Hybrid functional

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Hybrid functionals are a class of approximations to the exchange–correlation energy functional in density functional theory (DFT) that incorporate a portion of exact exchange from Hartree–Fock theory with exchange and correlation from other sources (*ab initio* or empirical). The exact exchange energy functional is expressed in terms of the Kohn–Sham orbitals rather than the density, so is termed an *implicit* density functional. One of the most commonly used versions is B3LYP, which stands for Becke, 3-parameter, Lee-Yang-Parr.

Contents

Origin

The hybrid approach to constructing density functional approximations was introduced by Axel Becke in 1993.[1] Hybridization with Hartree–Fock (exact) exchange provides a simple scheme for improving many molecular properties, such as atomization energies, bond lengths and vibration frequencies, which tend to be poorly described with simple "ab initio" functionals.[2]

Method

A hybrid exchange-correlation functional is usually constructed as a linear combination of the Hartree–Fock exact exchange functional, E_x^{HF}:

$$E_{\mathrm{x}}^{\mathrm{HF}} = -\frac{1}{2}\sum_{i,j}\int\int \psi_i^*(\mathbf{r_1})\psi_j^*(\mathbf{r_1})\frac{1}{r_{12}}\psi_i(\mathbf{r_2})\psi_j(\mathbf{r_2})d\mathbf{r_1}\,d\mathbf{r_2},$$

and any number of exchange and correlation explicit density functionals. The parameters determining the weight of each individual functional are typically specified by fitting the functional's predictions to experimental or accurately calculated thermochemical data, although in the case of the "adiabatic connection functionals" the weights can be set *a priori*.[2]

B3LYP

For example, the popular B3LYP (Becke, three-parameter, Lee-Yang-Parr)[3][4] exchange-correlation functional is:

$$E_{\mathrm{xc}}^{\mathrm{B3LYP}} = E_{\mathrm{x}}^{\mathrm{LDA}} + a_0(E_{\mathrm{x}}^{\mathrm{HF}} - E_{\mathrm{x}}^{\mathrm{LDA}}) + a_{\mathrm{x}}(E_{\mathrm{x}}^{\mathrm{GGA}} - E_{\mathrm{x}}^{\mathrm{LDA}}) + E_{\mathrm{c}}^{\mathrm{LDA}} + a_{\mathrm{c}}(E_{\mathrm{c}}^{\mathrm{GGA}} - E_{\mathrm{c}}^{\mathrm{LDA}}),$$

where $a_0 = 0.20$, $a_{\mathrm{x}} = 0.72$, and $a_{\mathrm{c}} = 0.81$. $E_{\mathrm{x}}^{\mathrm{GGA}}$ and $E_{\mathrm{c}}^{\mathrm{GGA}}$ are generalized gradient approximations: the Becke 88 exchange functional[5] and the correlation functional of Lee, Yang and Parr[6] for B3LYP, and $E_{\mathrm{c}}^{\mathrm{LDA}}$ is the VWN local-density approximation to the correlation functional.[7]

The three parameters defining B3LYP have been taken without modification from Becke's original fitting of the analogous B3PW91 functional to a set of atomization energies, ionization potentials, proton affinities, and total atomic energies.[8]

PBE0

The PBE0 functional[2] [9] mixes the Perdew–Burke-Ernzerhof (PBE) exchange energy and Hartree-Fock exchange energy in a set 3 to 1 ratio, along with the full PBE correlation energy:

$$E_{xc}^{PBE0} = \frac{1}{4}E_x^{HF} + \frac{3}{4}E_x^{PBE} + E_c^{PBE},$$

where E_x^{HF} is the Hartree–Fock exact exchange functional, E_x^{PBE} is the PBE exchange functional, and E_c^{PBE} is the PBE correlation functional.[10]

HSE

The HSE (Heyd-Scuseria-Ernzerhof)[11] exchange-correlation functional uses an error function screened Coulomb potential to calculate the exchange portion of the energy in order to improve computational efficiency, especially for metallic systems.

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

where a is the mixing parameter and ω is an adjustable parameter controlling the short-rangeness of the interaction. Standard values of $a = \frac{1}{4}$ and $\omega = 0.2$ (usually referred to as HSE06) have been shown to give good results for most systems. The HSE exchange-correlation functional degenerates to the PBE0 hybrid functional for $\omega = 0$. $E_x^{HF,SR}(\omega)$ is the short range Hartree–Fock exact exchange functional, $E_x^{PBE,SR}(\omega)$ and $E_x^{PBE,LR}(\omega)$ are the short and long range components of the PBE exchange functional, and $E_c^{PBE}(\omega)$ is the PBE [10] correlation functional.

Meta hybrid GGA

The M06 suite of functionals[12][13] is a set of four meta-hybrid GGA and meta-GGA DFT functionals. These functionals are constructed by empirically fitting their parameters, while being constrained to a uniform electron gas.

The family includes the functionals M06-L, M06, M06-2X and M06-HF, with a different amount of exact exchange for each one. M06-L is fully local without HF exchange (thus it cannot be considered hybrid), M06 has 27% HF exchange, M06-2X 54% and M06-HF 100%.

The advantages and usefulness of each functional are

- M06-L: Fast, Good for transition metals, inorganic and organometallics.
- M06: For main group, organometallics, kinetics and non-covalent bonds.
- M06-2X: Main group, kinetics.
- M06-HF: Charge transfer TD-DFT, systems where self interaction is pathological.

The suite gives good results for systems containing dispersion forces, one of the biggest deficiencies of standard DFT methods. The s6 scaling factors on Grimme's long-range dispersion correction are 0.20, 0.25 and 0.06 for M06-L, M06 and M06-2X, respectively.

References

1. A.D. Becke (1993). "A new mixing of Hartree-Fock and local density-functional theories". *J. Chem. Phys.* **98** (2): 1372–1377. Bibcode:1993JChPh..98.1372B (http://adsabs.harvard.edu/abs/1993JChP

h..98.1372B). doi:10.1063/1.464304 (https://doi.org/10.1063%2F1.464304).

2. John P. Perdew; Matthias Ernzerhof; Kieron Burke (1996). "Rationale for mixing exact exchange with density functional approximations" (http://dft.uci.edu/pubs/PEB96.pdf) (PDF). *J. Chem. Phys.* **105** (22): 9982–9985. Bibcode:1996JChPh.105.9982P (http://adsabs.harvard.edu/abs/1996JChPh.105.9982P). doi:10.1063/1.472933 (https://doi.org/10.1063%2F1.472933). Retrieved 2007-05-07.

3. K. Kim; K. D. Jordan (1994). "Comparison of Density Functional and MP2 Calculations on the Water Monomer and Dimer". *J. Phys. Chem.* **98** (40): 10089–10094. doi:10.1021/j100091a024 (https://doi.org/10.1021%2Fj100091a024).

4. P.J. Stephens; F. J. Devlin; C. F. Chabalowski; M. J. Frisch (1994). "*Ab Initio* Calculation of Vibrational Absorption and Circular Dichroism Spectra Using Density Functional Force Fields". *J. Phys. Chem.* **98** (45): 11623–11627. doi:10.1021/j100096a001 (https://doi.org/10.1021%2Fj100096a001).

5. A. D. Becke (1988). "Density-functional exchange-energy approximation with correct asymptotic behavior" (http://link.aps.org/abstract/PRA/v38/p3098). *Phys. Rev. A.* **38** (6): 3098–3100. Bibcode:1988PhRvA..38.3098B (http://adsabs.harvard.edu/abs/1988PhRvA..38.3098B). PMID 9900728 (https://www.ncbi.nlm.nih.gov/pubmed/9900728). doi:10.1103/PhysRevA.38.3098 (https://doi.org/10.1103%2FPhysRevA.38.3098).

6. Chengteh Lee; Weitao Yang; Robert G. Parr (1988). "Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density". *Phys. Rev. B.* **37** (2): 785–789. Bibcode:1988PhRvB..37..785L (http://adsabs.harvard.edu/abs/1988PhRvB..37..785L). doi:10.1103/PhysRevB.37.785 (https://doi.org/10.1103%2FPhysRevB.37.785).

7. S. H. Vosko; L. Wilk; M. Nusair (1980). "Accurate spin-dependent electron liquid correlation energies for local spin density calculations: a critical analysis". *Can. J. Phys.* **58** (8): 1200–1211. Bibcode:1980CaJPh..58.1200V (http://adsabs.harvard.edu/abs/1980CaJPh..58.1200V). doi:10.1139/p80-159 (https://doi.org/10.1139%2Fp80-159).

8. Becke, Axel D. (1993). "Density-functional thermochemistry. III. The role of exact exchange". *J. Chem. Phys.* **98** (7): 5648–5652. Bibcode:1993JChPh..98.5648B (http://adsabs.harvard.edu/abs/1993JChPh..98.5648B). doi:10.1063/1.464913 (https://doi.org/10.1063%2F1.464913).

9. Adamo, Carlo; Vincenzo Barone (1999-04-01). "Toward reliable density functional methods without adjustable parameters: The PBE0 model" (http://jcp.aip.org/resource/1/jcpsa6/v110/i13/p6158_s1). *The Journal of Chemical Physics.* **110** (13): 6158–6170. Bibcode:1999JChPh.110.6158A (http://adsabs.harvard.edu/abs/1999JChPh.110.6158A). ISSN 0021-9606 (https://www.worldcat.org/issn/0021-9606). doi:10.1063/1.478522 (https://doi.org/10.1063%2F1.478522). Retrieved 2013-06-21.

10. Perdew, John P.; Kieron Burke; Matthias Ernzerhof (1996-10-28). "Generalized Gradient Approximation Made Simple" (http://link.aps.org/doi/10.1103/PhysRevLett.77.3865). *Physical Review Letters.* **77** (18): 3865–3868. Bibcode:1996PhRvL..77.3865P (http://adsabs.harvard.edu/abs/1996PhRvL..77.3865P). PMID 10062328 (https://www.ncbi.nlm.nih.gov/pubmed/10062328). doi:10.1103/PhysRevLett.77.3865 (https://doi.org/10.1103%2FPhysRevLett.77.3865). Retrieved 2011-09-28.

11. Jochen Heyd; Gustavo E. Scuseria; Matthias Ernzerhof (2003). "Hybrid functionals based on a screened Coulomb potential". *J. Chem. Phys.* **118** (18): 8207. Bibcode:2003JChPh.118.8207H (http://adsabs.harvard.edu/abs/2003JChPh.118.8207H). doi:10.1063/1.1564060 (https://doi.org/10.1063%2F1.1564060).

12. Zhao, Yan; Donald G. Truhlar. "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". *Theor. Chem. Account.* **120**: 215. doi:10.1007/s00214-007-0310-x (https://doi.org/10.1007%2Fs00214-007-0310-x).

13. Zhao, Yan; Donald G. Truhlar. "Density Functional for Spectroscopy: No Long-Range Self-Interaction Error, Good Performance for Rydberg and Charge-Transfer States, and Better Performance on Average than B3LYP for Ground States". *J. Phys. Chem.* **110**: 13126. doi:10.1021/jp066479k (https://doi.org/10.1021%2Fjp066479k).