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Adiabatic integration formula for the correlation energy functional of the Hartree–Fock density

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Abstract. An adiabatic integration formula for the quantum chemistry correlation energy functional of the Hartree–Fock density, $E_c^{QC}[n]$, is presented. The functional $E_c^{QC}[n]$ is meant to be added to the completed Hartree–Fock energy to produce the exact ground-state energy of the system under consideration. The initial slope of the integrand in this connection formula is identified as a second-order energy and an explicit expression for the initial slope of the integrand is presented. Our expression should be useful for arriving at new improved approximations to $E_c^{QC}[n]$. Previous numerical results by Huang and Umrigar (1997) *Phys Rev A* 56:290, for two-electron densities are proved, and a generalization to more than two electrons is presented. Results obtained by means of the present density functional theory correlation energy functionals, when used to approximate the initial slope in our adiabatic integration formula for $E_c^{QC}[n]$, are compared against exact numbers.

Key words: Correlation energy functionals – Density functional theory

1 Introduction

The construction of accurate correlation energy functionals and the continuous improvement of present ones are crucial in achieving high-quality density functional calculations not only within the Kohn–Sham (KS) formalism [1–8], but also in hybrid schemes featuring density functionals as post-Hartree–Fock (HF) methods [8–15]. Knowledge of the exact properties of the unknown correlation energy functionals is very important because approximate functionals could then be made to satisfy these exact constraints. With these goals in mind, new relations between the conventional density functional theory (DFT) correlation energy functional, $E_c[n]$ [6, 8], and the traditional quantum chemistry (QC) correlation energy functional of the HF density, $E_c^{QC}[n]$, are presented. $E_c[n]$ is to be used in self-consistent KS calculations, in contrast to $E_c^{QC}[n]$ which is meant to be added to the completed HF energy to produce the exact ground-state energy of the system of interest. The utilization of this latter functional enables one to replace the time-consuming methods for calculating QC correlation energy which are usually based on many-body perturbation theory, with a simpler calculation involving $E_c^{QC}[n]$.

The present study has also been influenced by a recent work of Huang and Umrigar [16]. They numerically investigated the asymptotic high-nuclear charge (high-Z) expansion for the Coulombic potential and the asymptotic high-force constant expansion for the harmonic oscillator potential for the DFT and QC correlation energies for two-electron densities. For the two-electron systems studied, they found numerically that the respective asymptotic series begin with the same second-order energy term. We shall prove their numerical observations for two-electron systems, as well as derive an inequality connecting the second-order energies in both series studied for more than two electrons, with the caveat of nondegeneracy. Previous DFT–high-Z connections have been made by Perdew et al. [17], Chakravorty and Davidson [18], and Ivanov and Levy [19].

We shall introduce an adiabatic integration formula for $E_c^{QC}[n]$ and identify the initial slope of the integrand as a second-order energy. For certain atomic densities, the second-order energy is the leading term in the high-Z asymptotic series for the QC correlation energy. Since there are numbers available for the QC correlation energy for isoelectronic systems with infinite nuclear charge, $Z \to \infty$ [18, 20], and for Harmonium with infinite force constant [16, 21–23], we will compare these numbers against those obtained from different DFT functionals when used as approximations to $E_c^{QC}[n]$.

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2 Definitions and notation

In atomic units (hartree atomic units are to be used throughout the paper), the Hamiltonian operator ${}^{\gamma}\hat{\mathrm{H}}$ is defined as

$$ {}^{\gamma}\hat{\mathrm{H}}(\mathbf{R}) = \hat{\mathrm{T}}(\mathbf{R}) + \gamma\, \hat{\mathrm{V}}_{\mathrm{ee}}(\mathbf{R}) + \sum_{i=1}^{N} \mathrm{v}(\mathbf{r}_i) \ , \tag{1} $$

where $\mathbf{R}$ represents all coordinates. In the above formula, $\hat{\mathrm{T}}(\mathbf{R})$ and $\hat{\mathrm{V}}_{\mathrm{ee}}(\mathbf{R})$ are the kinetic energy and electron–electron repulsion operators, respectively, and $\mathrm{v}(\mathbf{r})$ is the external potential for the system of interest. In Eq. (1), γ is a coupling constant that turns on and off the electron–electron repulsion. Note that when $\gamma = 1$, the Hamiltonian in Eq. (1) corresponds to the full interactive Hamiltonian of some system in the external potential $\mathrm{v}(\mathbf{r})$.

The ground-state energy of ${}^{\gamma}\hat{\mathrm{H}}$, ${}^{\gamma}E_{\mathrm{GS}}$, is given by

$$ {}^{\gamma}E_{\mathrm{GS}} = \left\langle {}^{\gamma}\Psi_{\mathrm{GS}} | {}^{\gamma}\hat{\mathrm{H}} | {}^{\gamma}\Psi_{\mathrm{GS}} \right\rangle \ , \tag{2} $$

where ${}^{\gamma}\Psi_{\mathrm{GS}}$ is the wavefunction that minimizes the expectation value of ${}^{\gamma}\hat{\mathrm{H}}$. The restricted HF energy ${}^{\gamma}E_{\mathrm{HF}}$ is defined as

$$ {}^{\gamma}E_{\mathrm{HF}} = \left\langle {}^{\gamma}\Phi_{\mathrm{HF}} | {}^{\gamma}\hat{\mathrm{H}} | {}^{\gamma}\Phi_{\mathrm{HF}} \right\rangle \ , \tag{3} $$

where ${}^{\gamma}\Phi_{\mathrm{HF}}$ is the single determinant that minimizes $\langle {}^{\gamma}\hat{\mathrm{H}} \rangle$.

The traditional QC correlation energy ${}^{\gamma}E_{\mathrm{c}}^{\mathrm{QC}}[{}^{\gamma}n]$ is defined [24] as the difference between ${}^{\gamma}E_{\mathrm{GS}}$ and ${}^{\gamma}E_{\mathrm{HF}}$ and it is a unique functional of the HF density ${}^{\gamma}n(\mathbf{r})$, as shown independently by Harris and Pratt [12], and Levy [13], and extended by Davidson [14]. Namely

$$ \begin{aligned} {}^{\gamma}E_{\mathrm{c}}^{\mathrm{QC}}[{}^{\gamma}n] &= \left\langle {}^{\gamma}\Psi_{\mathrm{GS}} | {}^{\gamma}\hat{\mathrm{H}} | {}^{\gamma}\Psi_{\mathrm{GS}} \right\rangle \\ &\quad - \left\langle {}^{\gamma}\Phi_{\mathrm{HF}} | {}^{\gamma}\hat{\mathrm{H}} | {}^{\gamma}\Phi_{\mathrm{HF}} \right\rangle \ . \end{aligned} \tag{4} $$

In Eq. (4), ${}^{\gamma}n(\mathbf{r})$ is the HF density obtained from ${}^{\gamma}\Phi_{\mathrm{HF}}$, i.e. ${}^{\gamma}n(\mathbf{r}) = \langle {}^{\gamma}\Phi_{\mathrm{HF}} | \hat{\rho} | {}^{\gamma}\Phi_{\mathrm{HF}} \rangle$, $\hat{\rho}$ is the density operator. The HF density is not the same as the ground-state density ${}^{\gamma}n^{\mathrm{GS}}(\mathbf{r})$ obtained from ${}^{\gamma}\Psi_{\mathrm{GS}}$, except for the special case of the nondegenerate ground state for $\gamma = 0$. Note that the definition of the correlation energy ${}^{\gamma}E_{\mathrm{c}}^{\mathrm{QC}}[{}^{\gamma}n]$ depends upon γ, as well as upon the density.

3 Adiabatic connection formula

The Hamiltonian given in Eq. (1) is particularly useful for studying the actual QC correlation energy $E_{\mathrm{c}}^{\mathrm{QC}}[n]$ corresponding to systems with a full electron–electron repulsion, i.e. $E_{\mathrm{c}}^{\mathrm{QC}}[n] = {}^{\gamma}E_{\mathrm{c}}^{\mathrm{QC}}[{}^{\gamma}n]$ at $\gamma = 1$. In order to simplify our notation, when $\gamma = 1$ the superscript will be omitted. For systems with a nondegenerate ground state, $E_{\mathrm{c}}^{\mathrm{QC}}[n]$ can be obtained by

$$ E_{\mathrm{c}}^{\mathrm{QC}}[n] = \int_0^1 d\, {}^{\gamma}E_{\mathrm{c}}^{\mathrm{QC}}[{}^{\gamma}n] = \int_0^1 \frac{\partial\, {}^{\gamma}E_{\mathrm{c}}^{\mathrm{QC}}[{}^{\gamma}n]}{\partial \gamma} d\gamma \ . \tag{5} $$

Equation (5) follows directly from Eq. (4) because for a nondegenerate ground state at $\gamma = 0$, ${}^{0}\Psi_{\mathrm{GS}}$ is the same as ${}^{0}\Phi_{\mathrm{HF}}$, and ${}^{0}E_{\mathrm{c}}^{\mathrm{QC}}[{}^{o}n]$ becomes zero. By using the definition of ${}^{\gamma}E_{\mathrm{c}}^{\mathrm{QC}}[{}^{\gamma}n]$, and taking advantage of the minimizing (stationary) nature of ${}^{\gamma}\Psi_{\mathrm{GS}}$ and ${}^{\gamma}\Phi_{\mathrm{HF}}$, we obtain

$$ E_{\mathrm{c}}^{\mathrm{QC}}[n] = \int_0^1 {}^{\gamma}V_{\mathrm{c}}^{\mathrm{QC}}[{}^{\gamma}n]\, \mathrm{d}\gamma \ , \tag{6} $$

where

$$ \begin{aligned} {}^{\gamma}V_{\mathrm{c}}^{\mathrm{QC}}[{}^{\gamma}n] &= \frac{\partial\, {}^{\gamma}E_{\mathrm{c}}^{\mathrm{QC}}[{}^{\gamma}n]}{\partial \gamma} \\ &= \left\langle {}^{\gamma}\Psi_{\mathrm{GS}} | \hat{\mathrm{V}}_{\mathrm{ee}} | {}^{\gamma}\Psi_{\mathrm{GS}} \right\rangle - \left\langle {}^{\gamma}\Phi_{\mathrm{HF}} | \hat{\mathrm{V}}_{\mathrm{ee}} | {}^{\gamma}\Phi_{\mathrm{HF}} \right\rangle \ . \end{aligned} \tag{7} $$

In contrast to the adiabatic integration formula in DFT [25, 26], where the density is kept the same along the integration path, in our formula for $E_{\mathrm{c}}^{\mathrm{QC}}[n]$, Eq. (6), the density changes along the integration path γ. New improved approximations to $E_{\mathrm{c}}^{\mathrm{QC}}[n]$ can be developed by approximating the integrand ${}^{\gamma}V_{\mathrm{c}}^{\mathrm{QC}}[{}^{\gamma}n]$ in a similar way to what has recently been done by Ernzerhof [27], and by Perdew and coworkers [28–32] in their modeling of the DFT adiabatic connection integrand.

By applying standard Rayleigh–Schrödinger perturbation theory, we develop expansions for ${}^{\gamma}E_{\mathrm{GS}}$ and ${}^{\gamma}E_{\mathrm{HF}}$ and their respective wavefunctions ${}^{\gamma}\Psi_{\mathrm{GS}}$ and ${}^{\gamma}\Phi_{\mathrm{HF}}$. The energy expressions read

$$ \begin{aligned} {}^{\gamma}E_{\mathrm{GS}} &= E_{\mathrm{o}} + \gamma^1 E_{\mathrm{GS}}^{(1)} + \gamma^2 E_{\mathrm{GS}}^{(2)} + \gamma^3 E_{\mathrm{GS}}^{(3)} + \cdots \\ &= E_{\mathrm{o}} + \sum_{j=1}^{\infty} \gamma^j E_{\mathrm{GS}}^{(j)} \ , \end{aligned} \tag{8} $$

and

$$ \begin{aligned} {}^{\gamma}E_{\mathrm{HF}} &= E_{\mathrm{o}} + \gamma^1 E_{\mathrm{HF}}^{(1)} + \gamma^2 E_{\mathrm{HF}}^{(2)} + \gamma^3 E_{\mathrm{HF}}^{(3)} + \cdots \\ &= E_{\mathrm{o}} + \sum_{j=1}^{\infty} \gamma^j E_{\mathrm{HF}}^{(j)} \ . \end{aligned} \tag{9} $$

In Eqs. (8) and (9), E_{o} is the ground-state energy of ${}^{0}\hat{\mathrm{H}}$, i.e. ${}^{\gamma}\hat{\mathrm{H}}$ at $\gamma = 0$. The eigenvalue problem corresponding to ${}^{0}\hat{\mathrm{H}}$ is

$$ {}^{0}\hat{\mathrm{H}}\ \Phi_k = E_k\ \Phi_k; \ \ E_{\mathrm{o}} < E_1 \leq E_2 \leq \cdots \leq E_k \leq \cdots \ , \tag{10} $$

where we shall concern ourselves with situations where E_{o} is nondegenerate. For $k > 0$, Φ_k are the excited-state wavefunctions of ${}^{0}\hat{\mathrm{H}}$.

The corresponding series for the wavefunctions ${}^{\gamma}\Psi_{\mathrm{GS}}$ and ${}^{\gamma}\Phi_{\mathrm{HF}}$ are

$$ \begin{aligned} {}^{\gamma}\Psi_{\mathrm{GS}} &= \Psi_{\mathrm{GS}}^{(0)} + \gamma^1 \Psi_{\mathrm{GS}}^{(1)} + \gamma^2 \Psi_{\mathrm{GS}}^{(2)} + \gamma^3 \Psi_{\mathrm{GS}}^{(3)} + \cdots \\ &= \sum_{j=0}^{\infty} \gamma^j \Psi_{\mathrm{GS}}^{(j)} \end{aligned} \tag{11} $$

and

$$ \begin{aligned} {}^{\gamma}\Phi_{\mathrm{HF}} &= \Phi_{\mathrm{HF}}^{(0)} + \gamma^1 \Phi_{\mathrm{HF}}^{(1)} + \gamma^2 \Phi_{\mathrm{HF}}^{(2)} + \gamma^3 \Phi_{\mathrm{HF}}^{(3)} + \cdots \\ &= \sum_{j=0}^{\infty} \gamma^j \Phi_{\mathrm{HF}}^{(j)} \ . \end{aligned} \tag{12} $$

When ${}^{0}\hat{\mathrm{H}}$ has a nondegenerate ground state, both series begin with the same Φ_{o} which is the ground-state solution to Eq. (10), $k = 0$. In other words, $\Psi^{(0)}_{\mathrm{GS}} = \Phi^{(0)}_{\mathrm{HF}} = \Phi_{\mathrm{o}}$. Unless otherwise stated, this nondegeneracy shall be assumed.

The second and third terms in the corresponding expansions for ${}^{\gamma}E_{\mathrm{GS}}$ and ${}^{\gamma}E_{\mathrm{HF}}$, with nondegenerate E_{o}, are

$$E^{(1)}_{\mathrm{GS}} = E^{(1)}_{\mathrm{HF}} = \langle \Phi_{\mathrm{o}} | \hat{\mathrm{V}}_{\mathrm{ee}} | \Phi_{\mathrm{o}} \rangle \ , \tag{13}$$

$$E^{(2)}_{\mathrm{GS}} = \frac{1}{2}\langle \Phi_{\mathrm{o}} | \hat{\mathrm{V}}_{\mathrm{ee}} | \Psi^{(1)}_{\mathrm{GS}} \rangle + \frac{1}{2}\langle \Psi^{(1)}_{\mathrm{GS}} | \hat{\mathrm{V}}_{\mathrm{ee}} | \Phi_{\mathrm{o}} \rangle \ , \tag{14}$$

and

$$E^{(2)}_{\mathrm{HF}} = \frac{1}{2}\langle \Phi_{\mathrm{o}} | \hat{\mathrm{V}}_{\mathrm{ee}} | \Phi^{(1)}_{\mathrm{HF}} \rangle + \frac{1}{2}\langle \Phi^{(1)}_{\mathrm{HF}} | \hat{\mathrm{V}}_{\mathrm{ee}} | \Phi_{\mathrm{o}} \rangle \ . \tag{15}$$

For completeness of the presentation, we explicitly show the complex conjugate counterparts of the wavefunctions even though the energies are real. In the above equations, $\Psi^{(1)}_{\mathrm{GS}}$ is expanded in the usual way as

$$\Psi^{(1)}_{\mathrm{GS}} = \sum_{k=1}^{\infty} \frac{\langle \Phi_k | \hat{\mathrm{V}}_{\mathrm{ee}} | \Phi_{\mathrm{o}} \rangle}{E_{\mathrm{o}} - E_k} \Phi_k \ . \tag{16}$$

In terms of eigenfunctions of ${}^{0}\hat{\mathrm{H}}$, $\Phi^{(1)}_{\mathrm{HF}}$ is given by [19]

$$\begin{aligned}\Phi^{(1)}_{\mathrm{HF}} &= \sum_{k=1}^{\infty} \frac{\langle \Phi_k | \sum_{i=1}^{N} {}^{\mathrm{HF}}\hat{\mathrm{v}}([\Phi_{\mathrm{o}}]; \mathbf{r}_i) | \Phi_{\mathrm{o}} \rangle}{E_{\mathrm{o}} - E_k} \Phi_k \\ &= \sum_{\substack{k=1 \\ \text{S.E.}}}^{\infty} \frac{\langle \Phi_k | \hat{\mathrm{V}}_{\mathrm{ee}} | \Phi_{\mathrm{o}} \rangle}{E_{\mathrm{o}} - E_k} \Phi_k \ ,\end{aligned} \tag{17}$$

since ${}^{\mathrm{HF}}\hat{\mathrm{v}}([\Phi_{\mathrm{o}}]; \mathbf{r})$ is a one-body operator and for every determinant Φ_k corresponding to single excitation

$$\left\langle \Phi_k \left| \sum_{i=1}^{N} {}^{\mathrm{HF}}\hat{\mathrm{v}}([\Phi_{\mathrm{o}}]; \mathbf{r}_i) \right| \Phi_{\mathrm{o}} \right\rangle = \langle \Phi_k | \hat{\mathrm{V}}_{\mathrm{ee}} | \Phi_{\mathrm{o}} \rangle \ . \tag{18}$$

In Eq. (17), ${}^{\mathrm{HF}}\hat{\mathrm{v}}([\Phi_{\mathrm{o}}]; \mathbf{r})$ is the HF nonlocal effective potential which has two contributions: the nonlocal exchange potential ${}^{\mathrm{HF}}\hat{\mathrm{v}}_x([\Phi_{\mathrm{o}}]; \mathbf{r})$ built from the occupied one-particle orbitals of Φ_{o}, and the local Hartree potential $u([{}^{\mathrm{o}}n]; \mathbf{r})$, associated with the density ${}^{\mathrm{o}}n$ obtained from Φ_{o}. S.E. indicates that the summation is over single excitations only.

By subtracting Eq. (9) from Eq. (8), along with making use of Eq. (13), one obtains an expression for ${}^{\gamma}E^{\mathrm{QC}}_{\mathrm{c}}[{}^{\gamma}n]$ which begins with $\gamma^2 E^{\mathrm{QC},(2)}_{\mathrm{c}}$:

$${}^{\gamma}E^{\mathrm{QC}}_{\mathrm{c}}[{}^{\gamma}n] = \gamma^2 E^{\mathrm{QC},(2)}_{\mathrm{c}} + \gamma^3 E^{\mathrm{QC},(3)}_{\mathrm{c}} + \cdots = \sum_{j=2}^{\infty} \gamma^j E^{\mathrm{QC},(j)}_{\mathrm{c}} \ , \tag{19}$$

where

$$E^{\mathrm{QC},(j)}_{\mathrm{c}} \equiv E^{(j)}_{\mathrm{GS}} - E^{(j)}_{\mathrm{HF}} \ . \tag{20}$$

It follows that

$$\lim_{\gamma \to 0} \gamma^{-2}\, {}^{\gamma}E^{\mathrm{QC}}_{\mathrm{c}}[{}^{\gamma}n] = E^{\mathrm{QC},(2)}_{\mathrm{c}} \ . \tag{21}$$

When the ground state of ${}^{0}\hat{\mathrm{H}}$ is degenerate, the expansion for ${}^{\gamma}E^{\mathrm{QC}}_{\mathrm{c}}[{}^{\gamma}n]$ is expected, in general, to begin with a term linear in γ since $E^{(1)}_{\mathrm{GS}} < E^{(1)}_{\mathrm{HF}}$.

By making use of Eqs. (14)–(17), the second-order energy $E^{\mathrm{QC},(2)}_{\mathrm{c}}$, given in terms of eigenstates of ${}^{0}\hat{\mathrm{H}}$, becomes [19]

$$\begin{aligned}E^{\mathrm{QC},(2)}_{\mathrm{c}} &= \frac{1}{2}\langle \Phi_{\mathrm{o}} | \hat{\mathrm{V}}_{\mathrm{ee}} | \{ \Psi^{(1)}_{\mathrm{GS}} - \Phi^{(1)}_{\mathrm{HF}} \} \rangle \\ &\quad + \frac{1}{2}\langle \{ \Psi^{(1)}_{\mathrm{GS}} - \Phi^{(1)}_{\mathrm{HF}} \} | \hat{\mathrm{V}}_{\mathrm{ee}} | \Phi_{\mathrm{o}} \rangle \\ &= \sum_{\substack{k=1 \\ \text{D.E.}}}^{\infty} \frac{|\langle \Phi_k | \hat{\mathrm{V}}_{\mathrm{ee}} | \Phi_{\mathrm{o}} \rangle|^2}{E_{\mathrm{o}} - E_k} \ .\end{aligned} \tag{22}$$

In Eq. (22), D.E. signifies double excitations: in other words, the summation is over those eigenstates Φ_k of ${}^{0}\hat{\mathrm{H}}$ which are obtained by exciting two electrons from Φ_{o}. There is no contribution from singly excited states.

By differentiating Eq. (19) with respect to γ (see Eq. 7), we obtain an expression for ${}^{\gamma}V^{\mathrm{QC}}_{\mathrm{c}}[{}^{\gamma}n]$ for small γ, namely

$${}^{\gamma}V^{\mathrm{QC}}_{\mathrm{c}}[{}^{\gamma}n] = 2\gamma E^{\mathrm{QC},(2)}_{\mathrm{c}} + 3\gamma^2 E^{\mathrm{QC},(3)}_{\mathrm{c}} + \cdots \ . \tag{23}$$

Here, $2E^{\mathrm{QC},(2)}_{\mathrm{c}}$ is the initial slope of the integrand in Eq. (6) for $\gamma = 0$, and $E^{\mathrm{QC},(2)}_{\mathrm{c}}$ is given explicitly in terms of the eigenfunctions and eigenvalues of ${}^{0}\hat{\mathrm{H}}$ in Eq. (22).

It is worth mentioning that, for a nondegenerate ground state, the densities obtained from the wavefunctions ${}^{\gamma}\Psi_{\mathrm{GS}}$ and ${}^{\gamma}\Phi_{\mathrm{HF}}$ are the same through the first order in γ. This follows from the forms of $\Psi^{(1)}_{\mathrm{GS}}$ and $\Phi^{(1)}_{\mathrm{HF}}$, and the fact that the density operator $\hat{\rho}$ is a one-body operator. For the first order in γ, one has

$$\begin{aligned}&\langle \Psi^{(1)}_{\mathrm{GS}} | \hat{\rho} | \Phi_{\mathrm{o}} \rangle + \langle \Phi_{\mathrm{o}} | \hat{\rho} | \Psi^{(1)}_{\mathrm{GS}} \rangle \\ &\quad = \langle \Phi^{(1)}_{\mathrm{HF}} | \hat{\rho} | \Phi_{\mathrm{o}} \rangle + \langle \Phi_{\mathrm{o}} | \hat{\rho} | \Phi^{(1)}_{\mathrm{HF}} \rangle = n^{(1)} \ .\end{aligned} \tag{24}$$

4 Perturbation expansion for the DFT correlation energy

For the Hamiltonian in Eq. (1), the conventional DFT correlation energy functional ${}^{\gamma}E_{\mathrm{c}}[{}^{\gamma}n^{\mathrm{GS}}]$ is defined as [6, 8]

$$\begin{aligned}{}^{\gamma}E_{\mathrm{c}}[{}^{\gamma}n^{\mathrm{GS}}] &\equiv {}^{\gamma}E_{\mathrm{GS}} - {}^{\gamma}E_{\mathrm{KS}} \\ &= \langle {}^{\gamma}\Psi_{\mathrm{GS}} | {}^{\gamma}\hat{\mathrm{H}} | {}^{\gamma}\Psi_{\mathrm{GS}} \rangle - \langle {}^{\gamma}\Phi_{\mathrm{KS}} | {}^{\gamma}\hat{\mathrm{H}} | {}^{\gamma}\Phi_{\mathrm{KS}} \rangle \ .\end{aligned} \tag{25}$$

In Eq. (25), according to the constrained-search formulation of DFT [7], ${}^{\gamma}\Phi_{\mathrm{KS}}$ is the wavefunction which minimizes the expectation value of the kinetic energy operator only, and yields the actual ground-state density ${}^{\gamma}n^{\mathrm{GS}}$ for every γ. At $\gamma = 1$, one has the DFT correlation energy for the fully interacting system.

Next, we shall obtain perturbation expansions for ${}^{\gamma}E_{\mathrm{KS}}$ and ${}^{\gamma}\Phi_{\mathrm{KS}}$ for small-enough γ for systems with nondegenerate ground states at $\gamma = 0$.

The respective series for ${}^{\gamma}E_{\mathrm{KS}}$ and ${}^{\gamma}\Phi_{\mathrm{KS}}$ read

$$\begin{aligned}{}^{\gamma}E_{\mathrm{KS}} &= E_{\mathrm{o}} + \gamma^1 E^{(1)}_{\mathrm{KS}} + \gamma^2 E^{(2)}_{\mathrm{KS}} + \gamma^3 E^{(3)}_{\mathrm{KS}} + \cdots \\ &= E_{\mathrm{o}} + \sum_{j=1}^{\infty} \gamma^j E^{(j)}_{\mathrm{KS}} \ , \end{aligned} \tag{26}$$

and

$$\begin{aligned}{}^{\gamma}\Phi_{\mathrm{KS}} &= \Phi_{\mathrm{o}} + \gamma^1 \Phi^{(1)}_{\mathrm{KS}} + \gamma^2 \Phi^{(2)}_{\mathrm{KS}} + \gamma^3 \Phi^{(3)}_{\mathrm{KS}} + \cdots \\ &= \Phi_{\mathrm{o}} + \sum_{j=1}^{\infty} \gamma^j \Phi^{(j)}_{\mathrm{KS}} \ . \end{aligned} \tag{27}$$

The second and third terms in Eq. (26) are

$$E^{(1)}_{\mathrm{KS}} = \langle \Phi_{\mathrm{o}} | \hat{\mathrm{V}}_{\mathrm{ee}} | \Phi_{\mathrm{o}} \rangle \ , \tag{28}$$

and

$$E^{(2)}_{\mathrm{KS}} = \frac{1}{2} \langle \Phi_{\mathrm{o}} | \hat{\mathrm{V}}_{\mathrm{ee}} | \Phi^{(1)}_{\mathrm{KS}} \rangle + \frac{1}{2} \langle \Phi^{(1)}_{\mathrm{KS}} | \hat{\mathrm{V}}_{\mathrm{ee}} | \Phi_{\mathrm{o}} \rangle \ . \tag{29}$$

By subtracting Eq. (26) from Eq. (8) along with making use of Eq. (28), one arrives at an expression for ${}^{\gamma}E_{\mathrm{c}}[{}^{\gamma}n^{\mathrm{GS}}]$ which begins with $\gamma^2 E^{(2)}_{\mathrm{c}}$:

$${}^{\gamma}E_{\mathrm{c}}\left[{}^{\gamma}n^{\mathrm{GS}}\right] = \gamma^2 E^{(2)}_{\mathrm{c}} + \gamma^3 E^{(3)}_{\mathrm{c}} + \cdots = \sum_{j=2}^{\infty} \gamma^j E^{(j)}_{\mathrm{c}} \ , \tag{30}$$

or

$$\lim_{\gamma \to 0} \gamma^{-2}\, {}^{\gamma}E_{\mathrm{c}}\left[{}^{\gamma}n^{\mathrm{GS}}\right] = E^{(2)}_{\mathrm{c}} \ , \tag{31}$$

where

$$E^{(j)}_{\mathrm{c}} \equiv E^{(j)}_{\mathrm{GS}} - E^{(j)}_{\mathrm{KS}} \ . \tag{32}$$

In Eqs. (30) and (31), $E^{(2)}_{\mathrm{c}}$ is given by

$$\begin{aligned} E^{(2)}_{\mathrm{c}} &= \frac{1}{2} \langle \Phi_{\mathrm{o}} | \hat{\mathrm{V}}_{\mathrm{ee}} | \{ \Psi^{(1)}_{\mathrm{GS}} - \Phi^{(1)}_{\mathrm{KS}} \} \rangle \\ &\quad + \frac{1}{2} \langle \{ \Psi^{(1)}_{\mathrm{GS}} - \Phi^{(1)}_{\mathrm{KS}} \} | \hat{\mathrm{V}}_{\mathrm{ee}} | \Phi_{\mathrm{o}} \rangle \ . \end{aligned} \tag{33}$$

To obtain $\Phi^{(1)}_{\mathrm{KS}}$, we consider the equation to which ${}^{\gamma}\Phi_{\mathrm{KS}}$ is an eigenfunction:

$$\begin{aligned} &\left\{ \hat{\mathrm{T}} + \sum_{i=1}^{N} \left[\gamma v_{\mathrm{xu}}(\left[{}^{\gamma}n^{\mathrm{GS}}\right]; \mathbf{r}_i) + {}^{\gamma}v_{\mathrm{c}}(\left[{}^{\gamma}n^{\mathrm{GS}}\right]; \mathbf{r}_i) \right] + \sum_{i=1}^{N} (\mathbf{r}_i) \right\} \\ &\quad \times {}^{\gamma}\Phi_{\mathrm{KS}} = {}^{\gamma}\bar{\mathrm{E}}_{\mathrm{KS}} {}^{\gamma}\Phi_{\mathrm{KS}} \ . \end{aligned} \tag{34}$$

Note that ${}^{\gamma}\bar{E}_{\mathrm{KS}}$, which is a sum of the KS orbital energies, is different from ${}^{\gamma}E_{\mathrm{KS}}$. In Eq. (34), $v_{\mathrm{xu}}([{}^{\gamma}n^{\mathrm{GS}}]; \mathbf{r})$ and ${}^{\gamma}v_{\mathrm{c}}([{}^{\gamma}n^{\mathrm{GS}}]; \mathbf{r})$ are local spin-independent multiplicative potentials.

The correlation potential ${}^{\gamma}v_{\mathrm{c}}([{}^{\gamma}n^{\mathrm{GS}}]; \mathbf{r})$ is the functional derivative of ${}^{\gamma}E_{\mathrm{c}}[{}^{\gamma}n^{\mathrm{GS}}]$ and $v_{\mathrm{xu}}([{}^{\gamma}n^{\mathrm{GS}}]; \mathbf{r})$ is the functional derivative of $E_{\mathrm{xu}}[{}^{\gamma}n^{\mathrm{GS}}] \equiv \langle {}^{\gamma}\Phi_{\mathrm{KS}} | \hat{v}_{\mathrm{ee}} | {}^{\gamma}\Phi_{\mathrm{KS}} \rangle$, with respect to the density. Here ${}^{\gamma}\Phi_{\mathrm{KS}}$ is the single determinant that minimizes $\langle \hat{\mathrm{T}} \rangle$, and yields ${}^{\gamma}n^{\mathrm{GS}}$. The sum $\gamma v_{\mathrm{xu}}([{}^{\gamma}n^{\mathrm{GS}}]; \mathbf{r}) + {}^{\gamma} v_{\mathrm{c}}([{}^{\gamma}n^{\mathrm{GS}}]; \mathbf{r})$ makes the density obtained from ${}^{\gamma}\Phi_{\mathrm{KS}}$ the same as the density obtained from ${}^{\gamma}\Psi_{\mathrm{GS}}$. All potentials considered are adjusted by additive constants to vanish at infinity.

For small γ, ${}^{\gamma}\bar{E}_{\mathrm{KS}}$ is expanded in the following way

$$\begin{aligned}{}^{\gamma}\bar{E}_{\mathrm{KS}} &= E_{\mathrm{o}} + \gamma^1 \bar{E}^{(1)}_{\mathrm{KS}} + \gamma^2 \bar{E}^{(2)}_{\mathrm{KS}} + \gamma^3 \bar{E}^{(3)}_{\mathrm{KS}} + \cdots \\ &= E_{\mathrm{o}} + \sum_{j=1}^{\infty} \gamma^j \bar{E}^{(j)}_{\mathrm{KS}} \ . \end{aligned} \tag{35}$$

Next, assume Taylor expansions for $v_{\mathrm{xu}}([{}^{\gamma}n^{\mathrm{GS}}]; \mathbf{r})$ and ${}^{\gamma}v_{\mathrm{c}}([{}^{\gamma}n^{\mathrm{GS}}]; \mathbf{r})$ about $\gamma = 0$. Upon substituting Eqs. (27) and (35) in Eq. (34), and equating all terms of order γ, one obtains

$$\left[{}^{0}\hat{\mathrm{H}} - E_{\mathrm{o}}\right] \Phi^{(1)}_{\mathrm{KS}} = \left[\bar{E}^{(1)}_{\mathrm{KS}} - \sum_{i=1}^{N} v_{\mathrm{xu}}([{}^{\mathrm{o}}n]; \mathbf{r}_i) \right] \Phi_{\mathrm{o}} \ . \tag{36}$$

Note that in Eq. (36), there is no term linear in γ which comes from $\gamma v_{\mathrm{c}}([{}^{\gamma}n^{\mathrm{GS}}]; \mathbf{r})$ because of Eq. (30). Similar results appear in Görling–Levy perturbation theory [9, 32, 33].

In terms of eigenfunctions of ${}^{0}\hat{\mathrm{H}}$, $\Phi^{(1)}_{\mathrm{KS}}$ is given by

$$\Phi^{(1)}_{\mathrm{KS}} = \sum_{k=1}^{\infty} \frac{\langle \Phi_k | \sum_{i=1}^{N} v_{\mathrm{xu}}([{}^{\mathrm{o}}n]; \mathbf{r}_i | \Phi_{\mathrm{o}} \rangle}{E_{\mathrm{o}} - E_k} \Phi_k \ . \tag{37}$$

By subtracting Eq. (37) from Eq. (16), one finds

$$\Psi^{(1)}_{\mathrm{GS}} - \Phi^{(1)}_{\mathrm{KS}} = \sum_{k=1}^{\infty} \frac{\langle \Phi_k | \hat{\mathrm{V}}_{\mathrm{ee}} - \sum_{i=1}^{N} v_{\mathrm{xu}}([{}^{\mathrm{o}}n]; \mathbf{r}_i) | \Phi_{\mathrm{o}} \rangle}{E_{\mathrm{o}} - E_k} \Phi_k \ . \tag{38}$$

Since the densities obtained from ${}^{\gamma}\Psi_{\mathrm{GS}}$ and ${}^{\gamma}\Phi_{\mathrm{KS}}$ are identical by definition, i.e.

$$\langle {}^{\gamma}\Psi_{\mathrm{GS}} | \hat{\rho} | {}^{\gamma}\Psi_{\mathrm{GS}} \rangle = \langle {}^{\gamma}\Phi_{\mathrm{KS}} | \hat{\rho} | {}^{\gamma}\Phi_{\mathrm{KS}} \rangle \ , \tag{39}$$

for order 1 in γ, one has

$$\begin{aligned} &\langle \Psi^{(1)}_{\mathrm{GS}} | \hat{\rho} | \Phi_{\mathrm{o}} \rangle + \langle \Phi_{\mathrm{o}} | \hat{\rho} | \Psi^{(1)}_{\mathrm{GS}} \rangle \\ &\quad = \langle \Phi^{(1)}_{\mathrm{KS}} | \hat{\rho} | \Phi_{\mathrm{o}} \rangle + \langle \Phi_{\mathrm{o}} | \hat{\rho} | \Phi^{(1)}_{\mathrm{KS}} \rangle = n^{(1)} \ , \end{aligned} \tag{40}$$

or

$$\begin{aligned} &\left\langle \Phi_{\mathrm{o}} \left| \sum_{i=1}^{N} A(\mathbf{r}_i) \right| \{ \Psi^{(1)}_{\mathrm{GS}} - \Phi^{(1)}_{\mathrm{KS}} \} \right\rangle \\ &\quad + \left\langle \{ \Psi^{(1)}_{\mathrm{GS}} - \Phi^{(1)}_{\mathrm{KS}} \} \left| \sum_{i=1}^{N} A(\mathbf{r}_i) \right| \Phi_{\mathrm{o}} \right\rangle = 0 \ , \end{aligned} \tag{41}$$

where $A(\mathbf{r})$ is any one-body multiplicative operator. Note the similarity of Eqs. (24) and (40). Both wavefunctions $\Phi^{(1)}_{\mathrm{KS}}$ and $\Phi^{(1)}_{\mathrm{HF}}$ yield the same first-order density as the one obtained from $\Psi^{(1)}_{\mathrm{GS}}$; however, $\Phi^{(1)}_{\mathrm{KS}}$ is associated with a local multiplicative external potential, whereas $\Phi^{(1)}_{\mathrm{HF}}$ is associated with the HF nonlocal effective potential. Only for two-electron systems does the HF effective potential become local.

With Eq. (41) in mind, and with $A(\mathbf{r}) = v_{\mathrm{xu}}([{}^{\mathrm{o}}n]; \mathbf{r})$, the expression for $E^{(2)}_{\mathrm{c}}$ becomes

$$E^{(2)}_{\mathrm{c}} = \sum_{k=1}^{\infty} \frac{\left| \langle \Phi_k | \hat{\mathrm{V}}_{\mathrm{ee}} - \sum_{i=1}^{N} v_{\mathrm{xu}}([{}^{\mathrm{o}}n]; \mathbf{r}_i) | \Phi_{\mathrm{o}} \rangle \right|^2}{E_{\mathrm{o}} - E_k} \ . \tag{42}$$

By separating the infinite summation in Eq. (42) into a summation over single excitations and a summation over double excitations, one obtains

$$E_{\mathrm{c}}^{(2)} = \sum_{\substack{\underline{k=1}\\ \mathrm{D.E.}}}^{\infty} \frac{\left|\left\langle \Phi_k \middle| \hat{\mathrm{V}}_{\mathrm{ee}} \middle| \Phi_{\mathrm{o}} \right\rangle\right|^2}{E_{\mathrm{o}} - E_k} + \sum_{\substack{\underline{k=1}\\ \mathrm{S.E.}}}^{\infty} \frac{\left|\left\langle \Phi_k \middle| \hat{\mathrm{V}}_{\mathrm{ee}} - \sum_{i=1}^{N} v_{\mathrm{xu}}([{}^{\mathrm{o}}n];\mathbf{r}_i) \middle| \Phi_{\mathrm{o}} \right\rangle\right|^2}{E_{\mathrm{o}} - E_k} \quad . \tag{43}$$

The combination of Eqs. (22) and (43) leads to

$$E_{\mathrm{c}}^{(2)} = E_{\mathrm{c}}^{\mathrm{QC},(2)} + \sum_{\substack{\underline{k=1}\\ \mathrm{S.E.}}}^{\infty} \frac{\left|\left\langle \Phi_k \middle| \hat{\mathrm{V}}_{\mathrm{ee}} - \sum_{i=1}^{N} v_{\mathrm{xu}}([{}^{\mathrm{o}}n];\mathbf{r}_i) \middle| \Phi_{\mathrm{o}} \right\rangle\right|^2}{E_{\mathrm{o}} - E_k} \quad . \tag{44}$$

For two-electron systems, there is no contribution from single excitations and both series begin with the same second-order energy. For more than two electrons, a strict inequality applies. In general, for any number of electrons, the following relation is true

$$E_{\mathrm{c}}^{(2)} \le E_{\mathrm{c}}^{\mathrm{QC},(2)} \quad . \tag{45}$$

In a similar way, it can be shown that the correlation energy functional $E_{\mathrm{c}}^{\mathrm{HF}}\left[n^{\mathrm{GS}}\right]$ [8, 9], whose functional derivative is meant to be added to the HF nonlocal effective potential to produce, via self-consistency, the exact ground-state density and ground-state energy, satisfies the following limit

$$\lim_{\gamma\to 0} \gamma^{-2}\ {}^{\gamma}E_{\mathrm{c}}^{\mathrm{HF}}\left[{}^{\gamma}n^{\mathrm{GS}}\right] = E_{\mathrm{c}}^{\mathrm{QC},(2)} \quad . \tag{46}$$

In Eq. (46), ${}^{\gamma}E_{\mathrm{c}}\left[{}^{\gamma}n^{\mathrm{GS}}\right]$ is defined as

$$\begin{aligned} {}^{\gamma}E_{\mathrm{c}}^{\mathrm{HF}}\left[{}^{\gamma}n^{\mathrm{GS}}\right] &= \left\langle {}^{\gamma}\Psi_{\mathrm{GS}} \middle| {}^{\gamma}\hat{\mathrm{H}} \middle| {}^{\gamma}\Psi_{\mathrm{GS}} \right\rangle \\ &\quad - \left\langle {}^{\gamma}\Phi_{\mathrm{HF}} \middle| {}^{\gamma}\hat{\mathrm{H}} \middle| {}^{\gamma}\Phi_{\mathrm{HF}} \right\rangle \ , \end{aligned} \tag{47}$$

where ${}^{\gamma}\Phi_{\mathrm{HF}}$ is the HF single determinant which minimizes $\langle {}^{\gamma}\hat{\mathrm{H}} \rangle$ and yields the ground-state density ${}^{\gamma}n^{\mathrm{GS}}$ for every γ [7–9].

5 Homogeneous external potentials

Next, for a homogeneous external potential, $v^{\beta}(\mathbf{r})$, of degree s which depends on some positive constant β, i.e.

$$v^{\beta}(\lambda\mathbf{r}) = \lambda^{s} v^{\beta}(\mathbf{r}) \ , \tag{48}$$

we shall consider a canonical transformation of the coordinate system, as originally suggested by Hylleraas [35] and later utilized by Linderberg and Shull [36]. The interacting Hamiltonian $\hat{\mathrm{H}}(\mathbf{R})$ with some homogeneous external potential $v^{\beta}(\mathbf{r})$ of degree s, can be expressed equivalently in coordinate system $\lambda\mathbf{R}$ as

$$\hat{\mathrm{H}}(\mathbf{R}) = \lambda^2 \left\{ \hat{\mathrm{T}}(\lambda\mathbf{R}) + \frac{1}{\lambda}\hat{\mathrm{V}}_{\mathrm{ee}}(\lambda\mathbf{R}) + \lambda^{-s-2} \sum_{i=1}^{N} v^{\beta}(\lambda\mathbf{r}_i) \right\} \ . \tag{49}$$

With an appropriate choice of λ, which depends upon β, Eq. (49) takes on the form

$$\hat{\mathrm{H}}(\mathbf{R}) = \lambda^2 \left\{ \hat{\mathrm{T}}(\lambda\mathbf{R}) + \frac{1}{\lambda}\hat{\mathrm{V}}_{\mathrm{ee}}(\lambda\mathbf{R}) + \sum_{i=1}^{N} v(\lambda\mathbf{r}_i) \right\} \ . \tag{50}$$

In Eq. (50), $v(\mathbf{r})$ corresponds to an external potential which is independent of β. In other words, $v(\mathbf{r})$ has the form of $v^{\beta}(\mathbf{r})$ for $\beta = 1$. When the external potential is linear in β, this leads to a simple relationship between λ and β depending upon the degree of homogeneity s, i.e. $\beta = \lambda^{2+s}$. For example, if $v^{\beta}(\mathbf{r}) = -\beta/r$, then $\lambda = \beta$, and if $v^{\beta}(\mathbf{r}) = \beta r^2$, then $\lambda = \beta^{1/4}$.

Following Linderberg and Shull [36] and making use of Eqs. (8)–(22) with $\gamma = 1/\beta$ for large-enough β, the QC correlation energy for the Hamiltonian with $v^{\beta}(\mathbf{r})$ becomes

$$\begin{aligned} E_{\mathrm{c}}^{\mathrm{QC}}\left[n^{\beta}\right] &= E_{\mathrm{c}}^{\mathrm{QC},(2)} + \lambda^{-1} E_{\mathrm{c}}^{\mathrm{QC},(3)} + \cdots \\ &= \sum_{j=0}^{\infty} \lambda^{-j} E_{\mathrm{c}}^{\mathrm{QC},(j+2)} \ , \end{aligned} \tag{51}$$

with $\beta = \lambda^{2+s}$, for $s > -2$. The density $n^{\beta}(\mathbf{r})$ depends on the value of the constant β, but $E_{\mathrm{c}}^{\mathrm{QC},(2)}$ is independent of β. In turn, $E_{\mathrm{c}}^{\mathrm{QC},(2)}$ is the leading term in the asympotic high-β expansion for the whole isoelectronic series associated with some $v^{\beta}(\mathbf{r})$ [35], i.e.

$$\lim_{\beta\to\infty} E_{\mathrm{c}}^{\mathrm{QC}}\left[n^{\beta}\right] = E_{\mathrm{c}}^{\mathrm{QC},(2)} \ . \tag{52}$$

For the conventional DFT correlation energy following Huang and Umrigar [16], in a similar way we obtain

$$\lim_{\beta\to\infty} E_{\mathrm{c}}\left[n^{\mathrm{GS},\beta}\right] = E_{\mathrm{c}}^{(2)} \ . \tag{53}$$

By using Eq. (45), we arrive at an inequality connecting the asymptotic high-β expressions for $E_{\mathrm{c}}\left[n^{\mathrm{GS},\beta}\right]$ and $E_{\mathrm{c}}^{\mathrm{QC}}\left[n^{\beta}\right]$, namely

$$\lim_{\beta\to\infty} E_{\mathrm{c}}\left[n^{\mathrm{GS},\beta}\right] \le \lim_{\beta\to\infty} E_{\mathrm{c}}^{\mathrm{QC}}\left[n^{\beta}\right] \ . \tag{54}$$

The strict inequality in Eq. (54) is true only for two-electron densities (see Eq. 44). This equality has been observed numerically by Huang and Umrigar [16] in their studies on two-electron systems in homogeneous external potentials in the high-β limit.

For the functional $E_{\mathrm{c}}^{\mathrm{HF}}[n^{\mathrm{GS}}]$, defined in Eq. (47), one has

$$\lim_{\beta\to\infty} E_{\mathrm{c}}^{\mathrm{HF}}\left[n^{\mathrm{GS},\beta}\right] = E_{\mathrm{c}}^{\mathrm{QC},(2)} \ . \tag{55}$$

From the coordinate transformation in Eqs. (49) and (50), as pointed out by Chakravorty and Davidson [18], for large β, and respectively large λ, it follows that

$$n^{\beta}(x,y,z) \to \lambda^3\ {}^{\mathrm{o}}n(\lambda x, \lambda y, \lambda z) \ . \tag{56}$$

In Eq. (56), $\lambda^3\ {}^{\mathrm{o}}n(\lambda x, \lambda y, \lambda z)$ is the ground-state density of the scaled Hamiltonian in Eq. (50), for $\beta \to \infty$. Note that $\lambda^3\ {}^{\mathrm{o}}n(\lambda x, \lambda y, \lambda z)$ is also the scaled ground-state density of the Hamiltonian in Eq. (1) for $\gamma = 0$ and the homogeneous external potential $v^{\beta}(\mathbf{r})$ with $\beta = 1$. By combining Eqs. (52) and (56), for a homogeneous external potential with a nondegenerate ground state, we identify the second-order energy $E_c^{QC,(2)}$ through coordinate-scaling of the density as

$$\lim_{\beta\to\infty} E_c^{QC}\left[n^{\beta}\right] = \lim_{\lambda\to\infty} E_c^{QC}[{}^{o}n_{\lambda}] = E_c^{QC,(2)} \ . \tag{57}$$

Since for large β, and respectively large λ, $n^{GS,\beta}(x,y,z) \to \lambda^3 \ {}^{o}n(\lambda x, \lambda y, \lambda z)$, we obtain

$$\lim_{\beta\to\infty} E_c\left[n^{GS,\beta}\right] = \lim_{\lambda\to\infty} E_c[{}^{o}n_{\lambda}] = E_c^{(2)} \ , \tag{58}$$

and

$$\lim_{\beta\to\infty} E_c^{HF}\left[n^{GS,\beta}\right] = \lim_{\lambda\to\infty} E_c^{HF}[{}^{o}n_{\lambda}] = E_c^{QC,(2)} \ . \tag{59}$$

6 Numerical results

Since there are many published numbers for $E_c^{QC,(2)}$ [16, 18, 20, 21], we present these numbers as important values for approximating ${}^{\gamma}V_c^{QC}[{}^{\gamma}n]$, in Eq. (6). We can approximate the initial slope $2E_c^{QC,(2)}$ by approximating $\lim_{\lambda\to\infty} E_c^{QC}[{}^{o}n_{\lambda}]$, which, in turn, equals $E_c^{QC,(2)}$ (Eq. 57). These exact numbers are compared against the results obtained from three DFT correlation energy functionals – the one of Lee, Yang and Parr (LYP) [37], the functional of Wilson and Levy (WL) [38], and the recently derived generalized gradient approximation of Perdew, Burke and Ernzerhor (PBE) [39].

To test approximations to ${}^{\gamma}V_c^{QC}[{}^{\gamma}n]$, first we take the exact values for the second-order energy $E_c^{QC,(2)}$ for five different hydrogen-like densities. The model densities are the ground-state densities of ${}^{0}\hat{H}$ in Eq. (1) with $v(\mathbf{r}) = -\beta/r$. $E_c^{QC,(2)}$ is independent of β, even though the density depends on β. For homogeneous external potentials, when the scaled density is employed and the limit $\lambda \to \infty$ is considered, all densities corresponding to different finite positive β have the same scaling limit. In other words,

$$\lim_{\lambda\to\infty} \lambda^3 \ {}^{o}n^{\beta}(\lambda x, \lambda y, \lambda z) = \lim_{\lambda\to\infty} \lambda^3 \ {}^{o}n(\lambda x, \lambda y, \lambda z) \tag{60}$$

The two- and ten-electron densities are generated from the nondegenerate ground-state wavefunctions of the noninteracting ${}^{0}\hat{H}$. For the 3-, 9- and 11-electron densities, the ground state of ${}^{0}\hat{H}$ is degenerate, but the integrand ${}^{\gamma}V_c^{QC}[{}^{\gamma}n]$ still begins with $2E_c^{QC,(2)}$ because of symmetry, following Linderberg and Shull [35]. The 3-, 9- and 11-electron densities are obtained from wavefunctions that correspond to configurations $1s^2 2s$, $1s^2 2s^2 2p^5$ and $1s^2 2s^2 2p^6 3s$ respectively.

In Table 1, we compare the exact values of $2E_c^{QC,(2)}$ with those of $2E_c^{APP,(2)}$, where $E_c^{APP,(2)} = E_c^{APP}[{}^{o}n_{\lambda}]$ as $\lambda \to \infty$, and ${}^{o}n$ are the ground-state densities of ${}^{0}\hat{H}$ with $v(\mathbf{r}) = -\beta/r$. $E_c^{APP}[{}^{o}n_{\lambda}]$ refers to one of the three approximations – LYP, WL, or PBE.

In Table 2, we compare the exact value of $2E_c^{QC,(2)}$ with those of $2E_c^{APP,(2)}$, for the ground-state density of ${}^{0}\hat{H}$ with $v^{\beta}(\mathbf{r}) = \beta r^2$. The exact form of ${}^{o}n^{\beta}$ is then ${}^{o}n^{\beta}(\mathbf{r}) = 2\ (2\beta^2/\pi)^{3/2} \exp(-2\beta^2 r^2)$. Even though the density depends on β, the second-order energy is independent of β because of Eq. (60).

Table 1. Comparison of $2E_c^{QC,(2)}$ for $\hat{H}$ in Eq. (1) with $v(\mathbf{r}) = -\beta/r$ as $\beta \to \infty$ to $2E_c^{APP,(2)}$

Density	$2E_c^{QC,(2)}$	$2E_c^{PBE,(2)}$	$2E_c^{LYP,(2)}$	$2E_c^{WL,(2)}$
2-electron	−0.0934	−0.0958	−0.1134	−0.0960
3-electron	−0.1074	−0.1168	−0.1990	−0.1136
9-electron	−0.7388	−0.7712	−0.9330	−0.7652
10-electron	−0.8556	−0.9154	−1.0590	−0.9008
11-electron	−0.9068	−0.9506	−1.1780	−0.9436

Table 2. Comparison of $2E_c^{QC,(2)}$ for $\hat{H}$ in Eq. (1) with $v(\mathbf{r}) = \beta r^2$ as $\beta \to \infty$, to $2E_c^{APP,(2)}$

Density	$2E_c^{QC,(2)}$	$2E_c^{PBE,(2)}$	$2E_c^{LYP,(2)}$	$2E_c^{WL,(2)}$
$2(2\beta^2/\pi)^{3/2}\exp(-2\beta^2 r^2)$	−0.0994	−0.1626	−0.0710	−0.1564

The approximations tested give reasonable-to-excellent values, depending upon the functional, the number of electrons, and the external potential for the test density. In general, the results obtained by means of all approximations for the density of the harmonic oscillator external potential are significantly worse than those for hydrogenic densities. Also, when the adiabatic connection formula Eq. (6) is employed to generate a new approximation to $E_c^{QC}[n]$, with all three functionals there is room for improvement when these functionals are used to approximate the $2E_c^{QC,(2)}$ segment of the integrand, which is the initial slope in this adiabatic connection formula.

The numerical results partially explain the results obtained by Fuentealba and Savin [40]. They found that the WL functional gives better results than the LYP approximation when used as a"tack-on" functional. The data in Tables 1 and 2 suggest that the WL functional produces a quite good approximation to the integrand in Eq. (6). (For a review of the use of the WL approximation as a functional added to the completed HF energy see Ref. [41]) In line with this, the PBE functional is also expected to produce very good results when used as an approximation to $E_c^{QC}[n]$ or $E_c^{HF}[n^{GS}]$.

The numbers presented in Table 1 are the same as those in Ref. [19] but multiplied by a factor of 2. (There are slight differences between the numbers obtained with the LYP approximation in Ref. [19] and those presented in this work. Here, the results from the LYP functional are calculated with the exact value of a, given in Ref. [36], $a = 0.04918$, rather than $a = 0.049$ which was used in Ref. [19].) Ivanov and Levy [19] have established connections between known numbers from the asymptotic high-Z expansion for the QC correlation energy and the second-order energy in Görling–Levy perturbation theory for certain hydrogen-like densities in the context of the DFT adiabatic connection method.

7 Concluding comments

We have derived an adiabatic connection formula for the correlation energy functional, $E_c^{QC}[n]$, of the HF density. This functional is intended to be added to the completed HF energy to produce the exact ground-state energy. The initial slope of the integrand in this integration formula, Eq. (6), has been identified as $2E_{\mathrm{c}}^{\mathrm{QC},(2)}$, where $E_{\mathrm{c}}^{\mathrm{QC},(2)}$ is given in Eq. (23). $E_{\mathrm{c}}^{\mathrm{QC},(2)}$ can be easily computed through the variation-perturbation method of Hylleraas [34]. Since there are published numbers for $E_{\mathrm{c}}^{\mathrm{QC},(2)}$ from the asymptotic high-β expansions for the QC correlation energy, we have presented six numerical tests to assess approximations to the initial slope of the integrand in the adiabatic connection formula introduced. Viable DFT correlation energy functionals have been tested when used as approximations to $2E_{\mathrm{c}}^{\mathrm{QC},(2)}$. Further, Eq. (6) should prove valuable for developing new improved approximations to $E_{\mathrm{c}}^{\mathrm{QC}}[n]$. Our adiabatic integration formula enables one to connect available results at coupling constant 1 and results at low coupling constants in order to model the integrand in Eq. (6).

In order to prove recent numerical results by Huang and Umrigar for homogeneous external potentials $v^{\beta}(\mathbf{r})$, we have developed high-β expansions for $E_{\mathrm{c}}\left[n^{\mathrm{GS},\beta}\right]$ and $E_{\mathrm{c}}^{\mathrm{QC}}\left[n^{\beta}\right]$, where $n^{\mathrm{GS},\beta}$ is the ground-state density and n^{β} is the HF density of the same Hamiltonian. We have shown that $\lim_{\beta\to\infty} E_{\mathrm{c}}[n^{\mathrm{GS},\beta}] \leq \lim_{\beta\to\infty} E_{\mathrm{c}}^{\mathrm{QC}}[n^{\beta}]$, with equality for, and only for, two-electron densities. This equality has been numerically observed by Huang and Umrigar.

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