Gaussian-based range-separation approach on Hartree–Fock exchange interaction and second-order perturbation theory

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A B S T R A C T

A Gaussian-based range-separation approach is applied to the Hartree–Fock exchange interaction and the second-order perturbation theory, comparing the results with those provided through the *erfc* short-range potential approach. The Gaussian short-range potential's behavior resembles more that of the bare $1/r$ potential than that of the *erfc* short-range potential around the origin. Thus, the Gaussian-based range-separation of the exchange term agrees better with the ordinary HF method and the Møller–Plesset perturbation theory.

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1. Introduction

In first-principles quantum chemistry calculations, the range-separation technique is widely employed for efficient Hartree-term calculations, long-range corrections in hybrid density functional theory (DFT), and suppressions of the long-range contribution of the Hartree–Fock (HF) exchange term under the periodic boundary conditions (PBCs) [1–14]. To separate the bare $1/r$ potential, the error and complementary error functions are often adopted as follows:

$$\frac{1}{r} = \frac{erf(\eta r)}{r} + \frac{erfc(\eta r)}{r} \tag{1}$$

In addition, the following Gaussian-based range-separation approach was reported for the dielectric-dependent exchange potential method [15].

$$\frac{1}{r} = \frac{1 - \exp(-\omega r^2)}{r} + \frac{\exp(-\omega r^2)}{r} \tag{2}$$

Figure 1 depicts the Gaussian- and *erf*-based range separation approaches, where the Gaussian long-range potential of $(1 - \exp(-\omega r^2))/r$ shows a significantly different behavior from that of the *erf* long-range potential; at the origin ($r = 0$), the Gaussian

long-range potential become zero. Conversely, the *erf* long-range potential takes the finite value of $2\eta/\sqrt{\pi}$. This means the Gaussian short-range potential $\exp(-\omega r^2)/r$ can agree more with the bare $1/r$ potential around the origin than with the *erfc* short-range potential of $erfc(\eta r)/r$. However, only a few studies pay attention to the short-range exchange interaction with $\exp(-\omega r^2)/r$, whereas many use it to describe the Coulomb hole and the electron correlation cusp [6,13]. The Gaussian short-range exchange potential has several useful features. For example, it can be employed to develop efficient first-principles quantum chemistry methodologies. It is useful to construct novel DFT functionals [15–17]. The short-range exchange potential can improve the stability of the SCF procedure, especially in the PBC calculations [14,15]. In this letter, we discuss the Gaussian-based range-separation approach, focusing on the nonlocal HF exchange interaction.

Furthermore, the perturbation theory plays an essential role in first-principles calculations. For example, the second-order Møller–Plesset (MP2) method is frequently employed in quantum chemistry calculations [18–20], especially considering the van der Waals interactions. Recently, DFT functionals utilized the perturbation theory. In particular, double-hybrid DFT functionals employed the second-order perturbation terms in addition to the local potentials and the HF exchange term [21,22]. Furthermore, Ren et al. discussed the effect of a single excitation in the second-order perturbation method to improve the random-phase approximation (RPA) [23]. In addition, a PBC-MP2 method was employed to investigate polymers and materials [24–26]. Thus, this letter discusses a perturbation method based on the Gaussian short-range exchange potential.

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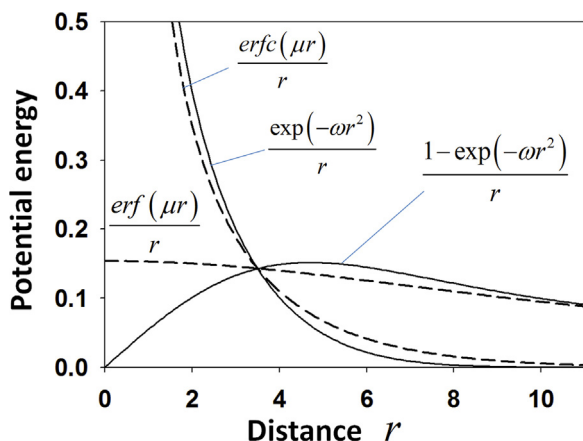
Figure 1. Long- and short-range potentials. The solid lines indicate the Gaussian-based range-separation potentials and the dashed lines indicate the *erf* and *erfc* potentials. The dotted line shows the bare $1/r$ potential.

2. Second-order perturbation theory based on short-range exchange potential

In this letter, we consider the Fock operator $\hat{F}_i^{SR-Ex}$ with the short-range exchange potential for electron i,

$$\hat{F}_i^{SR-Ex}\phi_i^{SR-Ex} = \varepsilon_i^{SR-Ex}\phi_i^{SR-Ex} \tag{3}$$

Here, ϕ_i^{SR-Ex} and ε_i^{SR-Ex} are the molecular orbital and the energy for the $\hat{F}_i^{SR-Ex}$ operator, respectively. The atomic orbital (AO)-based Fock matrix for closed-shell system is described as follows:

$$F_{\mu\nu}^{SR-Ex}=\langle\chi_\mu|\hat{F}^{SR-Ex}|\chi_\nu\rangle=h_{\mu\nu}+\sum_\lambda^{AO}\sum_\sigma^{AO} D_{\lambda\sigma}\left[(\mu\nu|\lambda\sigma)-\frac{1}{2}(\mu\lambda|\nu\sigma)_{SR}\right] \tag{4-1}$$

$$(\mu\nu|\lambda\sigma) = \int \chi_\mu(\mathbf{r}_1)\chi_\nu(\mathbf{r}_1)\frac{1}{r_{12}}\chi_\lambda(\mathbf{r}_2)\chi_\sigma(\mathbf{r}_2)d\mathbf{r}_1 d\mathbf{r}_2 \tag{4-2}$$

Here, $\chi(\mathbf{r})$ is the atomic orbital, and $D_{\lambda\sigma}$ is the AO-based density matrix. The Greek characters μ, ν, λ, and σ represent the atomic orbitals indexes. $h_{\mu\nu}$ is the AO-based matrix element for the core Hamiltonian $\hat{h}$, calculated from $h_{\mu\nu} = \langle\chi_\mu|\hat{h}|\chi_\nu\rangle$. $(\mu\nu|\lambda\sigma)$ is the AO-based electron repulsive integral (ERI). $(\mu\lambda|\nu\sigma)_{SR}$ is the short-range AO-based ERI. The only difference in the $\hat{F}_{\mu\nu}^{SR-Ex}$ from the ordinary HF method is the short-range exchange term in Eq. (4-1). In the Gaussian-based range-separation approach, the short-range AO integral is determined by

$$(\mu\lambda|\nu\sigma)_{Gauss-SR} = \int \chi_\mu(\mathbf{r}_1)\chi_\lambda(\mathbf{r}_1)\frac{\exp(-\omega r_{12}^2)}{r_{12}}\chi_\nu(\mathbf{r}_2)\chi_\sigma(\mathbf{r}_2)d\mathbf{r}_1 d\mathbf{r}_2 \tag{5}$$

The integrals $(\mu\lambda|\nu\sigma)_{Gauss-SR}$ can be calculated from the modified Obara–Saika (OS) recurrence relation [6,15,27]. This letter is a comparative study of the *erfc* short-range exchange potential, where the short-range AO integral is described by

$$(\mu\lambda|\nu\sigma)_{erfc-SR} = \int \chi_\mu(\mathbf{r}_1)\chi_\lambda(\mathbf{r}_1)\frac{erfc(\eta r_{12})}{r_{12}}\chi_\nu(\mathbf{r}_2)\chi_\sigma(\mathbf{r}_2)d\mathbf{r}_1 d\mathbf{r}_2 \tag{6}$$

In the perturbation theory, the zero-order Hamiltonian and the energy are obtained from the sums of the Fock operators and

the molecular energies, as $\hat{H}^{(0)} = \sum_i \hat{F}_i^{SR-Ex}$ and $E^{(0)} = \sum_i \varepsilon_i^{SR-Ex}$, respectively. The perturbation term is obtained from

$$\hat{H}^{(1)} = \hat{H} - \hat{H}^{(0)} = \hat{H} - \sum_i \hat{F}_i^{SR-Ex} \tag{7}$$

Here, $\hat{H} = \sum_i \hat{h}_i + \sum_{i<j} 1/r_{ij}$, which is the Hamiltonian for all electrons. The first-order energy is obtained from $E^{(1)} = \langle\Phi_0^{SR-Ex}|\hat{H}^{(1)}|\Phi_0^{SR-Ex}\rangle$, where Φ_0^{SR-Ex} is the Slater determinant constructed by one-electron ϕ_i^{SR-Ex} wave functions. The sum of the energies $E^{(0)}$, $E^{(1)}$, and E_{NN} is described as follows:

$$E^{(0)} + E^{(1)} + E_{NN} = \sum_i \varepsilon_i^{SR-Ex} + \langle\Phi_0^{SR-Ex}|\hat{H}^{(1)}|\Phi_0^{SR-Ex}\rangle + E_{NN}$$

$$= E_{SCF} + E_x^{LR} \tag{8-1}$$

$$E_{SCF} = \sum_{\mu,\nu}^{AO}D_{\mu\nu}h_{\mu\nu} + \frac{1}{2}\sum_{\mu,\nu,\lambda,\sigma}^{AO}D_{\mu\nu}D_{\lambda\sigma}\left[(\mu\nu|\lambda\sigma)-\frac{1}{2}(\mu\lambda|\nu\sigma)_{SR}\right]$$

$$+ E_{NN} \tag{8-2}$$

$$E_x^{LR} = -\frac{1}{2}\sum_{\mu,\nu,\lambda,\sigma}D_{\mu\nu}D_{\lambda\sigma}(\mu\lambda|\nu\sigma)_{LR} \tag{8-3}$$

where E_{NN} is the nuclear–nuclear repulsive energy. E_{SCF} is the SCF energy. E_x^{LR} is the long-range contribution of the HF exchange interaction, and $(\mu\lambda|\nu\sigma)_{LR}$ is the long-range AO-based integral. Here, the equations above represent the closed-shell system [28]. Two types of long-range integrals of $(\mu\lambda|\nu\sigma)_{Gauss-LR}$ and $(\mu\lambda|\nu\sigma)_{erf-LR}$ are employed for the Gaussian- and the *erfc*-based range-separation approaches, respectively. They are described as follows:

$$(\mu\lambda|\nu\sigma)_{Gauss-LR} = \int \chi_\mu(\mathbf{r}_1)\chi_\lambda(\mathbf{r}_1)\frac{1-\exp(-\omega r_{12}^2)}{r_{12}}\chi_\nu(\mathbf{r}_2)\chi_\sigma(\mathbf{r}_2)d\mathbf{r}_1 d\mathbf{r}_2 \tag{9-1}$$

$$(\mu\lambda|\nu\sigma)_{erf-LR} = \int \chi_\mu(\mathbf{r}_1)\chi_\lambda(\mathbf{r}_1)\frac{erf(\eta r_{12})}{r_{12}}\chi_\nu(\mathbf{r}_2)\chi_\sigma(\mathbf{r}_2)d\mathbf{r}_1 d\mathbf{r}_2 \tag{9-2}$$
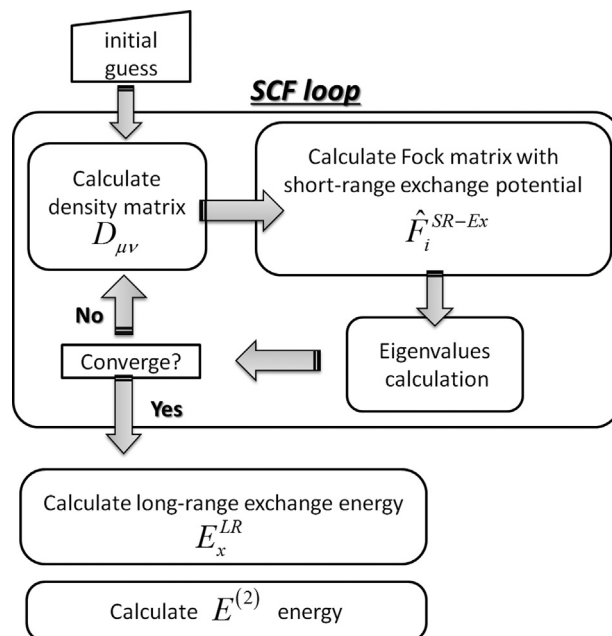

Figure 2. Self-consistent field (SCF) approach with the short-range exchange potential. The E_x^{LR} and MP2 energies are calculated after the SCF procedure.