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A new exchange-correlation functional free of delocalization and static correlation errors

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Abstract

Predicting the correct binding curves of H_2^+ and H_2 systems presents a great challenge in current applications of electronic density functional theory. Here we report a new functional for the exchange-correlation energy based on the weighted density approximation and the classical mapping method. With the exact sum rule for the exchange-correlation hole and accurate correlation functions of uniform electrons as the input, the new functional is free of delocalization and static correlation errors. It yields the exact results for any one-electron systems and the correct asymptotic limit of the binding energy between hydrogen atoms.

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Since proposed in the 1960s,[1, 2] the Kohn-Sham density functional theory (KSDFT) has evolved into one of the most powerful computational tools for predicting the properties of multi-body electronic systems.[3-14] The main idea behind KSDFT is to construct a virtually non-interacting reference system that reproduces the electronic structure of the target system of practical concern. While the mathematic procedure is formally exact, KSDFT calculations hinge on various approximations for the so-called exchange-correlation energy, $E_{\mathrm{xc}}[\rho]$, which accounts for multi-body correlation effects arising from addition of electrostatic interactions to the reference. Although KSDFT has been remarkably successful, all existing functionals fail to capture the asymptotic limit of binding energy even for systems as simple as H_2^+ and H_2.[15] In this work, we introduce a new exchange-correlation functional by utilizing the exact sum rule for the exchange-correlation hole and accurate radial distribution functions of uniform electron gases at all densities. The new functional is free of delocalization and static correlation errors and yields the correct binding behavior. The numerical performance of the new functional has been calibrated with exact results for the hydrogen test set (HTS).

Formulation of an accurate functional for $E_{\mathrm{xc}}[\rho]$ has been a perennial pursuit in the theoretical development of KSDFT.[16-21] Up to now, popular exchange-correlation functionals are almost exclusively based on the local density approximation (LDA) plus corrections with various forms of the generalized gradient approximation (GGA).[4-6] LDA represents $E_{\mathrm{xc}}[\rho]$ in terms of that corresponding to a uniform electron gas (UEG) at the local density:

$$E_{\mathrm{xc}}^{\mathrm{LDA}}[\rho] = \int \varepsilon_{\mathrm{xc}}^{\mathrm{UEG}}[\rho(\mathbf{r})]\,\mathrm{d}\,\mathbf{r} \tag{1}$$

Notwithstanding its simplicity, LDA performs surprisingly well for many electronic systems.[3] One possible reason for such good performance is that LDA obeys the exact sum rule for the exchange-correlation hole $\rho_{\mathrm{xc}}(\mathbf{r}_1,\mathbf{r}_2)$ [22]

$$\int \rho_{\mathrm{xc}}(\mathbf{r}_1,\mathbf{r}_2)\mathrm{d}\mathbf{r}_2 = -1 \tag{2}$$

While this important sum rule is preserved in various improvements of LDA, often through introduction of empirical parameters, one major limitation of existing exchange-correlation functionals, LDA and its GGA modifications included, lies in the erroneous inclusion of the self-interaction energy, i.e., the interaction of an electron with itself.[23] Unless the exchange-correlation energy exactly cancels the spurious electron-electron interaction, KSDFT is deemed to have the delocalization error as plainly manifested in one-electron systems such as H_2^+.

The exchange-correlation energy and the exchange correlation hole are formally related through, in atomic units (a.u.),

$$E_{\mathrm{xc}} = \frac{1}{2}\iint \frac{\rho(\mathbf{r})\rho_{\mathrm{xc}}(\mathbf{r},\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}' \tag{3}$$

According to the adiabatic connection for the exchange-correlation energy,[22, 24, 25] the exchange-correlation hole is given by

$$\rho_{\mathrm{xc}}(\mathbf{r},\mathbf{r}') = \int_0^1 \rho(\mathbf{r}')h(\mathbf{r},\mathbf{r}';\lambda)\mathrm{d}\lambda \equiv \rho(\mathbf{r}')\bar{h}(\mathbf{r},\mathbf{r}') \tag{4}$$

where $h(\mathbf{r},\mathbf{r}';\lambda)$ represents the two-body density correlation function of a reference system with the electron density profile identical to that of the real system but with the Coulomb potential scaled by a factor of $0 \le \lambda \le 1$. When $\lambda = 0$, we have non-interacting Fermions; and $\lambda = 1$ corresponds to the real system under consideration. Eq.(4) can be derived from a functional integration of the exchange-correlation energy with respect to the two-body Coulomb potential between electrons.

In terms of correlation functions, LDA amounts to the approximation of the exchange-correlation hole with that of a uniform system: [26]

$$\rho_{\mathrm{xc}}^{\mathrm{(LDA)}}(\mathbf{r},\mathbf{r}') = \rho(\mathbf{r})\bar{h}(|\mathbf{r}-\mathbf{r}'|;\rho(\mathbf{r})) \tag{5}$$

where $\bar{h}(r) = \int_0^1 h(r,\lambda)\,\mathrm{d}\lambda$ is the average density correlation function of a uniform electron gas with local density $\rho(\mathbf{r})$. With an accurate expression for the correlation functions of uniform electron systems, LDA naturally satisfies the sum rule given by Eq. (2). In conventional weighted density approximations (WDA), [27-30] the average pair correlation function of the inhomogeneous electron gas is expressed in terms of that a uniform system with a locally weighted density

$$\bar{h}(\mathbf{r},\mathbf{r}') = \bar{h}^{\mathrm{UEG}}[|\mathbf{r}-\mathbf{r}'|;\bar{\rho}(\mathbf{r})] \tag{6}$$

In Eq.(6), the weighted density, $\bar{\rho}(\mathbf{r})$, is defined by the exchange-correlation sum rule, *viz.* Eq.(2), and the density correlation functions of uniform electron systems are typically obtained from either the random phase approximation [3] or quantum Monte Carlo simulations (QMC)[31]. Recently, empirical means has also been proposed for best representation of the pair correlation functions of uniform electrons.[32] Eqs.(6) and (2) result in a complicated expression for the exchange-correlation potential

$$
\begin{aligned}
v_{xc}(\mathbf{r}) = \frac{\delta E_{\mathrm{xc}}}{\delta\rho(\mathbf{r})} &= \int \rho(\mathbf{r}_1)\frac{\bar{h}^{\mathrm{UEG}}(|\mathbf{r}-\mathbf{r}_1|,\bar{\rho}(\mathbf{r})) + \bar{h}^{\mathrm{UEG}}(|\mathbf{r}-\mathbf{r}_1|,\bar{\rho}(\mathbf{r}_1))}{2|\mathbf{r}-\mathbf{r}_1|}\mathrm{d}\mathbf{r}_1 \\
&-\frac{1}{2}\iint \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{r_{12}}\frac{\partial\bar{h}^{\mathrm{UEG}}(r_{12},\bar{\rho}(\mathbf{r}_1))}{\partial\bar{\rho}(\mathbf{r}_1)}\frac{\bar{h}^{\mathrm{UEG}}(|\mathbf{r}-\mathbf{r}_1|,\bar{\rho}(\mathbf{r}_1))}{\int\rho(\mathbf{r}_3)\frac{\partial\bar{h}^{\mathrm{UEG}}(r_{13},\bar{\rho}(\mathbf{r}_1))}{\partial\bar{\rho}(\mathbf{r}_1)}\mathrm{d}\mathbf{r}_3}\mathrm{d}\mathbf{r}_1\mathrm{d}\mathbf{r}_2
\end{aligned}
\tag{7}
$$

Whereas introduction of the weighted density improves the numerical performance of LDA, KSDFT calculations based on Eq. (7) are computationally much more demanding in comparison to those based on GGA. More important, Eq.(7) gives an incorrect asymptotic limit for the exchange-correlation potential, i.e., it predicts $v_{\mathrm{xc}}(\mathbf{r}) \sim 1/2r$ instead of $1/r$ as $r \to \infty$. This inconsistency is due to the lost of symmetry between **r** and **r**' in equation (6), which has once been treated by some specific methods. [29, 30] We can avoid both limitations using a simple weighted density approximation [27, 28]

$$
v_{xc}(\mathbf{r}) \approx \int \rho(\mathbf{r}_1)\frac{\bar{h}^{\mathrm{UEG}}(|\mathbf{r}-\mathbf{r}_1|,\bar{\rho}(\mathbf{r}))}{|\mathbf{r}-\mathbf{r}_1|}\mathrm{d}\mathbf{r}_1 \tag{8}
$$

where $\bar{\rho}(\mathbf{r})$ is determined from the sum rule the exchange-correlation hole

$$
\rho_{\mathrm{xc}}(\mathbf{r},\mathbf{r}') \approx \rho(\mathbf{r}')\bar{h}^{UEG}(|\mathbf{r}-\mathbf{r}'|;\bar{\rho}(\mathbf{r})) \tag{9}
$$

Apparently, Eq.(8) satisfies the asymptotic limit at large r and is computationally much simpler. The detailed algorithm of this method is presented in the supporting information.

To calculate the weighted density at each position, we need an efficient way to predict the radial distribution functions (RDFs) of uniform electrons at all densities. Toward that end, we use the classical mapping method.[33, 34] As shown in our previous work,[35, 36] classical mapping is computationally efficient and numerically accurate for predicting the RDFs in good agreement with QMC. For example, Figure 1 shows the theoretical predictions of $g(r) \equiv \bar{h}^{\mathrm{UEG}}(r)+1$ for three uniform electron gases with the Wigner-Seitz radius $r_s = (3/4\pi\rho)^{-1/3}$ = 1, 10 and 40 a.u., representing high, medium and low electron densities, respectively. While these functions look similar in dimensionless length scales (Fig 1a), we like to emphasize that they are drastically different in absolute units (Fig 1b). For r_s = 40 a.u., $g(r)$ is essentially 0 at the range of $r < 10$ a.u.. As discussed below, the disappearance of $g(r)$ at low density is critically important to describe the asymptotic behavior of chemical binding energy.

For systems containing only a single electron (such as H_2^+ binding), there is no electron-electron interaction. In this case, the exchange-correlation energy must cancel the Coulomb interaction

$$E_{xc} = -E_{ee} \tag{10}$$

Conventional functionals for E_{xc} do not exclude the self-interaction because Eq.(10) is not satisfied. By contrast, as demonstrate below, our new functional is exact for any one-electron systems. Figure 2 shows that the new functional is able to reproduce the whole binding curve of H_2^+ predicted by the Schrödinger equation. The H_2^+ system has been a benchmark to calibrate the delocalization error of new exchange-correlation functionals.

The perfect match of the results from the KSDFT and the Schrödinger equation for one-electron systems is not a coincidence. For one-electron systems, the electron density satisfies the normalization condition

$$\int \rho(\mathbf{r})\mathrm{d}\mathbf{r} = 1 \tag{11}$$

Comparing Eq.(11) with the sum rule

$$\int \rho(\mathbf{r}')\bar{h}^{\mathrm{UEG}}(|\mathbf{r}-\mathbf{r}'|,\bar{\rho}(\mathbf{r}))\mathrm{d}\mathbf{r}' = -1 \tag{12}$$

we find that the only solution for Eq.(12) is $\bar{\rho}(\mathbf{r})=0$. Because $\bar{h}^{\mathrm{UEG}}(r;\bar{\rho}(\mathbf{r})=0)=-1$, Eq.(10) is exactly satisfied and thus the KSDFT calculation leads to the correct results. The conventional exchange-correlation functionals, including previous WDA methods [29, 32], fail for one-electron systems because they do not automatically capture the correct behavior of $\bar{h}_{\mathrm{xc}}(\mathbf{r},\mathbf{r}')$, *viz.* $\bar{h}_{\mathrm{xc}}(\mathbf{r},\mathbf{r}')=-1$, at the one-electron limit. Apparently, the classical mapping method provides accurate descriptions of the pair correlation functions at the low density limit, leading to the exact prediction of one electron system.

For the H_2 system, the asymptotic limit of binding energy is related to the spin degeneracy of electrons, i.e., due to the static correlations. Such degeneracy effect is not automatically captured in conventional KSDFT calculations. However, our new exchange-correlation functional is immune to the statistic correlation fallacy. Figure 3 shows the binding energy for H_2 from this work in comparison with those from alternative methods in the literature. As indicated by Cohen *et al*., [15] LDA, Becke, three-parameter, Lee-Yang-Parr (B3LYP) and Hatree-Fock (HF) all predict erroneous binding energy at large separation. The static correlation error arises from the degeneracy of the spin states $[\uparrow,0]$ and $[\frac{1}{2}\uparrow,\frac{1}{2}\downarrow]$ for an isolated H atom. For the H_2 system, the electron spin densities are always identical, $\rho_{\uparrow}(\mathbf{r})=\rho_{\downarrow}(\mathbf{r})$. At infinite separation, each H atom has the energy of $E[\frac{1}{2}\uparrow,\frac{1}{2}\downarrow]$. Because we consider two isolated H atoms, each with only one spin type of energy $E[1\uparrow,0\downarrow]$, as the reference state for H_2 binding, the asymptotic limit of binding energy should be

$$\Delta E(r=\infty)=2\left\{E[\frac{1}{2}\uparrow,\frac{1}{2}\downarrow]-E[1\uparrow,0\downarrow]\right\}=0 \tag{13}$$

Eq.(13) is not automatically satisfied in conventional KSDFT calculations, leading to the incorrect asymptotic limit for the binding energy.

Our new functional captures the correct asymptotic limit of the H_2 binding energy because the classical mapping allows us to calculate the density correlation function accurately at very low electron densities. In classical mapping [37], the fractional spin effect is accounted for in the average pair correlation function $\bar{h}_{\mathrm{xc}}^{\mathrm{UEG}}(r,\rho,\zeta)$:

$$\bar{h}_{\mathrm{xc}}^{\mathrm{UEG}}(r;\rho,\zeta)=\left(\frac{1+\zeta}{2}\right)^2\bar{h}_{\uparrow\uparrow}^{\mathrm{UEG}}(r;\rho,\zeta)+\frac{1-\zeta^2}{2}\bar{h}_{\uparrow\downarrow}^{\mathrm{UEG}}(r;\rho,\zeta)+\left(\frac{1-\zeta}{2}\right)^2\bar{h}_{\downarrow\downarrow}^{\mathrm{UEG}}(r;\rho,\zeta) \tag{14}$$

where ζ is the spin polarization. When $\rho\to 0$, the asymptotic limits for $\bar{h}_{\uparrow\uparrow}^{\mathrm{UEG}}(r,\rho,\zeta)$, $\bar{h}_{\uparrow\downarrow}^{\mathrm{UEG}}(r,\rho,\zeta)$, and $\bar{h}_{\downarrow\downarrow}^{\mathrm{UEG}}(r,\rho,\zeta)$ become identical and independent of ζ. As a result, the low-density limit of $\bar{h}_{\mathrm{xc}}^{\mathrm{UEG}}(r,\rho,\zeta)$ is spin independent and approaches the exact result

$$\lim_{\rho\to 0}\bar{h}_{\mathrm{xc}}^{\mathrm{UEG}}(r,\rho,\zeta)=-1 \tag{15}$$

As discussed above for one-electron systems, a combination of Eq.(15) with the exchange-correlation sum rule, Eq.(2), leads to the exact results for both $E[\frac{1}{2}\uparrow,\frac{1}{2}\downarrow]$ and $E[1\uparrow,0\downarrow]$. In other words, our new functional is free from the static correlation error due to the theoretical construction rather than coincidence or artifact.

In spite of the correct asymptotic behavior, we must admit that our new functional yields the well depth of the binding curve not as accurate as that from B3LYP. The numerical error is introduced mainly in the approximation of the density correlation function of inhomogeneous systems, $h_{\mathrm{xc}}(\mathbf{r},\mathbf{r}')$, with those of reference uniform systems, $h_{\mathrm{xc}}^{UEG}(\mathbf{r},\bar{r})$. We believe that the numerical performance may be further improved by using a more sophisticated approximation for $h_{\mathrm{xc}}(\mathbf{r},\mathbf{r}')$. Figure 4 presents the exchange-correlation hole calculated from Eq. (4) and (6). The results may be compared with those from alternative methods (e.g., Figures 5 and 6 in reference [29]). We find that the uniform density approximation overestimates $\rho_{\mathrm{xc}}(\mathbf{r},\mathbf{r}')$ when $|\mathbf{r}-\mathbf{r}'|$ is large, implying too strong long-range correlations. At $r_{\text{H-H}} = 1.4$ bohr, $\rho_{\mathrm{xc}}(\mathbf{r},\mathbf{r}')$ from this work is similar to that from LDA (Fig 4a); while at $r_{\text{H-H}} = 5$ bohr, our result is close to that by Giesbertz *et al*. using the SX version of WDA. [29] The difference in the exchange-correlation hole explains why our prediction of the binding energy is much better than that by Giesbertz *et al*. [29]

In summary, we have proposed a new functional for the exchange-correlation energy based on the weighted density approximation and classical mapping. The new functional is free of the delocalization and static correlation errors commonly suffered in alternative methods. We have tested the numerical performance of the new functional for predicting both H_2^+ and H_2 binding curves, a standard test set for calibrating the strong correlations. For H_2^+, it exactly reproduces the whole binding curve; while for H_2, the theory reduces the correct asymptotic limit when $r \to \infty$.

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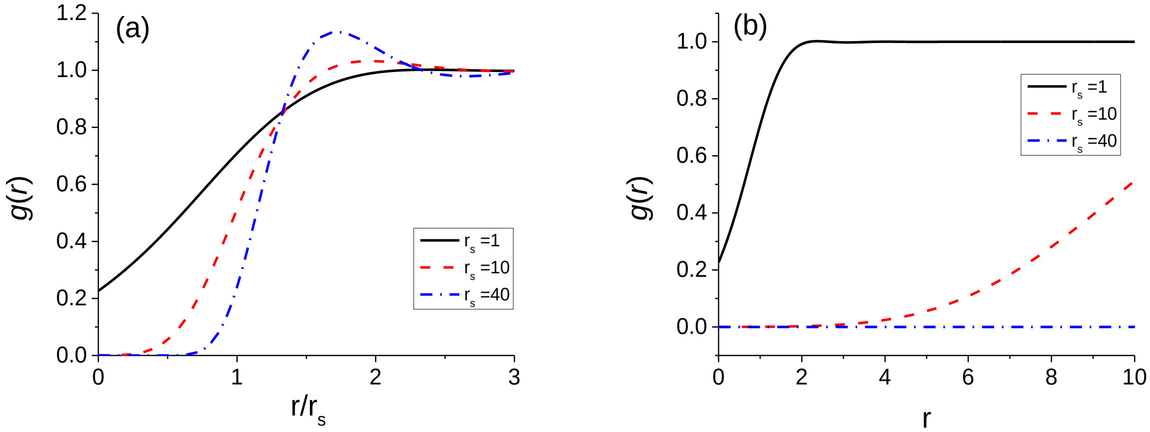

Figure 1. Radial distribution functions of three uniform electron gases with different densities. (a) distance in units of the Wigner-Seitz radius r_s ; (b) in atomic units, bohr.

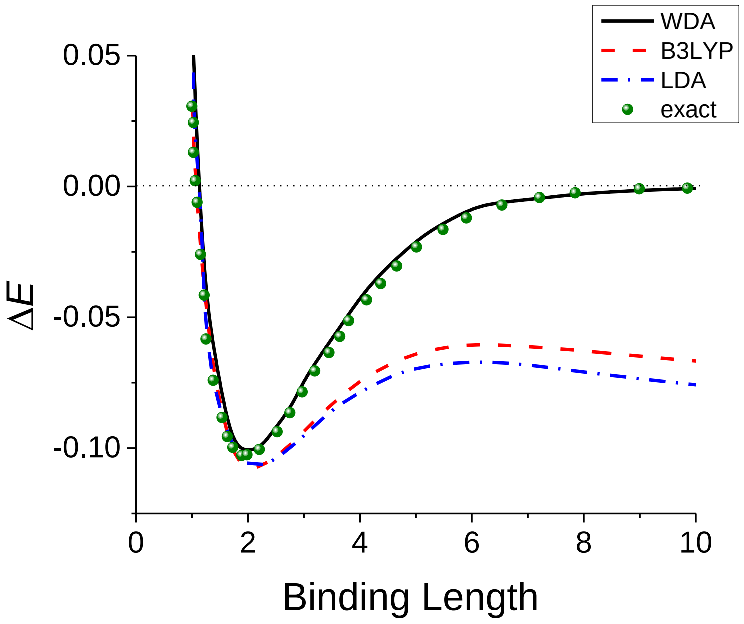

Figure 2. Binding energy curves (atom units) for H_2^+ calculated from different versions of KSDFT. B3LYP, LDA and exact results are from reference [15]. The binding length is referred to the center-to-center distance between the two H atoms.

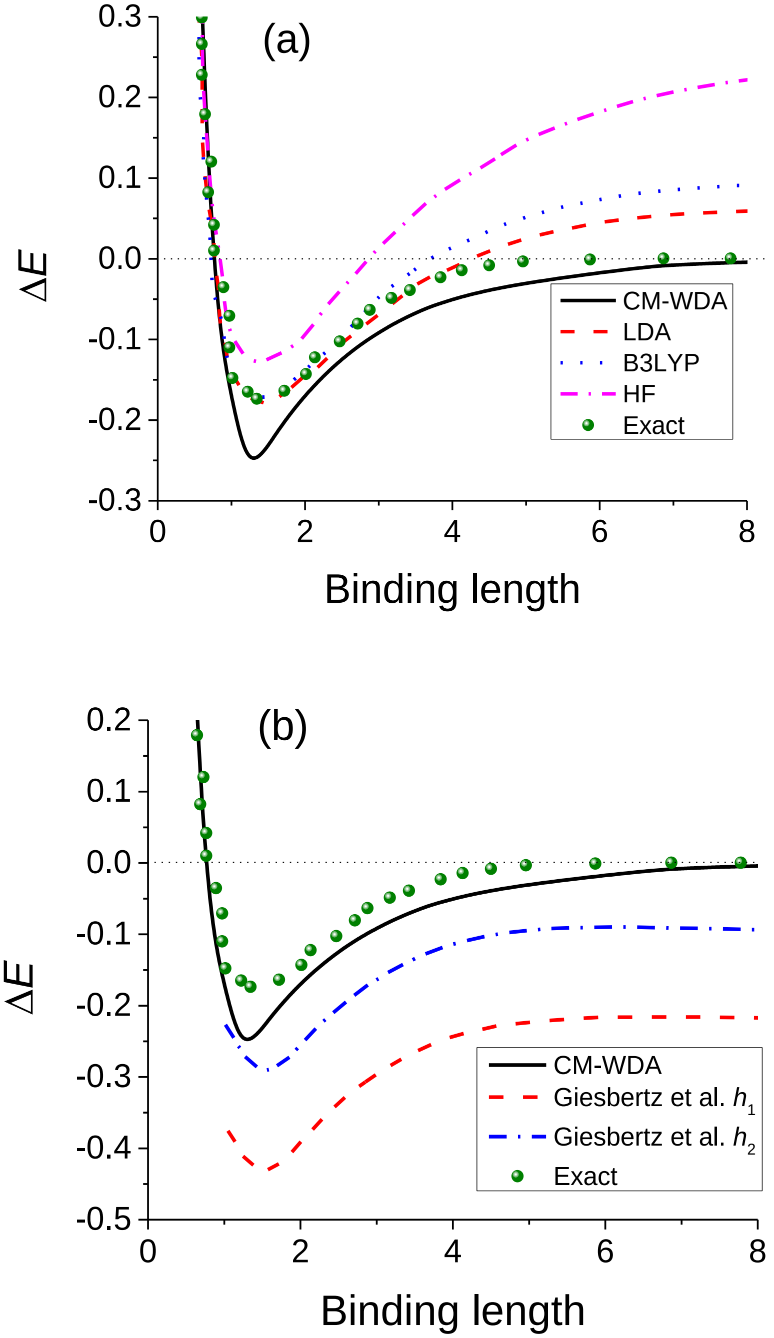

Figure 3. Binding energy curves for H_2 calculated from different methods (atom units). (a) Comparison of results from this work and those from alternative methods; [15] (b) Comparison of the binding energy curve from this work with those from several recent WDA methods. [29]

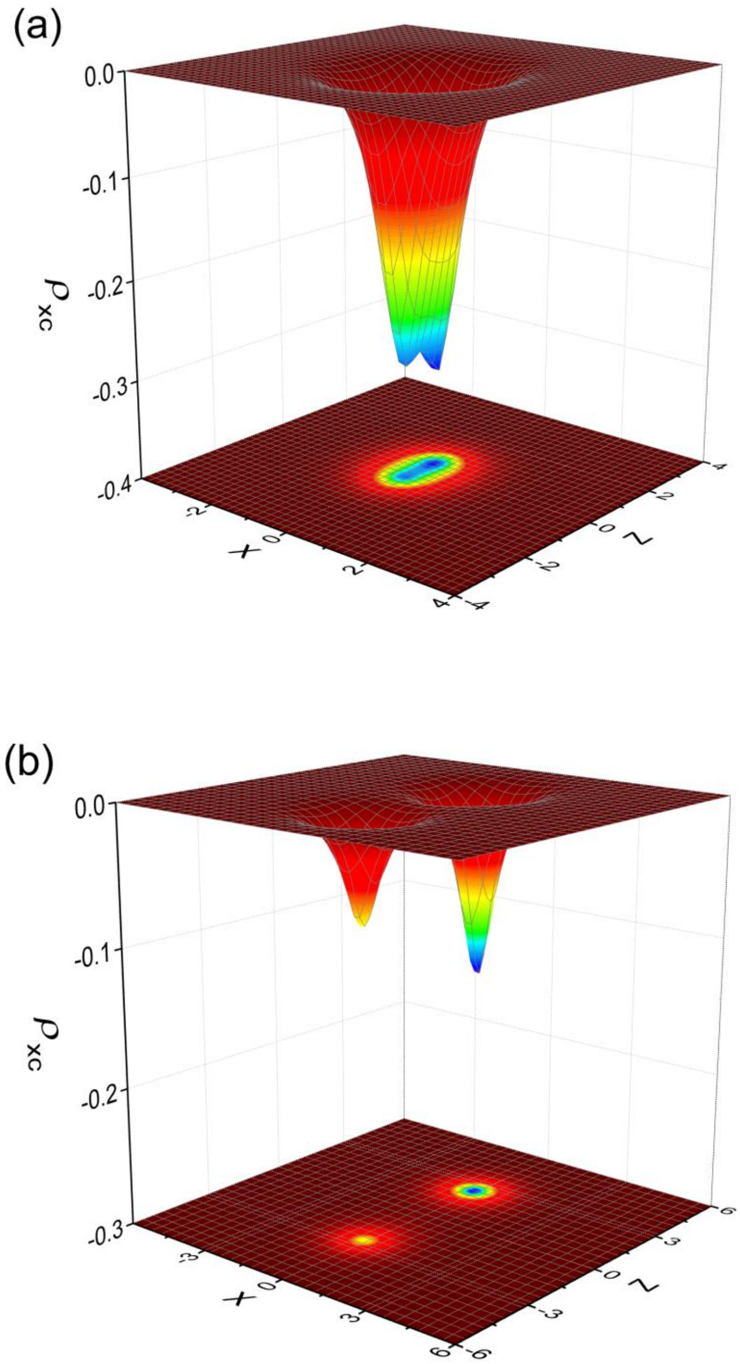

Figure 4 Exchange-correlation hole for the H_2 system with binding length (a) 1.4 bohr and (b) 5 bohr. The reference electron is set at 0.3 bohr to the left of the +*z* nucleus along *z* axis, i.e. (a) **r’** = (0 ,0 ,0.4); (b) **r’** = (0 ,0 ,2.2).

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Weighted density approximation and classical mapping result in a new exchange-correlation energy free of delocalization and static correlation errors