Fourteen Easy Lessons in Density Functional Theory

JOHN P. PERDEW, ADRIENN RUZSINSZKY

Department of Physics and Quantum Theory Group, Tulane University, New Orleans, LA 70118

ABSTRACT: Density functional theory (DFT) is now the most commonly used method of electronic structure calculation in both condensed matter physics and quantum chemistry, thanks in part to the focus it has received over the first 50 years of the Sanibel Symposium. We present a short history, and review fourteen short and easy but important lessons about nonrelativistic DFT, with some partiality but with a minimum of technical complication. © 2010 Wiley Periodicals, Inc. Int J Quantum Chem 110: 2801–2807, 2010

Key words: density functional theory; exchange–correlation energy; electronic structure theory; Kohn–Sham theory

Introduction and Short History of Density Functional Theory

This article summarizes a talk given at the 50th anniversary Sanibel Symposium on Quantum Chemistry. Its original title, "Some Things We have Learned About Exchange and Correlation in the Last Fifty Years," was somewhat too restrictive in both subject matter and time frame. It presents 14 easy lessons in nonrelativistic density functional theory (DFT) at a qualitative level. The selection of lessons is partial in both senses of the word: it is incomplete, and it reflects our own biases about what is most impor-

tant and interesting (or at least most familiar). The same can be said of the short history we present. Our subject is appropriate to the occasion, since the Sanibel Symposium has played a major role in the development of modern electronic structure theory, including but not limited to DFT. Possible companion pieces to this article are our short discussion [1] of "perplexing" issues in DFT and a detailed review [2] of the exact theory and its approximations.

Often we need to predict the ground-state properties of an atom, molecule, solid, nanostructure, or other system. We might need the equilibrium geometry or structure, vibrational frequencies, electron density, total energy, and various total energy differences such as atomization and surface energies, as well as the linear and nonlinear responses to external static probes. One way to find the needed properties is to solve the

N-electron Schroedinger equation for the N-electron ground-state wavefunction. This approach is potentially accurate and complete (providing all the information that can be known), but it is computationally inefficient and impractical for large N. A second way is to solve for more limited information, as provided by a Green's function, density matrix, or electron density. This approach may be less accurate and complete, but it can achieve a useful computational efficiency even for large N.

Kohn–Sham DFT [2, 3] uses spin orbitals to predict the ground-state electron density, total energy, and related important properties. It provides an often useful and improvable compromise between accuracy and computational efficiency. Thus, it is now the most widely used method of electronic structure calculation in both condensed matter physics and quantum chemistry, two subjects that have long been intertwined at the Sanibel Symposia. However, other methods [4], including full wavefunction methods, continue to improve in accuracy and efficiency, providing for selected systems a benchmark of accuracy.

Orbital-free DFT began in the 1920s with the Thomas–Fermi theory [5, 6], which expresses the total energy E approximately in terms of the electron density $n(\vec{r})$, where $n(\vec{r})d^3r$ is the average number of electrons in volume element d^3r at position $\vec{r}$, using the simplest density functional that makes sense. The density is then varied at fixed electron number $N = \int d^3r\, n(\vec{r})$ to minimize the energy functional. This approach gives simple and useful estimates for the density and total energy of an atom (defined as minus the minimum work to strip all the electrons from the nucleus) but it is far too crude for chemistry. In fact, Teller [7] proved that in Thomas–Fermi theory, atoms do not bind together to form molecules and solids. Without the exchange–correlation energy, "nature's glue" [8], chemical bonds are either absent or far too long and weak. However, orbital-free methods continue to improve; see recent work by Trickey and others [9–11].

Spin orbitals or fictitious one-electron wavefunctions $\psi_i(\vec{r}, \sigma)$ were introduced in the 1930s by Hartree, Fock, and Slater [12]. The energy (including sometimes exchange but not Coulomb correlation) was expressed in terms of these orbitals and their occupation numbers f_i (1 or 0, since electrons are fermions), and minimized with respect to them. This approach binds atoms into molecules and solids, although usually too weakly [8], and

generally improves the total energy E and electron density $n(\vec{r}) = \sum_{i\sigma} f_{i\sigma} |\psi_{i\sigma}(\vec{r})|^2$ over orbital-free methods.

The Hartree and Hartree-Fock methods were not easy to implement on early computers and omitted important correlation effects. In the 1950s, Slater combined the orbital and density functional approaches by creating a local density approximation (LDA) for the exchange–correlation energy and potential (which he called the $X\alpha$ approximation [12]). He found that it could be easily implemented self-consistently on the computer and that it included a rough but useful estimate of correlation. After retiring from MIT in 1966, Slater joined the Quantum Theory Project at the University of Florida, Gainesville, which held the first Sanibel Symposium in 1961.

In 1964–1965, the Hohenberg–Kohn [13] and Kohn–Sham [3] theorems, the twin pillars of modern DFT, were published. These theorems showed that, given the right density functionals, one can find the exact ground-state density and energy of an N-electron system in an external scalar potential using either the total density or the orbitals as variational objects. Kohn and Sham also proposed an LDA for the exchange–correlation energy, which, unlike Slater's, is exact for an electron gas of uniform or slowly varying density.

Kohn–Sham theory was not widely known until around 1970, when condensed matter physicists started to find that this theory in the LDA gives a remarkably realistic description of bulk solids and their surfaces. Since then, DFT has dominated electronic structure calculations for solids. For the surface energy [14, 15] of a solid, density functionals proved to be more accurate than early correlated wavefunction calculations.

The densities of many solids, especially simple metals, are sufficiently like those of uniform electron gases for the LDA to work well. However, it did not work so well for atoms and molecules. In particular, the atomization energies of molecules were strongly overestimated (although they were still better than those of Hartree-Fock theory). In the period 1970–1986, DFT in chemistry had only a few prophets, including notably Parr [16], Jones and Gunnarsson [17], and Levy [18]. This was however a time when theoretical work by Langreth and Perdew [19, 20], and by Gunnarsson and Lundqvist [21], explained why the local approximation worked as well as it did and suggested approaches to improve it. The new approaches included generalized gradient approximations and hybrid

functionals, which greatly increased the accuracy of atomization energies and thus the relevance of the theory to chemistry.

Since about 1992, DFT has swept chemistry, as it earlier swept condensed matter physics. This development was led notably by Becke [22], who proposed many creative approaches to functional construction, and by John Pople and Nick Handy.

Since the 1920s, many important lessons have been learned about DFT. We summarize 14 of these lessons below.

Lesson 1: Density vs. Correlated Wavefunction

The electron density $n(\vec{r})$ has a lower dimensionality than the N-electron wavefunction $\Psi(\vec{r}_1, \sigma_1, ..., \vec{r}_N, \sigma N)$. Using n instead of Ψ as the basic variational object makes electronic structure calculations much faster but typically much less accurate.

This lesson comes from Thomas [5] and Fermi [6]. In his lecture for the 1998 Nobel Prize in Chemistry [23], Walter Kohn explained this fact in a clear if oversimplified way, which we paraphrase here: suppose we use a mesh of points in real space, with 10 points along each of the x, y, and z axes. Then we can compute and store the density on the mesh as 10^3 numbers. A one-electron wavefunction can also be represented by 10^3 numbers, but a 10-electron correlated wavefunction must be represented by $(10^3)^{10} = 10^{30}$ numbers. There are of course cleverer ways [4] to compute a 10-electron wavefunction, but the fact remains that the effort to compute an N-electron wavefunction scales up very rapidly with N.

Lesson 2: Orbitals vs. Correlated Wavefunction

While too much accuracy can be lost by using the density $n(\vec{r})$ as the basic variational object, considerable accuracy can be restored by using also the occupied orbitals or fictitious one-electron wavefunctions $\psi_1(\vec{r}, \sigma)...\psi_N(\vec{r}, \sigma)$.

This lesson comes from Hartree and Fock in the 1920s and from Slater in the 1950s [12]. In our example from Lesson 1, an orbital description of

the 10-electron system requires computing and storing only $10 \times 10^3 = 10^4$ numbers.

Lesson 3: Something Proved to Exist That Cannot be Found

In principle, we can find the exact ground-state energy and density of N electrons in an external potential $v(\vec{r})$

a. by solving an Euler equation for the density $n(\vec{r})$ as proved by Hohenberg and Kohn [13], or

b. by solving self-consistent one-electron Schroedinger equations for the orbitals as proved by Kohn and Sham [3]. In approach (b), the functional derivative $\delta E_{xc}/\delta n(\vec{r})$ serves as the exchange–correlation contribution $v_{xc}(\vec{r})$ to the effective one-electron or Kohn–Sham potential $v_{KS}(\vec{r})$.

In practice, the exact density functional $E_v[n]$ for the total energy needed for approach (a), and the exact density functional $E_{xc}[n]$ for the exchange–correlation energy needed for approach (b), are not accessible in any practical way and must be approximated.

Although the Hohenberg–Kohn–Sham theorems are only existence theorems, the knowledge that exact density functionals exist has strongly driven the quest for better and more accurate approximations.

Lesson 4: From Uniform Electron Gas to Atoms, Molecules, and Solids

The local density approximation (LDA)

$$E_{xc}^{LDA}[n] = \int d^3 r n(\vec{r}) \varepsilon_{xc}^{unif}(n(\vec{r})), \qquad (1)$$

or better the local spin density approximation (LSDA)

$$E_{xc}^{LSDA}[n_\uparrow, n_\downarrow] = \int d^3 r n(\vec{r}) \varepsilon_{xc}^{unif}(n_\uparrow(\vec{r}), n_\downarrow(\vec{r})), \qquad (2)$$

which start from ε_{xc}^{unif}, the exchange–correlation energy per particle of a uniform electron gas, are

accurate enough for useful calculations on solids and solid surfaces but not accurate enough for atoms and molecules.

LDA comes from Kohn and Sham [3] and LSDA from von Barth and Hedin [24]. The accuracy of these local approximations for solids and surfaces was established by Lang and Kohn [25] and by Moruzzi et al. [26]. Jones and Gunnarsson [17] found good structures but overestimated atomization energies for molecules.

For open-shell or magnetic systems, in the absence of an external magnetic field, one can use either the total density or the separate spin densities in principle, but in practice LSDA is more accurate than LDA because it inputs more information about the system [27]. This was the first indication of a possible ladder of density functional approximations for the exchange–correlation energy to be discussed in Lessons 9 and 10 below. All rungs of the ladder are actually implemented on the spin densities, but we will use the total density below to simplify the notation.

Lesson 5: The Electron Digs a Hole

The exact exchange–correlation energy is [19–21] the electrostatic interaction between the electron density $n(\vec{r})$ and the density $n_{xc}(\vec{r}, \vec{r}')$ at $\vec{r}'$ of the exchange–correlation hole around an electron at $\vec{r}$:

$$E_{xc} = (1/2) \int d^3r n(\vec{r}) \int d^3r' n_{xc}(\vec{r}, \vec{r}')/|\vec{r}' - \vec{r}|. \quad (3)$$

The exchange–correlation hole $n_{xc} = n_x + n_c$ is the sum of the separate exchange and correlation holes. The exchange hole is the same as in Hartree–Fock theory, with the Hartree–Fock orbitals replaced by Kohn–Sham orbitals, and the correlation hole is an average of an expectation value over the coupling constant for the electron–electron interaction at fixed electron density. The exact holes satisfy the constraints

$$n_x < 0, \quad \int d^3r' n_x(\vec{r}, \vec{r}') = -1, \quad \int d^3r' n_c(\vec{r}, \vec{r}') = 0. \quad (4)$$

These constraints are also satisfied by the LDA hole (that of a uniform gas) and this fact explains why LDA works as well as it does. The con-

straints can also be imposed to develop other approximations that can improve over LDA by satisfying additional exact constraints.

This lesson comes from Langreth and Perdew [19, 20] and from Gunnarsson and Lundqvist [21].

Lesson 6: Searching Over Wavefunctions for the Density Functional

The original proof of the Hohenberg–Kohn theorem [13] was by reductio ad absurdum and thus not a constructive proof. Alternatively, the various density functionals, including $E_{xc}[n]$, can be defined by searches over N-electron wavefunctions constrained to yield a given electron density [18]. Thus, the functionals can be intuitively understood and their exact properties can be derived.

This lesson comes from Levy [18]. It is an important one because the derived exact properties (e.g., Refs. [28, 29]) can be used to constrain the needed approximations.

Lesson 7: After the Local Density Comes its Gradient

Second-order gradient expansions

$$E_{xc}^{GEA}[n] = E_{xc}^{LDA}[n] + \int d^3r C_{xc}(n)|\nabla n|^2/n^{4/3} \quad (5)$$

improve on LDA for very slowly varying densities but are typically less accurate than LDA for realistic densities [30, 31], because [31] the second-order gradient expansion of the hole violates the exact hole constraints of Lesson 5. However, generalized gradient approximations or GGAs [30–35]

$$E_{xc}^{GGA}[n] = \int d^3r n \varepsilon_{xc}^{GGA}(n, \nabla n) \quad (6)$$

can be derived with or without nonempirical parameters, and are more accurate than LDA for the separate exchange and correlation energies of atoms and for the atomization energies of molecules and solids.

Nonempirical constructions often impose exact constraints on (1) the hole [33], or (2) the energy

functional [35], or (3) the coupling constant dependence [36].

This lesson comes from Ma and Brueckner [30], Langreth and Perdew [31], Langreth and Mehl [32], Perdew and Wang [33], Becke [34, 22], Perdew et al. [35], and Seidl et al. [36]. It was the main development that made DFT of interest to chemists.

Lesson 8: What is a Fraction of an Electron?

The exact density functional $E_v[n]$ for the energy can be defined for an open system with noninteger average electron number N [37] by extending the constrained search of Lesson 6 from wavefunctions to ensembles. The energy E varies linearly between adjacent integer electron numbers, with derivative discontinuities at the integers. This explains why neutral molecules dissociate to integer-charged atoms, and why the fundamental band gap [38, 39] in the exact Kohn–Sham band structure is unphysical.

This lesson comes from Perdew et al. [37], Perdew and Levy [38], and Sham and Schlueter [39].

Lesson 9: The More Information Input, the More Accurate the Output

We can make more accurate functionals by adding ingredients to the exchange–correlation energy density beyond n and ∇n:

a. Meta-GGAs add the orbital kinetic energy density

$$\tau(\vec{r}) = (1/2) \sum_{i\sigma} f_{i\sigma} |\nabla \psi_{i\sigma}(\vec{r})|^2, \qquad (7)$$

as proposed by Becke [40] with other nonempirical constructions by Perdew et al. [41–43].

b. Hyper-GGAs or hybrid functionals add exact exchange information, such as the exact exchange energy or the exact exchange hole, as proposed by Becke [44] and refined by Savin [45], Vydrov and Scuseria [46], etc. Most hyper-GGAs do not properly scale to exact exchange under uniform density scal-

ing to the high-density limit but some do [47].

c. Random phase approximation (RPA)-like functionals add the unoccupied orbitals as developed by Furche [48, 49], Harl and Kresse [50], etc.

Lesson 10: We are Climbing Jacob's Ladder

There is a five-rung Jacob's ladder of common density functional approximations (LSDA, GGA, meta-GGA, hyper-GGA, and RPA-like functionals), as proposed by Perdew and Schmidt [51] and explained in Lesson 9. All rungs except the hyper-GGA rung now have nonempirical constructions. Accuracy tends to increase up the ladder. Computational cost increases modestly from LSDA to GGA to meta-GGA (the three semilocal rungs) but can increase considerably on ascent to higher rungs.

The Perdew-Burke-Ernzerhof (PBE) GGA [35] provides a moderately accurate description of atoms, molecules, and solids but is too simple to achieve high accuracy for all three kinds of systems. The optimum GGA for solids has a weaker gradient dependence than the optimum GGA for atoms and molecules, as argued by Perdew and coworkers [52–54]. However, a single nonempirical meta-GGA (revTPSS) can work well for the equilibrium properties of atoms, molecules, and solids, as shown by Perdew et al. [43]. A meta-GGA can provide different GGA descriptions for solids (especially metals), which have important regions of strong orbital overlap where $\tau(\vec{r}) \gg \tau_W(\vec{r}) \equiv |\nabla n|^2/(8n)$, and for atoms and molecules, which have important regions where a single orbital shape dominates the density (as in an electron-pair bond), making $\tau(\vec{r}) \approx \tau_W(\vec{r})$.

Lesson 11: Where Semilocal Functionals Fall Down

Semilocal functionals (LSDA, GGA, and meta-GGA) necessarily fail (and thus full nonlocality is needed) when the exact exchange–correlation hole has a long-range tail, because semilocal functionals know nothing about the electron density far from an electron. This failure occurs when long-

range van der Waals interactions between separating systems are important; the needed correction is present in RPA-like functionals [48–50] but neither in semilocal functionals nor in hyper-GGAs. The failure also occurs when electrons are shared across stretched bonds between distant centers (as in certain transition states and dissociation limits). Semilocal functionals cannot describe such stretched bonds, but hyper-GGAs and RPA-like functionals can do so by displaying more or less the right derivative discontinuities of Lesson 8.

Dramatic stretched-bond effects have been discussed by Ruzsinszky et al. [55, 56], Vydrov et al. [57], Tsuchimochi and Scuseria [58], and Yang and coworkers [59].

Lesson 12: Elaborate Functionals Need Corrections Too

The RPA, which uses the unoccupied orbitals in the simplest way that makes sense for all systems, is not quite good enough for chemistry. It underestimates atomization energies of molecules by about the same amount that the PBE GGA overestimates them as discovered by Furche [48]. For this property, RPA is far less accurate than meta- and hyper-GGAs. RPA uses exact exchange but makes the correlation energy too negative by roughly 0.02 hartree/electron. Thus, a correction to RPA is needed.

The needed correction to RPA is semilocal (describable by LSDA or GGA) in atoms and at solid surfaces [60] but it is fully nonlocal in molecules [61]. An accurate nonempirical nonlocal correction remains to be found.

Lesson 13: The Kohn–Sham Potential Shapes Up

Starting from an orbital functional, the exact Kohn–Sham potential $v_{KS}(\vec{r})$ of Lesson 3 can be constructed by the optimized effective potential method of Talman and Shadwick [62, 63].

Starting from the correlated N-electron wavefunction, we can directly construct the energy and electron density. However, it is also computationally practical to construct therefrom the exact Kohn–Sham potential and so to study its features. This can be done in two different ways: (1) The

Zhao et al. [64] approach first constructs the density and then numerically varies the Kohn–Sham potential to reproduce this density in a system of N noninteracting electrons. (2) Another approach due to Sahni [65] and others constructs the Kohn–Sham potential from expectation values computed from the correlated N-electron wavefunction.

Lesson 14: After Statics Comes Dynamics

DFT can be extended (exactly in principle and approximately in practice) to time-dependent and excited states. The essential idea is to solve time-dependent one-electron Schroedinger equations in which the time-dependent exchange–correlation potential $v_{xc}(\vec{r}, t)$ is a functional of the electron density $n(\vec{r}', t')$. Poles of the frequency-dependent linear density response function then yield the excitation energies.

This lesson comes from Runge and Gross [66] and from others [67].

References

1. Perdew, J. P.; Ruzsinszky, A.; Constantin, L. A.; Sun, J.; Csonka, G. I. J Chem Theory Comput 2009, 5, 902.

2. Perdew, J. P.; Kurth, S. In A Primer in Density Functional Theory; Fiolhais, C., Nogueira, F., Marques, M., Eds.; Lecture Notes in Physics; Springer: Berlin, 2003; Vol. 620, p 1.

3. Kohn, W.; Sham, L. J. Phys Rev 1965, 140, A1133.

4. Shavitt, I.; Bartlett, R. J. Many Body Methods in Chemistry and Physics: MBPT and Coupled-Cluster Theory; Cambridge University Press: Cambridge, 2009.

5. Thomas, L. H. Proc Cambridge Philos Soc 1926, 23, 542.

6. Fermi, E. Zeit fuer Physik 1928, 48, 73.

7. Teller, E. Rev Mod Phys 1962, 34, 627.

8. Kurth, S.; Perdew, J. P. Int J Quantum Chem 2000, 77, 819.

9. Perdew, J. P.; Constantin, L. A. Phys Rev B 2007, 75, 155109.

10. Karasiev, V. V.; Jones, R. S.; Trickey, S. B.; Harris, F. E. Phys Rev B 2009, 80, 245120.

11. Huang, C.; Carter, E. A. Phys Rev B 2010, 81, 045206.

12. Slater, J. C. The Self-Consistent Field for Molecules and Solids; McGraw-Hill: New York, 1974.

13. Hohenberg, P.; Kohn, W. Phys Rev 1964, 136, B864.

14. Fiolhais, C.; Perdew, J. P. Phys Rev B 1992, 45, 6207.

15. Constantin, L. A.; Pitarke, J. M.; Dobson, J. F.; Garcia-Lekue, A.; Perdew, J. P. Phys Rev Lett 2008, 100, 036401.

16. Parr, R. G.; Yang, W. Density Functional Theory of Atoms and Molecules; Oxford University Press: Oxford, 1989.

17. Jones, R. O.; Gunnarsson, O. Rev Mod Phys 1989, 61, 689.

18. Levy, M. Proc Nat Acad Sci USA 1979, 76, 6062.

19. Langreth, D. C.; Perdew, J. P. Solid State Commun 1975, 17, 1425.

20. Langreth, D. C.; Perdew, J. P. Phys Rev B 1977, 15, 2884.

21. Gunnarsson, O.; Lundqvist, B. I. Phys Rev B 1976, 13, 4274.

22. Becke, A. D. Phys Rev A 1988, 38, 3098.

23. Kohn, W. Rev Mod Phys 1999, 71, 1253.

24. von Barth, U.; Hedin, L. J Phys C: Solid State Phys 1972, 5, 1629.

25. Lang, N. D.; Kohn, W. Phys Rev B 1970, 1, 4555.

26. Moruzzi, V. L.; Janak, J. F.; Williams, A. R. Calculated Electronic Properties of Metals; Pergamon: New York, 1978.

27. Gunnarsson, O.; Lundqvist, B. I.; Wilkins, J. W. Phys Rev B 1974, 10, 1319.

28. Levy, M.; Perdew, J. P. Phys Rev A 1985, 32, 2010.

29. Oliver, G. L.; Perdew, J. P. Phys Rev A 1979, 20, 397.

30. Ma, S.-K.; Brueckner, K. A. Phys Rev 1968, 165, 18.

31. Langreth, D. C.; Perdew, J. P. Phys Rev B 1980, 21, 5469.

32. Langreth, D. C.; Mehl, M. J. Phys Rev B 1983, 20, 1809.

33. Perdew, J. P.; Wang, Y. Phys Rev B 1986, 33, 8800; Erratum: Perdew, J. P.; Wang, Y. Phys Rev B 1989, 40, 3399.

34. Becke, A. D. J Chem Phys 1986, 84, 4524.

35. Perdew, J. P.; Burke, K.; Ernzerhof, M. Phys Rev Lett 1996, 77, 3865; Erratum: Perdew, J. P.; Burke, K.; Ernzerhof, M. Phys Rev Lett 1997, 78, 1396.

36. Seidl, M.; Perdew, J. P.; Kurth, S. Phys Rev Lett 2000, 84, 5070.

37. Perdew, J. P.; Parr, R. G.; Levy, M.; Balduz, J. L. Phys Rev Lett 1982, 49, 1691.

38. Perdew, J. P.; Levy, M. Phys Rev Lett 1983, 51, 1884.

39. Sham, L. J.; Schlueter, M. J. Phys Rev Lett 1983, 51, 1888.

40. Becke, A. D.; Roussel, M. R. Phys Rev A 1989, 39, 3761, and references therein.

41. Perdew, J. P.; Kurth, S.; Zupan, A.; Blaha, P. Phys Rev Lett 1999, 82, 2544; Erratum: Perdew, J. P.; Kurth, S.; Zupan, A.; Blaha, P. Phys Rev Lett 1999, 82, 5179.

42. Tao, J.; Perdew, J. P.; Staroverov, V. N.; Scuseria, G. E. Phys Rev Lett 2003, 91, 146401.

43. Perdew, J. P.; Ruzsinszky, A.; Csonka, G. I.; Constantin, L. A.; Sun, J. Phys Rev Lett 2009, 103, 026403.

44. Becke, A. D. J Chem Phys 1993, 98, 5648.

45. Savin, A. In Recent Developments and Applications of Modern Density Functional Theory; Seminario, J. M., Ed.; Elsevier: Amsterdam, 1996; p 327.

46. Vydrov, O. A.; Scuseria, G. E. J Chem Phys 2006, 125, 234109.

47. Perdew, J. P.; Staroverov, V. N.; Tao, J.; Scuseria, G. E. Phys Rev A 2008, 78, 052513.

48. Furche, F. Phys Rev B 2001, 64, 195120.

49. Furche, F. J Chem Phys 2008, 129, 114105.

50. Harl, J.; Kresse, G. Phys Rev Lett 2009, 103, 056401.

51. Perdew, J. P.; Schmidt, K. In Density Functional Theory and Its Applications to Materials; Van Doren, V. E., Van Alsenoy, K., Geerlings, P., Eds.; American Institute of Physics: Melville, NY, 2001; p 1.

52. Perdew, J. P.; Constantin, L. A.; Sagvolden, E.; Burke, K. Phys Rev Lett 2006, 97, 223002.

53. Csonka, G. I.; Vydrov, O. A.; Scuseria, G. E.; Ruzsinszky, A.; Perdew, J. P. J Chem Phys 2007, 126, 244107.

54. Perdew, J. P.; Ruzsinszky, A.; Csonka, G. I.; Constantin, L. A.; Zhou, X.; Vydrov, O. A.; Scuseria, G. E.; Burke, K. Phys Rev Lett 2008, 100, 136406; Erratum: Perdew, J. P.; Ruzsinszky, A.; Csonka, G. I.; Constantin, L. A.; Zhou, X.; Vydrov, O. A.; Scuseria, G. E.; Burke, K. Phys Rev Lett 2009, 102, 039902.

55. Ruzsinszky, A.; Perdew, J. P.; Csonka, G. I.; Vydrov, O. A.; Scuseria, G. E. J Chem Phys 2006, 125, 194112.

56. Ruzsinszky, A.; Perdew, J. P.; Csonka, G. I.; Vydrov, O. A.; Scuseria, A. J Chem Phys 2007, 126, 104102.

57. Vydrov, O. A.; Scuseria, G. E.; Perdew, J. P. J Chem Phys 2007, 126, 154109.

58. Tsuchimochi, T.; Scuseria, G. E. J Chem Phys 2009, 131, 121102.

59. Cohen, A. J.; Mori-Sanchez, P.; Yang, W. Science 2008, 321, 792.

60. Yan, Z.; Perdew, J. P.; Kurth, S. Phys Rev B 2000, 61, 16430; Erratum: Yan, Z.; Perdew, J. P.; Kurth, S. Phys Rev B 2010, 81, 169902.

61. Ruzsinszky, A.; Perdew, J. P.; Csonka, G. I. J Chem Theory Comput 2010, 6, 127.

62. Talman, J. D.; Shadwick, W. F. Phys Rev A 1976, 14, 36.

63. Kuemmel, S.; Perdew, J. P. Phys Rev Lett 2003, 90, 043004.

64. Zhao, Q.; Morrison, R. C.; Parr, R. G. Phys Rev A 1994, 50, 2138.

65. Sahni, V. Quantal Density Functional Theory; Springer: Berlin, 2004, and references therein.

66. Runge, E.; Gross, E. K. U. Phys Rev Lett 1984, 52, 997.

67. Marques, M. A. L.; Ullrich, C. A.; Nogueira, F.; Rubio, A.; Burke, K.; Gross, E. K. U., Eds. Time-Dependent Density Functional Theory; Springer Lecture Notes in Physics; Springer: Berlin, 2006; Vol. 706.