\mathrm{LSDA}}$

Approximate area under the adiaabtic connection curve (trapezoidal rule)!

Issues with the “half and half” hybrid functional

Still not accurate enough for thermochemistry

$E_{xc,\lambda}$ curve really linear?

Should we really mix correlation?

Rationale for mixing exact exchange with density functional approximations

John P. Perdew and Matthias Ernzerhof
Department of Physics and Quantum Theory Group, Tulane University, New Orleans, Louisiana 70118

Kieron Burke
Department of Chemistry, Rutgers University, Camden, New Jersey 08102

(Received 11 June 1996; accepted 5 September 1996)

***J. Chem. Phys.* 105, 9982 (1996).**

Density functional approximations for the exchange-correlation energy E_{xc}^{DFA} of an electronic system are often improved by admixing some exact exchange E_x: $E_{xc} \approx E_{xc}^{DFA} + (1/n)(E_x - E_x^{DFA})$. This procedure is justified when the error in E_{xc}^{DFA} arises from the $\lambda=0$ or exchange end of the coupling-constant integral $\int_0^1 d\lambda\, E_{xc,\lambda}^{DFA}$. We argue that the optimum integer n is approximately the lowest order of Görling–Levy perturbation theory which provides a realistic description of the coupling-constant dependence $E_{xc,\lambda}$ in the range $0 \leqslant \lambda \leqslant 1$, whence $n \approx 4$ for atomization energies of typical molecules. We also propose a continuous generalization of n as an index of correlation strength, and a possible mixing of second-order perturbation theory with the generalized gradient approximation. © *1996 American Institute of Physics.* [S0021-9606(96)01846-6]

$$E_{xc,\lambda}^{hyb}(n) = E_{xc,\lambda}^{DFA} + (E_x - E_x^{DFA})(1-\lambda)^{n-1}$$

$$E_{xc}^{hyb} = \int_0^1 d\lambda\, E_{xc,\lambda}^{hyb} = E_{xc}^{DFA} + \frac{1}{n}(E_x - E_x^{DFA})$$

For n=4, DFA=PBE: The PBE0 functional !

Density-functional thermochemistry. III. The role of exact exchange

Axel D. Becke
Department of Chemistry, Queen's University, Kingston, Ontario, Canada K7L 3N6

J. Chem. Phys. 98, 1372 (1993).

(Received 30 October 1992; accepted 16 December 1992)

Despite the remarkable thermochemical accuracy of Kohn–Sham density-functional theories with gradient corrections for exchange-correlation [see, for example, A. D. Becke, J. Chem. Phys. **96**, 2155 (1992)], we believe that further improvements are unlikely unless *exact-exchange* information is considered. Arguments to support this view are presented, and a semiempirical exchange-correlation functional containing local-spin-density, gradient, and exact-exchange terms is tested on 56 atomization energies, 42 ionization potentials, 8 proton affinities, and 10 total atomic energies of first- and second-row systems. This functional performs significantly better than previous functionals with gradient corrections only, and fits experimental atomization energies with an impressively small average absolute deviation of 2.4 kcal/mol.

$$E_{\mathrm{XC}}=E_{\mathrm{XC}}^{\mathrm{LSDA}}+a_0(E_X^{\mathrm{exact}}-E_X^{\mathrm{LSDA}})+a_X\Delta E_X^{\mathrm{B88}}+a_C\Delta E_C^{\mathrm{PW91}},$$

$$a_0=0.20,\quad a_X=0.72,\quad a_C=0.81.$$

Fit for thermochemistry: The B3PW91 functional

From B3PW91 to B3LYP

$$E_{xc} = (1 - a_0)E_x^{LSDA} + a_0 E_x^{HF} + a_x \Delta E_x^{B88} + E_c^{LSDA} + a_c \Delta E_c^{PW91}$$

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

No parameter refitting, correlation readjustment

Stephens, Devlin, Chabalowski, Frisch,
J. Phys. Chem. 98, 11623 (1994)

Massively empirical hybrid functionals

Theor Chem Account (2008) 120:215–241
DOI 10.1007/s00214-007-0310-x

REGULAR ARTICLE

The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: two new functionals and systematic testing of four M06-class functionals and 12 other functionals

Yan Zhao · Donald G. Truhlar

Meta-GGA based family of hybrid functionals with varying degrees of exact exchange

36 parameters explicitly fit against extensive benchmark data

Can be highly effective for systems and properties that are chemically similar to those in the set

Range-separated hybrid functionals

Coulomb operator decomposition:

$$r^{-1} = \underbrace{r^{-1}\mathrm{erfc}(\gamma r)}_{\textbf{Short Range}} + \underbrace{r^{-1}\mathrm{erf}(\gamma r)}_{\textbf{Long Range}}$$

Emphasize long-range exchange, short-range exchange correlation!

A. Savin,
in *Recent Advances in Density Functional Methods Part (1995).*

$$\left(-\frac{1}{2}\nabla^2 + V_{ion}(r) + V_H([n];r) + \hat{V}_F^{lr,\gamma} + v_x^{sr,\gamma}([n];r) + v_c^{sl}([n];r)\right)\varphi_i(r) = \varepsilon_i \varphi_i(r)$$

See, e.g.: **Leininger et al., *Chem. Phys. Lett.* 275, 151 (1997)**
Iikura et al., J. *Chem. Phys.* 115, 3540 (2001)
Yanai et al., *Chem. Phys. Lett.* 393, 51 (2004)

Fully within the Generalized Kohn-Sham Scheme!

$$\left(-\frac{1}{2}\nabla^2 + V_{ion}(r) + V_H([n];r) + \hat{V}_F^{lr,\gamma} + v_x^{sr,\gamma}([n];r) + v_c^{sl}([n];r)\right)\varphi_i(r) = \varepsilon_i \varphi_i(r)$$

$$S[\Phi] = \langle \Phi | \hat{T} + \hat{V}_{ee}^{LR} | \Phi \rangle$$

Kronik, Stein, Refaely-Abrmason, Baer, J. Chem. Theo. Comp. 8, 1515 (2012).

Generalized range-separation

$$\frac{1}{r} = \underbrace{\frac{\alpha + \beta erf(\gamma r)}{r}}_{\text{Fock exchange}} + \underbrace{\frac{1-[\alpha + \beta erf(\gamma r)]}{r}}_{\text{GGA exchange}}$$

Yanai et al., Chem. Phys. Lett. 393, 51 (2004)

$$E_{xc}^{RSH} = \alpha E_{x,HF}^{SR,\gamma} + (1-\alpha) E_{x,PBE}^{SR,\gamma} + (\alpha+\beta) E_{x,HF}^{LR,\gamma} + (1-\alpha-\beta) E_{x,PBE}^{LR,\gamma} + E_{c,PBE}$$

Popular PBE-based choices (1)

α=0, β=1, γ=0.4 bohr^{-1} : LC-ωPBE

Vydrov & Scuseria,
J. Chem. Phys. 125, 234109 (2006)

α=0.2, β=0.8, γ=0.2 bohr^{-1} : LC-ωPBE0

Rohrdanz, Martins, Herbert
J. Chem. Phys. 125, 234109 (2006)

$$E_{\mathrm{xc}}^{\mathrm{RSH}} = \alpha E_{x,\mathrm{HF}}^{\mathrm{SR},\gamma} + (1-\alpha) E_{x,\mathrm{PBE}}^{\mathrm{SR},\gamma} + (\alpha+\beta) E_{x,\mathrm{HF}}^{\mathrm{LR},\gamma} + (1-\alpha-\beta) E_{x,\mathrm{PBE}}^{\mathrm{LR},\gamma} + E_{c,\mathrm{PBE}}$$

Popular PBE-based choices (2)

α=0.25, β=-0.25, γ=0.11 bohr^{-1} : HSE

Heyd, Scuseria, Ernzerhof
J. Chem. Phys. 118, 8207 (2003);
124, 219906 (Erratum, 2006).

HSE is a *short-range* exchange functional! Useful for the solid state!

$$E_{\mathrm{xc}}^{\mathrm{RSH}} = \alpha E_{x,\mathrm{HF}}^{\mathrm{SR},\gamma} + (1-\alpha) E_{x,\mathrm{PBE}}^{\mathrm{SR},\gamma} + (\alpha+\beta) E_{x,\mathrm{HF}}^{\mathrm{LR},\gamma} + (1-\alpha-\beta) E_{x,\mathrm{PBE}}^{\mathrm{LR},\gamma} + E_{c,\mathrm{PBE}}$$

Other well-known empirical RSH choices

CAM-B3LYP:

α=0.19, β=0.46, γ=0.33 bohr^{-1}

Yanai, Tew, Handy

Chem. Phys. Lett. 393, 51 (2004)

Fit against thermochemistry.

Not asymptotically correct!

ω-B97x: Massively empirical (16 parameters)

Chai & Head-Gordon,

J. Chem. Phys. 128, 084106 (2008).

Improved theromchemistry and kinetics

Double-hybrid functionals

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

Semiempirical hybrid density functional with perturbative second-order correlation

Stefan Grimme[a)]

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

where (in spin-orbital form)

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

B2PLYP: BLYP exchange-correlation components

Fitting: a_x=0.53; c=1-b=0.27

THE JOURNAL OF CHEMICAL PHYSICS **134**, 064113 (2011)

Double-hybrid density-functional theory made rigorous

Kamal Sharkas,[1,2,a)] Julien Toulouse,[1,b)] and Andreas Savin[1,c)]
[1]*Laboratoire de Chimie Théorique, Université Pierre et Marie Curie and CNRS, 75005 Paris, France*
[2]*Atomic Energy Commission of Syria, P.O. Box 6091, Damascus, Syria*

$$E_{xc}^{1\mathrm{DH},\lambda} = \lambda E_x^{\mathrm{HF}} + (1-\lambda)E_x[n] + (1-\lambda^2)E_c[n] + \lambda^2 E_c^{\mathrm{MP2}},$$

Fitting: λ=0.55

THE JOURNAL OF CHEMICAL PHYSICS **141**, 031101 (2014)

Communication: Double-hybrid functionals from adiabatic-connection The QIDH model

Éric Brémond,[1,2,a)] Juan Carlos Sancho-García,[3,b)] Ángel José Pérez-Jiménez,[3] and Carlo Adamo[2,4]

$$E_{xc,\lambda_x}^{\mathrm{QIDH}}[\rho] = \frac{\lambda_x+2}{3}E_x^{\mathrm{HF}} + \frac{1-\lambda_x}{3}E_x^{\mathrm{DFA}}[\rho] + \frac{1}{3}E_c^{\mathrm{MP2}} + \frac{2}{3}E_c^{\mathrm{DFA}}[\rho].$$

Scaling: $\lambda_x=3^{2/3}-2$

Double-hybrid functionals

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

where (in spin-orbital form)

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

B2PLYP: BLYP exchange-correlation components

Fitting: a_x=0.53; c=1-b=0.27

Grimme, J. Chem. Phys. 124, 034108 (2006).

ωB97M(2)
A semi-empirical range-separated double hybrid

Contains 14 empirical parameters

Performance for main-group chemistry database (4986 data points from 84 datasets)

Functional	Rung	Overall	NCED	NCEC	NCD	IE	ID	TCE	TCD	BH	EBL	EBE
ωB97M(2)	5	0.49	0.14	0.36	0.32	0.11	0.97	0.96	2.71	0.84	0.019	0.14
ωB97M-V	4	0.69	0.15	0.42	0.53	0.11	1.32	1.56	4.15	1.48	0.019	0.17
ωB97X-V	4	0.97	0.17	0.50	0.61	0.15	1.55	2.35	5.56	2.44	0.043	0.17
B97M-rV	3	1.23	0.18	0.57	1.10	0.24	4.24	1.88	5.47	3.12	0.030	0.16
B97-D3(BJ)	2	2.49	0.45	3.20	1.25	0.62	5.04	3.43	8.88	7.67	0.040	0.49
SPW92	1	6.51	1.91	27.76	5.11	1.26	5.58	10.13	32.20	15.53	0.202	1.48

Mardirossian and Head-Gordon, J. Chem. Phys. 148, 241736 (2018).

PHYSICAL REVIEW A **72**, 012510 (2005)

van der Waals forces in density functional theory: Perturbational long-range electron-interaction corrections

János G. Ángyán and Iann C. Gerber
Laboratoire de Cristallographie et de Modélisation des Matériaux Minéraux et Biologiques, UMR 7036, CNRS-Université Henri Poincaré, B.P. 239, F-54506 Vandœuvre-lès-Nancy, France

Andreas Savin and Julien Toulouse
Laboratoire de Chimie Théorique, UMR 7616, CNRS-Université Pierre et Marie Curie, 4 place Jussieu, F-75005 Paris, France
(Received 12 April 2005; published 19 July 2005)

Long-range exchange and correlation effects, responsible for the failure of currently used approximate density functionals in describing van der Waals forces, are taken into account explicitly after a separation of the electron-electron interaction in the Hamiltonian into short- and long-range components. We propose a "range-separated hybrid" functional based on a local density approximation for the short-range exchange-correlation energy, combined with a long-range exact exchange energy. Long-range correlation effects are added by a second-order perturbational treatment. The resulting scheme is general and is particularly well adapted to describe van der Waals complexes, such as rare gas dimers.

Range-separated hybrid density functionals made simple

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Éric Brémond,[1,a)] Ángel José Pérez-Jiménez,[2] Juan Carlos Sancho-García,[2] and Carlo Adamo[3,4]

ABSTRACT

In this communication, we present a new and simple route to derive range-separated exchange (RSX) hybrid and double hybrid density functionals in a nonempirical fashion. In line with our previous developments [Brémond *et al.*, J. Chem. Theory Comput. **14**, 4052 (2018)], we show that by imposing an additional physical constraint to the exchange-correlation energy, i.e., by enforcing to reproduce the total energy of the hydrogen atom, we are able to generalize the nonempirical determination of the range-separation parameter to a family of RSX hybrid density functionals. The success of the resulting models is illustrated by an accurate modeling of several molecular systems and properties, like ionization potentials, particularly prone to the one- and many-electron self-interaction errors.

Local hybrids

$$E_{\mathrm{xc}}^{\mathrm{lochyb}} = \int n(\vec{r})\{f([n];\vec{r})e_x^{\mathrm{sloc}}([n];\vec{r}) +$$

$$[1 - f([n];\vec{r})]e_x^{\mathrm{exact}}([n];\vec{r}) + e_c^{\mathrm{sloc}}([n];\vec{r})\}d^3r$$

Jaramillo, Scuseria, Ernzerhof, J. Chem. Phys. 118, 1068 (2003)

Maier, Arbuznikov, Kaupp, WIREs Comput. Mol. Sci. 2019;9:e1378

Conclusions

- Hybrid functionals are a rigorous concept within GKS (or OEP).
- Zoo of functionals can be confusing, but most can be classified into global, range-separated, double, and (possibly local) combinations thereof.
- Can be massively, minimally, or non-empirical
- Useful 4th and 5th rung functionals!