Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

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

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1. Solving $\bar{\rho}(\mathbf{r})$:

We define $M+1$ testing density:

$$\rho_i^{(t)} = i\Delta\rho^{(t)} \quad i = 0,1,\mathsf{L}\ M \qquad \text{* MERGEFORMAT (S1)}$$

Using classical mapping method, we calculate the corresponding pair correlation function of HEG:

$$h_i^{(t)}(r) = \bar{h}^{\mathrm{CM}}(r, \rho_i^{(t)}) \qquad \text{* MERGEFORMAT (S2)}$$

Once a density profile $\rho(\mathbf{r})$ is given, we calculate $M+1$ convolutions:

$$I_i(\mathbf{r}) = \int \rho(\mathbf{r}')h_i^{(t)}(|\mathbf{r}-\mathbf{r}'|)\,\mathrm{d}\mathbf{r}' \quad i = 0,1,\mathsf{L}\ M \qquad \text{* MERGEFORMAT (S3)}$$

Then, at each $\mathbf{r}$, we search an $I_j(\mathbf{r})$ from $\{I_0(\mathbf{r}), I_1(\mathbf{r}),\mathsf{L}\ I_M(\mathbf{r})\}$, by

$$I_j(\mathbf{r}) = -1 \qquad \text{* MERGEFORMAT (S4)}$$

And $\bar{\rho}(\mathbf{r})$ can be calculated by:

$$\bar{\rho}(\mathbf{r}) = \rho_j^{(t)} \qquad \text{* MERGEFORMAT (S5)}$$

According to this procedure, it is easy to check $\bar{\rho}(\mathbf{r})$ satisfy equation (2) in the main text. Additionally, the exchange correlation potential $v_{xc}(\mathbf{r})$ and Coulombic potential $v_{ee}(\mathbf{r})$ can be calculated together:

$$\begin{aligned} v_{xc}(\mathbf{r}) + v_{ee}(\mathbf{r}) &= \int \frac{\rho(\mathbf{r}')\bar{h}(|\mathbf{r}-\mathbf{r}'|)}{|\mathbf{r}-\mathbf{r}'|}\mathrm{d}\mathbf{r}' + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\mathrm{d}\mathbf{r}' \\ &= \int \rho(\mathbf{r}')\frac{1+\bar{h}(|\mathbf{r}-\mathbf{r}'|)}{|\mathbf{r}-\mathbf{r}'|}\mathrm{d}\mathbf{r}' \end{aligned} \qquad \text{* MERGEFORMAT (S6)}$$

We define:

$$\omega_i(r) = \frac{1+h_i^{(t)}(r)}{r} \quad i = 0,1,\mathrm{L}\ M \qquad \text{* MERGEFORMAT (S7)}$$

And

$$V_i(\mathbf{r}) = \int \rho(\mathbf{r}')\omega_i(|\mathbf{r}-\mathbf{r}'|)\mathrm{d}\mathbf{r}' \qquad \text{* MERGEFORMAT (S8)}$$

Then, $v_{xc}(\mathbf{r}) + v_{ee}(\mathbf{r})$ can be calculated from:

$$v_{xc}(\mathbf{r}) + v_{ee}(\mathbf{r}) = V_{j(\mathbf{r})}(\mathbf{r}) \qquad \text{* MERGEFORMAT (S9)}$$

In convolution of equation * MERGEFORMAT (S3) and * MERGEFORMAT (S8), Fast Fourier Transfer (FFT) is employed:

$$\int A(\mathbf{r}')B(\mathbf{r}-\mathbf{r}')\mathrm{d}\mathbf{r}' = \mathrm{F}^{-1}\{\mathrm{F}[A(\mathbf{r})]\mathrm{F}[B(\mathbf{r})]\} \qquad \text{* MERGEFORMAT (S10)}$$

In this way, direct integration can be avoid and the calculation speed is greatly improved.

2. Computational procedure

Self-consistent iteration is used to solve the density profile, the detailed procedure is as following:

1) Input necessary parameters, *e.g.*, number of electrons, coordinates of nucleus, pair correlation function calculated from classical mapping method.

2) Transform $h_i^{(t)}(r)$ and $\omega_i(r)$ into Fourier space, $h_i^{(t)}(k)$ and $\omega_i(k)$. (FFTW3 package)

3) Set initial guess of Kohn Sham potential, $v_{ks}(\mathbf{r}) = v_{ext}(\mathbf{r})$, set the converge flag as "false".

4) Solve one-body Schrödinger equation with Kohn Sham potential. (Janecek *et al.*'s package [1])

5) Generate new density profile from the wave function

$$\rho_{new}^{(i)}(\mathbf{r}) = \sum_j \psi_j^*(\mathbf{r})\psi_j(\mathbf{r}) \qquad \text{* MERGEFORMAT (S11)}$$

If it is the first step i =1, let $\rho^{(i)}(\mathbf{r}) = \rho_{new}^{(i)}(\mathbf{r})$; if $\rho^{(i)}(\mathbf{r})$ and $\rho_{new}^{(i)}(\mathbf{r})$ are close enough, set the converge flag as "true"; otherwise, let $\rho^{(i)}(\mathbf{r}) = (1-\kappa)\rho_{new}^{(i)}(\mathbf{r}) + \kappa\rho^{(i-1)}(\mathbf{r})$, where κ is set at 0.75 in this work.

6) Transform $\rho^{(i)}(\mathbf{r})$ into Fourier space and calculate $I_i(\mathbf{r})$ from equation * MERGEFORMAT (S3) and $V_i(\mathbf{r})$ from equation * MERGEFORMAT (S8) by FFT.

7) Obtain $j(\mathbf{r})$ form equation * MERGEFORMAT (S5) (discrete form of $\bar{\rho}(\mathbf{r})$).

8) Obtain $v_{xc}(\mathbf{r}) + v_{ee}(\mathbf{r})$ from equation * MERGEFORMAT (S9).

9) Calculate Kohn Sham potential $v_{ks}(\mathbf{r})$ as well as total energy.

10) If converge flag is “false”, go back to step 4, if “true”, go to the next step.

11) Output and end the calculation.

Reference:

1. S. Janecek and E. Krotscheck, *Computer Physics Communications*, 2008, **178**, 835-842.