Theor Chem Acc (2016) 135:255
DOI 10.1007/s00214-016-2013-7

REGULAR ARTICLE

Functional constructions with specified functional derivatives

K. Finzel[1] · **Paul W. Ayers**[2]

Received: 1 July 2016 / Accepted: 18 October 2016 / Published online: 28 October 2016
© Springer-Verlag Berlin Heidelberg 2016

Abstract A bifunctional construction depending on a specified density–potential pair and an approximate guiding electron density functional is presented. The proposed bifunctional construction properly transforms under homogeneous coordinate scaling and yields the specified functional derivative, which determines the electron density. Whereas the method is general and applicable to all functional types, it will prove especially helpful in the context of orbital-free density functional theory, where most existing approximate density functionals predict inaccurate potentials.

Keywords Potential functionals · Specified functional derivatives · Orbital-free density functional theory · Pauli potential · Kinetic energy density functional

1 Introduction

The Hohenberg–Kohn (HK) theorems [1] offer a seductive approach to the physical properties of a system without using wavefunctions [2]. However, finding reliable approximations to the HK functional is very difficult [3, 4]. Exact approaches [5–7] sacrifice conceptual simplicity and in practice require the same computational effort as wavefunction methods [8, 9]; simple approximations tend to fail unpredictably [3].

Especially in orbital-free density functional theory (OF-DFT), approximate functionals for the kinetic energy [10–31] often suffer from the lack of N-representability of density functionals [32–34], and consequently, they tend to fail during the variational optimization of the electron density, producing bosonic-like structureless electron densities. This failure is attributed to an insufficient incorporation of the Pauli exclusion principle in the approximate functional. The Pauli kinetic energy, which is defined as the difference between the non-interacting kinetic energy and the bosonic von Weizsäcker term [35], as well as the corresponding Pauli potential has been intensively studied in the literature [36–44] as they represent the only unknown part of the Kohn–Sham (KS) kinetic energy functional and its corresponding KS potential.

Recently, one of us showed how to design approximations for the Pauli potential that give electron densities with proper atomic shell structure [45–47]. An extension of this method, applicable to bound Coulomb systems, can be found in reference [48]. However, those approximations are given in terms of a position variable and as such do not provide a direct route for obtaining the corresponding parent functional using, for example, path integration techniques [49]. Of course, the corresponding functional of degree one can always be constructed [36, 50], but this functional expression does not fulfill known constraints on the kinetic energy, like homogeneous scaling [36], and is a poor approximation to total kinetic energy values even though it yields qualitatively correct binding energy curves for strong and moderately bound molecules [50].

In this work, we show how to construct functionals that correctly transform under homogeneous coordinate scaling and yield a specified functional derivative. Examples of the proposed bifunctional construction will be given for the exchange energy and the Pauli kinetic energy.

✉ K. Finzel
kati.finzel@cpfs.mpg.de

[1] (IFM) Department of Physics, Chemistry and Biology, Linköping University, 58183 Linköping, Sweden

[2] Department of Chemistry and Chemical Biology, McMaster University, Hamilton ON L8S 4M1, Canada

2 Theory

Our approach to functionals with specified functional derivative is a bifunctional construction, using a potential functional that specifies the functional derivative and an approximate density functional. Additionally, the bifunctional is designed to properly transform under homogeneous coordinate scaling [51].

A functional that is homogeneous with respect to coordinate scaling:

$$\begin{aligned} &Q[\rho_\alpha] = \alpha^\mu Q[\rho] \\ &\rho_\alpha(x,y,z) = \alpha^3 \rho_\alpha(\alpha x, \alpha y, \alpha z) \end{aligned} \tag{1}$$

can always be approximated by a local functional with the correct scaling:

$$\begin{aligned} Q[\rho_\alpha] &= C \int (\rho_\alpha(\mathbf{r}))^{\mu/3+1}\, \mathrm{d}\mathbf{r} \\ &= C \int\int\int \alpha^\mu \rho^{\mu/3+1}(\alpha x, \alpha y, \alpha z)\, \mathrm{d}(\alpha x)\, \mathrm{d}(\alpha y)\, \mathrm{d}(\alpha z) \\ &= \alpha^\mu Q[\rho], \end{aligned} \tag{2}$$

where C, α and μ are constants. This suggests that we consider a change in the argument of the density functional to the quantity $\rho^{\mu/3+1}(\mathbf{r})$, so that the functional is homogeneous of degree one and its functional derivative is homogenous of degree zero with respect to coordinate scaling:

$$\begin{aligned} \frac{\delta Q}{\delta\rho^{\mu/3+1}(\mathbf{r})} &= \int \frac{\delta Q}{\delta\rho(\mathbf{r}')} \frac{\delta\rho(\mathbf{r}')}{\delta\rho^{\mu/3+1}(\mathbf{r})}\, \mathrm{d}\mathbf{r}' \\ &= \int \frac{\delta Q}{\delta\rho(\mathbf{r}')} \frac{\delta(\mathbf{r}-\mathbf{r}')}{\delta\left(\frac{\mu}{3}+1\right)\rho^{\mu/3}(\mathbf{r})}\, \mathrm{d}\mathbf{r}' \\ &= \frac{3}{\mu+3}\rho^{-\mu/3}(\mathbf{r}) \frac{\delta Q}{\delta\rho(\mathbf{r})}. \end{aligned} \tag{3}$$

The advantage of this approach is that $\frac{\delta Q}{\delta\rho^{\mu/3+1}(\mathbf{r})}$ has the same scaling as a constant.

Finally, the bifunctional $Q_v[\rho]$ is constructed as the sum of an approximate density functional $\tilde{Q}[\rho]$ that obeys homogeneous scaling and the bifunctional correction:

$$\begin{aligned} Q_v[\rho] &= \tilde{Q}[\rho] \\ &\quad + \int \rho^{\mu/3+1}(\mathbf{r}) \left[\frac{\delta Q}{\delta\rho^{\mu/3+1}(\mathbf{r})}\Big|_{\mathrm{acc}} - \frac{\delta\tilde{Q}}{\delta\rho^{\mu/3+1}(\mathbf{r})}\Big|_{\mathrm{acc}} \right] \mathrm{d}\mathbf{r} \\ &= \tilde{Q}[\rho] + \left(\frac{3}{\mu+3}\right) \int \rho^{\mu/3+1}(\mathbf{r}) \\ &\quad \times \left\{ (\rho[v_{\mathrm{acc}};\mathbf{r}])^{-\mu/3} \left[v_{\mathrm{acc}}(\mathbf{r}) - \frac{\delta\tilde{Q}[\rho[v_{\mathrm{acc}};\mathbf{r}]]}{\delta\rho(\mathbf{r})} \right] \right\} \mathrm{d}\mathbf{r}, \end{aligned} \tag{4}$$

where $v_{\mathrm{acc}}(\mathbf{r}) = \frac{\delta Q}{\delta\rho(\mathbf{r})}|_{\mathrm{acc}}$ is an accurate functional derivative associated with the electron density $\rho[v_{\mathrm{acc}};\mathbf{r}]$. Notice that by construction the term in curly braces does not depend on the electron density. Because of this, both the first and the second terms of Eq. 4 have the correct scaling, and so the overall functional does also. In addition, taking the functional derivative at the solution point, one obtains:

$$\begin{aligned} \frac{\delta Q_v[\rho[v_{\mathrm{acc}};\mathbf{r}]]}{\delta\rho(\mathbf{r})} &= \frac{\delta\tilde{Q}[\rho[v_{\mathrm{acc}};\mathbf{r}]]}{\delta\rho(\mathbf{r})} \\ &\quad + \left(\frac{3}{\mu+3}\right)\left(\frac{\mu+3}{3}\right) (\rho[v_{\mathrm{acc}};\mathbf{r}])^{\mu/3} (\rho[v_{\mathrm{acc}};\mathbf{r}])^{-\mu/3} \\ &\quad \times \left[v_{\mathrm{acc}}(\mathbf{r}) - \frac{\delta\tilde{Q}[\rho[v_{\mathrm{acc}};\mathbf{r}]]}{\delta\rho(\mathbf{r})} \right] \\ &= v_{\mathrm{acc}}(\mathbf{r}) \end{aligned} \tag{5}$$

the desired potential expression $v_{\mathrm{acc}}(\mathbf{r})$, that can be chosen to be the accurate potential for the system of interest. Therefore, the functional defined by Eq. 4 obeys homogeneous coordinate scaling and has the specified functional derivative, as it shifts the minimum of the approximative functional $\tilde{Q}[\rho]$ to the specified expression for the potential. Notice that the desired minimizing density is obtained for all possible choices of approximate $\tilde{Q}[\rho]$. In practice, however, the density will be obtained from the corresponding potential expression alone. The energy evaluated from the proposed bifunctional $Q_v[\rho]$ depends on the approximation for $\tilde{Q}[\rho]$, where any approximation obeying homogeneous coordinate scaling [51] can be chosen. Alternatively, but equivalently, the energy can be evaluated by the virial theorem [51].

At the solution point, the proposed bifunctional construction with specified functional derivative:

$$\begin{aligned} Q_v[\rho_{\mathrm{acc}}] &= \tilde{Q}[\rho_{\mathrm{acc}}] + \left(\frac{3}{\mu+3}\right) \\ &\quad \times \int \rho_{\mathrm{acc}}(\mathbf{r}) \left[v_{\mathrm{acc}}(\mathbf{r}) - \frac{\delta\tilde{Q}[\rho[v_{\mathrm{acc}};\mathbf{r}]]}{\delta\rho(\mathbf{r})} \right] \mathrm{d}\mathbf{r} \end{aligned} \tag{6}$$

yields an improvement over the original functional approximation $\tilde{Q}[\rho]$ as the accurate electron density is obtained by construction. Moreover, in stark contrast to existing kinetic energy density functionals, the potential is evaluated at the accurate reference density, rather than the poor quality minimizing density associated with $\tilde{Q}[\rho]$. This corrects for density-driven errors in the functional [52–54]. Finally, because the functional scales correctly and the density and potential are correct, the value of Q is correct for the minimizing density (by the Euler theorem for homogeneous functionals). Finding an approximate functional in the form $F[\rho] = \int f(\rho, \ldots)\, \mathrm{d}\mathbf{r}$ that produces an accurate energy and potential expression for an actual reference density is less difficult than what the formulation in Eq. 5 achieves, which is a functional that gives this reference density by variational minimization of the functional.

As a first example of this formulation, consider the exchange energy density functional. For any electron density that is the Hartree–Fock ground state for some system, the exact exchange potential is given by the HFxc method [55]. Using the HFxc potential, $v_{\mathrm{HFxc}}(\mathbf{r})$, for a Hartree–Fock density $\rho_{\mathrm{HF}}(\mathbf{r})$, one can write the functional:

$$E_X[\rho] = \tilde{E}_X[\rho] + \frac{3}{4}\int \rho^{4/3}(\mathbf{r}) \times \left\{ (\rho_{\mathrm{HF}}(\mathbf{r}))^{-1/3} \left[v_{\mathrm{HFxc}}(\mathbf{r}) - \frac{\delta \tilde{E}_X[\rho_{\mathrm{HF}}]}{\delta \rho(\mathbf{r})} \right] \right\} \mathrm{d}\mathbf{r}. \tag{7}$$

The issue of designing functionals with appropriate functional derivatives is most critical in orbital-free density functional theory. Therefore, the proposed bifunctional is especially useful in this context. For the Pauli kinetic energy, the corresponding bifunctional construction at the solution point yields:

$$T_{\mathrm{P}}[\rho] = \tilde{T}_{\mathrm{P}}[\rho] + \frac{3}{5}\int \rho(\mathbf{r}) \left[v_{\mathrm{P}}(\mathbf{r}) - \frac{\delta \tilde{T}_{\mathrm{P}}[\rho[v_{\mathrm{P}};\mathbf{r}]]}{\delta \rho(\mathbf{r})} \right] \mathrm{d}\mathbf{r} \tag{8}$$

whereby $\tilde{T}_{\mathrm{P}}[\rho]$ can be any functional approximation for the Pauli kinetic energy that obeys homogeneous coordinate scaling.

3 Conclusions

In this work, a strategy for the design of functionals that transform correctly under homogeneous coordinate scaling and yield a specified functional derivative is presented. This goal was achieved with the help of a bifunctional construction, depending on the electron density and a specified potential–density pair, determining the functional derivative. By construction, this bifunctional always recovers this pair when it is variationally optimized. However, the corresponding energy is mainly determined by the chosen density functional approximation.

Acknowledgements K.F greatly acknowledges the support from the Alexander von Humboldt foundation in form of a Feodor Lynen fellowship and as the main funder of this work. Additionally, K.F. is thankful for financial support from the Swedish Government Strategic Research Area in Materials Science on Functional Materials at Linköping University (Faculty Grant SFO Mat LiU No. 2009 00971). P.W.A. acknowledges support from NSERC and Compute Canada.

References

1. Hohenberg P, Kohn W (1964) Phys Rev B 136:864
2. Parr RG, Yang W (1989) Density-functional theory of atoms and molecules. Oxford University Press, Oxford
3. Burke K (2012) J Chem Phys 136:150901
4. Becke AD (2014) J Chem Phys 140:18A301
5. Levy M (1979) Proc Natl Acad Sci 76:6062
6. Lieb EH (1983) Int J Quantum Chem 24:243
7. Kryachko ES, Ludeña (1991) Phys Rev A 43:2179
8. Colonna F, Savin A (1999) J Chem Phys 110:2828
9. Ayers PW, Parr RG (2014) Indian J Chem 53A:929
10. Thomas LH (1927) Proc Camb Philos Soc 23:542
11. Fermi E (1928) Z Phys 48:73–79
12. Kirzhnits DA (1957) Sov Phys JETP 5:64
13. Hodges CH (1973) Can J Phys 51:1428
14. Yang W (1986) Phys Rev A 34:4575
15. DePristo AE, Kress JD (1987) Phys Rev A 35:438
16. Thakkar AJ (1992) Phys Rev A 46:6920
17. Lacks DJ, Gordon RG (1994) J Chem Phys 100:4446
18. Wang YA, Carter EA (2000) Orbital-free kinetic-energy density functional theory. In: Schwarz SD (ed) Theoretical methods in condensed phase chemistry. Kluwer, New York, p 117
19. Ayers PW, Lucks JB, Parr RG (2002) Acta Chim Phys Debr 34:223
20. Ayers PW (2005) J Math Phys 46:062107
21. Chakraborty D, Ayers PW (2011) J Math Chem 49:1810
22. Tran F, Wesolowski TA (2002) Int J Quantum Chem 89:441
23. Levy M, Ayers PW (2009) Phys Rev A 79:064504
24. Lee D, Constantin LA, Perdew JP, Burke K (2009) J Chem Phys 130:034107
25. Karasiev V, Jones RS, Trickey SB, Harris FE (2009) Recent advances in developing orbital-free kinetic energy functionals. In: Paz EJ, Hernandez AJ (eds) New developments in quantum chemistry. Transworld Research Network, Trivandrum
26. Ghiringhelli LM, Delle Site L (2008) Phys Rev B 77:073104
27. Ghiringhelli LM, Hamilton IP, Delle Site L (2010) J Chem Phys 132:014106
28. Trickey S, Karasiev VV, Vela A (2011) Phys Rev B 84:075146
29. Karasiev VV, Trickey SB (2012) Comput Phys Commun 183:2519
30. Karasiev V, Chakraborty D, Trickey SB (2014) Progress on new approaches to old ideas: orbital-free density functionals. In: Delle Site L, Bach V (eds) Many-electron approaches in physics, chemistry and mathematics. Springer, Heidelberg, p 113
31. Karasiev V, Trickey SB (2015) Adv Quantum Chem 71:221
32. Ayers PW, Liu S (2007) Phys Rev A 75:022514
33. Ludeña EV, Illas F, Ramirez-Solis A (2008) Int J Mod Phys B 22:4642
34. Kryachko ES, Ludeña EV (2014) Phys Rep 544:123
35. March NH (1986) Phys Lett A 113:476
36. Levy M, Ou-Yang H (1988) Phys Rev A 38:625
37. Nagy A (1991) Acta Phys Hung 70:321
38. Nagy A, March NH (1991) Int J Quantum Chem 39:615
39. Nagy A, March NH (1992) Phys Chem Liq 25:37
40. Holas A, March NH (1995) Int J Quantum Chem 56:371
41. Amovilli C, March NH (1998) Int J Quantum Chem 66:281
42. Nagy A (2008) Chem Phys Lett 460:343
43. Nagy A (2010) Int J Quantum Chem 110:2117
44. Nagy A (2011) J Chem Phys 135:044106
45. Finzel K (2015) Int J Quantum Chem 115:1629
46. Finzel K (2016a) J Chem Phys 144:034108
47. Finzel K (2016b) Theor Chem Acc 135:87

48. Finzel K (2016c) Int J Quantum Chem 116:1261
49. Gaiduk AP, Chulkov SK, Staroverov VN (2009) J Chem Theory Comput 5:699
50. Finzel K, Davidsson J, Abrikosov AI (2016) Int J Quantum Chem 116:1337
51. Levy M, Perdew JP (1985) Phys Rev A 32:2010
52. Kim MC, Sim E, Burke K (2013) Phys Rev Lett 111:073003
53. Kim MC, Sim E, Burke K (2014) J Chem Phys 140:18a528
54. Kim MC, Park H, Son S, Sim E, Burke K (2015) J Phys Chem Lett 6:3802
55. Ryabinkin IG, Kananenka AA, Staroverov VN (2013) Phys Rev Lett 111:074112