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Analytic Second Variational Derivative of the Exchange-Correlation Functional

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Abstract

A general analytic expression for the second variational derivative of gradient-corrected exchange-correlation energy functionals is derived, and the terms for the widely used Becke/Perdew, Becke/Lee-Yang-Parr, and Perdew-Burke-Ernzerhof exchange-correlation functionals are given. These analytic derivatives can be used for all applications employing linear-response theory or time-dependent density-functional theory. Calculations are performed in a plane-wave scheme and shown to be numerically more stable, more accurate, and computationally less costly than the most widely used finite-difference scheme.

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I. INTRODUCTION

Density-functional theory (DFT) in the Kohn-Sham (KS) formulation [1–3] is the most widely used nonempirical tool for studying the geometric and electronic structures of systems in condensed phase. The many-electron problem is reduced to many one-electron problems in a self-consistent effective potential. The part of this potential accounting for the many-electron effects is called the exchange-correlation (XC) functional and also contains the electron self-interaction. Its full nonlocal form is not known, but is usually approximated with the local-density approximation (LDA) or the generalized-gradient approximation (GGA). A plane-wave basis is particularly well suited for calculations in condensed phase. Fast Fourier transforms (FFTs) can be used for conveniently transforming electronic wavefunctions and density distributions between direct and reciprocal space, and the XC functional is normally evaluated on the real-space mesh given by the Fourier transform of the plane-wave basis (see e.g. Ref. [4]).

Often, the response of a many-electron system to an external influence is best described with density-functional perturbation theory [5, 6] (DFPT). Examples of problems that can be solved with DFPT include interactions with a changing electric field, such as light, and nuclear motions, such as phonons or colliding particles. In most cases, limiting the response functions to linear terms is sufficient. Moreover, time-dependent DFT [7] (TDDFT) can be formulated as a perturbation theory to the ground state to obtain excitation energies [8] and even excited-state geometries [9]. Therefore the same techniques as for DFPT can be used.

To calculate the linear-response wavefunctions, the variation of the effective potential acting on the electrons with respect to the external perturbation needs to be determined. Because the effective potential contains the external potential as well as the potential from electron-electron interactions, calculating the variation of the effective one-electron potential will always involve the variation of the electron-electron potential, i.e., the Hartree potential (electrostatics), and the XC potential. While the variation of the Hartree potential, i.e., the second variational derivative of the Hartree energy with respect to the electronic density distribution, is trivial, its XC counterpart of the popular GGA functionals currently either has to be approximated or is calculated using a finite-difference method [6, 9] because its fully analytic implementation is considered to be cumbersome to derive, numerically unstable in regions of low density, and, lastly, too expensive to calculate [6, 9]. We shall show that all three problems can be overcome.

A brief motivation will be given in Section II. Section III will propose an analytic functional form of the second derivative of the gradient-corrected XC energy as well as show in which order the terms need to be evaluated in order to avoid numerical problems in regions of low electron density. In addition to a general expression, specific expressions will be given for the widely used Becke88 [10] / Perdew86 [11] (BP), Becke88 / Lee-Yang-Parr [12] (BLYP), and Perdew-Burke-Ernzerhof [13–15] (PBE) XC functionals. In Section IV, we will show the practical feasibility of the proposed analytic method in an implementation using plane waves, and demonstrate that it actually outperforms the finite-difference scheme, Eq. (7), in terms of accuracy, convergence control, and computational performance. The appendix will give the specific terms for the BP, BLYP, and PBE functionals.

II. THE XC POTENTIAL IN DFPT

The effective one-electron (KS) Hamiltonian $\hat{H}_{\mathrm{KS}}^{(0)} = \hat{V}_{\mathrm{ext}} + \hat{V}_{\mathrm{el}} + \hat{V}_{\mathrm{xc}} + \hat{T}$ of the unperturbed system is composed of the external potential $\hat{V}_{\mathrm{ext}}$ due to the atomic nuclei, the Hartree potential $\hat{V}_{\mathrm{el}}$ of the electrostatic repulsion between electrons, the noninteracting kinetic energy $\hat{T}$, and the XC potential $\hat{V}_{\mathrm{xc}}$,

$$V_{\mathrm{xc}}[n](\mathbf{r}_0) = \frac{\delta E_{\mathrm{xc}}[n]}{\delta n(\mathbf{r}_0)}. \tag{1}$$

This potential is the variational derivative of the XC energy E_{xc} with respect to the electron density $n(\mathbf{r}_0)$. The XC energy can be written as [16]

$$E_{\mathrm{xc}}[n] = \int \mathrm{d}\mathbf{r}\ \varepsilon_{\mathrm{xc}}(n)n(\mathbf{r})\ , \tag{2}$$

where $\varepsilon_{\mathrm{xc}}$ is the XC energy per electron.

Consider a system described by the KS Hamiltonian $\hat{H}_{\mathrm{KS}}(\lambda) = \hat{H}_{\mathrm{KS}}^{(0)} + \lambda \hat{H}_{\mathrm{KS}}^{(1)}$ responding to a time-dependent or time-independent perturbation $\lambda \hat{H}_{\mathrm{KS}}^{(1)}$, e.g., a nuclear displacement due to a phonon or an electric field caused by a photon. To determine the linear-response electron density $n^{(1)} = \partial n/\partial \lambda$, the partial derivative $\partial \hat{H}_{\mathrm{KS}}/\partial \lambda$ of the KS Hamiltonian with respect to the perturbation parameter λ needs to be calculated.

Because the electron density $n(\mathbf{r}, \lambda) = n^{(0)}(\mathbf{r}) + \lambda n^{(1)}(\mathbf{r})$ at point $\mathbf{r}$ will generally react to such a perturbation, the calculation of the derivative,

$$\frac{\partial}{\partial \lambda} \hat{H}_{\mathrm{KS}}[n(\lambda)](\lambda) = \left.\frac{\partial \hat{H}_{\mathrm{KS}}(\lambda)}{\partial \lambda}\right|_{n(\lambda)} + \int \mathrm{d}\mathbf{r}\ \frac{\delta \hat{H}_{\mathrm{KS}}[n(\lambda)]}{\delta n(\mathbf{r}, \lambda)} \frac{\partial n(\mathbf{r}, \lambda)}{\partial \lambda}, \tag{3}$$

also includes the variational derivation of the electron-electron terms with respect to the density distribution:

$$\int \mathrm{d}\mathbf{r}\ \frac{\delta \hat{H}_{\mathrm{KS}}}{\delta n(\mathbf{r})} \frac{\partial n(\mathbf{r})}{\partial \lambda} = \int \mathrm{d}\mathbf{r}\ \frac{\delta \hat{V}_{\mathrm{el}} + \delta \hat{V}_{\mathrm{xc}}}{\delta n(\mathbf{r})} \frac{\partial n(\mathbf{r})}{\partial \lambda}\ . \tag{4}$$

In the LDA, $\varepsilon_{\mathrm{xc}}$ is a local function of the density only and can be expressed in the form $\varepsilon_{\mathrm{xc}}(n)n(\mathbf{r}) \approx f_{\mathrm{xc}}(n(\mathbf{r}))$, and the second variational derivative of the XC energy is easily evaluated:

$$\int \mathrm{d}\mathbf{r}\ \frac{\delta V_{\mathrm{xc}}(\mathbf{r}_0)}{\delta n(\mathbf{r})} \frac{\partial n(\mathbf{r})}{\partial \lambda} = \int \mathrm{d}\mathbf{r}\ \frac{\partial n(\mathbf{r})}{\partial \lambda}\ \delta(\mathbf{r}_0 - \mathbf{r})\ \left.\frac{\partial^2 f_{\mathrm{xc}}}{\partial n^2}\right|_{\mathbf{r}_0,\mathbf{r}} = \frac{\partial n(\mathbf{r}_0)}{\partial \lambda}\ \left.\frac{\partial^2 f_{\mathrm{xc}}}{\partial n^2}\right|_{\mathbf{r}_0,\mathbf{r}_0}\ . \tag{5}$$

The situation is more complicated for the GGA. We concentrate here on the popular gradient-corrected functionals of the form $\varepsilon_{\mathrm{xc}}(n)n(\mathbf{r}) \approx f_{\mathrm{xc}}(n(\mathbf{r}), \nabla n(\mathbf{r}))$ and their corresponding one-electron potential $\hat{V}_{\mathrm{xc}}$,

$$V_{\mathrm{xc}}[n](\mathbf{r}_0) = \frac{\delta E_{\mathrm{xc}}[n]}{\delta n(\mathbf{r}_0)} = \left.\left(\frac{\partial f_{\mathrm{xc}}}{\partial n} - \nabla \cdot \frac{\partial f_{\mathrm{xc}}}{\partial \nabla n}\right)\right|_{\mathbf{r}_0}\ . \tag{6}$$

Note that with a plane-wave basis, these terms can be conveniently evaluated on a mesh in real space using FFTs to evaluate both the gradient of the density and the divergence operator, but special care has to be taken not to introduce artificial high Fourier components due to the mesh. In practice, this is achieved by applying a cutoff density $n_{\rm cut}$, below which the gradient correction is neglected.

For the GGA class of density functionals, the analytic evaluation of an expression analogous to Eq. (5) was considered to be cumbersome to implement, numerically unstable in regions of low density, and computationally expensive [6, 9, 17]. Therefore, numerical methods that include approximations and finite-difference schemes are used (see e.g. Refs. [6, 9, 17]). For example, good results are obtained with the two-point formula [6],

$$\int \mathrm{d}\mathbf{r} \frac{\delta V_{\rm xc}[n](\mathbf{r}_0)}{\delta n(\mathbf{r})} n^{(1)}(\mathbf{r}) \simeq \frac{V_{\rm xc}[n+\varepsilon_n n^{(1)}](\mathbf{r}_0) - V_{\rm xc}[n-\varepsilon_n n^{(1)}](\mathbf{r}_0)}{2\varepsilon_n} \; . \tag{7}$$

The drawbacks of finite-difference schemes for this task are less obvious than those of approximations to the full functional: the accuracy of such finite-difference methods is difficult to control not only for large displacements ε_n because of higher-order terms but also for small values of ε_n because of amplified numerical ripple, particularly when using a plane-wave basis with the XC potential evaluated on a real-space mesh.

III. ANALYTIC VARIATIONAL DERIVATIVE OF THE XC POTENTIAL

For the second variation of the XC energy, we need to introduce a Dirac distribution to bring the semi-local functional $V_{\rm xc}[n](\mathbf{r}_0)$ into its integrated form, $F(y) = \int \mathrm{d}x \; L(x, y(x))$:

$$V_{\rm xc}[n](\mathbf{r}_0) = \int \mathrm{d}\mathbf{r} \; V_{\rm xc}[n](\mathbf{r}) \, \delta(\mathbf{r}-\mathbf{r}_0) \; , \tag{8}$$

which is suitable for variational differentiation. Substituting expression (6) for $V_{\rm xc}$, we arrive at

$$V_{\rm xc}[n](\mathbf{r}_0) = \int \mathrm{d}\mathbf{r} \; \left(\frac{\partial f_{\rm xc}}{\partial n(\mathbf{r})} - \nabla \cdot \frac{\partial f_{\rm xc}}{\partial |\nabla n(\mathbf{r})|} \frac{\nabla n(\mathbf{r})}{|\nabla n(\mathbf{r})|} \right) \delta(\mathbf{r}-\mathbf{r}_0) \; , \tag{9}$$

where we have used the identity

$$\frac{\partial f_{\rm xc}}{\partial \nabla n} = \frac{\partial f_{\rm xc}}{\partial |\nabla n|} \frac{\nabla n}{|\nabla n|} \tag{10}$$

because the practical gradient-corrected density functionals do not depend explicitly on the gradient but rather on its absolute value because of rotational invariance.

The variational derivative can be defined as follows [16]: If the following relation holds for any well-behaved function $\vartheta(x)$

$$\frac{\mathrm{d}}{\mathrm{d}\alpha} F[y+\alpha\vartheta] \Big|_{\alpha=0} = \int \mathrm{d}x \; \frac{\delta F[y]}{\delta y(x)} \, \vartheta(x) \; , \tag{11}$$

then $\delta F[y]/\delta y(x)$ is called variational derivative of $F[y]$. Inserting Eq. (9), we find

$$\begin{aligned}&\frac{\mathrm{d}}{\mathrm{d}\alpha}V_{\mathrm{xc}}[n+\alpha\vartheta](\mathbf{r}_0)\Big|_{\alpha=0}\\&=\int\mathrm{d}\mathbf{r}\,\left\{\frac{\partial^2 f_{\mathrm{xc}}}{\partial n^2}\vartheta+\frac{\partial^2 f_{\mathrm{xc}}}{\partial|\nabla n|\partial n}\frac{\nabla n}{|\nabla n|}\cdot\nabla\vartheta-\nabla\cdot\left[\frac{\nabla n}{|\nabla n|}\left(\frac{\partial^2 f_{\mathrm{xc}}}{\partial n\partial|\nabla n|}\vartheta+\frac{\partial^2 f_{\mathrm{xc}}}{\partial|\nabla n|^2}\frac{\nabla n}{|\nabla n|}\cdot\nabla\vartheta\right)\right.\right.\\&\qquad\left.\left.+\frac{\partial f_{\mathrm{xc}}}{\partial|\nabla n|}\left(\frac{\nabla\vartheta}{|\nabla n|}-\frac{\nabla n}{|\nabla n|^3}\nabla n\cdot\nabla\vartheta\right)\right]\right\}\,\delta(\mathbf{r}-\mathbf{r}_0)\end{aligned}\tag{12}$$

The first term corresponds to (11). By partial integration, we could bring terms with $\nabla\vartheta$ to this form:

$$\int\mathrm{d}\mathbf{r}\;g(\mathbf{r})\delta(\mathbf{r}-\mathbf{r}_0)\nabla\vartheta(\mathbf{r})=-\int\mathrm{d}\mathbf{r}\;\nabla\left(g(\mathbf{r})\,\delta(\mathbf{r}-\mathbf{r}_0)\right)\vartheta(\mathbf{r})\;,\tag{13}$$

which, by comparison with (11), would imply that

$$-\nabla\left(g\left(\mathbf{r}\right)\;\delta(\mathbf{r}-\mathbf{r}_0)\right)=-\nabla g(\mathbf{r})\,\delta(\mathbf{r}-\mathbf{r}_0)+g(\mathbf{r})\nabla\,\delta(\mathbf{r}-\mathbf{r}_0)\tag{14}$$

is the variational derivative. But recalling our objective, which is to calculate

$$\int\mathrm{d}\mathbf{r}\;\frac{\delta V_{\mathrm{xc}}[n](\mathbf{r}_0)}{\delta n(\mathbf{r})}n^{(1)}(\mathbf{r})\;,\tag{15}$$

it would be necessary to apply the Dirac distribution and its gradient to $n^{(1)}$. This would however lead to numerically unstable terms. But we can in fact skip this step: Because Eq. (11) must hold for any function ϑ, we set $\vartheta=n^{(1)}$ and from Eqs. (11) and (12) obtain

$$\begin{aligned}\int\mathrm{d}\mathbf{r}\;\frac{\delta V_{\mathrm{xc}}[n](\mathbf{r}_0)}{\delta n(\mathbf{r})}n^{(1)}(\mathbf{r})=&\left\{\frac{\partial^2 f_{\mathrm{xc}}}{\partial n^2}n^{(1)}+\frac{\partial^2 f_{\mathrm{xc}}}{\partial|\nabla n|\partial n}\frac{\nabla n}{|\nabla n|}\cdot\nabla n^{(1)}\right.\\&-\nabla\cdot\left[\frac{\nabla n}{|\nabla n|}\left(\frac{\partial^2 f_{\mathrm{xc}}}{\partial n\partial|\nabla n|}n^{(1)}+\frac{\partial^2 f_{\mathrm{xc}}}{\partial|\nabla n|^2}\frac{\nabla n}{|\nabla n|}\cdot\nabla n^{(1)}\right)\right.\\&\left.\left.+\frac{\partial f_{\mathrm{xc}}}{\partial|\nabla n|}\left(\frac{\nabla n^{(1)}}{|\nabla n|}-\frac{\nabla n}{|\nabla n|^3}\nabla n\cdot\nabla n^{(1)}\right)\right]\right\}\Bigg|_{\mathbf{r}=\mathbf{r}_0}\;.\end{aligned}\tag{16}$$

Note that this equation differs considerably from the one given in Ref. [17]. For the PBE exchange (PBE96) functional [13], Eq. (16) can be simplified:

$$\begin{aligned}\int\mathrm{d}\mathbf{r}\;\frac{\delta V_{\mathrm{x}}^{\mathrm{PBE96}}[n](\mathbf{r}_0)}{\delta n(\mathbf{r})}n^{(1)}(\mathbf{r})=&\left\{\frac{\partial^2 f_{\mathrm{x}}^{\mathrm{PBE96}}}{\partial n^2}n^{(1)}+\frac{\partial^2 f_{\mathrm{x}}^{\mathrm{PBE96}}}{\partial|\nabla n|^2\partial n}2\nabla n\cdot\nabla n^{(1)}\right.\\&-\nabla\cdot\left[2\nabla n\left(\frac{\partial^2 f_{\mathrm{x}}^{\mathrm{PBE96}}}{\partial n\partial|\nabla n|^2}n^{(1)}+\frac{\partial^2 f_{\mathrm{x}}^{\mathrm{PBE96}}}{\partial(|\nabla n|^2)^2}2\nabla n\cdot\nabla n^{(1)}\right)\right.\\&\left.\left.+\frac{\partial f_{\mathrm{x}}^{\mathrm{PBE96}}}{\partial|\nabla n|^2}2\nabla n^{(1)}\right]\right\}\Bigg|_{\mathbf{r}=\mathbf{r}_0}\;.\end{aligned}\tag{17}$$

Generalization to spin-polarized calculations is straightforward for the exchange potential because there is no exchange antisymmetry between electrons with different magnetic quantum number. The total density $n = n_\alpha + n_\beta$ in Eq. (16) merely has to be substituted by the corresponding density of electrons with spin up or down, n_α or n_β, and the constants adjusted accordingly. For the correlation potentials, $V_{\mathrm{c},\alpha}(\mathbf{r}_0) = \delta E_c/\delta n_\alpha(\mathbf{r}_0)$, this restriction does not apply, and terms containing n_α, n_β, $|\nabla n_\alpha|$, $|\nabla n_\beta|$, and $\nabla n_\alpha \cdot \nabla n_\beta$ are possible in a rotationally invariant GGA. The spin-polarized equivalent of Eq. (16) for the Perdew86 (P86) correlation functional [11] contains all possible terms:

$$
\begin{aligned}
\int \mathrm{d}r\, \frac{\delta V^{\mathrm{P86}}_{\mathrm{c},\alpha}[n](r_0)}{\delta n(r)} n^{(1)}(r) = \Bigg\{ & \frac{\partial^2 f_c^{\mathrm{P86}}}{\partial n_\alpha^2} n_\alpha^{(1)} + \frac{\partial^2 f_c^{\mathrm{P86}}}{\partial n_\beta \partial n_\alpha} n_\beta^{(1)} \\
& + \frac{\partial^2 f_c^{\mathrm{P86}}}{\partial |\nabla n_\alpha| \partial n_\alpha} \frac{\nabla n_\alpha \cdot \nabla n_\alpha^1}{|\nabla n_\alpha|} + \frac{\partial^2 f_c^{\mathrm{P86}}}{\partial |\nabla n_\beta| \partial n_\alpha} \frac{\nabla n_\beta \cdot \nabla n_\beta^1}{|\nabla n_\beta|} \\
& + \frac{\partial^2 f_c^{\mathrm{P86}}}{\partial (\nabla n_\alpha \cdot \nabla n_\beta) \partial n_\alpha} (\nabla n_\beta \cdot \nabla n_\alpha^{(1)} + \nabla n_\alpha \cdot \nabla n_\beta^{(1)}) \\
& - \nabla \cdot \Bigg[\frac{\nabla n_\alpha}{|\nabla n_\alpha|} \Bigg(\frac{\partial^2 f_c^{\mathrm{P86}}}{\partial n_\alpha \partial |\nabla n_\alpha|} n_\alpha^{(1)} + \frac{\partial^2 f_c^{\mathrm{P86}}}{\partial n_\beta \partial |\nabla n_\alpha|} n_\beta^{(1)} \\
& + \frac{\partial^2 f_c^{\mathrm{P86}}}{\partial (\nabla n_\alpha \cdot \nabla n_\beta) \partial |\nabla n_\alpha|} (\nabla n_\beta \cdot \nabla n_\alpha^{(1)} + \nabla n_\alpha \cdot \nabla n_\beta^{(1)}) \\
& + \frac{\partial^2 f_c^{\mathrm{P86}}}{\partial |\nabla n_\alpha|^2} \frac{\nabla n_\alpha \cdot \nabla n_\alpha^1}{|\nabla n_\alpha|} + \frac{\partial^2 f_c^{\mathrm{P86}}}{\partial |\nabla n_\beta| \partial |\nabla n_\alpha|} \frac{\nabla n_\beta \cdot \nabla n_\beta^1}{|\nabla n_\beta|} - \frac{\partial f_c^{\mathrm{P86}}}{\partial |\nabla n_\alpha|} \frac{\nabla n_\alpha \cdot \nabla n_\alpha^1}{|\nabla n_\alpha|^2} \Bigg) \\
& + \nabla n_\beta \Bigg(\frac{\partial^2 f_c^{\mathrm{P86}}}{\partial n_\alpha \partial (\nabla n_\alpha \cdot \nabla n_\beta)} n_\alpha^{(1)} + \frac{\partial^2 f_c^{\mathrm{P86}}}{\partial |\nabla n_\alpha| \partial (\nabla n_\alpha \cdot \nabla n_\beta)} \frac{\nabla n_\alpha \cdot \nabla n_\alpha^1}{|\nabla n_\alpha|} \\
& + \frac{\partial^2 f_c^{\mathrm{P86}}}{\partial n_\beta \partial (\nabla n_\alpha \cdot \nabla n_\beta)} n_\beta^{(1)} + \frac{\partial^2 f_c^{\mathrm{P86}}}{\partial |\nabla n_\beta| \partial (\nabla n_\alpha \cdot \nabla n_\beta)} \frac{\nabla n_\beta \cdot \nabla n_\beta^1}{|\nabla n_\beta|} \\
& + \frac{\partial^2 f_c^{\mathrm{P86}}}{\partial (\nabla n_\alpha \cdot \nabla n_\beta)^2} (\nabla n_\beta \cdot \nabla n_\alpha^{(1)} + \nabla n_\alpha \cdot \nabla n_\beta^{(1)}) \Bigg) \\
& + \frac{\partial f_c^{\mathrm{P86}}}{\partial |\nabla n_\alpha|} \frac{\nabla n_\alpha^{(1)}}{|\nabla n_\alpha|} + \frac{\partial f_c^{\mathrm{P86}}}{\partial (\nabla n_\alpha \cdot \nabla n_\beta)} \nabla n_\beta^{(1)} \Bigg] \Bigg\} \Bigg|_{r=r_0} . \qquad (18)
\end{aligned}
$$

It can be simplified for the Lee-Yang-Parr (LYP) correlation functional [12]:

$$\begin{aligned}\int \mathrm{d}r \, \frac{\delta V_{\mathrm{c},\alpha}^{\mathrm{LYP}}[n](r_0)}{\delta n(r)} n^{(1)}(r) = \Bigg\{ & \frac{\partial^2 f_{\mathrm{c}}^{\mathrm{LYP}}}{\partial n_\alpha^2} n_\alpha^{(1)} + \frac{\partial^2 f_{\mathrm{c}}^{\mathrm{LYP}}}{\partial n_\beta \partial n_\alpha} n_\beta^{(1)} \\ & + \frac{\partial^2 f_{\mathrm{c}}^{\mathrm{LYP}}}{\partial |\nabla n_\alpha| \partial n_\alpha} \frac{\nabla n_\alpha}{|\nabla n_\alpha|} \cdot \nabla n_\alpha^{(1)} + \frac{\partial^2 f_{\mathrm{c}}^{\mathrm{LYP}}}{\partial |\nabla n_\beta| \partial n_\alpha} \frac{\nabla n_\beta}{|\nabla n_\beta|} \cdot \nabla n_\beta^{(1)} \\ & + \frac{\partial^2 f_{\mathrm{c}}^{\mathrm{LYP}}}{\partial (\nabla n_\alpha \cdot \nabla n_\beta) \partial n_\alpha} (\nabla n_\beta \cdot \nabla n_\alpha^{(1)} + \nabla n_\alpha \cdot \nabla n_\beta^{(1)}) \\ & - \nabla \cdot \Bigg[\frac{\nabla n_\alpha}{|\nabla n_\alpha|} \left(\frac{\partial^2 f_{\mathrm{c}}^{\mathrm{LYP}}}{\partial n_\alpha \partial |\nabla n_\alpha|} n_\alpha^{(1)} + \frac{\partial^2 f_{\mathrm{c}}^{\mathrm{LYP}}}{\partial n_\beta \partial |\nabla n_\alpha|} n_\beta^{(1)} \right) \\ & + \nabla n_\beta \left(\frac{\partial^2 f_{\mathrm{c}}^{\mathrm{LYP}}}{\partial n_\alpha \partial (\nabla n_\alpha \cdot \nabla n_\beta)} n_\alpha^{(1)} + \frac{\partial^2 f_{\mathrm{c}}^{\mathrm{LYP}}}{\partial n_\beta \partial (\nabla n_\alpha \cdot \nabla n_\beta)} n_\beta^{(1)} \right) \\ & + \frac{\partial f_{\mathrm{c}}^{\mathrm{LYP}}}{\partial |\nabla n_\alpha|} \frac{\nabla n_\alpha^{(1)}}{|\nabla n_\alpha^{(1)}|} + \frac{\partial f_{\mathrm{c}}^{\mathrm{LYP}}}{\partial (\nabla n_\alpha \cdot \nabla n_\beta)} \nabla n_\beta^{(1)} \Bigg] \Bigg\} \Bigg|_{r=r_0} . \end{aligned} \tag{19}$$

The corresponding terms for the gradient-corrected [14] Perdew-Wang correlation (PW92) functional [15], often referred to as the correlation part of the PBE XC functional, are:

$$\begin{aligned}\int \mathrm{d}r \, \frac{\delta V_{\mathrm{c},\alpha}^{\mathrm{PW92}}[n](r_0)}{\delta n(r)} n^{(1)}(r) = \Bigg\{ & \frac{\partial^2 f_c^{\mathrm{PW92}}}{\partial n_\alpha^2} n_\alpha^{(1)} + \frac{\partial^2 f_c^{\mathrm{PW92}}}{\partial n_\beta \partial n_\alpha} n_\beta^{(1)} \\ & + \frac{\partial^2 f_c^{\mathrm{PW92}}}{\partial |\nabla n_\alpha|^2 \partial n_\alpha} 2 \nabla n_\alpha \cdot \nabla n_\alpha^1 + \frac{\partial^2 f_c^{\mathrm{PW92}}}{\partial |\nabla n_\beta|^2 \partial n_\alpha} 2 \nabla n_\beta \cdot \nabla n_\beta^1 \\ & + \frac{\partial^2 f_c^{\mathrm{PW92}}}{\partial (\nabla n_\alpha \cdot \nabla n_\beta) \partial n_\alpha} (\nabla n_\beta \cdot \nabla n_\alpha^{(1)} + \nabla n_\alpha \cdot \nabla n_\beta^{(1)}) \\ & - \nabla \cdot \Bigg[2 \nabla n_\alpha \Bigg(\frac{\partial^2 f_c^{\mathrm{PW92}}}{\partial n_\alpha \partial |\nabla n_\alpha|^2} n_\alpha^{(1)} + \frac{\partial^2 f_c^{\mathrm{PW92}}}{\partial n_\beta \partial |\nabla n_\alpha|^2} n_\beta^{(1)} \\ & + \frac{\partial^2 f_c^{\mathrm{PW92}}}{\partial (\nabla n_\alpha \cdot \nabla n_\beta) \partial |\nabla n_\alpha|^2} (\nabla n_\beta \cdot \nabla n_\alpha^{(1)} + \nabla n_\alpha \cdot \nabla n_\beta^{(1)}) \\ & + \frac{\partial^2 f_c^{\mathrm{PW92}}}{\partial (|\nabla n_\alpha|^2)^2} 2 \nabla n_\alpha \cdot \nabla n_\alpha^1 + \frac{\partial^2 f_c^{\mathrm{PW92}}}{\partial |\nabla n_\beta|^2 \partial |\nabla n_\alpha|^2} 2 \nabla n_\beta \cdot \nabla n_\beta^1 \Bigg) \\ & + \nabla n_\beta \Bigg(\frac{\partial^2 f_c^{\mathrm{PW92}}}{\partial n_\alpha \partial (\nabla n_\alpha \cdot \nabla n_\beta)} n_\alpha^{(1)} + \frac{\partial^2 f_c^{\mathrm{PW92}}}{\partial |\nabla n_\alpha|^2 \partial (\nabla n_\alpha \cdot \nabla n_\beta)} 2 \nabla n_\alpha \cdot \nabla n_\alpha^{(1)} \\ & + \frac{\partial^2 f_c^{\mathrm{PW92}}}{\partial n_\beta \partial (\nabla n_\alpha \cdot \nabla n_\beta)} n_\beta^{(1)} + \frac{\partial^2 f_c^{\mathrm{PW92}}}{\partial |\nabla n_\beta|^2 \partial (\nabla n_\alpha \cdot \nabla n_\beta)} 2 \nabla n_\beta \cdot \nabla n_\beta^1 \\ & + \frac{\partial^2 f_c^{\mathrm{PW92}}}{\partial (\nabla n_\alpha \cdot \nabla n_\beta)^2} (\nabla n_\beta \cdot \nabla n_\alpha^{(1)} + \nabla n_\alpha \cdot \nabla n_\beta^{(1)}) \Bigg) \\ & + \frac{\partial f_c^{\mathrm{PW92}}}{\partial |\nabla n_\alpha|^2} 2 \nabla n_\alpha^{(1)} + \frac{\partial f_c^{\mathrm{PW92}}}{\partial (\nabla n_\alpha \cdot \nabla n_\beta)} \nabla n_\beta^{(1)} \Bigg] \Bigg\} \Bigg|_{r=r_0} \end{aligned} \tag{20}$$

We have explicitly calculated the terms for the widely used Becke88 (B88) [10] and PBE96 [13] exchange functionals, and for the LYP [12], P86 [11], and PW92 correlation functionals. The individual terms are given in the appendix.

IV. TEST CALCULATIONS: SETUP AND RESULTS

We have implemented the methods presented in this letter in the DFT-based program CPMD [18], which uses a plane-wave basis. For programs using this basis, FFTs play a central role, allowing a convenient and efficient evaluation of both spatial derivatives and operators that are either local in direct or reciprocal space. In practice, the computational efficiency of a method in a plane-wave code is often determined by the possibility to use FFTs and the number of FFTs needed. Note that all terms in Eqs. (9) and (16) can be conveniently evaluated using FFTs [4, 19]. The variational formulation of DFPT [6] as implemented in CPMD has been used.

The NO_2 radical was chosen as a test system. The Becke-Lee-Yang-Parr (BLYP) XC functional [10, 12] has been used throughout. Spin-polarized calculations were performed in a cubic cell of 24.0-Bohr edge. The cutoff of the plane-wave basis was 70 Ry. Unless indicated otherwise, all values are given in atomic units. For test purposes, the robustness of the integral

$$I[f] = \int\int \mathrm{d}\mathbf{r}_0 \; \mathrm{d}\mathbf{r} \; \frac{\delta V_{\mathrm{xc}}(\mathbf{r}_0)}{\delta n(\mathbf{r})} \frac{\partial n(\mathbf{r})}{\partial R_{\mathrm{N}}} \; f(\mathbf{r}_0) \; , \tag{21}$$

was tested against arbitrary choices of numerical parameters. δR_{N} corresponds to a displacement of the nitrogen atom towards one of the two oxygen atoms. The test density distribution $f(\mathbf{r}_0)$ was either the linear-response density or the overlap density,

$$f(\mathbf{r}_0) = \begin{cases} f_o(\mathbf{r}_0) = \phi_d^*(\mathbf{r}_0)\phi_s(\mathbf{r}_0) & \text{response density} \\ f_r(\mathbf{r}_0) = \partial n(\mathbf{r}_0)/\partial R_{\mathrm{N}} & \text{overlap density} \end{cases} , \tag{22}$$

where $|\phi_d\rangle$ and $|\phi_s\rangle$ represent the KS orbitals of the highest doubly occupied and the singly occupied state, respectively. All integrals were evaluated for the Slater transition-state density (see e.g. Ref. [3]) for the excitation between these two states.

Table I compares the results of numerical calculations of the second variational derivative of the XC energy, Eq. (7), with the value calculated analytically using Eq. (16), both as a function of the finite-difference displacement ε_n and of the cutoff density n_{cut} for the calculation of the gradient corrections. Clearly, the analytic calculation is more robust than the finite-difference calculation. This can be explained by inspection of the values of $\int \mathrm{d}\mathbf{r} \; (\delta V_{\mathrm{xc}}(\mathbf{r}_0)/\delta n(\mathbf{r}))\,(\partial n(\mathbf{r})/\partial R_{\mathrm{N}})$, which had approximately hundredfold larger fluctuations in the finite-difference case than in the analytic case owing to amplified numerical ripple in $V_{\mathrm{xc}}(\mathbf{r}_0)$. When using Eq. (16) instead of Eqs. (13) and (14), the predicted instabilities due to large inverse powers of the density[6] can be avoided because these terms are multiplied on the fly with a linear-response density distribution or its gradient, which are small in the same regions where the total electron density distribution is also small.

The CPU time required for both methods is approximately the same. For spin-polarized calculations, the analytic method requires 16 forward and 10 inverse Fourier transforms, compared with 16 forward and 12 inverse Fourier transforms for the finite-difference calculation[1]. For the BLYP [10, 12] functional, the analytic calculation is slightly faster: On four

[1] Note that these counts exploit the fact that the density distribution in position space is real, and therefore,

TABLE I: Convergence of the second variational derivative of the XC functional with respect to the finite-difference displacement ε_n and to the base-10 logarithm of the cutoff density n_{cut} for calculating the gradient corrections, calculated with the finite-difference formula ("FD"), Eq. (7), and analytically ("Ana") with Eq. (16). Tabulated are the integrals $I[f_r]$ ("Response") and $I[f_o]$ ("Overlap") of Eqs. (21) and (22). All values are given in atomic units.

Method	ε_n	$\log(n_{\text{cut}})$	Integral	
			Response	Overlap
FD	0.0001	–5	–0.5937	–0.0086585
FD	0.0005	–5	–0.5938	–0.00865863
FD	0.001	–5	–0.59370	–0.00865862
FD	0.01	–5	–0.59372	–0.00865863
FD	0.1	–5	–0.585	–0.0086588
FD	0.0005	–4	–0.594	–0.0086582
FD	0.0005	–5	–0.5938	–0.00865863
FD	0.0005	–6	–0.59371	–0.008658654
FD	0.0005	–7	–0.59370	–0.008658659
FD	0.0005	–8	–0.59371	–0.00865869
FD	0.0005	–9	–0.593724	–0.00865870
FD	0.0005	–10	–0.593723	–0.008658696
FD	0.0005	–11	–0.593722	–0.008658687
Ana	—	–4	–0.59370	–0.008658662
Ana	—	–5	–0.593675	–0.008658658
Ana	—	–6	–0.593686	–0.008658667
Ana	—	–7	–0.593698	–0.008658671
Ana	—	–8	–0.593706	–0.008658673
Ana	—	–9	–0.593720	–0.0086586815
Ana	—	–10	–0.593721117	–0.00865868179326
Ana	—	–11	–0.593721118	–0.00865868179334

processors of an IBM RS/6000 7044-270, one evaluation of the analytic formula, Eq. (16), took 24.28 s, whereas 27.43 s were required for the finite-difference formula, Eq. (7).[2]

two independent density distributions in position space or momentum space can be obtained using only one FFT.

[2] Of this difference of 2.15 s, the two additional FFTs accounted for 0.78 s, the evaluation of the individual terms for 1.21 s, and the remaining 0.16 s could be saved by omitting the calculation of $|\nabla n^{(1)}|$ from its components.

V. CONCLUSIONS

This letter demonstrated that the calculation of the analytic variational derivative of a gradient-corrected exchange-correlation functional does not lead to the anticipated numerical instabilities if implemented correctly. Indeed, it is numerically much more robust and more accurate than the finite-difference schemes currently used, and its calculation does not require any additional computational effort compared with the finite-difference schemes but rather slightly reduces them. The generalization from the currently available terms of the widely used BP [10, 11], BLYP [10, 12], and PBE [13–15] functionals to other density functionals is straightforward. With the increasing use of TDDFT and DFPT to calculate electronic excitation energies, phonon spectra, electron-phonon couplings, and many other properties in molecular and solid-state systems, the calculation of all these properties will benefit from the accuracy and efficiency of the new analytic method proposed here.

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[1] P. Hohenberg and W. Kohn, Phys.Rev. **136**, B864 (1964).
[2] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).
[3] R. M. Dreizler and E. K. U. Gross, *Density Functional Theory* (Springer, Berlin and Heidelberg, 1990).
[4] D. Marx and J. Hutter, in *Modern Methods and Algorithms of Quantum Chemistry*, edited by J. Grotendorst (John von Neumann Institute for Computing, Jülich, 2000), vol. 1 of *NIC*, pp. 301–449.
[5] X. Gonze, Phys. Rev. A **52**, 1096 (1995).
[6] A. Putrino, D. Sebastiani, and M. Parrinello, J. Chem. Phys. **113**, 7102 (2000).
[7] E. Runge and E. K. U. Gross, Phys. Rev. Lett. **52**, 997 (1984).
[8] M. E. Casida, in *Recent Advances in Density Functional Methods*, edited by D. P. Chong (World Scientific, Singapore, 1995), vol. 1, p. 155.
[9] J. Hutter, J. Chem. Phys. **118**, 3928 (2003).
[10] A. D. Becke, Phys. Rev. A **38**, 3098 (1988).
[11] J. P. Perdew, Phys. Rev. B **33**, 8822 (1986).
[12] C. Lee, W. Yang, and R. G. Parr, Phys. Rev. B **37**, 785 (1988).
[13] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett **77**, 3865 (1996).
[14] J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, and C. Fiolhais, Phys. Rev. B **46**, 6671 (1992).
[15] J. P. Perdew and Y. Wang, Phys. Rev. B **45**, 13244 (1992).
[16] U. Scherz, *Quantenmechanik, Eine Einführung mit Anwendungen auf Atome, Moleküle und Festkörper* (B.G. Teubner, Leipzig, 1999).

[17] A. Dal Corso, S. Baroni, and R. Resta, Phys. Rev. B **49**, 5323 (1994).
[18] *CPMD*, Copyright IBM Corp 1990–2003 and MPI für Festkörperforschung, Stuttgart, Germany, 1997–2001.
[19] J. A. White and D. M. Bird, Phys. Rev. B **50**, 4954 (1994).

APPENDIX. SECOND DERIVATIVE OF SOME WIDELY USED XC FUNCTIONALS

Partial derivatives of the Becke88 [10] and Perdew-Burke-Ernzerhof [13] (PBE) exchange functionals, and for the Lee-Yang-Parr [12] (LYP), Perdew86 [11], and PBE correlation functionals [14, 15], used in Eqs. (16) and (19). Where the configuration argument in this section is omitted, $\mathbf{r}$ must be assumed. A term $\tilde{F}$ corresponds to F with the spin of all densities inversed. For the spin-unpolarised case, just set $n_\alpha = n_\beta = n/2$.
The Becke88 [10] exchange functional reads

$$f_x^{\text{B88}} = -\sum_{\sigma=\alpha,\beta} A n_\sigma^{4/3} + \beta n_\sigma^{4/3} x_\sigma^2 Z_\sigma$$

$$x = \frac{|\nabla n|}{n^{4/3}}\,, \qquad Z = \frac{1}{1+6\beta x \sinh^{-1}(x)}\,, \qquad A = \frac{3}{4}\left(\frac{6}{\pi}\right)^{1/3}\,, \qquad \beta = 0.0042\,.$$

Its partial derivatives are

$$\frac{\partial^2 f_x^{\text{B88}}}{\partial n^2} = -\frac{4}{9}An^{-2/3} - \beta|\nabla n|\left[x'\left(\frac{4}{3}n^{-1}Z + 3Z'\right) + x(-\frac{4}{3}(n^{-2}Z + n^{-1}Z') + Z'') + 2x''Z\right]$$

$$x' = -\frac{4}{3}|\nabla n|n^{-7/3}\,, \qquad x'' = \frac{28}{9}|\nabla n|n^{-10/3}\,, \qquad Z' = -6\beta Z^2(x'\sinh^{-1}(x) + xS')\,, \qquad S' = \frac{x'}{1+x^2}$$

$$\frac{\partial^2 f_x^{\text{B88}}}{\partial n \partial |\nabla n|} = -\beta(Z(\frac{4}{3}n^{-1}x + 2x') + xZ') - \beta|\nabla n|(\frac{4}{3}n^{-1}(\dot{x}Z + x\dot{Z}) + 2\dot{x}'Z + 2x'\dot{Z} + \dot{x}Z' + x\dot{Z}')$$

$$\dot{x}' = -\frac{4}{3}n^{-7/3}\,, \qquad \dot{S}' = -\frac{4}{3}\dot{S}^3 n^{5/3}\,, \qquad \dot{Z}' = -12Z\dot{Z}\beta(x'S + xS') - 6Z^2\beta(\dot{x}'S + x'\dot{S} + \dot{x}S' + x\dot{S}')$$

$$\frac{\partial^2 f_x^{\text{B88}}}{\partial |\nabla n|^2} = -\beta(2\dot{Z}x + 2Z\dot{x} + n^{4/3}(2x\dot{x}\dot{Z} + x^2\ddot{Z}))$$

$$\ddot{S} = -\dot{S}^3|\nabla n|\,, \qquad \ddot{Z} = -12\beta Z\dot{Z}(\dot{x}S + x\dot{S}) - 6\beta Z^2(2\dot{x}\dot{S} + x\ddot{S})\,.$$

The LYP [12] correlation functional reads

$$f_c^{\text{LYP}} = -4aD\frac{n_\alpha n_\beta}{n} - \omega K$$

$$K = n_\alpha n_\beta L - \frac{2}{3}n^2|\nabla n|^2 + \left(\frac{2}{3}n^2 - n_\alpha^2\right)|\nabla n_\beta|^2 + \left(\frac{2}{3}n^2 - n_\beta^2\right)|\nabla n_\alpha|^2$$

$$L = C_F(n_\alpha^{8/3} + n_\beta^{8/3}) + \left(\frac{47}{18} - \frac{7}{18}\delta\right)|\nabla n|^2 - \left(\frac{5}{2} - \frac{1}{18}\delta\right)(|\nabla n_\alpha|^2 + |\nabla n_\beta|^2) - \frac{\delta - 11}{9}\left(\frac{n_\alpha}{n}|\nabla n_\alpha|^2 + \frac{n_\beta}{n}|\nabla n_\beta|^2\right)$$

$$D = \frac{1}{1+dn^{-1/3}}\,, \qquad \omega = abe^{-cn^{-1/3}}Dn^{-11/3}\,, \qquad \delta = cn^{-1/3} + \frac{dn^{-1/3}}{1+dn^{-1/3}}\,, \qquad C_F = 2^{11/3}\frac{3}{10}(3\pi^2)^{2/3}$$

$$a = 0.04918\,, \qquad b = 0.132\,, \qquad c = 0.2533\,, \qquad d = 0.349\,.$$

Its partial derivatives are

$$\frac{\partial^2 f_c^{\text{LYP}}}{\partial |\nabla n_\alpha|^2} = -\omega\dot{K}$$

$$\dot{K} = n_\alpha n_\beta \dot{L} - n_\beta^2\,, \qquad \dot{L} = \frac{1}{9} - \frac{1}{3}\delta - \frac{1}{9}(\delta - 11)n_\alpha n^{-1}$$

$$\frac{\partial^2 f_c^{\mathrm{LYP}}}{\partial n_\alpha^2} = -4a(D''\frac{n_\alpha n_\beta}{n} + 2D'n_\beta^2 n^{-2} - 2Dn_\beta^2 n^{-3}) - \omega'' K - 2\omega' K' - \omega K''$$

$$D' = \frac{1}{3} d D^2 n^{-4/3} \ , \qquad D'' = \frac{1}{3} d(2DD'n^{-4/3} - \frac{4}{3} n^{-7/3} D^2) \ ,$$

$$\omega' = ab \frac{e^{-cn^{-1/3}}(cn^{1/3} + cd - 10n^{1/3}d - 11n^{2/3})}{3n^{14/3}(n^{1/3}+d)^2} \ ,$$

$$\omega'' = \frac{e^{-cn^{-1/3}}(c^2d^2 + n(282d - 26c) + n^{1/3}(2c^2 - 24cd^2) + n^{2/3}(c^2 - 50cd + 130d^2) + 154n^{4/3})}{9n^6(n^{1/3}+d)^3} \ ,$$

$$K' = n_\beta L + n_\alpha n_\beta L' + \left(\frac{4}{3}n - 2n_\alpha\right)|\nabla n_\beta|^2 + \frac{4}{3}n(|\nabla n_\alpha|^2 - |\nabla n|^2) \ ,$$

$$K'' = 2n_\beta L' + n_\alpha n_\beta L'' - \frac{4}{3}(|\nabla n|^2 + 2|\nabla n_\beta|^2 - |\nabla n_\alpha|^2) \ ,$$

$$L' = \frac{8}{3} C_F n_\alpha^{5/3} - \frac{1}{9}(\delta - 11)n_\beta n^{-2}\left(|\nabla n_\alpha|^2 - |\nabla n_\beta|^2\right) - \frac{7}{18}|\nabla n|^2 \delta' - \frac{1}{9}\delta' \frac{n_\alpha n_\beta}{n} + \frac{1}{18}\delta'(|\nabla n_\alpha|^2 + |\nabla n_\beta|^2)$$

$$L'' = \frac{40}{9} C_F n_\alpha^{2/3} - \frac{2}{9}\delta' n_\beta n^{-2}(|\nabla n_\alpha|^2 - |\nabla n_\beta|^2) + \frac{2}{9}(\delta - 11)n_\beta n^{-3}(|\nabla n_\alpha|^2 - |\nabla n_\beta|^2)$$
$$+ \delta''\left(\frac{1}{18}(|\nabla n_\alpha|^2 + |\nabla n_\beta|^2) - \frac{1}{9}\frac{n_\alpha n_\beta}{n} - \frac{7}{18}|\nabla n|^2\right)$$

$$\frac{\partial^2 f_c^{\mathrm{LYP}}}{\partial n_\beta \partial n_\alpha} = -4a(D''\frac{n_\alpha n_\beta}{n} + D'n_\alpha^2 n^{-2} + D'n_\beta^2 n^{-2} + 2Dn_\alpha n_\beta n^{-3}) - \omega'' K - \omega' \tilde{K}' - \omega' K'$$
$$- \omega\left(n_\beta \tilde{L}' + L + n_\alpha L' + n_\alpha n_\beta \left(\frac{1}{9}\delta' n^{-2}(|\nabla n_\alpha|^2 - |\nabla n_\beta|^2)(n_\beta - n_\alpha)(1 + \frac{1}{9}(\delta - 11)n^{-1})\right.\right.$$
$$\left.\left. + \delta''\left(\frac{1}{18}(|\nabla n_\alpha|^2 + |\nabla n_\beta|^2) - \frac{1}{9}\frac{n_\alpha n_\beta}{n} - \frac{7}{18}|\nabla n|^2\right)\right) - \frac{4}{3}(|\nabla n|^2 - |\nabla n_\beta|^2 - |\nabla n_\alpha|^2)\right)$$

$$\frac{\partial^2 f_c^{\mathrm{LYP}}}{\partial n_\alpha \partial |\nabla n_\alpha|^2} = -\omega' \dot{K} - \omega \dot{K}'$$

$$\dot{K}' = n_\beta \dot{L} + n_\alpha n_\beta \dot{L}' \ , \qquad \dot{L}' = -\frac{1}{9}\delta'(3 + n_\alpha n^{-1}) - \frac{1}{9}(\delta - 11)n_\beta n^{-2}$$

$$\frac{\partial^2 f_c^{\mathrm{LYP}}}{\partial n_\beta \partial |\nabla n_\alpha|^2} = -\omega' \dot{K} - \omega(n_\alpha \dot{L} + n_\alpha n_\beta(-\frac{1}{3}\delta' - n_\alpha(\frac{1}{9}\delta' n^{-1} - \frac{1}{9}(\delta - 11)n^{-2})) - 2n_\beta)$$

$$\frac{\partial^2 f_c^{\mathrm{LYP}}}{\partial |\nabla n_\beta|^2 \partial n_\alpha} = -\omega'(n_\alpha n_\beta \tilde{\dot{L}} - n_\alpha^2) - \omega(n_\beta \tilde{\dot{L}} + n_\alpha n_\beta\left(-\frac{1}{3}\delta'(3 + n_\beta n^{-1}) + \frac{1}{9}(\delta - 11)n_\beta n^{-2}\right) - 2n_\alpha$$

$$\frac{\partial^2 f_c^{\mathrm{LYP}}}{\partial(\nabla n_\alpha \cdot \nabla n_\beta)\partial n_\alpha} = 2\left(-\omega\left(n_\alpha n_\beta\left(\frac{47}{18} - \frac{7}{18}\delta\right) - \frac{2}{3}n^2\right) - \omega\left(-\frac{4}{3}n + n_\beta\left(\frac{47}{18} - \frac{7}{18}\delta\right) - n_\alpha n_\beta \frac{7}{18}\delta'\right)\right)$$

$$\frac{\partial^2 f_c^{\mathrm{LYP}}}{\partial(\nabla n_\alpha \cdot \nabla n_\beta)} = -\omega\left(2n_\alpha n_\beta\left(\frac{47}{18} - \frac{7}{18}\delta\right) - \frac{4}{3}n^2\right) \qquad .$$

The P86 [11] correlation functional reads

$$f_c^{\mathrm{P86}} = Z + e^{-\Phi} C(r_\mathrm{s}) \frac{|\nabla n|^2}{n^{\frac{4}{3}} d}$$

$$Z = \epsilon^\mathrm{p}(r_\mathrm{s}) + \left(\epsilon^\mathrm{f}(r_\mathrm{s}) - \epsilon^\mathrm{p}(r_\mathrm{s})\right) f(\zeta), \quad \Phi = 0.19195 C(\infty) \frac{|\nabla n|}{n^{\frac{7}{6}} C(r_\mathrm{s})}, \quad d = 2^{\frac{1}{3}} \left(\frac{(\zeta+1)}{2}^{\frac{5}{3}} + \frac{(\zeta-1)}{2}^{\frac{5}{3}} \right)^{\frac{1}{2}}$$

$$C(r_\mathrm{s}) = 0.001667 + \frac{P_0 + P_1 r_\mathrm{s} + P_2 r_\mathrm{s}^2}{1 + P_3 r_\mathrm{s} + P_4 r_\mathrm{s}^2 + P_5 r_\mathrm{s}^3}, \quad f(\zeta) = \frac{(\zeta+1)^{\frac{4}{3}} + (\zeta-1)^{\frac{4}{3}} - 2}{2^{\frac{4}{3}} - 2}$$

$$n = n_\alpha + n_\beta, \quad \zeta = \frac{n_\alpha - n_\beta}{n}, \quad r_\mathrm{s} = \left(\frac{3}{4\pi n}\right)^{\frac{1}{3}}, \quad \epsilon = A\log(r_\mathrm{s}) + B + C r_\mathrm{s} \log(r_\mathrm{s}) + D r_\mathrm{s}$$

$$P_0 = 0.002568, \quad P_1 = 0.023266, \quad P_2 = 7.38910^{-6}, \quad P_3 = 8.723, \quad P_4 = 0.472, \quad P_5 = 0.07389$$

$$A^\mathrm{p} = 0.0311, \quad A^\mathrm{f} = 0.01555, \quad B^\mathrm{p} = -0.048, \quad B^\mathrm{f} = -0.269, \quad C^\mathrm{p} = 0.0020,$$

$$C^\mathrm{f} = 0.0007, \quad D^\mathrm{p} = -0.0116, \quad D^\mathrm{f} = -0.0048$$

Its partial derivatives are

$$\frac{\partial f_c^{\mathrm{P86}}}{\partial |\nabla n_\alpha|} = \frac{C(r_\mathrm{s})}{d n^{\frac{4}{3}}} e^{-\dot{\Phi}} \left(-\dot{\Phi} |\nabla n|^2 + 2|\nabla n_\alpha| \right)$$

$$\dot{\Phi} = \frac{0.19195 C(\infty)}{n^{\frac{7}{6}|\nabla n|}} |\nabla n_\alpha|$$

$$\frac{\partial^2 f_c^{\mathrm{P86}}}{\partial n_\alpha^2} = 2Z' + nZ'' - |\nabla n|^2 e^{-\Phi} \left(d^{-1} \left(-\Phi' C(r_\mathrm{s}) + C'(r_\mathrm{s}) - C(r_\mathrm{s})(d' d^{-1} + \frac{4}{3} n^{-1}) \right) (\Phi' n^{-\frac{4}{3}} + \frac{4}{3} n^{-\frac{7}{3}}) \right.$$

$$-n^{-\frac{4}{3}} \left(\frac{d'}{d^2} \left(-\Phi' C(r_\mathrm{s}) + C'(r_\mathrm{s}) - C d^{-1} d' - \frac{4}{3} C(r_\mathrm{s}) n^{-1} \right) \right.$$

$$\left. \left. + \left(-\Phi'' C(r_\mathrm{s}) - \Phi' C' + C'' - C'(r_\mathrm{s})(d' d^{-1} + \frac{4}{3} n^{-1}) - C(r_\mathrm{s})(-d'^2 d^{-2} + d'' d^{-1} - \frac{4}{3} n^{-2}) \right) d^{-1} \right) \right)$$

$$\frac{\partial^2 f_c^{\mathrm{P86}}}{\partial n_\beta \partial n_\alpha} = \tilde{Z} + Z' + n\tilde{Z}' + |\nabla n|^2 e^{-\Phi} \left(d^{-1} \left(-\Phi' C(r_\mathrm{s}) + C'(r_\mathrm{s}) - C(r_\mathrm{s})(d' d^{-1} + \frac{4}{3} n^{-1}) \right) (\Phi' n^{-\frac{4}{3}} + \frac{4}{3} n^{-\frac{7}{3}}) \right.$$

$$- n^{-\frac{4}{3}} \frac{\tilde{d}}{d^2} \left(-\Phi' C(r_\mathrm{s}) + C'(r_\mathrm{s}) - C d^{-1} d' - \frac{4}{3} C(r_\mathrm{s}) n^{-1} \right)$$

$$\left. + \left(-\Phi'' C(r_\mathrm{s}) - \Phi' C' + C'' - C'(r_\mathrm{s})(d' d^{-1} + \frac{4}{3} n^{-1}) - C(r_\mathrm{s})(-\tilde{d} d' d^{-2} + \tilde{d}' d^{-1} - \frac{4}{3} n^{-2}) \right) d^{-1} \right)$$

$$r_\mathrm{s}' = -\frac{1}{3} \left(\frac{3}{4\pi n}\right)^{\frac{1}{3}} n^{-\frac{4}{3}}, \quad r_\mathrm{s}'' = \frac{4}{9} \left(\frac{3}{4\pi n}\right)^{\frac{1}{3}} n^{-\frac{7}{3}}$$

$$\epsilon' = \left(\frac{A}{r_\mathrm{s}} + C\left(\log(r_\mathrm{s}) + 1\right) + D \right) r_\mathrm{s}', \quad \epsilon'' = \left(-\frac{A}{r_\mathrm{s}^2} + \frac{C}{r_\mathrm{s}} \right) r_\mathrm{s}'^2 + \frac{\epsilon'}{r_\mathrm{s}'} r_\mathrm{s}''$$

$$f^{'}(\zeta) = \frac{4}{3}\frac{\zeta^{'}\left((\zeta+1)^{\frac{1}{3}} - (\zeta-1)^{\frac{1}{3}}\right)}{2^{\frac{4}{3}}-2}, \quad \tilde{f}(\zeta) = -f^{'}(\zeta)\frac{n_\alpha}{n_\beta}, \quad \zeta^{'} = 2\frac{n_\beta}{n^2}, \quad \tilde{\zeta} = -\zeta^{'}\frac{n_\alpha}{n_\beta}$$

$$Z^{'} = \epsilon^{p^{'}} + f(\zeta)^{'}\left(\epsilon^{\mathrm{f}} - \epsilon^{\mathrm{p}}\right) + f(\zeta)\left(\epsilon^{f^{'}} - \epsilon^{p^{'}}\right), \quad \tilde{Z} = \epsilon^{p^{'}} + \tilde{f}(\zeta)\left(\epsilon^{\mathrm{f}} - \epsilon^{\mathrm{p}}\right) + f(\zeta)\left(\epsilon^{f^{'}} - \epsilon^{p^{'}}\right)$$

$$C^{'}(r_{\mathrm{s}}) = \frac{(P_1 + 2P_2 r_{\mathrm{s}})}{1 + P_3 r_{\mathrm{s}} + P_4 r_{\mathrm{s}}^2 + P_5 r_{\mathrm{s}}^3} - \left(P_0 + P_1 r_{\mathrm{s}} + P_2 r_{\mathrm{s}}^2\right)\left(P_3 + 2P_4 r_{\mathrm{s}} + 3P_5 r_{\mathrm{s}}^2\right)$$

$$d^{'} = \frac{1}{2d}\frac{5}{6}\zeta^{'}\left((\zeta+1)^{\frac{2}{3}} - (\zeta-1)^{\frac{2}{3}}\right), \quad \tilde{d} = -d^{'}\frac{n_\alpha}{n_\beta}$$

$$\Phi^{'} = -0.19195C(\infty)|\nabla n|\left(\frac{\frac{7}{6}}{C(r_{\mathrm{s}})n^{\frac{13}{6}}} + \frac{C^{'}(r_{\mathrm{s}})}{C(r_{\mathrm{s}})^2 n^{\frac{7}{6}}}\right), \quad \hat{\Phi} = 0.19195C(\infty)n^{\frac{7}{6}|\nabla n|}|\nabla n_\beta|$$

$$\zeta^{''} = -4\frac{n_\beta}{n^3}, \quad \tilde{\zeta}^{'} = 2\frac{n_\alpha - n_\beta}{n^3}$$

$$f^{''} = \frac{4}{3}\frac{\frac{1}{3}\frac{\zeta^{'2}}{(\zeta+1)^{\frac{2}{3}}} + (\zeta+1)^{\frac{1}{3}}\zeta^{''} + \frac{1}{3}\frac{\zeta^{'2}}{(\zeta-1)^{\frac{2}{3}}} - (\zeta-1)^{\frac{1}{3}}\zeta^{''}}{2^{\frac{4}{3}}-2}$$

$$\tilde{f}^{'} = \frac{4}{3}\frac{\tilde{\zeta}^{'}\left((\zeta+1)^{\frac{1}{3}} - (\zeta-1)^{\frac{1}{3}}\right) + \frac{1}{3}\zeta^{'}\tilde{\zeta}(\zeta-1)^{-\frac{2}{3}} + (\zeta-1)^{-\frac{2}{3}}}{2^{\frac{4}{3}}-2}$$

$$Z^{''} = \epsilon^{p^{''}} + f^{''}\left(\epsilon^{\mathrm{f}} - \epsilon^{\mathrm{p}}\right) + 2f^{'}\left(\epsilon^{f^{'}} - \epsilon^{p^{'}}\right) + f\left(\epsilon^{f^{''}} - \epsilon^{p^{''}}\right)$$

$$\tilde{Z}^{'} = \epsilon^{p^{''}} + \tilde{f}^{'}\left(\epsilon^{\mathrm{f}} - \epsilon^{\mathrm{p}}\right) + f^{'}\left(\epsilon^{f^{'}} - \epsilon^{p^{'}}\right)\left(1 - \frac{n_\alpha}{n_\beta}\right) + f\left(\epsilon^{f^{''}} - \epsilon^{p^{''}}\right)$$

$$C^{''}(r_{\mathrm{s}}) = \Big[2\frac{P_2}{1 + P_3 r_{\mathrm{s}} + P_4 r_{\mathrm{s}}^2 + P_5 r_{\mathrm{s}}^3} - \Big\{2(P_1 + 2P_2 r_{\mathrm{s}})\left(P_3 + 2P_4 r_{\mathrm{s}} + 3P_5 r_{\mathrm{s}}^2\right)$$

$$+ \frac{\left(P_0 + P_1 r_{\mathrm{s}} + P_2 r_{\mathrm{s}}^2\right)(2P_4 + 6P_5 r_{\mathrm{s}})}{(1 + P_3 r_{\mathrm{s}} + P_4 r_{\mathrm{s}}^2 + P_5 r_{\mathrm{s}}^3)^2}\Big\} + \frac{2\left(P_0 + P_1 r_{\mathrm{s}} + P_2 r_{\mathrm{s}}^2\right)\left(P_3 + 2P_4 r_{\mathrm{s}} + 3P_5 r_{\mathrm{s}}^2\right)^2}{(P_0 + P_1 r_{\mathrm{s}} + P_2 r_{\mathrm{s}}^2)^3}\Big] r_{\mathrm{s}}^{'2} + \frac{C^{'}(r_{\mathrm{s}})}{r_{\mathrm{s}}^{'}} r_{\mathrm{s}}^{''}$$

$$d^{''} = -\frac{d^{'2}}{d} + \frac{2^{-\frac{1}{3}}}{d}\frac{5}{3}\left(2^{\frac{1}{3}}\frac{1}{6}\zeta^{'2}\left((\zeta+1)^{-\frac{1}{3}} + (\zeta-1)^{-\frac{1}{3}}\right) + 2^{-\frac{2}{3}}\left((\zeta+1)^{\frac{2}{3}} - (\zeta-1)^{\frac{2}{3}}\right)\frac{\zeta^{''}}{2}\right)$$

$$\tilde{d}^{'} = \frac{5}{12}\left(\frac{\zeta^{'}}{d}((\zeta+1)^{\frac{2}{3}} - (\zeta-1)^{\frac{2}{3}})(-\frac{\tilde{b}}{d} + \frac{\tilde{\zeta}^{'}}{\zeta^{'}}) + \frac{2}{3}\frac{\zeta^{'}}{d}\tilde{\zeta}^{'}((\zeta+1)^{-\frac{1}{3}} + (\zeta-1)^{-\frac{1}{3}})\right)$$

$$\Phi^{''} = 0.19195C(\infty)|\nabla n|(\frac{91}{36}\frac{n^{\frac{19}{6}}}{C(r_{\mathrm{s}})} + \frac{7}{3}\frac{n^{-\frac{13}{6}}}{C(r_{\mathrm{s}})^2}C^{'}(r_{\mathrm{s}}) + \frac{2}{C(r_{\mathrm{s}})^3}C^{'}(r_{\mathrm{s}})^2 n^{-\frac{7}{6}} - \frac{C^{''}(r_{\mathrm{s}})}{C(r_{\mathrm{s}})^2}n^{-\frac{7}{6}})$$

$$\frac{\partial^2 f_c^{\mathrm{P86}}}{\partial n_\alpha \partial |\nabla n_\alpha|} = n^{-\frac{4}{3}}d^{-1}\left(C^{'}(r_{\mathrm{s}})e^{-\Phi}(-\dot{\Phi}|\nabla n|^2 + 2|\nabla n_\alpha|) + C(r_{\mathrm{s}})e^{-\Phi}(\Phi^{'}\dot{\Phi}|\nabla n|^2 - \dot{\Phi}^{'}|\nabla n|^2 - \Phi^{'}2|\nabla n_\alpha|)\right)$$

$$+ C(r_{\mathrm{s}})e^{-\Phi}(-\dot{\Phi}|\nabla n|^2 + 2|\nabla n_\alpha|)(-\frac{4}{3}n^{-\frac{7}{3}}d^{-1} - d^{'}d^{-2}n^{-\frac{4}{3}})$$

$$\dot{\Phi}^{'} = 0.19195C(\infty)\left(-\frac{7}{6}n^{-\frac{13}{6}}C(r_{\mathrm{s}})^{-1} - C^{'}C(r_{\mathrm{s}})^{-2}n^{-\frac{7}{6}}\right)|\nabla n|^{-1}|\nabla n_\alpha|$$

$$\frac{\partial^2 f_c^{\mathrm{P86}}}{\partial n_\beta \partial|\nabla n_\alpha|} = n^{-\frac{4}{3}} d^{-1} \left(C^{'}(r_{\mathrm{s}}) e^{-\Phi} (-\dot{\Phi}|\nabla n|^2 + 2|\nabla n_\alpha|) + C(r_{\mathrm{s}}) e^{-\Phi} (\Phi^{'} \dot{\Phi} |\nabla n|^2 - \dot{\Phi}^{'} |\nabla n|^2 - \Phi^{'} 2|\nabla n_\alpha|) \right)$$
$$+ C(r_{\mathrm{s}}) e^{-\Phi} (-\dot{\Phi}|\nabla n|^2 + 2|\nabla n_\alpha|)(-\frac{4}{3} n^{-\frac{7}{3}} d^{-1} - \tilde{d} d^{-2} n^{-\frac{4}{3}})$$

$$\frac{\partial^2 f_c^{\mathrm{P86}}}{\partial n_\alpha \partial|\nabla n_\beta|} = \frac{\partial^2 f_c^{\mathrm{P86}}}{\partial n_\alpha \partial|\nabla n_\alpha|} \frac{|\nabla n_\beta|}{|\nabla n_\alpha|}$$

$$\frac{\partial^2 f_c^{\mathrm{P86}}}{\partial|\nabla n|^2} = C(r_{\mathrm{s}}) n^{-\frac{4}{3}} d^{-1} e^{-\Phi} \left((\dot{\Phi}^2 - \ddot{\Phi})|\nabla n|^2 - \dot{\Phi} 4|\nabla n_\alpha| + 2 \right)$$
$$\ddot{\Phi} = 0.19195 C(\infty) n^{-\frac{7}{6}} C(r_{\mathrm{s}})^{-1} \left(|\nabla n|^{-1} - \frac{|\nabla n_\alpha|^2}{|\nabla n|^3} \right)$$

$$\frac{\partial^2 f_c^{\mathrm{P86}}}{\partial|\nabla n_\beta| \partial|\nabla n_\alpha|} = C(r_{\mathrm{s}}) n^{-\frac{4}{3}} d^{-1} e^{-\Phi} \left((\hat{\Phi}\dot{\Phi} - \hat{\dot{\Phi}})|\nabla n|^2 - \dot{\Phi} 2|\nabla n_\beta| - \hat{\Phi} 2|\nabla n_\alpha| \right)$$
$$\hat{\dot{\Phi}} = 0.19195 C(\infty) n^{-\frac{7}{6}} C^{-1} \left(-|\nabla n_\alpha||\nabla n_\beta||\nabla n|^{-3} \right)$$

$$\frac{\partial f_c^{\mathrm{P86}}}{\partial(\nabla n_\alpha \cdot \nabla n_\beta)} = \frac{\partial f_c^{\mathrm{P86}}}{\partial|\nabla n_\alpha|} |\nabla n_\alpha|^{-1}$$

$$\frac{\partial^2 f_c^{\mathrm{P86}}}{\partial(\nabla n_\alpha \cdot \nabla n_\beta) \partial n_\alpha} = \frac{\partial^2 f_c^{\mathrm{P86}}}{\partial n_\alpha \partial|\nabla n_\beta|} |\nabla n_\beta|^{-1}$$

$$\frac{\partial^2 f_c^{\mathrm{P86}}}{\partial n_\beta \partial(\nabla n_\alpha \cdot \nabla n_\beta)} = n^{-\frac{4}{3}} d^{-1} e^{-\Phi} (-\bar{\Phi}|\nabla n|^2 + 2)(C^{'}(r_{\mathrm{s}}) - \frac{4}{3} C(r_{\mathrm{s}}) n^{-1}$$
$$- C(r_{\mathrm{s}}) d^{-1} \tilde{b} - C(r_{\mathrm{s}}) \Phi^{'}) - C(r_{\mathrm{s}}) n^{-\frac{4}{3}} d^{-1} e^{-\Phi} \bar{\Phi}^{'} |\nabla n|^2$$
$$\bar{\Phi} = 0.19195 C(\infty) C^{-1} n^{-\frac{7}{6}} |\nabla n|^{-1}$$
$$\bar{\Phi}^{'} = 0.19195 C(\infty)(-\frac{7}{6} n^{-\frac{13}{6}} C(r_{\mathrm{s}})^{-1} - C^{'} C^{-2} n^{-\frac{7}{6}})|\nabla n|^{-1}$$

$$\frac{\partial^2 f_c^{\mathrm{P86}}}{\partial(\nabla n_\alpha \cdot \nabla n_\beta)^2} = C(r_{\mathrm{s}}) n^{-\frac{4}{3}} d^{-1} e^{-\Phi} (\bar{\Phi}^2 |\nabla n|^2 - \bar{\bar{\Phi}} |\nabla n|^2 - 4\bar{\Phi})$$
$$\bar{\bar{\Phi}} = 0.19195 C(\infty) n^{-\frac{7}{6}} C(r_{\mathrm{s}})^{-1} |\nabla n|^{-3}$$

$$\frac{\partial^2 f_c^{\mathrm{P86}}}{\partial(\nabla n_\alpha \cdot \nabla n_\beta)\partial|\nabla n_\alpha|} = \frac{\partial^2 f_c^{\mathrm{P86}}}{\partial|\nabla n_\beta|\partial|\nabla n_\alpha|}|\nabla n_\beta|^{-1}$$

$$\frac{\partial^2 f_c^{\mathrm{P86}}}{\partial(\nabla n_\alpha \cdot \nabla n_\beta)\partial|\nabla n_\beta|} = \frac{\partial^2 f_c^{\mathrm{P86}}}{\partial(\nabla n_\alpha \cdot \nabla n_\beta)^2}|\nabla n_\beta|$$

The PBE [13] exchange functional reads

$$f_x^{\mathrm{PBE96}} = \frac{1}{2}\sum_{\sigma=\alpha,\beta} E(2n_\sigma)$$

$$E(n) = -\frac{3}{4}bn^{\frac{4}{3}}F, \quad F = 1 + R - \frac{R}{(1+\mu\frac{S^2}{R})^2}$$

$$b = \left(\frac{3}{\pi}\right)^{\frac{1}{3}}, \quad \mu = 0.066725\frac{\pi^2}{3}, \quad S = \chi a, \quad \chi = \frac{|\nabla n|}{n^{\frac{4}{3}}}, \quad a = \frac{1}{2(3\pi^2)^{\frac{1}{3}}}$$

Its partial derivatives are

$$\frac{\partial E}{\partial|\nabla n|^2} = -\frac{3}{2}bn^{\frac{4}{3}}\mu\frac{1}{(1+\mu\frac{S^2}{R})^2}a^2 n^{-\frac{8}{3}}$$

$$\frac{\partial^2 E}{\partial(|\nabla n|^2)^2} = 12bn^{\frac{4}{3}}\mu^2\frac{a^2}{R}n^{-\frac{16}{3}}\frac{1}{(1+\mu\frac{S^2}{R})^3}$$

$$\frac{\partial^2 E}{\partial n^2} = 2b\left(-\frac{1}{3}n^{-\frac{2}{3}} - 2n^{\frac{1}{3}}F^{'} - \frac{3}{4}n^{\frac{4}{3}}F^{''}\right)$$

$$F^{'} = 2\frac{1}{(1+\mu\frac{S^2}{R})^2}\mu S\chi^{'}a, \quad \chi^{'} = -\frac{4}{3}|\nabla n|n^{-\frac{7}{3}}$$

$$F^{''} = -\mu\left(\frac{8\mu}{R}\frac{1}{(1+\mu\frac{S^2}{R})^3}S^2\chi^{'2}a^2 - \frac{2}{(1+\mu\frac{S^2}{R})^2}(\chi^{'2}a^2 + S\chi^{''}a)\right), \quad \chi^{''} = \frac{28}{9}|\nabla n|n^{-\frac{10}{3}}$$

$$\frac{\partial^2 E}{\partial|\nabla n|^2\partial n} = 4\left(-bn^{\frac{1}{3}}\mu\frac{1}{(1+\mu\frac{S^2}{R})^2}a^2 n^{-\frac{8}{3}} - \frac{3}{4}bn^{\frac{4}{3}}\dot{F}'\right)$$

$$\dot{F}' = \frac{\mu}{|\nabla n|^2}\left(2SS^{'}\frac{1}{(1+\mu\frac{S^2}{R})^2} - 4\frac{\mu}{R}S^3S^{'}\frac{1}{(1+\mu\frac{S^2}{R})^3}\right)$$

The PW92 [14, 15] correlation functional[3] reads

$$f_c^{\mathrm{PW92}} = n\,(\epsilon + L)$$

$$\epsilon = e_1 - e_3\omega\frac{(1-\zeta^4)}{c} + (e_2 - e_1)\,\omega\zeta^4$$

$$r_{\mathrm{s}} = \left(\frac{3}{4\pi n}\right)^{\frac{1}{3}}, \quad \zeta = \frac{n_\alpha - n_\beta}{n}, \quad \omega = \frac{(1+\zeta)^f 3 + (1-\zeta)^f 3 - 2}{2^f 3 - 2}$$

$$e_i = e(r_{\mathrm{s}}, T_i, U_i, V_i, W_i, X_i, Y_i) = -2T_i(1 + U_i r_{\mathrm{s}})\log\left(1 + \frac{1}{2T_i(V_i\sqrt{r_{\mathrm{s}}} + W_i r_{\mathrm{s}} + X_i r_{\mathrm{s}}^{\frac{3}{2}} + Y_i r^2)}\right)$$

$$c = 1.709921, \quad T = [0.031091, 0.015545, 0.016887], \quad U = [0.21370, 0.20548, 0.11125]$$

$$V = [7.5957, 14.1189, 10.357], \quad W = [3.5876, 6.1977, 3.6231], \quad X = [1.6382, 3.3662, 0.88026]$$

$$Y = [0.49294, 0.62517, 0.49671]$$

$$L = \frac{u^3\lambda^2}{2\iota}\log\left(1 + 2\frac{\iota(d^2 + Ad^4)}{\lambda(1 + Ad^2 + A^2d^4)}\right)$$

$$u = \frac{1}{2}\left(1 + zp23 + zm23\right), \quad d = \frac{|\nabla n|}{4u}k_1 n^{-7}, \quad A = \frac{2\iota}{\lambda}\left(e^{-\frac{2\iota\epsilon}{u^3\lambda^2}} - 1\right)^{-1}, \quad k_1 = \left(\frac{\pi}{3}\right)^{\frac{1}{6}}$$

$$\iota = 0.0715996577859519, \quad \lambda = 0.0667245506031492$$

[3] Note that, consistently with the implementation of the PBE XC functional in CPMD [18], the term called H_1 in Ref. [14] has been dropped.

Its partial derivatives are

$$\frac{\partial^2 f_c^{\mathrm{PW92}}}{\partial n_\alpha^2} = 2\epsilon^{'} + n\epsilon^{''} + 2L^{'} + nL^{''}$$

$$\epsilon^{'} = e_1^{'} - e_3^{'}\omega\frac{(1-\zeta^4)}{c} - e_3(\omega^{'}\frac{(1-\zeta^4)}{c} - \omega\frac{4\zeta^3\zeta^{'}}{c}) + (e_2^{'} - e_1^{'})\omega\zeta^4 + (e_2 - e_1)(\omega^{'}\zeta^4 + \omega 4\zeta^3\zeta^{'})$$

$$\omega^{'} = k_2 n_\beta(n_\alpha^{\frac{1}{3}} - n_\beta^{\frac{1}{3}})n^{-\frac{7}{3}}, \quad \zeta^{'} = 2\frac{n_\beta}{n^2}, \quad k_2 = 6.4630961358174301$$

$$e_i^{'} = -2T_i\left(U_i r_{\mathrm{s}}^{'}\log\left(1 + \frac{1}{2T_i(V_i\sqrt{r_{\mathrm{s}}} + W_i r_{\mathrm{s}} + X_i r_{\mathrm{s}}^{\frac{3}{2}} + Y_i r^2)}\right)\right.$$

$$-\frac{1+U_i r_{\mathrm{s}}}{1 + 2T_i(V_i\sqrt{r_{\mathrm{s}}} + W_i r_{\mathrm{s}} + X_i r_{\mathrm{s}}^{\frac{3}{2}} + Y_i r^2)}\left(2T_i(V_i\sqrt{r_{\mathrm{s}}} + W_i r_{\mathrm{s}} + X_i r_{\mathrm{s}}^{\frac{3}{2}} + Y_i r^2)\right)^{-1}$$

$$\left.\times\left(2T_i(\frac{1}{2}V_i r_{\mathrm{s}}^{-\frac{1}{2}} + W_i + \frac{3}{2}X_i\sqrt{r_{\mathrm{s}}} + 2Y_i r_{\mathrm{s}})r_{\mathrm{s}}^{'}\right)\right)$$

$$\epsilon^{''} = e_1^{''} - e_3^{''}\omega\frac{(1-\zeta^4)}{c} - e_3^{'}(\omega^{'}\frac{(1-\zeta^4)}{c} - 2\omega\frac{4\zeta^3\zeta^{'}}{c})$$

$$- e_3\left(\omega^{''}\frac{(1-\zeta^4)}{c} - 2\omega^{'}\frac{4\zeta^3\zeta^{'}}{c} - \omega c^{-1}(12\zeta^2\zeta^{'2} + 4\zeta^3\zeta^{''})\right)$$

$$+ (e_2^{''} - e_1^{''})\omega\zeta^4 + 2(e_2^{'} - e_1^{'})(\omega^{'}\zeta^4 + \omega 4\zeta^3\zeta^{'}) + (e_2 - e_1)(\omega^{''}\zeta^4 + 2\omega^{'}4\zeta^3\zeta^{'} + \omega(12\zeta^2\zeta^{'2} + 4\zeta^3\zeta^{''}))$$

$$\zeta^{''} = -4\frac{n_\beta}{n^3}, \quad \omega^{''} = k_2 n_\beta\left(\frac{1}{3}n_\alpha^{-\frac{2}{3}}n^{-\frac{7}{3}} - (n_\alpha^{\frac{1}{3}} - n_\alpha^{\frac{1}{3}})\frac{7}{3}n^{-\frac{10}{3}}\right)$$

$$L^{'} = \frac{\lambda^2}{2\iota}\left(3u^2u^{'}\log\left(1 + \frac{2\iota}{\lambda}\frac{Z_1}{N_1}\right) + \frac{u^3}{1 + \frac{2\iota}{\lambda}\frac{Z_1}{N_1}}\left(\frac{Z_1^{'}}{N_1} - \frac{Z_1 N_1^{'}}{N_1^2}\right)\right)$$

$$Z_1^{'} = 2dd^{'} + A^{'}d^4 + 4Ad^3d^{'}, \quad N_1^{'} = A^{'}d^2 + 2Add^{'} + 2AA^{'}d^4 + 4A^2d^3d^{'}$$

$$u^{'} = (\frac{1}{3}zp - 13 - \frac{1}{3}zm - 13)\zeta^{'}, \quad A^{'} = 2\lambda\left(e^{-\frac{2\iota\epsilon}{u^3\lambda^2}} - 1\right)^{-2}e^{-\frac{2\iota\epsilon}{u^3\lambda^2}}\frac{2\iota}{\lambda^2}(\epsilon^{'}u^{-3} - \epsilon u^{'}u^{-4})$$

$$d^{'} = \frac{|\nabla n|}{4}k_1(-u^{-2}u^{'}n^{-\frac{7}{6}} - \frac{7}{6}u^{-1}n^{-\frac{13}{6}})$$

$$L^{''} = \frac{\lambda^2}{2\iota}\left(6u^2\frac{u^{'}}{1 + \frac{2\iota}{\lambda}\frac{Z_1}{N_1}}\frac{2\iota}{\lambda}\left(\frac{Z_1^{'}}{N_1} - \frac{Z_1N_1^{'}}{N_1^2}\right) + \log\left(1 + \frac{2\iota}{\lambda}\frac{Z_1}{N_1}\right)(6uu^{'2} + 3u^2u^{''})\right.$$

$$+ u^3\left(-4\frac{\iota^2}{\lambda^2}\left(\frac{Z_1^{'}}{N_1} - \frac{Z_1N_1^{'}}{N_1^2}\right)^2\left(1 + \frac{2\iota}{\lambda}\frac{Z_1}{N_1}\right)^{-2}\right.$$

$$\left.\left.+\left(1 + \frac{2\iota}{\lambda}\frac{Z_1}{N_1}\right)^{-1}\frac{2\iota}{\lambda}\left(\frac{Z_1^{''}}{N_1} - \frac{Z_1^{'}N_1^{'}}{N_1^2} - \frac{Z_1^{'}N_1^{'} + Z_1N_1^{''}}{N_1^2} + 2\frac{Z_1N_1^{'2}N_1}{N_1^4}\right)\right)\right)$$

$$Z_1^{''} = 2(d^{'2} + dd^{''}) + A^{''}d^4 + 8A^{'}d^3d^{'} + 4A(3d^2d^{'2} + d^3d^{''})$$

$$N_1^{''} = A^{''}d^2 + 4A^{'}dd^{'} + 2A(d^{'2} + dd^{''}) + 2A^{'2}d^4 + 2A(A^{''}d^4 + 4A^{'}d^3d^{'}) + 8AA^{'}d^3d^{'} + 4A^2(3d^2d^{'2} + d^3d^{''})$$

$$d^{''} = \frac{|\nabla n|}{4}k_1\left(2u^{-3}u^{'2}n^{-\frac{7}{6}} - u^{-2}(u^{''}n^{-\frac{7}{6}} - \frac{7}{6}u^{'}n^{-\frac{13}{6}}) - \frac{7}{6}(-u^{-2}u^{'}n^{-\frac{13}{6}} - \frac{13}{6}u^{-1}n^{-\frac{19}{6}})\right)$$

$$u^{''} = \zeta^{''}u^{'} + \frac{1}{2}\zeta^{'2}\left(-\frac{2}{9}zp - 43 - \frac{2}{9}zm - 43\right)$$

$$A^{''} = \frac{2\iota}{\lambda}\left(-2\left(e^{-\frac{2\iota\epsilon}{u^3\lambda^2}} - 1\right)^{-3}e^{-\frac{4\iota\epsilon}{u^3\lambda^2}}\left(\frac{2\iota}{\lambda^2}\epsilon^{'}u^{-3} - \epsilon u^{'}u^{-4}\right)^2 + \left(e^{-\frac{2\iota\epsilon}{u^3\lambda^2}} - 1\right)^{-2}\right.$$

$$\left.\times\left(e^{-\frac{2\iota\epsilon}{u^3\lambda^2}}\left(\frac{2\iota}{\lambda^2}\epsilon^{'}u^{-3} - \epsilon u^{'}u^{-4}\right)^2 + e^{-\frac{2\iota\epsilon}{u^3\lambda^2}}\left(-\frac{2\iota}{\lambda^2}(\epsilon^{''}u^{-3} - \epsilon^{'}6u^{'}u^{-4} - 3\epsilon(u^{''}u^{-4} - 4u^{'2}u^{-5}))\right)\right)\right)$$

$$\frac{\partial^2 f_c^{\rm PW92}}{\partial n_\beta \partial n_\alpha} = \epsilon^{'} + \tilde{\epsilon} + n\tilde{\epsilon}^{'} + \tilde{L} + L^{'} + n\tilde{L}^{'}$$

$$\tilde{\epsilon} = e_1^{'} - e_3^{'}\omega\frac{(1-\zeta^4)}{c} - e_3\left(\tilde{\omega}\frac{(1-\zeta^4)}{c} - 4\omega\zeta^3\tilde{\zeta}c^{-1}\right) + (e_2^{'} - e_1{}')(\tilde{\omega}\zeta^4 + 4\omega\zeta^3\tilde{\zeta}), \quad \tilde{\omega} = -\frac{n_\alpha}{n_\beta}\omega^{'}$$

$$\tilde{\epsilon}^{'} = e_1^{''} - e_3^{''}\omega\frac{(1-\zeta^4)}{c} - e_3^{'}(\tilde{\omega}\frac{(1-\zeta^4)}{c} - 2\omega\frac{4\zeta^3\zeta^{'}}{c})$$

$$-e_3\left(\tilde{\omega^{'}}\frac{(1-\zeta^4)}{c} - \omega^{'}\frac{4\zeta^3\tilde{\zeta}}{c} - \tilde{\omega}\frac{4\zeta^3\zeta^{'}}{c} - \omega c^{-1}(12\zeta^2\zeta^{'}\tilde{\zeta} + 4\zeta^3\tilde{\zeta^{'}})\right)$$

$$+ (e_2^{''} - e_1^{''})\omega\zeta^4 + 2(e_2^{'} - e_1^{'})(\omega^{'}\zeta^4 + \omega 4\zeta^3\zeta^{'}) + (e_2 - e_1)(\tilde{\omega^{'}}\zeta^4 + \omega^{'}4\zeta^3\tilde{\zeta^{'}} + \tilde{\omega}4\zeta^3\zeta^{'} + \omega(12\zeta^2\zeta^{'}\tilde{\zeta} + 4\zeta^3\tilde{\zeta^{'}}))$$

$$\tilde{\omega}^{'} = k_2(\frac{n_\alpha^{\frac{1}{3}} - n_\beta^{\frac{1}{3}}}{n^{\frac{7}{3}}} + n_\beta(-\frac{1}{3}n_\beta^{-\frac{2}{3}}n^{-\frac{7}{3}} - (n_\alpha^{\frac{1}{3}} - n_\beta^{\frac{1}{3}})\frac{7}{3}n^{-\frac{10}{3}}, \quad \tilde{\zeta}^{'} = 2\frac{\zeta}{n^2}$$

$$\tilde{L} = \frac{\lambda^2}{2\iota}\left(3u^2\tilde{u}\log\left(1 + \frac{2\iota}{\lambda}\frac{Z_1}{N_1}\right) + \frac{u^3}{1+\frac{2\iota}{\lambda}\frac{Z_1}{N_1}}\left(\frac{\tilde{Z}_1}{N_1} - \frac{Z_1\tilde{N}_1}{N_1^2}\right)\right)$$

$$\tilde{Z}_1 = 2d\tilde{d} + \tilde{A}d^4 + 4Ad^3\tilde{d}, \quad \tilde{N}_1 = \tilde{A}d^2 + 2Ad\tilde{d} + 2A\tilde{A}d^4 + 4A^2d^3\tilde{d}$$

$$\tilde{d} = \frac{|\nabla n|}{4}k_1(-u^{-2}\tilde{u}n^{-\frac{7}{6}} - \frac{7}{6}u^{-1}n^{-\frac{13}{6}}), \quad \tilde{u} = (\frac{1}{3}zp - 13 - \frac{1}{3}zm - 13)\tilde{\zeta}$$

$$\tilde{A} = 2\lambda\left(e^{-\frac{2\iota\epsilon}{u^3\lambda^2}} - 1\right)^{-2} e^{-\frac{2\iota\epsilon}{u^3\lambda^2}}\frac{2\iota}{\lambda^2}(\tilde{\epsilon}u^{-3} - \epsilon\tilde{u}u^{-4})$$

$$\tilde{L}^{'} = \frac{\lambda^2}{2\iota}\left(3u^2\frac{u^{'}}{1+\frac{2\iota}{\lambda}\frac{Z_1}{N_1}}\frac{2\iota}{\lambda}\left(\frac{\tilde{Z}_1}{N_1} - \frac{Z_1\tilde{N}_1}{N_1^2}\right) + \log\left(1+\frac{2\iota}{\lambda}\frac{Z_1}{N_1}\right)(6u\tilde{u}u^{'} + 3u^2\tilde{u^{'}})\right.$$

$$+3u^2\frac{\tilde{u}}{1+\frac{2\iota}{\lambda}\frac{Z_1}{N_1}}\frac{2\iota}{\lambda}\left(\frac{Z_1^{'}}{N_1} - \frac{Z_1N_1^{'}}{N_1^2}\right) + u^3\left(-\frac{\iota^2}{\lambda^2}\left(\frac{Z_1^{'}}{N_1} - \frac{Z_1N_1^{'}}{N_1^2}\right)\left(1+\frac{2\iota}{\lambda}\frac{Z_1}{N_1}\right)^{-2}\left(\frac{\tilde{Z}_1}{N_1} - \frac{Z_1\tilde{N}_1}{N_1^2}\right)\right.$$

$$\left.\left.+\left(1+\frac{2\iota}{\lambda}\frac{Z_1}{N_1}\right)^{-1}\frac{2\iota}{\lambda}\left(\frac{\tilde{Z_1^{'}}}{N_1} - \frac{Z_1^{'}\tilde{N}_1}{N_1^2} - \frac{\tilde{Z}N_1^{'} + Z_1\tilde{N_1^{'}}}{N_1^2} + 2\frac{Z_1N_1^{'}\tilde{N}_1 2N_1}{N_1^4}\right)\right)\right)$$

$$\tilde{Z_1}^{'} = 2(d^{'}\tilde{d} + d\tilde{d^{'}}) + \tilde{A}^{'}d^4 + 4A^{'}d^3\tilde{d} + 4\tilde{A}d^3d^{'} + 4A(3d^2\tilde{d}d^{'} + d^3\tilde{d^{'}})$$

$$\tilde{N_1}^{'} = \tilde{A}^{'}d^2 + 2A^{'}d\tilde{d} + 2\tilde{A}dd^{'} + 2A(d^{'}\tilde{d} + d\tilde{d^{'}}) + 2A^{'}\tilde{A}d^4 + 2A(\tilde{A}^{'}d^4 + 4A^{'}d^3\tilde{d}) + 8A\tilde{A}d^3d^{'} + 4A^2(3d^2d^{'}\tilde{d} + d^3\tilde{d^{'}})$$

$$\tilde{d}^{'} = \frac{|\nabla n|}{4}k_1\left(2u^{-3}u^{'}\tilde{u}n^{-\frac{7}{6}} - u^{-2}(\tilde{u^{'}}n^{-\frac{7}{6}} - \frac{7}{6}u^{'}n^{-\frac{13}{6}}) - \frac{7}{6}(-u^{-2}\tilde{u}n^{-\frac{13}{6}} - \frac{13}{6}u^{-1}n^{-\frac{19}{6}})\right)$$

$$\tilde{u}^{'} = \tilde{\zeta}^{'}u^{'} + \frac{1}{2}\zeta^{'}\tilde{\zeta}\left(-\frac{2}{9}zp - 43 - \frac{2}{9}zm - 43\right)$$

$$\tilde{A}^{'} = \frac{2\iota}{\lambda}\left(-2\left(e^{-\frac{2\iota\epsilon}{u^3\lambda^2}} - 1\right)^{-3} e^{-\frac{4\iota\epsilon}{u^3\lambda^2}}\left(\frac{2\iota}{\lambda^2}\epsilon^{'}u^{-3} - \epsilon\tilde{u}u^{-4}\right)^2 + \left(e^{-\frac{2\iota\epsilon}{u^3\lambda^2}} - 1\right)^{-2}\right.$$

$$\left.\times\left(e^{-\frac{2\iota\epsilon}{u^3\lambda^2}}\left(\frac{2\iota}{\lambda^2}\tilde{\epsilon}u^{-3} - \epsilon\tilde{u}u^{-4}\right)^2 + e^{-\frac{2\iota\epsilon}{u^3\lambda^2}}\left(-\frac{2\iota}{\lambda^2}(\tilde{\epsilon^{'}}u^{-3} - \epsilon^{'}6\tilde{u}u^{-4} - 3\epsilon(\tilde{u^{'}}u^{-4} - 4u^{'}\tilde{u}u^{-5}))\right)\right)\right)$$

$$\frac{\partial f_c^{\rm PW92}}{\partial|\nabla n_\alpha|^2} = n\dot{L}$$

$$\dot{L} = \lambda u^3\left(1 + \frac{2\iota}{\lambda}\frac{Z_1}{N_1}\right)^{-1}\left(\frac{\dot{Z}_1}{N_1} - \frac{Z_1\dot{N}_1}{N_1^2}\right)$$

$$\dot{Z}_1 = \frac{d^2 + 2Ad^4}{|\nabla n|^2}, \quad \dot{N}_1 = \frac{Ad^2 + 2A^2d^4}{|\nabla n|^2}$$

$$\frac{\partial^2 f_c^{\mathrm{PW92}}}{\partial(|\nabla n_\alpha|^2)^2} = n\ddot{L}$$

$$\ddot{L} = \frac{\lambda^2}{2\iota}u^3\left(-\frac{4\iota^2}{\lambda^2}\left(\frac{\dot{Z}_1}{N_1} - \frac{Z_1\dot{N}_1}{N_1^2}\right)^2\left(1 + \frac{2\iota}{\lambda}\frac{Z_1}{N_1}\right)^{-2} + \left(\frac{\ddot{Z}_1}{N_1} - \frac{\dot{Z}_1\dot{N}_1}{N_1^2} - \frac{\dot{Z}_1\dot{N}_1 + Z_1\ddot{N}_1}{N_1^2} + 2\frac{Z_1\dot{N}_1{}^2 N_1}{N_1^4}\right)\right)$$

$$\ddot{Z}_1 = \frac{2Ad^4}{|\nabla n|^4}, \quad \ddot{N}_1 = \frac{2A^2d^4}{|\nabla n|^4}$$

$$\frac{\partial^2 f_c^{\mathrm{PW92}}}{\partial|\nabla n_\alpha|^2\partial n_\alpha} = \dot{L} + n\dot{L}'$$

$$\dot{L}' = \frac{\lambda^2}{2\iota}\left(3u^2u'\frac{2\iota}{\lambda}\left(1 + \frac{2\iota}{\lambda}\frac{Z_1}{N_1}\right)^{-1}\left(\frac{\dot{Z}_1}{N_1} - \frac{Z_1\dot{N}_1}{N_1^2}\right) + u^3\left(-\left(1 + \frac{2\iota}{\lambda}\frac{Z_1}{N_1}\right)^{-2}\left(\frac{\dot{Z}_1}{N_1} - \frac{Z_1\dot{N}_1}{N_1^2}\right)\frac{2\iota}{\lambda}\left(\frac{Z_1'}{N_1} - \frac{Z_1N_1'}{N_1^2}\right)\right.\right.$$
$$\left.\left. + \left(1 + \frac{2\iota}{\lambda}\frac{Z_1}{N_1}\right)^{-1}\left(\frac{2\iota}{\lambda}\frac{\dot{Z}_1{}'}{N_1} - \frac{\dot{Z}_1N_1'}{N_1^2} - \frac{Z_1'\dot{N}_1 + Z_1\dot{N}_1{}'}{N_1^2} + 2\frac{Z_1N_1'\dot{N}_1N_1}{N_1^4}\right)\right)\right)$$

$$\dot{Z}_1{}' = \frac{2dd' + 2A'd^4 + 8Ad^3d'}{|\nabla n|^2}, \quad \dot{N}_1{}' = \frac{A'd^2 + 2Add' + 4AA'd^4 + 8A^2d^3d'}{|\nabla n|^2}$$

$$\frac{\partial^2 f_c^{\mathrm{PW92}}}{\partial|\nabla n_\alpha|^2\partial n_\beta} = \dot{L} + n\dot{\tilde{L}}$$

$$\dot{\tilde{L}} = \frac{\lambda^2}{2\iota}\left(3u^2\tilde{u}\frac{2\iota}{\lambda}\left(1 + \frac{2\iota}{\lambda}\frac{Z_1}{N_1}\right)^{-1}\left(\frac{\dot{Z}_1}{N_1} - \frac{Z_1\dot{N}_1}{N_1^2}\right) + u^3\left(-\left(1 + \frac{2\iota}{\lambda}\frac{Z_1}{N_1}\right)^{-2}\left(\frac{\dot{Z}_1}{N_1} - \frac{Z_1\dot{N}_1}{N_1^2}\right)\frac{2\iota}{\lambda}\left(\frac{\tilde{Z}_1}{N_1} - \frac{Z_1\tilde{N}_1}{N_1^2}\right)\right.\right.$$
$$\left.\left. + \left(1 + \frac{2\iota}{\lambda}\frac{Z_1}{N_1}\right)^{-1}\left(\frac{2\iota}{\lambda}\frac{\dot{\tilde{Z}}_1}{N_1} - \frac{\dot{Z}_1\tilde{N}_1}{N_1^2} - \frac{\tilde{Z}_1\dot{N}_1 + Z_1\dot{\tilde{N}}_1}{N_1^2} + 2\frac{Z_1\tilde{N}_1\dot{N}_1N_1}{N_1^4}\right)\right)\right)$$

$$\dot{\tilde{Z}}_1 = \frac{2d\tilde{d} + 2\tilde{A}d^4 + 8Ad^3\tilde{d}}{|\nabla n|^2}, \quad \dot{\tilde{N}}_1 = \frac{\tilde{A}d^2 + 2Add\tilde{d} + 4A\tilde{A}d^4 + 8A^2d^3\tilde{d}}{|\nabla n|^2}$$

$$\frac{\partial^2 f_c^{\mathrm{PW92}}}{\partial(\nabla n_\alpha \cdot \nabla n_\beta)\partial n_\alpha} = 2\frac{\partial^2 f_c^{\mathrm{PW92}}}{\partial|\nabla n_\alpha|^2\partial n_\alpha}$$

$$\frac{\partial^2 f_c^{\mathrm{PW92}}}{\partial(\nabla n_\alpha \cdot \nabla n_\beta)\partial|\nabla n_\alpha|^2} = 2\frac{\partial^2 f_c^{\mathrm{PW92}}}{(\partial|\nabla n_\alpha|^2)^2}$$

$$\frac{\partial f_c^{\mathrm{PW92}}}{\partial(\nabla n_\alpha \cdot \nabla n_\beta)} = 2\frac{\partial f_c^{\mathrm{PW92}}}{\partial|\nabla n_\alpha|^2}$$

$$\frac{\partial^2 f_c^{\mathrm{PW92}}}{\partial(\nabla n_\alpha \cdot \nabla n_\beta)^2} = 4\frac{\partial^2 f_c^{\mathrm{PW92}}}{(\partial|\nabla n_\alpha|^2)^2}$$

$$\frac{\partial^2 f_c^{\mathrm{PW92}}}{\partial|\nabla n_\beta|^2\partial|\nabla n_\alpha|^2} = \frac{\partial^2 f_c^{\mathrm{PW92}}}{(\partial|\nabla n_\alpha|^2)^2}$$

$$\frac{\partial^2 f_c^{\mathrm{PW92}}}{\partial|\nabla n_\beta|^2\partial n_\alpha} = \frac{\partial^2 f_c^{\mathrm{PW92}}}{\partial|\nabla n_\alpha|^2\partial n_\alpha}$$

$$\frac{\partial^2 f_c^{\mathrm{PW92}}}{\partial(\nabla n_\alpha \cdot \nabla n_\beta)\partial|\nabla n_\beta|^2} = 2\frac{\partial^2 f_c^{\mathrm{PW92}}}{(\partial|\nabla n_\alpha|^2)^2}$$

$$\frac{\partial^2 f_c^{\mathrm{PW92}}}{\partial(\nabla n_\alpha \cdot \nabla n_\beta)\partial\nabla n_\beta} = 2\frac{\partial^2 f_c^{\mathrm{PW92}}}{\partial|\nabla n_\alpha|^2\partial n_\beta}$$