Electron-nucleus correlation functional for multicomponent density-functional theory

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An electron-nucleus Colle-Salvetti-type correlation functional for multicomponent density-functional theory is proposed. We demonstrate that our correlation functional quantitatively reproduces the quantum mechanical effects of protons; the mean absolute deviation value is 2.8 millihartrees for the optimized structures of hydrogen-containing molecules, and the effective potential energy curve of the hydrogen molecule is well reproduced. Since this functional is derived without any unphysical assumption, the strategy taken in this development will be a promising recipe to make new functionals for the potentials of other particles' interactions, such as electron-positron and electron-muon.

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Density-functional theory (DFT) [1–3] has become one of the most successful and powerful approaches to calculate the electronic structure of atoms, molecules, and solids, in the general areas of physics and materials and life sciences. Using the Born-Oppenheimer approximation, DFT is constructed on the Hohenberg-Kohn theorem, which establishes the one-to-one correspondence of density to the electrostatic potential of clamped fixed nuclei [1]. Therefore, the quantum effects of nuclear motions have been basically neglected in the conventional DFT calculations. Many recent studies, however, have reported [4,5] that nuclear quantum effects significantly contribute to various phenomena such as proton tunneling, hydrogen bonding, and so on. To adequately include such effects in DFT calculations, nuclear quantum effects should be explicitly taken into consideration in the functionals used.

Multicomponent DFT (MCDFT) is one of the main straightforward strategies for incorporating nuclear quantum effects in DFT. Capitani and co-workers first proposed MCDFT by proving the Hohenberg-Kohn theorem for multicomponent systems [6], and nowadays several groups have developed MCDFT methods based on this theorem [7–14]. In MCDFT calculations, Gross and co-workers [9,10] have found the qualitative reproduction for the structures of small molecules using a simple electron-nuclear correlation functional based on the Hartree approximation. They, however, failed to describe the effective potential energy curve of simple hydrogen molecules without an approximation for the conditional density based on the scaled atomic orbital approach [10]. Hammes-Schiffer and co-workers [11–14] also proposed an electron-proton correlation functional that uses the pair density obtained in the nuclear-electronic orbital explicitly correlated Hartree-Fock (NEOXCHF) calculations [14], for the MCDFT method. We have also developed a MCDFT method for qualitatively reproducing the geometric H-D isotope effects of porphyrin and porphycene molecules [15]. No "electron-nucleus (*en*)" correlation functional, however, has been used

in the practical calculations of our previous MCDFT method. We have highly confirmed that the *en* correlation, as well as the electron-electron correlation, is indispensable for giving quantitatively accurate results for multicomponent systems. To incorporate such *en* correlation effects, we have already proposed perturbation and configuration interaction approaches beyond the mean-field approximation [16,17]. In spite of the accurate *en* correlation, however, we should address here that these approaches incur enormous computational cost from the practical point of view. In this paper, we thus propose an *en* correlation functional using the physical model of the Colle-Salvetti (CS)-type correlation functional [18].

In MCDFT methods, the Fock operators of the Kohn-Sham equation for electrons (*e*) and nuclei (*n*) are defined as

$$\hat{f}_e^{\mathrm{MCDFT}} = \hat{h}_e + \sum_i^{N_e} \hat{J}_i - \sum_n^{N_n} \hat{J}_n + V_{\mathrm{XC}(ee)}^{\mathrm{MCDFT}} + V_{\mathrm{C}(en)}^{\mathrm{MCDFT}}, \quad (1)$$

$$\hat{f}_n^{\mathrm{MCDFT}} = \hat{h}_n + \sum_n^{N_n} \hat{J}_n - \sum_i^{N_e} \hat{J}_i + V_{\mathrm{XC}(nn)}^{\mathrm{MCDFT}} + V_{\mathrm{C}(en)}^{\mathrm{MCDFT}}, \quad (2)$$

where $\hat{h}_e$, $\hat{J}_i$, and $\hat{J}_n$ are one-electron, electronic Coulomb, and nuclear Coulomb operators, and N_e and N_n are the number of electrons and nuclei, respectively. Although many types of functionals have been proposed for electron-electron (*ee*) exchange-correlation potential, $V_{\mathrm{XC}(ee)}^{\mathrm{MCDFT}}$ [19–21], only a few types of functionals have been given for *en* correlation potential, $V_{\mathrm{C}(en)}^{\mathrm{MCDFT}}$, and nucleus-nucleus (*nn*) exchange-correlation potential, $V_{\mathrm{XC}(nn)}^{\mathrm{MCDFT}}$, as far as we know. To construct the correlation functional for $V_{\mathrm{C}(en)}^{\mathrm{MCDFT}}$, we adopt the physical model of the CS-type *ee* correlation functional [18].

The CS-type functional for the electron-nucleus (*en*) correlation is derived from the correlated wave function Ψ_{CS}^{en}, which is the Kohn-Sham (KS) wave function containing electron-electron correlations, Ψ_{KS}, multiplied by a Jastrow factor,

$$\Psi_{\mathrm{CS}}^{en} = \Psi_{\mathrm{KS}} \prod_{i,n} [1 - \phi^{en}(\mathbf{r}_i, \mathbf{r}_n)], \quad (3)$$

$$\phi^{en}(\mathbf{r}_i, \mathbf{r}_n) = \exp\left(-\beta_{en}^2 r^2\right)\left\{1 - \Phi^{en}(\mathbf{R})\left[1 + \eta_{\mathrm{cusp}}^{en} r\right]\right\}, \quad (4)$$

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where ϕ^{en} is the CS correlation factor for the en correlation, $\mathbf{r}_i$ and $\mathbf{r}_n$ are the position vectors of electrons and nuclei, respectively. $r = |\mathbf{r}_i - \mathbf{r}_n|$, $\mathbf{R} = \alpha\mathbf{r}_i + (1 - \alpha)\mathbf{r}_n \approx \mathbf{r}_n$, and η_{cusp}^{en} is the constant from cusp condition: e.g., $-Z_n$ for electron-nucleus case, where Z_n is the nuclear charge of nucleus n. The original CS-type ee-correlated wave function satisfies two physical conditions: (a) for electrons far apart from each other, the ee-correlated wave function should be reduced to the ee-uncorrelated Hartree-Fock wave function, and (b) for electrons close to each other the wave function should satisfy the correlation cusp condition. These physical conditions are applicable to the en correlations. Note that the en-correlated wave function should reproduce the KS wave function for electrons far apart from nuclei, and that electrons undergo only the electrostatic attractions from nuclei in the KS wave function. Therefore, the CS correlation factor, ϕ^{en}, in Eq. (4) is now written as

$$\phi^{en}(\mathbf{r}_i,\mathbf{r}_n) = \exp\left(-\beta_{en}^2 r^2\right)\{1 - \Phi^{en}(\mathbf{r}_n)[1 - Z_n r]\}. \quad (5)$$

In the case that the electron and nucleus are close to each other, the en-correlated wave function should satisfy the en cusp condition:

$$\frac{\partial \Psi^{en}}{\partial r}\bigg|_{r=0} = -Z_n \Psi^{en}|_{r=0}. \quad (6)$$

Therefore, Z_n in Eq. (5) is determined to be the nuclear charge to obey the en cusp condition. In Eq. (5), the function Φ^{en} is given by assuming that the KS first-order reduced density matrix is a reasonable approximation of the exact one [18]. Recently, Imamura and co-workers also proposed a CS-type correlation functional for en correlations [8]. In developing this functional, Φ^{en} was derived to obey the normalization condition. This Φ^{en}, however, unfortunately causes a singularity in this functional due to the minus nuclear charge term, $-Z_n$.

For determining the en CS correlation factor, ϕ^{en} in Eq. (5), it is interesting to note that similar Jastrow factors have been used in the correlated wave functions of quantum Monte Carlo
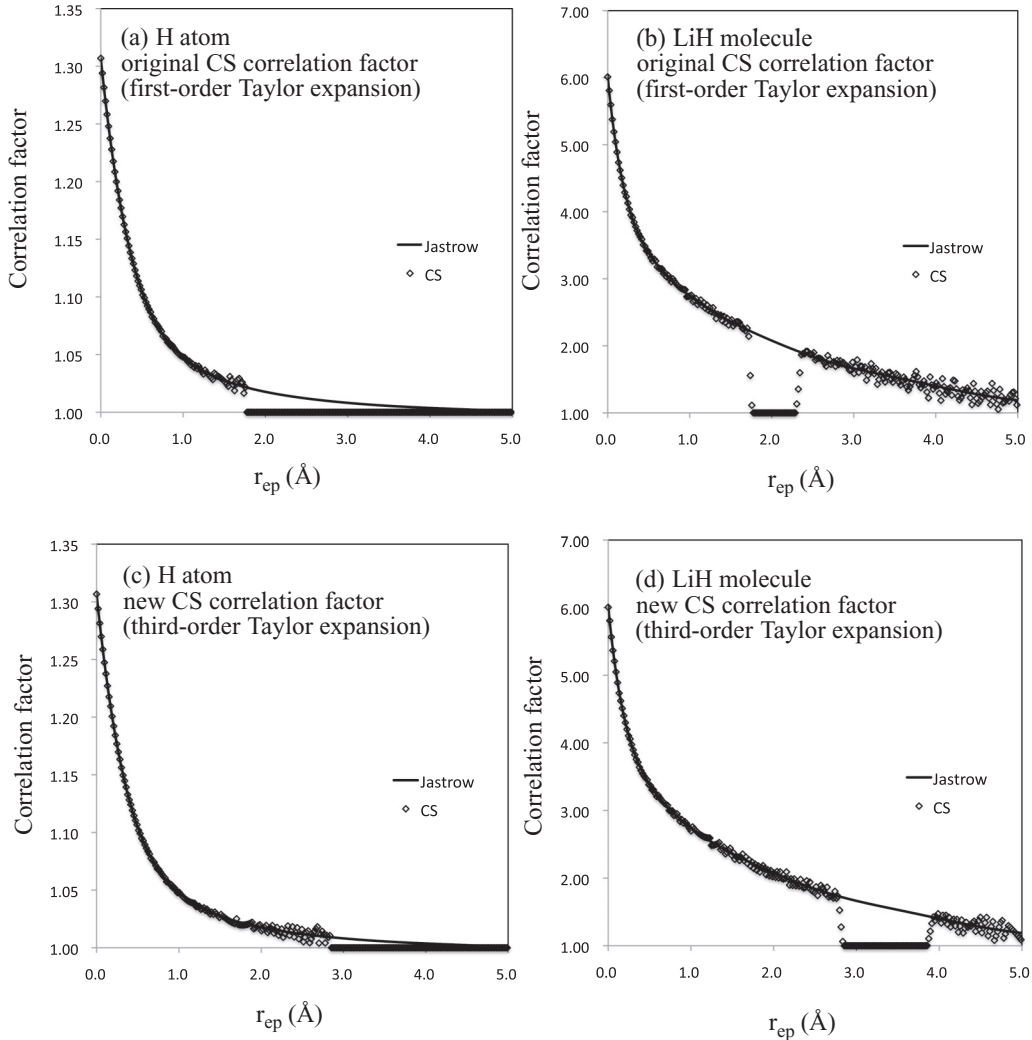

FIG. 1. The electron-proton correlation factor of the Jastrow factor given by multicomponent quantum Monte Carlo (MCQMC) calculations and the original Colle-Salvetti (CS) correlation factor for (a) H atom and (b) LiH molecule, and that given by MCQMC calculations and our CS correlation factor for (c) H atom and (d) LiH molecule. The Jastrow factor for LiH molecule was obtained considering electron-electron correlations.
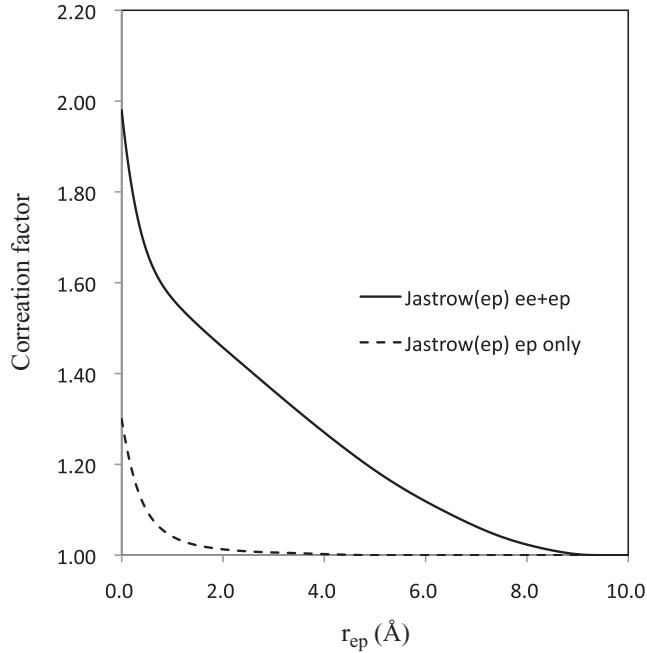
FIG. 2. Optimized Jastrow correlation factor for electron-proton correlation in H^- atom.

(QMC) calculations. We have therefore optimized the Jastrow factor by the multicomponent QMC (MCQMC) method [22] and have fitted the electron-proton (ep) CS correlation factor to the optimized Jastrow factor in Fig. 1. This figure displays the fitted CS correlation factor and the optimized Jastrow factor for (a) the H atom and (b) the LiH molecule. In Fig. 1(a), we found that the original CS correlation factor appropriately reproduces the Jastrow factor only for the short ep distance up to about 1.8 Å in the H atom. On the other hand, Fig. 1(b) shows that the original CS factor gives correct ep correlations for the long ep distance in the LiH molecule. This, however, provides zero ep correlation factor around 2.0 Å due to the insufficiency of the first-order Taylor-expanded CS correlation factor. This may cause a serious problem in reproducing correct ep correlations, because ep correlations affect for the ep distance longer than 2.0 Å as mentioned later. Comparing Figs. 1(a) and 1(b) also shows that the CS correlation factor shows smaller curvature for $H^{\delta-}$ in the LiH molecule than that for the H atom.

Figure 2 compares the optimized Jastrow factors of the electron-proton correlations for the H^- anion in MCQMC calculations: The solid line corresponds to the optimized Jastrow factor for incorporating both the ee and ep correlations, and the dashed line indicates the factor for including only the ep correlations. In this figure, we found that the ep correlations contribute to the long ep distance more than 8.0 Å if ee correlations are combined, though the ep correlations with no ee correlations are efficient only for the short ep distance up to about 4.0 Å. This result is in contrast to the conclusion in the study of Hammes-Schiffer and co-workers [14] that the ep correlations are uncoupled with the ee correlations and provide only additive effects to the total energy. As shown in the present result, the ee correlations significantly affect the distribution of the ep correlation. The impact distances (4.0 and 8.0 Å) are much longer than the range of the distance

where the original CS factor gives zero ep correlation (around 2.0 Å) mentioned above. To extend the effective region of the CS factor, we have reformulated the original CS correlation factor for electron-nucleus correlations, ϕ^{en} in Eq. (5), by using the third-order Taylor expansion as

$$\phi^{en}(\mathbf{r}_i,\mathbf{r}_n) = \exp\left(-\beta_{en}^2 r^2\right)\left\{1 - \Phi^{en}(\mathbf{r}_n)\right. \\ \left. \times \left[1 - Z_n r + \tfrac{1}{2}Z_n^2 r^2 - \tfrac{1}{6}Z_n^3 r^3\right]\right\}, \quad (7)$$

where Z_n is the nuclear charge. Figures 1(c) and 1(d) display the CS correlation factor, in which β_{en} is optimized in Eq. (7). In these figures, the CS correlation factor is confirmed to reproduce the Jastrow factor correctly up to about 2.8 Å.

What remains is to determine the exponent β_{en} in Eq. (7), which corresponds to the amplitude of correlation region. In the original paper of the CS correlation functional [18], Colle and Salvetti assumed for ee correlations that the volume of the region, in which the function for the ee correlations, $\phi^{ee}(\mathbf{r}_i,\mathbf{r}_j)$, is appreciably different from zero, is proportional to the Wigner's exclusion volume [23,24]. Consequently, they obtained the relation of $\beta_{ee} = q\rho_e^{1/3}$, where ρ_e is electronic density and q is a fitted parameter. According to Becke's definition of correlation length, Tsuneda and Hirao [25] proposed an approach for determining β_{ee} in the CS correlation factor that the volume of the ee exchange hole is proportional to that of the correlation hole. Note that these previous approaches are not applicable to the case of en correlations, because en correlations have no straightforward relation with electronic exchange interactions. Instead, we assumed that the volume of the en correlation hole is proportional to that of the ee correlation hole, because we consider that the en correlation energy, which increases the electronic density near atomic nuclei, is balanced with the ee correlation, which decreases the electronic density near nuclei, on the basis of the different sign of Z_n in Eq. (6). This assumption is also supported by the fact that the effective region of the correlation factor for en correlation is found to be significantly short by excluding ee correlations in many-electron systems, as mentioned above. As mentioned later, the en correlations turn out to be related to the ee exchange interactions through the ee correlations.

The en correlation functional is derived following the development of the one-parameter progressive (OP) ee correlation functional [21]. The volume of the ee correlation hole in the OP functional is presumed to be proportional to the volume of the ee exchange hole, which is determined by the exchange functional used together. Since the volume of the en correlation hole should be assumed to be proportional to that of the ee correlation hole, the former is also taken to be proportional to that of the exchange hole. Therefore, we determine the volume of the ee correlation potential [25] in our correlation functional similarly to that in the OP functional as

$$V_{CS}^{ee} = \text{const.}\left(\frac{4\pi}{3}\right)\left(\frac{z_{ee}}{2}\right)^3, \quad (8)$$

where z_{ee} is the Becke correlation length [26]. Colle and Salvetti [18] suggested that the volume of the correlation hole, V_{CS}^{ee}, where the correlation energy differs appreciably from

TABLE I. The sum of the Kohn-Sham BOP energies and the corresponding zero-point vibrational energies ($E^{\mathrm{BOP}} + E^{\mathrm{ZPE}}$) (hartree), sum of MCBOP and electron-proton correlation energies ($E^{\mathrm{MCBOP}} + E^{\mathrm{EPC}}$) (hartree), and deviations (E^{Dev}) (millihartree) are displayed for various systems. The mean absolute deviation value is 2.8 millihartrees.

	H$_2$							HeH$^+$
$E^{\mathrm{BOP}} + E^{\mathrm{ZPE}}$	−1.16148							−2.96621
$E^{\mathrm{MCBOP}} + E^{\mathrm{EPC}}$	−1.16130							−2.97605
E^{Dev}	0.1							−9.8
	LiH	BeH$_2$	BH$_3$	CH$_4$	NH$_3$	H$_2$O	FH	NeH$^+$
$E^{\mathrm{BOP}} + E^{\mathrm{ZPE}}$	−8.07197	−15.88387	−26.55590	−40.43552	−56.47276	−76.34735	−100.37958	−128.95422
$E^{\mathrm{MCBOP}} + E^{\mathrm{EPC}}$	−8.06673	−15.87819	−26.55287	−40.44337	−56.47904	−76.35237	−100.38158	−128.95672
E^{Dev}	5.2	2.8	1.0	−2.0	−2.1	−2.5	−2.0	−2.5
	NaH	MgH$_2$	AlH$_3$	SiH$_4$	PH$_3$	H$_2$S	HCl	ArH$^+$
$E^{\mathrm{BOP}} + E^{\mathrm{ZPE}}$	−162.82428	−201.19665	−244.12415	−291.76988	−343.03396	−399.29519	−460.72476	−527.58919
$E^{\mathrm{MCBOP}} + E^{\mathrm{EPC}}$	−162.81851	−201.18783	−244.11501	−291.76319	−343.03200	−399.29530	−460.72569	−527.59295
E^{Dev}	5.8	4.4	3.0	1.7	0.7	−0.1	−0.9	−3.8

zero, is expressed as

$$V_{\mathrm{CS}}^{ee} = 4\pi \int_0^{\infty} \exp\left(-\beta_{ee}^2 r^2\right) r^2 dr = \left(\frac{\pi^{1/2}}{\beta_{ee}}\right)^3. \quad (9)$$

By assuming that the volume of the *en* correlation hole, V_{CS}^{en}, where β_{ee} in Eq. (9) is substituted by β_{en}, is proportional to V_{CS}^{ee} in Eq. (8), the exponential coefficient β_{en} can be given by

$$\beta_{en} = q_{en} \left(\frac{1}{\rho_\alpha^{1/3} K_\alpha} + \frac{1}{\rho_\beta^{1/3} K_\beta}\right)^{-1}, \quad (10)$$

where q_{en} is a parameter, ρ_σ is the electronic density, and K_σ is defined in the usual *ee* exchange functional formulation [21],

$$E_x = -\frac{1}{2} \sum_\sigma \rho_\sigma^{4/3} K_\sigma d^3 \mathbf{r}. \quad (11)$$

Using the volume of the *en* correlation hole proportional to that of the *ee* correlation hole, the *en* correlation energy is supposed to be well balanced with the *ee* correlation energy.

Using Eqs. (3), (7), and (10), we analytically derived a CS-type *en* correlation functional in a similar way to the one-parameter progressive (OP) *ee* correlation functional [21]. As a result, we obtained a CS-type *en* correlation energy, E^{ENC}, as

$$E^{\mathrm{ENC}} = -4\pi \int d^3 \mathbf{r}_n \rho_e \rho_n \left\{ -\frac{3}{4\beta_{en}^3} + \frac{32\beta_{en}^3 + (8\sqrt{2\pi} - 32\sqrt{\pi})Z_n\beta_{en}^2 + 24Z_n^2\beta_{en} + (\sqrt{2\pi} - 8\sqrt{\pi})Z_n^3}{64\beta_{en}^5} \Phi^{en}(\mathbf{r}_n) \right.$$

$$\left. + \frac{384\beta_{en}^6 - 192\sqrt{2\pi}Z_n\beta_{en}^5 + 384Z_n^2\beta_{en}^4 - 96\sqrt{2\pi}Z_n^3\beta_{en}^3 + 112Z_n^4\beta_{en}^2 - 15\sqrt{2\pi}Z_n^5\beta_{en} + 8Z_n^6}{1536\beta_{en}^8} \Phi^{en}(\mathbf{r}_n)^2 \right\}, \quad (12)$$

where ρ_n and Z_n are nuclear density and charge, respectively. The CS-type *en* correlation energy is determined by specifying Z_n and β_{en} in Eq. (12).

In this study, we took the quantum nature of only protons into account for the nuclei, as well as electrons, and therefore, only electron-proton (*ep*) correlations arose. The only parameter, β_{en} ($=\beta_{ep}$ in this case), is determined by fitting the sum of the *ep* correlation (EPC) energy given by our *en* correlation functional, E^{EPC}, and the energy of MCDFT using the Becke electronic exchange [19] +OP correlation (BOP) functional, E^{MCBOP}, to the sum of the BOP energy given in the conventional DFT, E^{BOP}, and the zero-point vibrational energy (ZPE), E^{ZPE}, for H$_2$, LiH, and HeH$^+$ systems, in which the H atom is neutral, anionic, and cationic, respectively [8]. The 6-31G electronic basis set and [1s1p1d] Gaussian-type basis function are employed. Consequently, we obtained $q_{en} = 18.0$. For the fitting and all benchmark calculations below, we have used the development version of the GAUSSIAN 03 program package [27].

To examine the availability of our *en* correlation functional, we calculated the total energies of 18 systems, which are composed of both hydrogen and first- or second-row atoms. We took the quantum nature of only protons into account for the nuclei, as well as electrons, as mentioned above. Following the study of Ishikawa and Quiney [28], we have employed Gaussian-type basis functions: 6-31G and [1s1p1d] functions for electrons and protons, respectively. The molecular geometries were optimized using the BOP functional with the 6-31G basis set and MCBOP and EPC energies were calculated at such optimized geometries. Table I displays the sum of the BOP energies and the zero-point vibrational energies ($E^{\mathrm{BOP}} + E^{\mathrm{ZPE}}$), the sum of MCBOP and EPC energies ($E^{\mathrm{MCBOP}} + E^{\mathrm{EPC}}$), and the difference between them per proton (E^{Dev}). This result indicates that the multicomponent CS-type *en* correlation functional quantitatively reproduces the quantum mechanical effects of protons for various molecules with the mean absolute deviation of 2.8 millihartrees. Strictly speaking, the errors are large for quantum-treated hydrogen
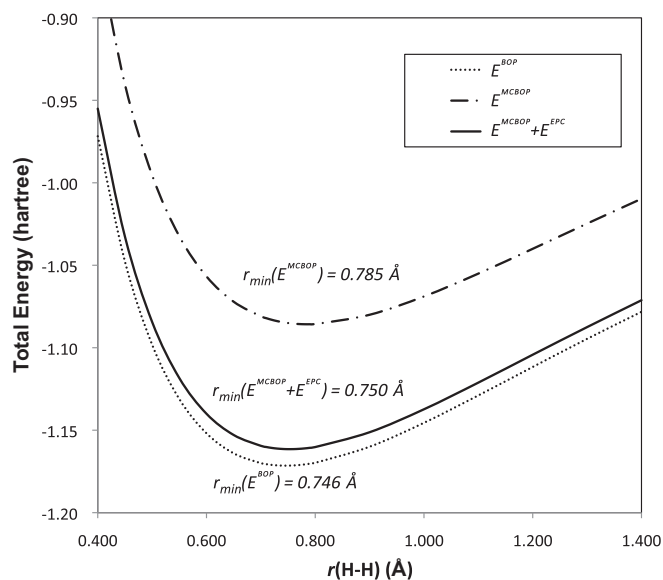
FIG. 3. Potential energy curves (PECs) calculated with the Kohn-Sham method with BOP functional, and effective PECs with MCBOP and MCBOP with our electron-nucleus correlation functional.

atoms with cationic character such as HeH^+ and with anionic character such as LiH and NaH as shown in Table I. We suppose that these large errors come from the extremely low or extremely high electron densities of H atom.

To confirm the validity and behavior of our *en* correlation functional, we have calculated the effective potential energy curve (PEC) of the H_2 molecule by using the BOP, MCBOP, and MCBOP + EPC methods (Fig. 3). The figure shows that the MCBOP energies are about 0.08 hartree higher than the BOP energies, which are clearly overestimated due to the simultaneous determination of nuclear and electronic wave functions in the MCBOP method. The optimum H-H bond distance of MCBOP is 0.785 Å, which is much longer than that of BOP, 0.746 Å, due to the overestimation of anharmonic effect on the PEC along the covalent bond direction. By including the *en* correlation effects, the overall PEC shape of MCBOP + EPC is similar to that of BOP, and the optimum bond distance, 0.750 Å, reasonably becomes shorter. Thus, these results clearly support that our functional provides accurate *en* correlation to reproduce the PEC of the H_2 molecule around the equilibrium structure. In the near future, we will discuss the behavior of our correlation functional for the large internuclear distance, which requires both unrestricted and multireference treatments to reproduce the PEC correctly.

In summary, we have proposed a CS-type electron-nucleus (*en*) correlation functional with the aid of the third-order Taylor expansion and the definition of β_{en}. We have found that our functional accurately reproduces *ep* correlations for the optimized structures of various H-contained molecules. We have also demonstrated that MCBOP using the our *en* correlation functional provides the physically correct effective potential energy curve of the H_2 molecule. In the present paper, we determined the parameter β_{en} to reproduce the BOP energies corrected with zero-point vibrations. We, however, expect that the performance of our *en* correlation functional would be improved by fitting it to reproduce more accurate factors such as the MCQMC-optimized Jastrow factor mentioned above. Furthermore, we need a general formula for the *en* functional to evaluate the *en* correlations comprehensively and to be applied to time-dependent external potential issue [29,30].

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