CORRELATED ORBITAL THEORIES WITH BOTH LOCAL AND NON-LOCAL ONE-BODY POTENTIALS

NORMAN H. MARCH[a]

(Communication presented by Prof. Paolo V. Giaquinta)

ABSTRACT. After a brief survey of current density functional theory (DFT), based on an incompletely known one-body potential $V(\mathbf{r})$, a method due to Cordero, March, and Alonso (CMA) is summarized. This obtains the ground-state density $n(\mathbf{r})$, for spherical atoms as yet, from a semi-empirical fine-tuning of Hartree-Fock (HF) theory, which of course involves a non-local potential because of the presence of the Fock operator. This leads to $n(\mathbf{r})$ for spherical atoms of quantum Monte Carlo quality. A more recent proposal, related to CMA but different, by Bartlett, is also reviewed.

1. Introduction

While the forerunner of modern density functional theory (DFT) [1], namely the Thomas-Fermi (TF) theory, was orbital-free, being based on a ground-state density $n(\mathbf{r})$ obtained from the energy functional $E_{\mathrm{TF}}[n]$ given by [2, 3]

$$E_{\mathrm{TF}}[n] = c_k \int n^{5/3}(\mathbf{r})d^3\mathbf{r} + \int V_{\mathrm{ext}}(\mathbf{r})n(\mathbf{r})d^3\mathbf{r} + \frac{1}{2}e^2 \int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d^3\mathbf{r}d^3\mathbf{r}', \quad (1)$$

where $c_k = (3h^2/10m)(3/8\pi)^{2/3}$, via the variational principle

$$\delta(E - \mu N) = 0, \quad (2)$$

where μ is the chemical potential and N the total number of electrons in the molecule or cluster being considered, the local density approximation (LDA) to the single-particle kinetic energy $t_1 \propto n^{5/3}(\mathbf{r})$ integrated through space is bypassed now in DFT [1] by returning to 'correlated orbitals' generated by the local one-body potential

$$V(\mathbf{r}) = V_{\mathrm{ext}}(\mathbf{r}) + V_{\mathrm{electrostatic}}(\mathbf{r}) + V_{\mathrm{xc}}(\mathbf{r}). \quad (3)$$

Here, unfortunately, uncontrolled approximations are involved in constructing the exchange (x) – correlation (c) potential $V_{\mathrm{xc}}(\mathbf{r})$ given in terms of the, as yet unknown, exchange-correlation functional $E_{\mathrm{xc}}[n]$ by [1, 4]

$$V_{\mathrm{xc}}(\mathbf{r}) = \frac{\delta}{\delta n(\mathbf{r})}E_{\mathrm{xc}}[n]. \quad (4)$$

In Appendix A, following Amovilli *et al.* [5], we show that of four of the more popular current energy density functionals, only one, by PBE, satisfies to date the required variational principle in Eq. (2). This means that only the PBE functional of the four considered can have, underpinning it, an antisymmetric N-electron correlated ground-state wavefunction.

While the local potential $V(\mathbf{r})$ defined above, given $V_{\mathrm{xc}}(\mathbf{r})$ 'exactly', generates (in principle) the formally exact ground-state density, we give some attention below to a summary of recent studies by Cordero, March, and Alonso [6], and later by Bartlett [7], which return to correlated orbitals but relax the requirement that they are generated by a local potential.

2. One-body potential theory of molecules and solids modified semiempirically for electron correlation

Some six decades ago, March and Murray [8, 9], by means of infinite order perturbation theory, set up a one-body potential theory suitable for treating molecules and defective solids. Their approach adopted a local potential $V(\mathbf{r})$, already considered by Slater [10] as a simplification of the Hartree-Fock method, the latter involving essentially a non-local one-body potential due to the presence of the Fock operator [11]. Subsequently, Slater's work on the one-body potential $V(\mathbf{r})$ was formally completed by Kohn and Sham [4]. These authors demonstrated that the potential $V(\mathbf{r})$ had an exchange-correlation component $V_{\mathrm{xc}}(\mathbf{r})$ which must be added to the Hartree potential:

$$V(\mathbf{r}) = V_{\mathrm{H}}(\mathbf{r}) + V_{\mathrm{xc}}(\mathbf{r}), \tag{5}$$

involving the as yet unknown energy functional $E_{\mathrm{xc}}[n]$ in Eq. (4), where n is the electron density.

While major progress in quantum chemistry has resulted from a number of proposed approximate energy functionals E_{xc} [5], there is presently no systematic procedure to ensure that 'refinements' of such available functionals will converge to the exact ground-state energy E. And indeed, while the Slater-Kohn-Sham (SKS) form of density functional theory (see, *e.g.,* Parr and Yang [1]) is a variationally based method for Fermions, Amovilli *et al.* [5] have recently shown in this Journal that three out of four currently popular forms of $E_{\mathrm{xc}}[n]$ lead to ground-state energies below the exact E for some of the trial test cases for which E is known from correlated wave function theory or quantum Monte Carlo (QMC) simulations. This, of course, is a deeply serious matter for it means that some of the widely used forms of E_{xc} and hence V_{xc} in Eq. (4) cannot have any underlying antisymmetric many-electron wave function.

Subsequent to the work of [6], Bartlett has recently written a frontier article [7] entitled 'towards an exact correlated orbital theory for electrons'. In this review, Bartlett also stresses that DFT methods 'are fraught with difficulty', and he notes in specific terms numerous errors in present functionals, in addition to the possible violation of the variational principle by some choices of $E_{\mathrm{xc}}[n]$ which are currently widely used in quantum chemistry, as demonstrated in [5].

However, one aim in the present article is to compare and contrast the proposal of Bartlett on a correlated orbital theory, with the earlier study of Cordero, March, and Alonso [6]. This is especially prompted by Bartlett's writing, and we quote again here, 'our one-particle theory will look almost like Hartree-Fock theory ...'. That description will be

shown to apply quite precisely also to [6], with, however, the, of course major, difference that Cordero *et al.* invoke semiempirical 'fine-tuning' of the ground-state Hartree-Fock (HF) density. However, given that Cordero *et al.* impose, in a spherical atom like Be or Ne, the experimental ionization potential I (as they stress, to be corrected by a method they outline for usually small relativistic effects when necessary), their approach already constitutes one example of a (now approximate, of course) correlated orbital theory for electrons. Briefly, the idea underlying [6] is to 'fine tune' the already highly accurate $n(\mathbf{r})$ of HF theory [12] to remove the difference between the ionization potential of Koopmans, denoted there by I_K, and the exact (non-relativistic) ionization potential I.

Put precisely, following [13], the asymptotic large r limit of the ground-state electron density of a non-relativistic spherical atom is given in atomic units by

$$n(r)\big|_{r\to\infty} = Ar^\gamma \exp(-2\sqrt{2I}r) . \tag{6}$$

In HF theory with its non-local potential, all the individual orbitals building up the density in Eq. (6) fall off in the same exponential manner governed by I_K in marked contrast to the case of a local potential $V(r)$.

The achievement of Cordero *et al.* is to modify HF theory to retain the Kato cusp at the nucleus (see Eq. (8) below) but to ensure the correct asymptotic form (6) by building in the measured I, as mentioned already, into Eq. (6).

The semiempirical correlated orbital theory of CMA, in the language of RJB [7], consists of the following, published so far for the spherical atoms Be, Ne, Mg and Ar ground-states:

(i) Solve the self-consistent field (SCF) HF equations [6] numerically. However, this solution is now, because of semiempirical inclusion of correlation, not for the integral atomic number Z (*i.e.* 4 for Be: 10 for Ne etc.), but for a fractional value, Z' say, near to Z. The value of Z' is fixed precisely by appeal to the experimentally measured ionization potential I (corrected, when necessary, for usually small relativistic effects (see [6]). The resulting normalized density $n(r, Z')$ thereby obtained from occupied normalized HF orbitals $\psi_i(r, Z')$ for neutral atoms with N electrons, *i.e.* $n(r, Z')$ has $N = Z$, not Z'. This density $n(r, Z')$, before final modification, describes either fractional cations or anions, but not neutral atoms.

(ii) This density is then scaled to a final density

$$n_\lambda(r) = \lambda^3 n(\lambda r, Z') \tag{7}$$

where λ is to be determined to satisfy the Kato cusp condition [14]. For atoms this reads

$$\frac{\partial n(r)}{\partial r}\bigg|_{r=0} = -\frac{2Z}{a_0}n(r=0) : a_0 = \frac{\hbar^2}{me^2} . \tag{8}$$

By detailed comparison with available QMC simulations, it turns out for the four atoms cited above that the ground-state densities thereby obtained are of QMC quality. The fact that this semiempirical fine-tuned HF density: to be determined by steps (i) and (ii) explained above, is an excellent approximation to the true ground-state density $n(r)$, has its origins in the work of Møller and Plesset, some $6\frac{1}{2}$ decades ago [12], who by HF perturbation theory proved that the HF ground-state density was correct to second-order in the difference between the Fock operator and the exact non-relativistic Hamiltonian.

We stress again that, as with the recent RJB proposal [7], the SKS requirement of an exact ground-state density [1] is relaxed slightly, in the CMA correlated orbital theory, by means of adapting the one-body HF potential which is, as mentioned above, intrinsically non-local. Returning for a moment to the RJB method [7], there it is explicitly concluded that 'our one-particle theory will look almost like Hartree-Fock theory etc.', making clear the similarities between the CMA semiempirical theory and the method of RJB. A second important similarity is the insistence in both methods that the ionization potential I is exact: as explained above this is put in 'by hand' in the CMA method by making use of the experimentally measured value. RJB in this latter respect goes further, at least in principle, in insisting that his approach guarantees a correct one-particle energy spectrum, but with an approximate density paralleling that in the CMA theory.

Returning to semiempirical approaches, we want to emphasize here that the ultimate aim of these would be to utilize the measured ground-state electron density $n(\mathbf{r})$ for molecules and solids. As a specific example we cite the work of Howard *et al.* [15] on a crystal of formamide. Following an approach now referred to as 'quantum crystallography' by workers in the field; notable names being J. Karle and L. Massa, one sets up an approximate, but nevertheless idempotent, density matrix of Dirac [16] single-particle(s) form

$$\gamma_s(\mathbf{r}, \mathbf{r}') = \sum_{\text{occupied } i} \psi_i^*(\mathbf{r})\psi_i(\mathbf{r}') \tag{9}$$

where the $\psi_i(\mathbf{r})$ denote orthonormal orbitals. The property of idempotency, plus the fact that Eq. (9) is such that $\gamma_s(\mathbf{r}, \mathbf{r}) = n(\mathbf{r})$, the measured ground-state density from, say, X-ray diffraction experiments, are the important characteristics of Eq. (9).

But, in practice, the approach of the crystallographers is less directly related to correlated orbital theory than Eq. (9) would suggest. Therefore, below, we shall (i) emphasize the precise procedure adapted in current applications of quantum crystallography and (ii) stress that approximations to $\gamma_s(\mathbf{r}, \mathbf{r}')$ in Eq. (9) can lead us to link correlated orbital theory, as in the CMA approach, to current DFT theory.

Starting with step (i) immediately above, Eq. (9) is approximated by (cf. Holas and March [17]) an expansion in a finite basis of K orbitals $\chi_i(\mathbf{r})$ as

$$\gamma_s(\mathbf{r}, \mathbf{r}') = \sum_{ij}^{K} P_{ij}\chi_i(\mathbf{r})\chi_j(\mathbf{r}'). \tag{10}$$

The orbitals χ_i may be chosen as real, which is always possible in the absence of a magnetic field. The symmetric matrix P_{ij} entering Eq. (10) is a compact representation of the parameters used in quantum crystallography to fit the measured Bragg reflection data, say on the solid in question.

We take as an immediate example the work of Howard *et al.* [15] on formamide, already referred to. An X-ray experiment on this molecule in its crystalline geometry had earlier been carried out by Stevens [18]. The analysis reported in [15] leads to an idempotent matrix which has the experimentally determined ground-state density $n(\mathbf{r})$ as its diagonal element $\gamma_s(\mathbf{r}, \mathbf{r})$.

But this now takes us back to correlated orbital theories distinguished by the use of local potentials, as in the SKS method, and the HF-like non-local potential of the CMA approach. For the former case, the idempotent Dirac matrix $\gamma_s(\mathbf{r}, \mathbf{r}')$ defined via Eq. (9),

satisfies the equation of motion [19]

$$\nabla_{\mathbf{r}}^2 \gamma_s - \nabla_{\mathbf{r}'}^2 \gamma_s = \frac{2m}{\hbar^2} \left[V(\mathbf{r}) - V(\mathbf{r}') \right] \gamma_s \tag{11}$$

where $V(\mathbf{r})$ is given in Eq. (5). Idempotency must, of course, be imposed on the physical solution of Eq. (11). But immediately we encounter the difficulties spelt out above concerning the exchange-correlation potential $V_{\text{xc}}(\mathbf{r})$ in Eq. (5).

Thus, Holas and March [17] have advocated an extension of the quantum crystallographic approach discussed above by applying a potential-locality constraint to the approach of Howard *et al.* [15]. This specific constraint has not yet, to the present writer's knowledge, been applied to the experimental data on formamide, but the way to do this is set out very specifically in section III of Holas and March [17].

In the absence of this necessary data on a semiempirical Dirac density matrix $\gamma_s(\mathbf{r}, \mathbf{r}')$ constructed from experiment X-ray intensities, which we regard as the 'ultimate' semiempirical approach, let us approach our conclusion by returning to the correlated orbital approach of CMA, in which only the experimental ionization potential is introduced semiempirically. The CMA approach has been subsequently generalized off the diagonal by Amovilli, March, and Talman [20], to form a Dirac density matrix $\gamma_s(\mathbf{r}, \mathbf{r}')$ with the CMA density as its diagonal element $\gamma_s(\mathbf{r}, \mathbf{r}')$. We must reiterate that this γ_s does not satisfy Eq. (11), since the Amovilli *et al.* γ_s is generated by a HF-like non-local potential. Nevertheless, there is a way, set out below, in which this 'non-locally' generated γ_s can be used to make intimate contact with current DFT [1].

The essence of the approach proposed below to connect, albeit approximately, the CMA correlated orbital theory with current DFT is to utilize the differential virial theorem derived by Holas and March [21]. Essential input is then the kinetic energy tensor t_{ij}, constructed from the Dirac density matrix $\gamma_s(\mathbf{r}, \mathbf{r}')$ as (in atomic units)

$$t_{ij} = \frac{1}{4} \left[\left(\frac{\partial^2}{\partial r_i \partial r_j'} + \frac{\partial^2}{\partial r_j \partial r_i'} \right) \gamma_s(\mathbf{r}, \mathbf{r}') \right]_{\mathbf{r}' = \mathbf{r}} \tag{12}$$

which leads to the force $\mathbf{F}_K$ given by its components $(F_K)_i$ as

$$(F_K)_i = \frac{2}{n(r)} \sum_{j=1}^{3} \frac{\partial t_{ij}}{\partial r_j} . \tag{13}$$

Then in Eq. (13) of Amovilli and March [22] the desired exchange-correlation potential in Eq. (5) above is given by

$$V_{\text{xc}}(\mathbf{r}) = -V_{\text{electrostatic}}(\mathbf{r}) + \frac{1}{16\pi} \int \frac{[\nabla n \cdot \nabla \nabla^2 n]}{n^2(\mathbf{r}')|\mathbf{r} - \mathbf{r}'|}(\mathbf{r}')d\mathbf{r}'$$
$$- \frac{1}{16\pi} \int \frac{\nabla^4 n(\mathbf{r}')}{n(\mathbf{r}')|\mathbf{r} - \mathbf{r}'|}d\mathbf{r}' + \frac{1}{4\pi} \int \frac{\nabla \cdot \mathbf{F}_K(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}d\mathbf{r}' . \tag{14}$$

In Eq. (14) $V_{\text{electrostatic}}(\mathbf{r})$ is the electrostatic potential, while, of course, to obtain $V_{\text{xc}}(\mathbf{r})$ exactly we need in Eq. (14) the exact ground-state density $n(\mathbf{r})$ for, say, the molecule or cluster under investigation, plus the force $\mathbf{F}_K(\mathbf{r})$ determined by the Dirac idempotent matrix $\gamma_s(\mathbf{r}, \mathbf{r}')$ through Eqs. (13) and (12).

System	Basis set	LDA	PBE	PW91	B3LYP	Best *ab initio*[a]
H⁻	UGBS	−0.54335	−0.52439	−0.52697	−0.53477	−0.52775
He	UGBS	−2.87217	−2.89293	−2.90005	−2.91522	−2.90372
Li	UGBS	−7.39838	−7.46216	−7.47423	−7.49296	−7.47806
Li⁻	UGBS	−7.43146	−7.47926	−7.49237	−7.51171	−7.50040
Be	UGBS	−14.52049	−14.62993	−14.64801	−14.67333	−14.66735
Ne	UGBS	−128.43480	−128.86640	−128.94669	−128.98096	−128.9376
H_2O	cc-pvqz	−76.10341	−76.38317	−76.44145	−76.46961	−76.4274
LiBO	cc-pvqz	−107.04496	−107.53627	−107.63019	−107.69329	−107.540(5)[b]

Table 1. Ground-state energies for the systems studied in [5] at various levels of DFT calculation and comparison with the best available variational non-relativistic data. (a) After Refs. [23, 24, 25, 26]. (b) From diffusion quantum Monte Carlo [5].

One use of the CMA correlated orbital theory, which is a major proposal of the present Letter, is to now use instead of the exact $n(\mathbf{r})$ entering Eq. (14) the CMA semiempirical fine-tuned HF density. The second approximation is to note that since $\mathbf{F}_K(\mathbf{r})$ appears inside a volume integration in the final term in Eq. (14), we substitute for the idempotent Dirac matrix $\gamma_s(\mathbf{r}, \mathbf{r}')$, which should be generated from the exact local one-body potential $V(\mathbf{r})$ in Eq. (5) via Eq. (11), the off-diagonal idempotent matrix given by Amovilli, March, and Talman [20]. Of course, this has a QMC accuracy on the diagonal, but off the diagonal it is generated by a non-local HF-like potential [20, 6]. It would seem of considerable interest for the many-electron theory of molecules and solids if one can finally pull together correlated orbital theories such as CMA or RJB with current formulations of DFT, by means of Eqs. (12) to (14) above.

Acknowledgements

Appendix A. Classification of available density functionals

Here, we summarize a classification of available energy density functionals into two groups, which we term (i) heuristic (H) and (ii) possibly variationally valid (PV). One reason for such a classification emerges directly from what is today the biggest challenge DFT faces: the problem of a systematic development of more and more accurate density functionals. Variational validity can be a natural part of such a development. A functional proving to be variationally valid on a large domain of chemical systems can be an important indicator regarding the direction of functional development [5]. A further point concerns the comparison with quantum Monte Carlo (QMC) techniques. Nowadays, DFT and QMC

System	LDA	PBE	PW91	B3LYP
H^-	H	PV	PV	H
He	PV	PV	PV	H
Li	PV	PV	PV	H
Li^-	PV	PV	PV	H
Be	PV	PV	PV	H
Ne	PV	PV	H	H
H_2O	PV	PV	H	H
LiBO	PV	PV	H	H

Table 2. Classification of the density functionals considered in [5] as heuristic (H) or possibly variational (PV) according to results of Table 1.

are the best candidates among the existing theoretical methods which could be able to overcome the well-known computer problems related to the use of the most accurate quantum chemistry methods.

While it seemed natural to test the still widely used LDA, there is a degree of arbitrariness about the selection of the further three exchange-correlation energy functionals considered in this review, namely the functional of Perdew, Burke and Ernzerhof (PBE) [27], of Perdew and Wang (PW91) [28] and the Becke three parameter Lee, Yang and Parr functional (B3LYP) [29, 30]. However, B3LYP and PBE are certainly among the most widely used. In the literature there are several studies on the performance of these functionals; a resumé can be found in Refs. [31, 32].

For the study in [5] some realistic electronic systems were chosen in which electron correlation plays a significant effect. Although the strongest effects occur in the Wigner regime, for instance in an assembly of interacting electrons weakly confined in a quantum dot, where correlation kinetic energy could be more than 10 % of the Kohn-Sham single particle kinetic energy [33], our attention was limited in [5] to some systems whose energy can be readily reproduced by the use of a standard package for quantum chemistry calculations.

Table 1 then records from [5] results obtained using the above functionals for the ground-state energies of a few selected anionic and neutral atomic systems and the two molecules H_2O and LiOB, the latter molecule having been studied by Forte *et al.* [34] at the coupled cluster singles and doubles (CCSD) level. Table 2 displays the grouping of the four functionals tested in [5].

The fact that PBE is variationally valid in all species studied is clearly the most striking conclusion in [5]. In marked contrast, for B3LYP all ground-state energies fall below the known and highly accurate quantum-chemical results for the species studied. Thus, some Fermion constraint is missing (which is of course beyond the formally exact framework of DFT) when the analogue of the (TF) variational principle (2) is employed on the energy density functional with a B3LYP exchange-correlation term. (Note that the LYP correlation-energy density functional has been developed from the strongly heuristic Colle-Salvetti correlation-energy formula [35, 36].) While, needless to say, B3LYP is a huge improvement on the TF statistical functional (1), which has been known for decades to approach the correct non-relativistic ground-state energy for neutral atoms,

namely $-0.77Z^{7/3}$ a.u., from below at large atomic number Z [3], and therefore in the present grouping is in category H, the conclusion that B3LYP intrinsically overestimates the exchange-correlation energy is hard to avoid [5].

References

[1] R. G. Parr and W. Yang, *Density Functional Theory of Atoms and Molecules* (Oxford University Press, Oxford, 1989).

[2] N. H. March, *Self-Consistent Fields in Atoms* (Pergamon Press, Oxford, 1975).

[3] N. H. March, *Electron density theory of atoms and molecules* (Academic Press, New York, 1992).

[4] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).

[5] C. Amovilli, N. H. March, F. Bogár, and T. Gál, Phys. Lett. A **373**, 3158 (2009).

[6] N. A. Cordero, N. H. March, and J. A. Alonso, Phys. Rev. A **75**, 052502 (2007).

[7] R. J. Bartlett, Chem. Phys. Lett. **484**, 1 (2009).

[8] N. H. March and A. M. Murray, Phys. Rev. **120**, 830 (1960), reprinted in Ref. [37].

[9] N. H. March and A. M. Murray, Proc. Roy. Soc. A **261**, 119 (1961), reprinted in Ref. [37].

[10] J. C. Slater, Phys. Rev. **81**, 385 (1951).

[11] N. H. March and J. F. Mucci, *Chemical Physics of Free Molecules* (Plenum Press, New York, 1993).

[12] Ch. Møller and M. S. Plesset, Phys. Rev. **46**, 618 (1934).

[13] T. Hoffmann-Ostenhof, M. Hoffmann-Ostenhof, and R. Ahlrichs, Phys. Rev. A **18**, 328 (1978).

[14] T. Kato, Commun. Pure Appl. Math. **10**, 151 (1957).

[15] S. T. Howard, J. P. Huke, P. R. Mallinson, and C. S. Frampton, Phys. Rev. B **49**, 7124 (1994).

[16] P. A. M. Dirac, Proc. Camb. Phil. Soc. **26**, 376 (1930).

[17] A. Holas and N. H. March, Phys. Rev. B **55**, 9422 (1997).

[18] E. D. Stevens, Acta Cryst. B **34**, 544 (1978).

[19] N. H. March and W. H. Young, Nucl. Phys. **12**, 237 (1959), reprinted in Ref. [37].

[20] C. Amovilli, N. H. March, and J. D. Talman, Phys. Rev. A **77**, 032503 (2008).

[21] A. Holas and N. H. March, Phys. Rev. A **51**, 2040 (1995), reprinted in Ref. [37].

[22] C. Amovilli and N. H. March, Chem. Phys. Lett. **423**, 94 (2006).

[23] F. R. Mandby and P. J. Knowles, Chem. Phys. Lett. **310**, 561 (1999).

[24] E. R. Davidson, S. A. Hagstrom, S. J. Chakravorty, V. M. Umar, and C. F. Fischer, Phys. Rev. A **44**, 7071 (1991).

[25] S. J. Chakravorty, S. R. Gwaltney, E. R. Davidson, F. A. Parpia, and C. F. Fischer, Phys. Rev. A **47**, 3649 (1993).

[26] A. Luchow, J. B. Anderson, and D. Feller, J. Chem. Phys. **106**, 7706 (1997).

[27] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).

[28] J. P. Perdew and Y. Wang, Phys. Rev. B **45**, 13244 (1992).

[29] A. D. Becke, J. Chem. Phys. **98**, 5648 (1993).

[30] C. Lee, W. Yang, and R. G. Parr, Phys. Rev. B **37**, 785 (1988).

[31] J. P. Perdew and K. Schmidt, in *Density Functional Theory and Its Applications to Materials*, edited by V. Van Doren, C. Van Alsenoy, and P. Geerlings (AIP, New York, 2001).

[32] *A Primer in Density Functional Theory*, edited by C. Fiolhais, F. Nogueria, and M. Marques (Springer-Verlag, Berlin, 2003).

[33] C. Amovilli and N. H. March, Phys. Lett. A **324**, 46 (2004).

[34] G. Forte, A. Grassi, G. M. Lombardo, G. G. N. Angilella, N. H. March, and R. Pucci, Phys. Lett. A **372**, 3253 (2008).

[35] R. Colle and O. Salvetti, Theor. Chim. Acta **37**, 329 (1975).

[36] R. Colle and O. Salvetti, J. Chem. Phys. **79**, 1404 (1983).

[37] *Many-body Theory of Molecules, Clusters, and Condensed Phases*, edited by N. H. March and G. G. N. Angilella (World Scientific, Singapore, 2009).

[a]   Oxford University, Oxford, UK

and

Department of Physics, University of Antwerp,
Groenenborgerlaan 171, B-2020 Antwerp, Belgium