Double-hybrid density-functional theory with meta-generalized-gradient approximations: Supplementary material

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(Dated: February 4, 2014)

In this supplementary material, we show that the nonlinear Rayleigh-Schrödinger perturbation theory first introduced in Ref. 1 and applied to double-hybrid approximations in Ref. 2 can be extended to meta-GGA functionals depending explicitly on both the density $n(\mathbf{r})$ and the positive kinetic-energy density $\tau(\mathbf{r})$.

Given a Hamiltonian $\hat{H}^{(0)}$, a perturbation operator $\hat{W}$ and a functional $F[n,\tau]$, we define the following energy expression by minimizing over N-electron normalized wave functions Ψ,

$$E^\alpha = \min_\Psi \Big\{ \langle \Psi | \hat{H}^{(0)} + \alpha \hat{W} | \Psi \rangle + F[n_\Psi, \tau_\Psi] \Big\}, \quad (1)$$

where $n_\Psi(\mathbf{r}) = \langle \Psi | \hat{n}(\mathbf{r}) | \Psi \rangle$ and $\tau_\Psi(\mathbf{r}) = \langle \Psi | \hat{\tau}(\mathbf{r}) | \Psi \rangle$ are the density and the positive kinetic-energy density of the wave function Ψ, respectively, expressed with the second-quantized operators $\hat{n}(\mathbf{r}) = \sum_{\sigma=\uparrow,\downarrow} \hat{\psi}^\dagger_\sigma(\mathbf{r}) \hat{\psi}_\sigma(\mathbf{r})$ and $\hat{\tau}(\mathbf{r}) = (1/2) \sum_{\sigma=\uparrow,\downarrow} \boldsymbol{\nabla}_\mathbf{r}\, \hat{\psi}^\dagger_\sigma(\mathbf{r}) \cdot \boldsymbol{\nabla}_\mathbf{r}\, \hat{\psi}_\sigma(\mathbf{r})$. In Eq. (1), α is the perturbation parameter; we are ultimately interested in the case $\alpha = 1$. The minimizing wave function Ψ^α satisfies the Euler-Lagrange equation

$$\left(\hat{H}^{(0)} + \alpha \hat{W} + \hat{\Omega}^\alpha \right) | \Psi^\alpha \rangle = \mathcal{E}^\alpha | \Psi^\alpha \rangle, \quad (2)$$

where the eigenvalue $\mathcal{E}^\alpha$ comes from the normalization condition and $\hat{\Omega}^\alpha$ is a potential operator (non linear in α) coming from the variation of $F[n,\tau]$,

$$\hat{\Omega}^\alpha = \int d\mathbf{r} \frac{\delta F[n^\alpha, \tau^\alpha]}{\delta n(\mathbf{r})} \hat{n}(\mathbf{r}) + \int d\mathbf{r} \frac{\delta F[n^\alpha, \tau^\alpha]}{\delta \tau(\mathbf{r})} \hat{\tau}(\mathbf{r}), \quad (3)$$

where $n^\alpha(\mathbf{r}) = \langle \Psi^\alpha | \hat{n}(\mathbf{r}) | \Psi^\alpha \rangle$ and $\tau^\alpha(\mathbf{r}) = \langle \Psi^\alpha | \hat{\tau}(\mathbf{r}) | \Psi^\alpha \rangle$.

Starting from the reference $\alpha = 0$, we develop a perturbation theory in α. We introduce the intermediate normalized wave function $\tilde{\Psi}^\alpha = \Psi^\alpha / \langle \Psi^{\alpha=0} | \Psi^\alpha \rangle$, and expand $\tilde{\Psi}^\alpha$, n^α, τ^α, $\hat{\Omega}^\alpha$ and $\mathcal{E}^\alpha$ in powers of α: $\tilde{\Psi}^\alpha = \sum_{k=0}^\infty \tilde{\Psi}^{(k)} \alpha^k$, $n^\alpha = \sum_{k=0}^\infty n^{(k)} \alpha^k$, $\tau^\alpha = \sum_{k=0}^\infty \tau^{(k)} \alpha^k$, $\hat{\Omega}^\alpha = \sum_{k=0}^\infty \hat{\Omega}^{(k)} \alpha^k$ and $\mathcal{E}^\alpha = \sum_{k=0}^\infty \mathcal{E}^{(k)} \alpha^k$. The coefficients $n^{(k)}$ and $\tau^{(k)}$ are obtained from the expansion of $\tilde{\Psi}^\alpha$ through

$$n^\alpha(\mathbf{r}) = \frac{\langle \tilde{\Psi}^\alpha | \hat{n}(\mathbf{r}) | \tilde{\Psi}^\alpha \rangle}{\langle \tilde{\Psi}^\alpha | \tilde{\Psi}^\alpha \rangle}, \quad (4)$$

$$\tau^\alpha(\mathbf{r}) = \frac{\langle \tilde{\Psi}^\alpha | \hat{\tau}(\mathbf{r}) | \tilde{\Psi}^\alpha \rangle}{\langle \tilde{\Psi}^\alpha | \tilde{\Psi}^\alpha \rangle}, \quad (5)$$

and the coefficients $\hat{\Omega}^{(k)}$ are found from the expansions of n^α and τ^α, after expanding $\hat{\Omega}^\alpha$ around $n^{(0)}$ and $\tau^{(0)}$,

$$\begin{aligned} \hat{\Omega}^\alpha \; = \; & \int d\mathbf{r} \frac{\delta F[n^{(0)}, \tau^{(0)}]}{\delta n(\mathbf{r})} \hat{n}(\mathbf{r}) + \int d\mathbf{r} \frac{\delta F[n^{(0)}, \tau^{(0)}]}{\delta \tau(\mathbf{r})} \hat{\tau}(\mathbf{r}) \\ & + \iint d\mathbf{r} d\mathbf{r}' \frac{\delta^2 F[n^{(0)}, \tau^{(0)}]}{\delta n(\mathbf{r}) \delta n(\mathbf{r}')} \Delta n^\alpha(\mathbf{r}') \hat{n}(\mathbf{r}) \\ & + \iint d\mathbf{r} d\mathbf{r}' \frac{\delta^2 F[n^{(0)}, \tau^{(0)}]}{\delta n(\mathbf{r}) \delta \tau(\mathbf{r}')} \Delta \tau^\alpha(\mathbf{r}') \hat{n}(\mathbf{r}) \\ & + \iint d\mathbf{r} d\mathbf{r}' \frac{\delta^2 F[n^{(0)}, \tau^{(0)}]}{\delta \tau(\mathbf{r}) \delta n(\mathbf{r}')} \Delta n^\alpha(\mathbf{r}') \hat{\tau}(\mathbf{r}) \\ & + \iint d\mathbf{r} d\mathbf{r}' \frac{\delta^2 F[n^{(0)}, \tau^{(0)}]}{\delta \tau(\mathbf{r}) \delta \tau(\mathbf{r}')} \Delta \tau^\alpha(\mathbf{r}') \hat{\tau}(\mathbf{r}) + \cdots , \end{aligned} \quad (6)$$

where $\Delta n^\alpha = n^\alpha - n^{(0)}$ and $\Delta \tau^\alpha = \tau^\alpha - \tau^{(0)}$. The zeroth-order equation is

$$\left(\hat{H}^{(0)} + \hat{\Omega}^{(0)} \right) | \tilde{\Psi}^{(0)} \rangle = \mathcal{E}^{(0)} | \tilde{\Psi}^{(0)} \rangle, \quad (7)$$

and of course $\tilde{\Psi}^{(0)} = \Psi^{\alpha=0}$. For the general order $k \geq 1$,

$$\begin{aligned} & \left(\hat{H}^{(0)} + \hat{\Omega}^{(0)} - \mathcal{E}^{(0)} \right) | \tilde{\Psi}^{(k)} \rangle + \hat{W} | \tilde{\Psi}^{(k-1)} \rangle \\ & \quad + \sum_{i=1}^k \hat{\Omega}^{(i)} | \tilde{\Psi}^{(k-i)} \rangle = \sum_{i=1}^k \mathcal{E}^{(i)} | \tilde{\Psi}^{(k-i)} \rangle. \end{aligned} \quad (8)$$

The corresponding eigenvalue correction of order k is

$$\mathcal{E}^{(k)} = \langle \tilde{\Psi}^{(0)} | \hat{W} | \tilde{\Psi}^{(k-1)} \rangle + \sum_{i=1}^k \langle \tilde{\Psi}^{(0)} | \hat{\Omega}^{(i)} | \tilde{\Psi}^{(k-i)} \rangle, \quad (9)$$

containing, besides the usual first term, a "non-linearity" term as well. Introducing the reduced resolvent, $\hat{R}_0$,

$$\hat{R}_0 \; = \; \sum_I \frac{|\tilde{\Psi}_I^{(0)} \rangle \langle \tilde{\Psi}_I^{(0)}|}{\mathcal{E}_I^{(0)} - \mathcal{E}^{(0)}}, \quad (10)$$

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where $\tilde{\Psi}_I^{(0)}$ and $\mathcal{E}_I^{(0)}$ are the excited eigenfunctions and eigenvalues of $\hat{H}^{(0)} + \hat{\Omega}^{(0)}$, the wave function correction of order k writes

$$|\tilde{\Psi}^{(k)}\rangle = -\hat{R}_0 \hat{W} |\tilde{\Psi}^{(k-1)}\rangle - \hat{R}_0 \hat{\Omega}^{(k)} |\tilde{\Psi}^{(0)}\rangle -\hat{R}_0 \sum_{i=1}^{k-1} \left(\hat{\Omega}^{(i)} - \mathcal{E}^{(i)} \right) |\tilde{\Psi}^{(k-i)}\rangle. \quad (11)$$

The total energy can be re-expressed in terms of the eigenvalue $\mathcal{E}^\alpha$ and the "double counting correction" D^α

$$E^\alpha = \mathcal{E}^\alpha + D^\alpha, \quad (12)$$

where

$$D^\alpha = F[n^\alpha, \tau^\alpha] - \int d\mathbf{r} \frac{\delta F[n^\alpha, \tau^\alpha]}{\delta n(\mathbf{r})} n^\alpha(\mathbf{r}) - \int d\mathbf{r} \frac{\delta F[n^\alpha, \tau^\alpha]}{\delta \tau(\mathbf{r})} \tau^\alpha(\mathbf{r}). \quad (13)$$

We expand E^α and D^α in powers of α: $E^\alpha = \sum_{k=0}^{\infty} E^{(k)} \alpha^k$ and $D^\alpha = \sum_{k=0}^{\infty} D^{(k)} \alpha^k$. The coefficients $D^{(k)}$ are found from the expansions of n^α and τ^α, after expanding D^α around $n^{(0)}$ and $\tau^{(0)}$,

$$\begin{aligned}
D^\alpha &= F[n^{(0)}, \tau^{(0)}] + \int d\mathbf{r} \frac{\delta F[n^{(0)}, \tau^{(0)}]}{\delta n(\mathbf{r})} \Delta n^\alpha(\mathbf{r}) \\
&+ \int d\mathbf{r} \frac{\delta F[n^{(0)}, \tau^{(0)}]}{\delta \tau(\mathbf{r})} \Delta \tau^\alpha(\mathbf{r}) \\
&+ \frac{1}{2} \iint d\mathbf{r} d\mathbf{r}' \frac{\delta^2 F[n^{(0)}, \tau^{(0)}]}{\delta n(\mathbf{r}) \delta n(\mathbf{r}')} \Delta n^\alpha(\mathbf{r}') \Delta n^\alpha(\mathbf{r}) \\
&+ \frac{1}{2} \iint d\mathbf{r} d\mathbf{r}' \frac{\delta^2 F[n^{(0)}, \tau^{(0)}]}{\delta n(\mathbf{r}) \delta \tau(\mathbf{r}')} \Delta \tau^\alpha(\mathbf{r}') \Delta n^\alpha(\mathbf{r}) \\
&+ \frac{1}{2} \iint d\mathbf{r} d\mathbf{r}' \frac{\delta^2 F[n^{(0)}, \tau^{(0)}]}{\delta \tau(\mathbf{r}) \delta n(\mathbf{r}')} \Delta n^\alpha(\mathbf{r}') \Delta \tau^\alpha(\mathbf{r}) \\
&+ \frac{1}{2} \iint d\mathbf{r} d\mathbf{r}' \frac{\delta^2 F[n^{(0)}, \tau^{(0)}]}{\delta \tau(\mathbf{r}) \delta \tau(\mathbf{r}')} \Delta \tau^\alpha(\mathbf{r}') \Delta \tau^\alpha(\mathbf{r}) + \cdots \\
&- \int d\mathbf{r} \frac{\delta F[n^{(0)}, \tau^{(0)}]}{\delta n(\mathbf{r})} n^\alpha(\mathbf{r}) - \int d\mathbf{r} \frac{\delta F[n^{(0)}, \tau^{(0)}]}{\delta \tau(\mathbf{r})} \tau^\alpha(\mathbf{r}) \\
&- \iint d\mathbf{r} d\mathbf{r}' \frac{\delta^2 F[n^{(0)}, \tau^{(0)}]}{\delta n(\mathbf{r}) \delta n(\mathbf{r}')} \Delta n^\alpha(\mathbf{r}') n^\alpha(\mathbf{r}) \\
&- \iint d\mathbf{r} d\mathbf{r}' \frac{\delta^2 F[n^{(0)}, \tau^{(0)}]}{\delta n(\mathbf{r}) \delta \tau(\mathbf{r}')} \Delta \tau^\alpha(\mathbf{r}') n^\alpha(\mathbf{r}) \\
&- \iint d\mathbf{r} d\mathbf{r}' \frac{\delta^2 F[n^{(0)}, \tau^{(0)}]}{\delta \tau(\mathbf{r}) \delta n(\mathbf{r}')} \Delta n^\alpha(\mathbf{r}') \tau^\alpha(\mathbf{r}) \\
&- \iint d\mathbf{r} d\mathbf{r}' \frac{\delta^2 F[n^{(0)}, \tau^{(0)}]}{\delta \tau(\mathbf{r}) \delta \tau(\mathbf{r}')} \Delta \tau^\alpha(\mathbf{r}') \tau^\alpha(\mathbf{r}) - \cdots .
\end{aligned} \quad (14)$$

The zeroth-order total energy is simply

$$E^{(0)} = \mathcal{E}^{(0)} + F[n^{(0)}, \tau^{(0)}] - \int d\mathbf{r} \frac{\delta F[n^{(0)}, \tau^{(0)}]}{\delta n(\mathbf{r})} n^{(0)}(\mathbf{r}) - \int d\mathbf{r} \frac{\delta F[n^{(0)}, \tau^{(0)}]}{\delta \tau(\mathbf{r})} \tau^{(0)}(\mathbf{r}). \quad (15)$$

The general correction of order $k \geq 1$ writes

$$E^{(k)} = \langle \tilde{\Psi}^{(0)} | \hat{W} | \tilde{\Psi}^{(k-1)} \rangle + \Delta^{(k)} \quad (16)$$

where $\Delta^{(k)}$ is

$$\Delta^{(k)} = \sum_{i=1}^{k} \langle \tilde{\Psi}^{(0)} | \hat{\Omega}^{(i)} | \tilde{\Psi}^{(k-i)} \rangle + D^{(k)}. \quad (17)$$

At first order, it can be verified that the nonlinearity term of the eigenvalue and the double counting correction cancel each other, i.e. $\Delta^{(1)} = 0$, and we obtain the conventional first-order energy correction

$$E^{(1)} = \langle \tilde{\Psi}^{(0)} | \hat{W} | \tilde{\Psi}^{(0)} \rangle. \quad (18)$$

At second order, the situation is analogous, i.e. $\Delta^{(2)} = 0$, and again the conventional form of the energy correction is retrieved

$$E^{(2)} = \langle \tilde{\Psi}^{(0)} | \hat{W} | \tilde{\Psi}^{(1)} \rangle. \quad (19)$$

The nonlinearity effects are "hidden" in the first-order wave function correction, which can be obtained from the self-consistent equation:

$$|\tilde{\Psi}^{(1)}\rangle = -\hat{R}_0 \hat{W} |\tilde{\Psi}^{(0)}\rangle - \hat{R}_0 \hat{\Omega}^{(1)} |\tilde{\Psi}^{(0)}\rangle \quad (20)$$

Since the first-order potential operator is, for real wave functions,

$$\begin{aligned}
\hat{\Omega}^{(1)} &= 2 \iint d\mathbf{r} d\mathbf{r}' \frac{\delta^2 F[n^{(0)}, \tau^{(0)}]}{\delta n(\mathbf{r}) \delta n(\mathbf{r}')} \langle \tilde{\Psi}^{(0)} | \hat{n}(\mathbf{r}') | \tilde{\Psi}^{(1)} \rangle \hat{n}(\mathbf{r}) \\
&+ 2 \iint d\mathbf{r} d\mathbf{r}' \frac{\delta^2 F[n^{(0)}, \tau^{(0)}]}{\delta n(\mathbf{r}) \delta \tau(\mathbf{r}')} \langle \tilde{\Psi}^{(0)} | \hat{\tau}(\mathbf{r}') | \tilde{\Psi}^{(1)} \rangle \hat{n}(\mathbf{r}) \\
&+ 2 \iint d\mathbf{r} d\mathbf{r}' \frac{\delta^2 F[n^{(0)}, \tau^{(0)}]}{\delta \tau(\mathbf{r}) \delta n(\mathbf{r}')} \langle \tilde{\Psi}^{(0)} | \hat{n}(\mathbf{r}') | \tilde{\Psi}^{(1)} \rangle \hat{\tau}(\mathbf{r}) \\
&+ 2 \iint d\mathbf{r} d\mathbf{r}' \frac{\delta^2 F[n^{(0)}, \tau^{(0)}]}{\delta \tau(\mathbf{r}) \delta \tau(\mathbf{r}')} \langle \tilde{\Psi}^{(0)} | \hat{\tau}(\mathbf{r}') | \tilde{\Psi}^{(1)} \rangle \hat{\tau}(\mathbf{r}),
\end{aligned} \quad (21)$$

Eq. (20) can be re-expressed as

$$|\tilde{\Psi}^{(1)}\rangle = -\hat{R}_0 \hat{W} |\tilde{\Psi}^{(0)}\rangle - \hat{R}_0 \hat{G}_0 |\tilde{\Psi}^{(1)}\rangle, \quad (22)$$

where

$$\begin{aligned}
\hat{G}_0 &= 2 \iint d\mathbf{r} d\mathbf{r}' \hat{n}(\mathbf{r}) |\tilde{\Psi}^{(0)}\rangle \frac{\delta^2 F[n^{(0)}, \tau^{(0)}]}{\delta n(\mathbf{r}) \delta n(\mathbf{r}')} \langle \tilde{\Psi}^{(0)} | \hat{n}(\mathbf{r}') \\
&+ 2 \iint d\mathbf{r} d\mathbf{r}' \hat{n}(\mathbf{r}) |\tilde{\Psi}^{(0)}\rangle \frac{\delta^2 F[n^{(0)}, \tau^{(0)}]}{\delta n(\mathbf{r}) \delta \tau(\mathbf{r}')} \langle \tilde{\Psi}^{(0)} | \hat{\tau}(\mathbf{r}') \\
&+ 2 \iint d\mathbf{r} d\mathbf{r}' \hat{\tau}(\mathbf{r}) |\tilde{\Psi}^{(0)}\rangle \frac{\delta^2 F[n^{(0)}, \tau^{(0)}]}{\delta \tau(\mathbf{r}) \delta n(\mathbf{r}')} \langle \tilde{\Psi}^{(0)} | \hat{n}(\mathbf{r}') \\
&+ 2 \iint d\mathbf{r} d\mathbf{r}' \hat{\tau}(\mathbf{r}) |\tilde{\Psi}^{(0)}\rangle \frac{\delta^2 F[n^{(0)}, \tau^{(0)}]}{\delta \tau(\mathbf{r}) \delta \tau(\mathbf{r}')} \langle \tilde{\Psi}^{(0)} | \hat{\tau}(\mathbf{r}').
\end{aligned} \quad (23)$$

The final expression of the second-order energy correction can be written as the series

$$
\begin{aligned}
E^{(2)} &= -\langle\tilde{\Psi}^{(0)}|\hat{W}\big(1+\hat{R}_0\hat{G}_0\big)^{-1}\hat{R}_0\hat{W}|\tilde{\Psi}^{(0)}\rangle \\
&= -\langle\tilde{\Psi}^{(0)}|\hat{W}\hat{R}_0\hat{W}|\tilde{\Psi}^{(0)}\rangle \\
&\quad +\langle\tilde{\Psi}^{(0)}|\hat{W}\hat{R}_0\hat{G}_0\hat{R}_0\hat{W}|\tilde{\Psi}^{(0)}\rangle - \cdots . \qquad (24)
\end{aligned}
$$

To define meta-GGA double-hybrid approximations, we apply this perturbation theory with the following choices. The Hamiltonian $\hat{H}^{(0)}$ is

$$
\hat{H}^{(0)} = \hat{T} + \hat{V}_{\text{ext}} + \lambda\hat{V}_{\text{H}x}^{\text{HF}}[\Phi^{\lambda}], \qquad (25)
$$

where λ is a fixed parameter, $\hat{T}$ is the kinetic energy operator, $\hat{V}_{\text{ext}}$ is an external potential operator, and $\hat{V}_{\text{H}x}^{\text{HF}}[\Phi^{\lambda}]$ is the Hartree-Fock-like Hartree-exchange potential operator evaluated for the DS1H single-determinant wave function Φ^{λ}. The perturbation operator $\hat{W}$ is

$$
\hat{W} = \lambda\left(\hat{W}_{ee} - \hat{V}_{\text{H}x}^{\text{HF}}[\Phi^{\lambda}]\right), \qquad (26)
$$

where $\hat{W}_{ee}$ is the Coulomb electron-electron interaction operator. The functional $F[n,\tau]$ is

$$
F[n,\tau] = \bar{E}_{\text{H}}^{\lambda}[n] + \bar{E}_{xc}^{\lambda}[n,\tau], \qquad (27)
$$

where $\bar{E}_{\text{H}}^{\lambda}[n]$ and $\bar{E}_{xc}^{\lambda}[n,\tau]$ are the complement λ-dependent Hartree and exchange-correlation functionals, respectively. With these choices, the zeroth-order wave function is the DS1H single-determinant wave function $\tilde{\Psi}^{(0)} = \Phi^{\lambda}$, and due to the Møller-Plesset form of the perturbation operator of Eq. (26), single excitations in $\hat{R}_0$ give vanishing matrix elements for $\hat{W}$ in Eq. (24), $\langle\Phi_{i\to a}^{\lambda}|\hat{W}|\Phi^{\lambda}\rangle = 0$, so only double excitations give non zero matrix elements $\langle\Phi_{i,j\to a,b}^{\lambda}|\hat{W}|\Phi^{\lambda}\rangle$. Moreover, the action of $\hat{G}_0$ on double excitations gives zero due to the presence of the one-electron operators $\hat{n}(\mathbf{r})$ and $\hat{\tau}(\mathbf{r})$ in Eq. (23), so the nonlinearity terms in Eq. (24) vanish, and the second-order energy correction is given by the standard MP2 correlation energy expression

$$
E^{\lambda,(2)} = \lambda^2 \sum_{\substack{i<j\\a<b}} \frac{|\langle ij||ab\rangle|^2}{\varepsilon_i+\varepsilon_j-\varepsilon_a-\varepsilon_b} = \lambda^2 E_c^{\text{MP2}}, \qquad (28)
$$

where i,j and a,b refer to occupied and virtual DS1H spin-orbitals, respectively, with associated orbital eigenvalues ε_k, and $\langle ij||ab\rangle$ are the antisymmetrized two-electron integrals.

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