

The density per particle can be used as the fundamental descriptor for systems with rapidly decaying external potentials

Paul W. Ayers

Received: 11 April 2012 / Accepted: 25 September 2012 / Published online: 20 October 2012
© Springer-Verlag Berlin Heidelberg 2012

Abstract For systems of electrons bound by potentials that decay faster than $1/r$ asymptotically, the density per particle determines the number of electrons and therefore the electron density. The density per particle, commonly called the shape function, can thus be used as the fundamental descriptor of systems with rapidly decaying external potentials. This result is analogous to a result that is known for Coulomb potentials. Possible extensions of the result to include broader classes of external potentials and alternative density-like descriptors are discussed.

Keywords Shape function · Coulomb systems · Density functional theory

Introduction

Many descriptors satisfy a restricted Hohenberg–Kohn-like theorem in which no two Coulombic external potentials can have the same value for the descriptor [1–19]. The resulting Coulomb-restricted functionals are useful in many cases, partly because less-divergent functionals are obtained [6, 9, 20] and partly because this provides a way to treat ground and excited states on an equal footing [1, 2, 4, 5, 7, 12–17, 21]. The proofs of these theorems usually rest on two key results: the Kato–Steiner cusp condition [22–24] and its excited-state generalizations [2, 7, 13, 14] (which allows one to determine the external potential from the cusp in

the electron density and descriptors related to it) and the characteristic asymptotic decay of the electron density (which allows one to determine the number of electrons and the level of excitation) [25–34]. Based on these arguments, it is possible to determine the Hamiltonian—and then, through the Schrödinger equation, all observable properties of the system—for any system whose external potential is created by a distribution of point charges,

$$v_{\text{Coul}}(r) = \sum_{\alpha=1}^L \frac{-q_{\alpha}}{|r - R_{\alpha}|}. \quad (1)$$

Such external potentials are called Coulombic. This type of approach originates with Bright Wilson, who invoked it to dismiss the Hohenberg–Kohn theorems as trivial (as discussed by Handy [35]). In its modern form, it is primarily associated with the work of Nagy (on excited states [1]) and the present author, who demonstrated that the state of a Coulomb system is determined by the density per particle, or shape function [7],

$$\sigma(r) = \frac{\rho(r)}{N}. \quad (2)$$

This result revived an old idea of Bartolotti and Parr [36], leading to a surge of research in what is often called shape functional theory [7, 10, 11, 18, 37–45]. This result also led to proofs that the Fukui function [8, 10, 46–48], the local temperature and local kinetic energy [3, 49–54], the electrostatic potential [8, 55–57], and many other density-functional descriptors [3, 8] can also be used as fundamental descriptors for Coulomb systems.

However, all of these results hold only for the very special case of Coulomb potentials. The purpose of this paper is to show that the shape function, Eq. 2, also determines all

P. W. Ayers (✉)
Department of Chemistry & Chemical Biology,
McMaster University,
Hamilton, Ontario, Canada
e-mail: ayers@mcmaster.ca

properties of systems with external potentials that have faster-than-Coulombic asymptotic decay, i.e., external potentials that decay asymptotically faster than $1/r$. These external potentials can be identified using the “normalization” of the potential [58–61],

$$0 = \int \frac{-1}{4\pi} \nabla^2 v(r) dr. \quad (3)$$

Alternatively, we can consider only those $v(\mathbf{r})$ for which, for every $\varepsilon > 0$, there is an R such that for all $r > R$, $|v(r)| < \varepsilon r^{-1}$ almost everywhere. Here, r is the distance from the center of the system, $r = |\mathbf{r}|$. The latter description is somewhat more general because it does not require the Laplacian of the external potential to be integrable. We refer to these potentials as *rapidly decaying*.

The shape function determines all properties of systems with rapidly decaying external potential

To show that $\sigma(\mathbf{r})$ determines all properties of any electronic system bound by a rapidly decaying external potential, an argument from [7] is adapted. First, using the methods of Almbladh and von Barth [32], the asymptotic decay of the electron density in a rapidly decaying external potential is derived. The Kohn–Sham equations are [62]

$$\left\{ \left(-\frac{\nabla^2}{2} + v(r) + v_J(r) + v_{xc}(r) \right) \varphi_i(r) = \varepsilon_i \varphi_i(r) \right\}_{i=1}^{N_{\text{occ}}} \quad (4)$$

where ϕ_i is the i th Kohn–Sham orbital, ε_i is the i th Kohn–Sham orbital energy, N_{occ} is the number of occupied orbitals, $v(\mathbf{r})$ is the external potential, $v_J(\mathbf{r})$ is the potential due to the classical electrostatic repulsion between particles, and $v_{xc}(\mathbf{r})$ is the potential due to exchange and correlation effects. For large r , v_J and v_{xc} fall off as N/r and $-1/r$, respectively, where N is the number of electrons [32, 63–65]. The asymptotic decay of the external potential is

$$v(\mathbf{r}) \sim \frac{K(\mathbf{r})}{r}, \quad (5)$$

and, because the external potential is assumed to be rapidly decaying,

$$\lim_{r \rightarrow \infty} K(r) = 0, \quad (6)$$

except possibly on a set of zero measure. (For example, sometimes the external potential may have a different asymptotic rate of decay on a symmetry plane of the system.) Substituting the asymptotic behavior of v , v_J , and v_{xc} into Eq. 4 gives the asymptotic Kohn–Sham equations (valid far from a finite system)

$$\left\{ \left(-\frac{1}{2} \frac{d^2}{dr^2} + \frac{1}{r} \cdot \frac{d}{dr} + \frac{K(r) + N - 1}{r} \right) \varphi_i(r) = \varepsilon_i \varphi_i(r) \right\}_{i=1}^{N_{\text{occ}}}, \quad (7)$$

with the asymptotic solution

$$\varphi_i(r) \sim r^{\frac{-K(r)+1-N}{\sqrt{-2\varepsilon_i}}-1} e^{-\sqrt{-2\varepsilon_i}r}. \quad (8)$$

The asymptotic decay of the electron density of this system is then

$$\rho(r) \sim \sum_{i=1}^{N_{\text{occ}}} n_i |\varphi_i(r)|^2 = \sum_{i=1}^{N_{\text{occ}}} n_i r^{2 \left(\frac{-K(r)-N+1}{\sqrt{-2\varepsilon_i}} - 1 \right)} e^{-r\sqrt{-8\varepsilon_i}}, \quad (9)$$

where n_i is the occupation number of the i th Kohn–Sham orbital. For large r , the density is dominated by contributions from the orbital (or orbitals) with the highest ε_i , since all other contributions to the density decay exponentially faster than these orbitals. (The one exception is on a nodal plane of the highest-occupied molecular orbital(s); that case requires specialized analysis [66–68].) Accordingly, for large r ,

$$\begin{aligned} \left[\frac{\partial \ln(\rho(r))}{\partial r} \right] &\sim -\sqrt{-8 \cdot \varepsilon_{\text{HOMO}}} \\ &+ 2 \left[\frac{(-K(r) - N + 1)}{\sqrt{-2 \cdot \varepsilon_{\text{HOMO}}} - 1} \right] \left(\frac{1}{r} \right) \\ &+ \left(\text{higher powers of } \frac{1}{r} \right). \end{aligned} \quad (10)$$

We can find $\varepsilon_{\text{HOMO}}$ from a formula analogous to the result for Coulomb systems [7],

$$\varepsilon_{\text{HOMO}} = \lim_{r \rightarrow \infty} \left[\frac{-1}{8} \cdot \left(\frac{\partial \ln(\rho(r))}{\partial r} \right)^2 \right]. \quad (11)$$

Similarly,

$$\begin{aligned} \lim_{r \rightarrow \infty} \left[\frac{\partial \left(\frac{\partial \ln(\rho(r))}{\partial r} \right)}{\partial \left(\frac{1}{r} \right)} \right] &= \lim_{r \rightarrow \infty} \left[2 \left(\frac{(-K(r) - N + 1)}{\sqrt{-2 \cdot \varepsilon_{\text{HOMO}}} - 1} \right) \right] \\ &= 2 \left(\frac{(-N + 1)}{\sqrt{-2 \cdot \varepsilon_{\text{HOMO}}} - 1} \right). \end{aligned} \quad (12)$$

The second equality follows from the rapid decay of the external potential, Eq. 6. This gives an explicit formula for the number of electrons in terms of the asymptotic decay of the electron density,

$$N[\rho] = 1 + \frac{1}{4} \cdot \lim_{r \rightarrow \infty} \left(\frac{\partial \ln(\rho(r))}{\partial r} \right) \left(2 + \frac{\partial^2 \ln(\rho(r))}{\partial \left(\frac{1}{r} \right) \partial r} \right). \quad (13)$$

However, because the electron density and the shape function differ by a multiplicative constant, their logarithmic

derivative with respect to any spatial function is the same,

$$\frac{\partial \ln(\sigma(r))}{\partial g(r)} = \frac{\partial [\ln(\rho(r)) - \ln(N)]}{\partial g(r)} = \frac{\partial \ln(\rho(r))}{\partial g(r)}. \tag{14}$$

Therefore, the shape function of a system with a rapidly decaying external potential also determines the number of electrons,

$$N[\sigma] = 1 + \frac{1}{4} \cdot \lim_{r \rightarrow \infty} \left(\frac{\partial \ln(\sigma(r))}{\partial r} \right) \left(2 + \frac{\partial^2 \ln(\sigma(r))}{\partial \left(\frac{1}{r}\right) \partial r} \right). \tag{15}$$

This means that the electron density, $\rho(\mathbf{r}) = N[\sigma]\sigma(\mathbf{r})$, is also a functional of the shape function. The shape function can then be used as the fundamental descriptor of the system via the Hohenberg–Kohn theorem [68].

The same analysis can be performed using the equations for the generalized overlap amplitudes instead of the Kohn–Sham equations [25]. If one does this, one discovers that the exponential rate of asymptotic decay of an excited-state shape function is controlled by the ionization potential of the excited state [7],

$$E_k^{(N)} - E_0^{(N-1)} = \lim_{r \rightarrow \infty} \left[\frac{-1}{8} \cdot \left(\frac{\partial \ln(\sigma_k(r))}{\partial r} \right)^2 \right]. \tag{16}$$

(Again, there are exceptions to this rule in the rare but interesting cases where the ground state of the $(N-1)$ -electron system has zero overlap with the k th excited state of the N -electron system [21, 25, 69], and potentially in cases where the highest-occupied Dyson orbital has an angular node at infinity [Gori-Giorgi P, Gal T, Baerends EJ (2012) in preparation].) This implies that the shape function of a system with rapidly decaying external potential determines both the number of electrons (via Eq. 15) and the excitation level (via Eq. 16) and permits the construction of an excited-state shape-functional theory for this class of systems. More interestingly, this allows the *density functional theory* construction in [21] to be applied to systems with rapidly decaying external potentials.

Discussion and extensions

An immediate and interesting extension of this result allows shape-functional theory to be applied to potentials that decay asymptotically as Kr^{-1} with known K . This is true of Coulomb systems (K can be deduced from the sharpness of the cusps in the shape function), but if one is given K for a non-Coulomb system, then N can be determined using Eq. 12.

There are many fundamental descriptors for Coulombic external potentials [3, 8, 10], and it is reasonable to ask

whether reactivity indicators like the Fukui function or the local temperature might suffice as descriptors of systems with rapidly decaying external potentials. *In general, the answer is no.* The class of rapidly decaying external potentials is just too large. However, if one restricts oneself to external potentials that are created by a system of second-order poles,

$$v(\mathbf{r}) = \sum_{\beta=1}^M \frac{p_\beta}{|\mathbf{r} - \mathbf{R}_\beta|^2}, \tag{17}$$

then the electron density is either zero at \mathbf{R}_β (but in a way that reveals the value of $p_\beta > 0$) or the electron density diverges at \mathbf{R}_β (but in a way that reveals the value of $p_\beta < 0$). Derivatives of the electron density (like the Fukui function) and other related quantities (like the local temperature) should then suffice to describe systems with external potentials of the form described by Eq. 17.

One may also speculate as to whether there might be a “supertheorem” that allows us to combine the result for rapidly decaying external potentials with the result for Coulombic external potentials. *In general, the answer is no.* An explicit counterexample is given by the shape function of the hydride anion. This is the shape function of a two-electron Coulomb system, but it is also the shape function of the one-electron system whose external potential is the Kohn–Sham potential of the hydride ion, $v_s(\mathbf{r}) = -\frac{1}{2}\nabla^2 \sqrt{\sigma(\mathbf{r})} / \sqrt{\sigma(\mathbf{r})}$. The Kohn–Sham potential of any anion decays as r^{-2} or faster because the Kohn–Sham potential decays as

$$v_s(r) \sim \frac{-Q - 1}{r} + O\left(\frac{1}{r^2}\right), \tag{18}$$

where Q is the charge on the system. However, if one is willing to restrict oneself to rapidly decaying potentials of the form described by Eq. (17), a combined theory does seem to exist. That is, given any external potential composed only of simple poles and quadratic poles, with no two poles coinciding,

$$v(\mathbf{r}) = \sum_{\alpha=1}^L \frac{-q_\alpha}{|\mathbf{r} - \mathbf{R}_\alpha|} + \sum_{\beta=1}^M \frac{p_\beta}{|\mathbf{r} - \mathbf{R}_\beta|^2} \quad \mathbf{R}_\alpha \neq \mathbf{R}_\beta, \tag{19}$$

the external potential can be determined by cusps (simple poles) or zeros and divergences (quadratic poles) of the shape function, and the number of electrons can be determined from the asymptotic decay of the shape function. *This theory cannot be extended to excited-states* because the higher-order cusp conditions for the shape function have the same form as the zeros associated with quadratic poles when $p_\beta > 0$ [2, 7, 13, 14]. However, it is probably possible to show that reactivity indicators like the Fukui function can be used as the fundamental descriptors of systems governed by external potentials like Eq. 19.

Based on [7] and subsequent work by this author and others, people often conclude that Coulombic external potentials are remarkably special. Coulombic external potentials are not *that* special. Indeed, for a sufficiently small class of external potentials, there will never be two shape functions with the same external potential. An example is the space of rapidly decaying external potentials focused upon in this paper. Similarly, for any sufficiently large class of external potentials (e.g., all external potentials decaying as r^{-1} or faster), there will be two different external potentials with the same shape function (e.g., the hydride anion and the one-electron system bound by the Kohn–Sham potential of H^-). One nice feature of the result given in this paper is that the class of rapidly decaying external potentials is a *mathematical space*. The class of Coulomb potentials is not a space because in the limit where the number of point charges goes to infinity, Coulomb-like potentials become continuous charge distributions. However, the Coulomb class of potentials is much more interesting for chemistry.

Acknowledgments PWA acknowledges the Natural Sciences and Engineering Research Council (NSERC) and the Canada Research Chairs for funding. I also acknowledge Peter Politzer, whom I admire because he exemplifies how to balance “interesting” and “useful” science.

References

- Nagy A (1998) Excited states in density functional theory. *Int J Quantum Chem* 70:681–691
- Nagy A, Sen KD (2001) Ground- and excited-state cusp conditions for the electron density. *J Chem Phys* 115:6300–6308
- Ayers PW, Nagy A (2007) Alternatives to the electron density for describing Coulomb systems. *J Chem Phys* 126:144108
- Nagy A (1998) Density functional. Theory and application to atoms and molecules. *Phys Rep* 298:2–79
- Ayers PW, Levy M (2009) Time-independent (static) density-functional theories for pure excited states: extensions and unification. *Phys Rev A* 80:012508
- Ayers PW, Golden S, Levy M (2006) Generalizations of the Hohenberg–Kohn theorem: I. Legendre transform constructions of variational principles for density matrices and electron distribution functions. *J Chem Phys* 124:054101
- Ayers PW (2000) Density per particle as a descriptor of coulombic systems. *Proc Natl Acad Sci USA* 97:1959–1964
- Ayers PW (2007) Using reactivity indicators instead of the electron density to describe Coulomb systems. *Chem Phys Lett* 438:148–152
- Ayers PW, Fuentealba P (2009) Density-functional theory with additional basic variables: extended Legendre transform. *Phys Rev A* 80:032510
- De Proft F, Ayers PW, Sen KD, Geerlings P (2004) On the importance of the “density per particle” (shape function) in the density functional theory. *J Chem Phys* 120:9969–9973
- Ayers PW, Cedillo A (2009) Density-functional theory. In: Chattaraj PK (ed) *Chemical reactivity theory: a density functional view*. Taylor and Francis, Boca Raton, p 269
- Nagy A (1998) Density functional theory for excited states. *Adv Quantum Chem* 29:159–178
- Nagy A, Sen KD (2000) Exact results on the curvature of the electron density at the cusp in certain highly excited states of atoms. *Chem Phys Lett* 332:154–158
- Nagy A, Sen KD (2000) Higher-order cusp of the density in certain highly excited states of atoms and molecules. *J Phys B* 33:1745–1751
- Nagy A (2003) Theories for excited states. *Adv Quantum Chem* 42:363–381
- Nagy A (2004) Theories for individual excited states. *Int J Quantum Chem* 99:256–264
- Nagy A, Levy M, Ayers PW (2009) Time-independent theory for a single excited state. In: Chattaraj PK (ed) *Chemical reactivity theory: a density functional view*. Taylor and Francis, Boca Raton, p 121
- Geerlings P, De Proft F, Ayers PW (2007) Chemical reactivity and the shape function. *Theor Comput Chem* 19:1–17
- Parr RG (2000) Density-functional theory and chemistry. In: Anagnostatos GS, Bishop RF, Gernoth KA, Giapitzakis J, Ginis P, Theophilou A (eds) *Condensed matter theories*, vol 15. Nova Science, Huntington, pp 297–302
- Ayers PW, Levy M (2005) Generalized density-functional theory: Conquering the N-representability problem with exact functionals for the electron pair density and the second-order reduced density matrix. *J Chem Sci* 117:507–514
- Ayers PW, Nagy A, Levy M (2012) Time-independent density-functional theory for excited states of Coulomb systems. *Phys Rev A* 85:042518
- Kato T (1957) On the eigenfunctions of many-particle systems in quantum mechanics. *Commun Pure Appl Math* 10:151–177
- Pack RT, Brown WB (1966) Cusp conditions for molecular wavefunctions. *J Chem Phys* 45:556–559
- Steiner E (1963) Charge densities in atoms. *J Chem Phys* 39:2365–2366
- Katriel J, Davidson ER (1980) Asymptotic behavior of atomic and molecular wave functions. *Proc Natl Acad Sci USA* 77:4403–4406
- Morrell MM, Parr RG, Levy M (1975) Calculation of ionization potentials from density matrices and natural functions, and the long-range behavior of natural orbitals and electron density. *J Chem Phys* 62:549–554
- Levy M, Parr RG (1976) Long-range behavior of natural orbitals and electron density. *J Chem Phys* 64:2707–2708
- Levy M, Perdew JP, Sahni V (1984) Exact differential-equation for the density and ionization-energy of a many-particle system. *Phys Rev A* 30:2745–2748
- Hoffmann-Ostenhof M, Hoffmann-Ostenhof T (1977) “Schrodinger inequalities” and asymptotic behavior of the electron density of atoms and molecules. *Phys Rev A* 16:1782–1785
- Ahlich R, Hoffmann-Ostenhof M, Hoffmann-Ostenhof T, Morgan JD III (1981) Bounds on the decay of electron densities with screening. *Phys Rev A* 23:2106–2117
- Fournais S, Hoffmann-Ostenhof M, Hoffmann-Ostenhof T, Sorensen TO (2009) Analytic structure of many-body coulombic wave functions. *Commun Math Phys* 289:291–310
- Almladh CO, von Barth U (1985) Exact results for the charge and spin-densities, exchange-correlation potentials, and density-functional eigenvalues. *Phys Rev B* 31:3231–3244
- Patil SH (1989) Asymptotic structure of atomic wave functions. *J Phys B* 22:2051–2056
- Patil SH (1984) Asymptotic behavior of 2-electron atomic wavefunctions. *J Chem Phys* 80:2689–2692
- Handy NC (1995) Density functional theory. In: Bicout D, Field M (eds) *Quantum mechanical simulation methods for studying biological systems: Les Houches Workshop, May 2–7, 1995*. Springer, Berlin, pp 1–35
- Parr RG, Bartolotti LJ (1983) Some remarks on the density functional theory of few-electron systems. *J Phys Chem* 87:2810–2815

37. Ayers PW (2005) Proof-of-principle functionals for the shape function. *Phys Rev A* 71:062506
38. Ayers PW, De Proft F, Geerlings P (2007) Comparison of the utility of the shape function and electron density for predicting periodic properties: atomic ionization potentials. *Phys Rev A* 75:012508
39. Borgoo A, De Proft F, Geerlings P, Sen KD (2007) Complexity of Dirac–Fock atom increases with atomic number. *Chem Phys Lett* 444(1–3):186–191
40. Borgoo A, Godefroid M, Indelicato P, De Proft F, Geerlings P (2007) Quantum similarity study of atomic density functions: insights from information theory and the role of relativistic effects. *J Chem Phys* 126(4):044102
41. Gal T (2007) The mathematics of functional differentiation under conservation constraint. *J Math Chem* 42:661–676
42. Ayers PW (2006) Information theory, the shape function, and the Hirshfeld atom. *Theor Chem Acc* 115:370–378
43. Geerlings P, Boon G, Van Alsenoy C, De Proft F (2005) Density functional theory and quantum similarity. *Int J Quantum Chem* 101(6):722–732
44. Sen KD, De Proft F, Borgoo A, Geerlings P (2005) N-derivative of Shannon entropy of shape function for atoms. *Chem Phys Lett* 410(1–3):70–76
45. Bultinck P, Carbó-Dorca R (2004) A mathematical discussion on density and shape functions, vector semispaces and related questions. *J Math Chem* 36(2):191–200
46. Parr RG, Yang WT (1984) Density functional approach to the frontier-electron theory of chemical reactivity. *J Am Chem Soc* 106:4049–4050
47. Yang WT, Parr RG, Pucci R (1984) Electron density, Kohn–Sham frontier orbitals, and Fukui functions. *J Chem Phys* 81:2862–2863
48. Ayers PW, Levy M (2000) Perspective on “Density functional approach to the frontier-electron theory of chemical reactivity” by Parr RG, Yang W (1984). *Theor Chem Acc* 103:353–360
49. Ghosh SK, Berkowitz M, Parr RG (1984) Transcription of ground-state density-functional theory into a local thermodynamics. *Proc Natl Acad Sci USA* 81:8028–8031
50. Ghosh SK, Berkowitz M (1985) A classical fluid-like approach to the density-functional formalism of many-electron systems. *J Chem Phys* 83:2976–2983
51. Ayers PW, Parr RG, Nagy A (2002) Local kinetic energy and local temperature in the density-functional theory of electronic structure. *Int J Quantum Chem* 90:309–326
52. Janosfalvi Z, Sen KD, Nagy A (2005) Cusp conditions for non-interacting kinetic energy density of the density functional theory. *Phys Lett A* 344(1):1–6
53. Anderson JSM, Ayers PW, Hernandez JIR (2010) How ambiguous is the local kinetic energy? *J Phys Chem A* 114:8884–8895
54. Chattaraj PK, Chamorro E, Fuentealba P (1999) Chemical bonding and reactivity: a local thermodynamic viewpoint. *Chem Phys Lett* 314:114–121
55. Politzer P, Truhlar D (1981) Chemical applications of atomic and molecular electrostatic potentials. Plenum, New York
56. Politzer P (1980) Electrostatic potential–electronic density relationships in atoms. *J Chem Phys* 72(5):3027–3033
57. Politzer P (1980) Electrostatic potential–electronic density relationships in atoms. 2. *J Chem Phys* 73(7):3264–3267
58. Ayers PW, Levy M (2001) Sum rules for exchange and correlation potentials. *J Chem Phys* 115:4438–4443
59. Andrade X, Aspuru-Guzik A (2011) Prediction of the derivative discontinuity in density functional theory from an electrostatic description of the exchange and correlation potential. *Phys Rev Lett* 107:183002
60. Liu SB, Ayers PW, Parr RG (1999) Alternative definition of exchange-correlation charge in density functional theory. *J Chem Phys* 111:6197–6203
61. Gorling A (1999) New KS method for molecules based on an exchange charge density generating the exact local KS exchange potential. *Phys Rev Lett* 83:5459–5462
62. Kohn W, Sham LJ (1965) Self-consistent equations including exchange and correlation effects. *Phys Rev* 140:A1133–A1138
63. Qian ZX, Sahn V (1998) Analytical asymptotic structure of the Pauli, Coulomb, and correlation-kinetic components of the Kohn–Sham theory exchange-correlation potential in atoms. *Int J Quantum Chem* 70:671–680
64. Ayers PW, Morrison RC, Parr RG (2005) Fermi–Amaldi model for exchange-correlation: atomic excitation energies from orbital energy differences. *Mol Phys* 103:2061–2072
65. Savin A, Umrigar CJ, Gonze X (1998) Relationship of Kohn–Sham eigenvalues to excitation energies. *Chem Phys Lett* 288(2–4):391–395
66. Wu Q, Ayers PW, Yang WT (2003) Density-functional theory calculations with correct long-range potentials. *J Chem Phys* 119:2978–2990
67. Holas A (2008) Comment on “Asymptotic form of the Kohn–Sham correlation potential”. *Phys Rev A* 77:026501
68. Hohenberg P, Kohn W (1964) Inhomogeneous electron gas. *Phys Rev* 136:B864–B871
69. Vanfleteren D, van Neck D, Ayers PW, Morrison RC, Bultinck P (2009) Exact ionization potentials from wavefunction asymptotics: the extended Koopmans’ theorem, revisited. *J Chem Phys* 130:194104