Supplementary Materials for "When the density of the noninteracting reference system is not the density of the physical system in Density Functional Theory"

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I. DERIVATION

Here we derive in details the density of the physical system from the linear response theory for optimized effective potential (OEP)[1–3] and generalized OEP (GOEP) methods[4]. The total energy functional is

$$E_{v_{ext}} = T_s[\rho_s^\sigma(\mathbf{r},\mathbf{r}')] + J[\rho_s(\mathbf{r})] + \int d\mathbf{r} v_{\text{ext}}(\mathbf{r})\rho_s(\mathbf{r}) + E_{\text{xc}}^{\text{DFA}}, \tag{1}$$

where the first three terms on the right hand side are the kinetic energy, Hartree energy, and external energy respectively, which are explicit functionals of $\rho_s^\sigma(\mathbf{r})$ and $\rho_s^\sigma(\mathbf{r},\mathbf{r}')$; $E_{\text{xc}}^{\text{DFA}}$ is the exchange-correlation (XC) energy whose exact functional form is unknown, three types of functionals will be discussed below, i.e. $E_{\text{xc}}^{\text{DFA}}[\rho_s^\sigma(\mathbf{r})]$, $E_{\text{xc}}^{\text{DFA}}[\rho_s^\sigma(\mathbf{r},\mathbf{r}')]$, and $E_{\text{xc}}^{\text{DFA}}[\{\phi_{p\sigma}(\mathbf{r})\}, v_{\text{ext}}(\mathbf{r})]$. Here orbitals $\{\phi_{p\sigma}(\mathbf{r})\}$ and orbital energies $\{\varepsilon_{p\sigma}\}$ are obtained from the following one-electron Schrödinger equation

$$h_s^\sigma \phi_{p\sigma} = (-\frac{1}{2}\nabla^2 + v_s^\sigma)\phi_{p\sigma} = \varepsilon_{p\sigma}\phi_{p\sigma}. \tag{2}$$

The determination of OEP is formulated as an optimization problem with the following construction for the OEP,

$$v_s^\sigma(\mathbf{r}) = v_{\text{ext}}(\mathbf{r}) + v_{\text{Hxc}}^\sigma(\mathbf{r}). \tag{3}$$

Here the external potential $v_{\text{ext}}(\mathbf{r})$ is deliberately separated from the total effective potential $v_s^\sigma(\mathbf{r})$. $v_{\text{ext}}(\mathbf{r})$ remains unchanged for a specific system. $v_{\text{Hxc}}^\sigma(\mathbf{r})$ is the Hartree-exchange-correlation (Hxc) potential, which includes the rest of the effective potential and is different for different methods.

For OEP, when the minimal energy is reached for a specific system, the stationary condition is

$$\frac{\delta E_{v_{ext}}}{\delta v_s^\sigma(\mathbf{r})} = \frac{\delta E_{v_{ext}}}{\delta v_{\text{Hxc}}^\sigma(\mathbf{r})} = \sum_p \int d\mathbf{r}d\mathbf{r}' \frac{\delta E}{\delta \phi_{p\sigma}(\mathbf{r})}\left(\frac{\delta \phi_{p\sigma}(\mathbf{r})}{\delta v_s^\sigma(\mathbf{r}')}\right) + c.c. = 0. \tag{4}$$

In the direct optimization method of Yang and Wu[2, 5], $v_s^\sigma(\mathbf{r})$ is further selected as $v_s^\sigma(\mathbf{r}) = v_0(\mathbf{r}) + \sum_t b_t^\sigma g(\mathbf{r})$, where $v_0(\mathbf{r})$ is a fixed reference potential including the external potential, and $\{b_t^\sigma\}$ are the coefficients for the linear combination of a set of basis functions $\{g_t(\mathbf{r})\}$. This makes it more practical, because $\{g_t(\mathbf{r})\}$ only need to expand a small part of the effective potential.

The GOEP, $v_s^\sigma(\mathbf{r},\mathbf{r}')$,on the other hand, is a nonlocal potential in space and can be represented in the orbital basis as

$$v_s^\sigma(\mathbf{r},\mathbf{r}') = \sum_{pq}\langle\mathbf{r}|\phi_{p\sigma}\rangle v_{s,pq}^\sigma \langle\phi_{q\sigma}|\mathbf{r}'\rangle, \tag{5}$$

where p and q are orbital indices. Unlike the OEP method, the orbitals density matrix and orbitals from GOEP is fully relaxed because there is no restriction of the locality in real space[4]. When the energy minimum is reached, the derivatives below should be zero,

$$\frac{\partial E}{\partial v_{s,pq}^\sigma} = 0. \tag{6}$$

It has been proved that the optimization of the total energy with respect to the GOEP is equivalent to the orbital optimization (OO) method[6], thus at the stationary point of GOEP, the orthonormalization constrained derivatives of the total energy with respect to oribital obey[4]

$$\left(\frac{\delta E}{\delta \phi_{p\sigma}(\mathbf{r})}\right)_{\mathrm{O}} = 0, \tag{7}$$

where $(\delta E_{tot}/\delta\phi_{p\sigma}(\mathbf{r}))_{\mathrm{O}}$ is the energy functional derivative with respect to the orbital under the orthonormalization constraint $\langle\phi_{p\sigma}|\phi_{q\sigma}\rangle = \delta_{pq}$[7], as indicated by the subscript O. Now we discuss the electron densities in three different types of functionals.

A. When $E_{\mathrm{xc}}^{\mathrm{DFA}}$ is an explicit and continuous functional of the density $\rho_s^\sigma(\mathbf{r})$, the total energy functional is

$$E^{\mathrm{DFA}}[\rho_s^\sigma(\mathbf{r},\mathbf{r}')] = T_s[\rho_s^\sigma(\mathbf{r},\mathbf{r}')] + J[\rho_s(\mathbf{r})] + \int d\mathbf{r} v_{\mathrm{ext}}(\mathbf{r})\rho_s(\mathbf{r}) + E_{\mathrm{xc}}^{\mathrm{DFA}}[\rho_s^\sigma(\mathbf{r})]. \tag{8}$$

The g.s. energy is

$$E_v^{\mathrm{DFA}}(N) = \min_{\rho_s^\sigma(\mathbf{r},\mathbf{r}')} E^{\mathrm{DFA}}[\rho_s^\sigma(\mathbf{r},\mathbf{r}')], \tag{9}$$

which leads to one-electron Schrödinger equation with local potential. In this scenario, the nonlocal GOEP will reduce to a local potential. Therefore, $\rho_s(\mathbf{r})$ of Inv-OEP, OEP and GOEP are the same, which is equal to $\rho(\mathbf{r})$ from the linear response

$$\rho(\mathbf{r}) = \frac{\delta E_v^{\mathrm{DFA}}(N)}{\delta v_{\mathrm{ext}}(\mathbf{r})} = \rho_s(\mathbf{r}). \tag{10}$$

B. When $E_{\mathrm{xc}}^{\mathrm{DFA}}$ is an explicit and continuous functional of the noninteracting reference density matrix $\rho_s^\sigma(\mathbf{r},\mathbf{r}')$, the total energy functional is

$$E^{\mathrm{DFA}}[\rho_s^\sigma(\mathbf{r},\mathbf{r}')] = T_s[\rho_s^\sigma(\mathbf{r},\mathbf{r}')] + J[\rho_s(\mathbf{r})] + \int d\mathbf{r} v_{\mathrm{ext}}(\mathbf{r})\rho_s(\mathbf{r}) + E_{\mathrm{xc}}^{\mathrm{DFA}}[\rho_s^\sigma(\mathbf{r},\mathbf{r}')]. \tag{11}$$

Now, OEP and GKS/GOEP are not the same.

For OEP, the ground-state energy is the minimum with the local potential constraint,

$$E_v^{\mathrm{DFA}}(N) = \min_{\mathrm{v_s}(\mathbf{r})} E^{\mathrm{DFA}}[\rho_s^\sigma(\mathbf{r},\mathbf{r}')]. \tag{12}$$

The density of the physical system is

$$\begin{aligned}\rho(\mathbf{r}) &= \frac{\delta E_v^{\mathrm{DFA}}(N)}{\delta v_{\mathrm{ext}}(\mathbf{r})} \\ &= \rho_s(\mathbf{r}) + \sum_{i\sigma}\left[\int d\mathbf{r}_3 d\mathbf{r}_4 \left(\frac{\delta E^{\mathrm{DFA}}[\rho_s^\sigma(\mathbf{r}_1,\mathbf{r}_2)]}{\delta\phi_{i\sigma}(\mathbf{r}_3)}\right)_{\mathrm{O}} \left(\frac{\delta\phi_{i\sigma}(\mathbf{r}_3)}{\delta v_{\mathrm{s}}^\sigma(\mathbf{r}_4)}\right)\left(\frac{\delta v_{\mathrm{s}}^\sigma(\mathbf{r}_4)}{\delta v_{\mathrm{ext}}(\mathbf{r})}\right) + c.c.\right] &(13)\\ &= \rho_s(\mathbf{r}) + \sum_{i\sigma}\left[\int d\mathbf{r}_3 \left(\frac{\delta E^{\mathrm{DFA}}[\rho_s^\sigma(\mathbf{r}_1,\mathbf{r}_2)]}{\delta\phi_{i\sigma}(\mathbf{r}_3)}\right)_{\mathrm{O}} \left(\frac{\delta\phi_{i\sigma}(\mathbf{r}_3)}{\delta v_{\mathrm{s}}^\sigma(\mathbf{r})}\right) + c.c.\right] &(14)\end{aligned}$$

We now define the effective (nonlocal) one-electron effective Hamiltonian $h_{eff}^\sigma = -\frac{1}{2}\nabla^2 + v_{eff}^\sigma(\mathbf{r}_1,\mathbf{r}_2)$ through

$$\left(\frac{\delta E^{\mathrm{DFA}}[\rho_s^\sigma(\mathbf{r}_1,\mathbf{r}_2)]}{\delta\phi_{i\sigma}^*(\mathbf{r}_3)}\right) = h_{eff}^\sigma\phi_{i\sigma}(\mathbf{r}_3) = <\mathbf{r}_3|h_{eff}^\sigma\phi_{i\sigma}> . \tag{15}$$

For any hybrid functional, h_{eff}^σ is just the nonlocal GKS Hamiltonian. $\left(\frac{\delta E^{\mathrm{DFA}}[\rho_s^\sigma(\mathbf{r}_1,\mathbf{r}_2)]}{\delta\phi_{i\sigma}^*(\mathbf{r}_3)}\right)_{\mathrm{O}} = <\mathbf{r}_3|(I-P_\sigma)h_{eff}^\sigma\phi_{i\sigma}>$, where $P_\sigma = \sum_i|\phi_{i_\sigma}\rangle\langle\phi_{i\sigma}|$ [7]. Using the first-order perturbation theory, we have

$$\frac{\delta\phi_{i\sigma}(\mathbf{r}_3)}{\delta v_{\mathrm{s}}^\sigma(\mathbf{r})} = \sum_{q\neq i}\phi_{q\sigma}(\mathbf{r}_3)\frac{\phi_{q\sigma}^*(\mathbf{r})\phi_{i\sigma}(\mathbf{r})}{\varepsilon_{i\sigma}-\varepsilon_{q\sigma}}. \tag{16}$$

Combing Eqs. 13,15, and 16, we obtain

$$\begin{aligned}\rho(\mathbf{r}) &= \frac{\delta E_v^{\mathrm{DFA}}(N)}{\delta v_{\mathrm{ext}}(\mathbf{r})} \\ &= \rho_s(\mathbf{r}) + \sum_{i,a\neq i,\sigma}\left[\langle\phi_{i\sigma}|\,h^\sigma_{eff}\,|\phi_{a\sigma}\rangle\frac{\phi^*_{a\sigma}(\mathbf{r})\phi_{i\sigma}(\mathbf{r})}{\varepsilon_{i\sigma}-\varepsilon_{a\sigma}} + c.c.\right] \end{aligned} \tag{17}$$

This is the density of the physical system for functionals of the density matrix like hybrid functionals.

With GOEP/OO calculations, the ground-state energy is

$$E_v^{\mathrm{DFA}}(N) = \min_{v_s^\sigma(\mathbf{r},\mathbf{r}')} E^{\mathrm{DFA}}[\rho_s^\sigma(\mathbf{r},\mathbf{r}')] = \min_{\phi_{p\sigma}(\mathbf{r})} E^{\mathrm{DFA}}[\rho_s^\sigma(\mathbf{r},\mathbf{r}')], \tag{18}$$

which is equivalent to the GKS method with a nonlocal XC potential. The density of the physical system is

$$\begin{aligned}\rho(\mathbf{r}) &= \frac{\delta E_v^{\mathrm{DFA}}(N)}{\delta v_{\mathrm{ext}}(\mathbf{r})} \\ &= \rho_s(\mathbf{r}) + \sum_i\left[\int d\mathbf{r}_3 d\mathbf{r}_4 d\mathbf{r}_5\left(\frac{\delta E^{\mathrm{DFA}}[\rho_s^\sigma(\mathbf{r}_1,\mathbf{r}_2)]}{\delta\phi_{i\sigma}(\mathbf{r}_3)}\right)_{\mathrm{O}}\frac{\delta\phi_{i\sigma}(\mathbf{r}_3)}{\delta v_s^\sigma(\mathbf{r}_4,\mathbf{r}_5)}\frac{\delta v_s^\sigma(\mathbf{r}_4,\mathbf{r}_5)}{\delta v_{\mathrm{ext}}(\mathbf{r})} + c.c.\right] \\ &= \rho_s(\mathbf{r}). \end{aligned} \tag{19}$$

Therefore, GOEP and GKS fully minimize the total energy and give the density of the physical system as $\rho_s(\mathbf{r})$.

C. When $E_{\mathrm{xc}}^{\mathrm{DFA}}$ is an implicit functional of the noninteracting reference density matrix $\rho_s^\sigma(\mathbf{r},\mathbf{r}')$, and having explicit dependence on orbitals $\{\phi_{p\sigma}(\mathbf{r})\}$ and the external potential $v_{\mathrm{ext}}(\mathbf{r})$ (e.g. through eigenvalues), the total energy functional is

$$E^{\mathrm{DFA}}_{v_{ext}}[\{\phi_{p\sigma}(\mathbf{r})\}] = T_s[\rho_s^\sigma(\mathbf{r},\mathbf{r}')] + J[\rho_s(\mathbf{r})] + \int d\mathbf{r} v_{\mathrm{ext}}(\mathbf{r})\rho_s(\mathbf{r}) + E_{\mathrm{xc}}^{\mathrm{DFA}}[\{\phi_{p\sigma}(\mathbf{r})\}, v_{\mathrm{ext}}(\mathbf{r})]. \tag{20}$$

For OEP, the approximate ground-state energy is minimization with local potential constraint,

$$E^{\mathrm{DFA}}_{v_{ext}}(N) = \min_{v_s^\sigma(\mathbf{r})} E^{\mathrm{DFA}}_{v_{ext}}[\{\phi_{p\sigma}(\mathbf{r})\}]. \tag{21}$$

The density of the physical system is

$$\begin{aligned}\rho(\mathbf{r}) &= \frac{\delta E^{\mathrm{DFA}}_{v_{ext}}(N}{\delta v_{\mathrm{ext}}(\mathbf{r})} \\ &= \rho_s(\mathbf{r}) + \sum_{i\sigma}\left[\int d\mathbf{r}_3 d\mathbf{r}_4\left(\frac{\delta E^{\mathrm{DFA}}_{v_{ext}}[\{\phi_{p\sigma}(\mathbf{r})\}]}{\delta\phi_{p\sigma}(\mathbf{r}_3)}\right)_{\mathrm{O}}\left(\frac{\delta\phi_{p\sigma}(\mathbf{r}_3)}{\delta v_{\mathrm{s}}^\sigma(\mathbf{r}_4)}\right)\left(\frac{\delta v_{\mathrm{s}}^\sigma(\mathbf{r}_4)}{\delta v_{\mathrm{ext}}(\mathbf{r})}\right) + c.c.\right] + \frac{\delta E_{\mathrm{xc}}^{\mathrm{DFA}}[\{\phi_{p\sigma}(\mathbf{r})\}, v_{\mathrm{ext}}(\mathbf{r})]}{\delta v_{\mathrm{ext}}(\mathbf{r})} \end{aligned} \tag{22}$$

$$\begin{aligned} &= \rho_s(\mathbf{r}) + \sum_{p\sigma}\left[\int d\mathbf{r}_3\left(\frac{\delta E^{\mathrm{DFA}}[\rho_s^\sigma(\mathbf{r}_1,\mathbf{r}_2)]}{\delta\phi_{p\sigma}(\mathbf{r}_3)}\right)_{\mathrm{O}}\left(\frac{\delta\phi_{p\sigma}(\mathbf{r}_3)}{\delta v_{\mathrm{s}}^\sigma(\mathbf{r})}\right) + c.c.\right] + \frac{\delta E_{\mathrm{xc}}^{\mathrm{DFA}}[\{\phi_{p\sigma}(\mathbf{r})\}, v_{\mathrm{ext}}(\mathbf{r})]}{\delta v_{\mathrm{ext}}(\mathbf{r})} \\ &= \rho_s(\mathbf{r}) + \sum_{p,q\neq p,\sigma}\left[\int d\mathbf{r}_3\left(\frac{\delta E^{\mathrm{DFA}}[\rho_s^\sigma(\mathbf{r}_1,\mathbf{r}_2)]}{\delta\phi_{p\sigma}(\mathbf{r}_3)}\right)_{\mathrm{O}}\phi_{q\sigma}(\mathbf{r}_3)\frac{\phi^*_{q\sigma}(\mathbf{r})\phi_{p\sigma}(\mathbf{r})}{\varepsilon_{p\sigma}-\varepsilon_{q\sigma}} + c.c.\right] + \frac{\delta E_{\mathrm{xc}}^{\mathrm{DFA}}[\{\phi_{p\sigma}(\mathbf{r})\}, v_{\mathrm{ext}}(\mathbf{r})]}{\delta v_{\mathrm{ext}}(\mathbf{r})} \end{aligned} \tag{23}$$

Thus, the density of the physical system is not the same as the reference density $\rho_s(\mathbf{r})$ from OEP.

With GOEP or OO calculations, the ground-state energy is

$$E^{\mathrm{DFA}}_{v_{ext}}(N) = \min_{v_s^\sigma(\mathbf{r},\mathbf{r}')} E^{\mathrm{DFA}}_{v_{ext}}[\{\phi_{p\sigma}(\mathbf{r})\}] = \min_{\phi_{p\sigma}(\mathbf{r})} E^{\mathrm{DFA}}_{v_{ext}}[\{\phi_{p\sigma}(\mathbf{r})\}], \tag{24}$$

GOEP minimizes the total energy (without constraint on the potential being local). The density of the physical system is

$$\begin{aligned}
\rho(\mathbf{r}) &= \frac{\delta E_v^{\mathrm{DFA}}(N)}{\delta v_{\mathrm{ext}}(\mathbf{r})} \\
&= \rho_s(\mathbf{r}) + \sum_{p\sigma}\left[\int d\mathbf{r}_3 d\mathbf{r}_4 d\mathbf{r}_5 \left(\frac{\delta E^{\mathrm{DFA}}_{v_{ext}}[\{\phi_{p\sigma}(\mathbf{r})\}]}{\delta\phi_{p\sigma}(\mathbf{r}_3)}\right)_{\mathrm{O}} \frac{\delta\phi_{p\sigma}(\mathbf{r}_3)}{\delta v_s^\sigma(\mathbf{r}_4,\mathbf{r}_5)}\frac{\delta v_s^\sigma(\mathbf{r}_4,\mathbf{r}_5)}{\delta v_{\mathrm{ext}}(\mathbf{r})} + c.c.\right] \\
&+ \frac{\delta E_{\mathrm{xc}}^{\mathrm{DFA}}[\{\phi_{p\sigma}(\mathbf{r})\}, v_{\mathrm{ext}}(\mathbf{r})]}{\delta v_{\mathrm{ext}}(\mathbf{r})} \\
&= \rho_s(\mathbf{r}) + \frac{\delta E_{\mathrm{xc}}^{\mathrm{DFA}}[\{\phi_{p\sigma}(\mathbf{r})\}, v_{\mathrm{ext}}(\mathbf{r})]}{\delta v_{\mathrm{ext}}(\mathbf{r})}
\end{aligned} \tag{25}$$

Therefore, the GOEP/OO reference density $\rho_s(\mathbf{r})$ is not equal to the density of the physical system.

II. DENSITY OF PH-RPA

To illustrate our idea, we derive and calculate the density of the physical system with ph-RPA, MP2 and pp-RPA under the GOEP or OO formulation and compare it with the noninteracting reference density. Ph-RPA is denoted here as RPA for simplicity. The total energy of RPA is

$$E^{\mathrm{tot}} = E^{\mathrm{HF}} + E_{\mathrm{c}}^{\mathrm{RPA}}. \tag{26}$$

The first term, E^{HF}, is the HF total energy evaluated with the reference DFA $\rho_s(\mathbf{r}', \mathbf{r})$; while the second term is the RPA correlation energy

$$\begin{aligned}
E_{\mathrm{c}}^{\mathrm{RPA}} &= \frac{1}{2}\sum_{n>0}\omega_n - \frac{1}{2}\mathrm{Tr}\mathbf{A} \\
&= \frac{1}{2}\sum_{n>0}\sum_{ai,bj}[(X_n)^*_{ai}A_{ai,bj}(X_n)_{bj} + (X_n)^*_{ai}B_{ai,bj}(Y_n)_{bj} \\
&+ (Y_n)^*_{ai}B_{ai,bj}(X_n)_{bj} + (Y_n)^*_{ai}A_{ai,bj}(Y_n)_{bj}] - \frac{1}{2}\sum_{ai}A_{ai,ai},
\end{aligned} \tag{27}$$

with A and B being the RPA matrix components

$$\begin{aligned}
A_{ai,bj} &= h_{ab}\delta_{ij} - h_{ij}\delta_{ab} + \langle aj|ib\rangle; \\
B_{ai,bj} &= \langle ab|ij\rangle.
\end{aligned} \tag{28}$$

Here h is the DFA Hamiltonian of the noninteracting reference system. X_n and Y_n are eigenvectors of the RPA matrix

$$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ -\mathbf{B}^\dagger & -\mathbf{A}^\dagger \end{pmatrix}\begin{pmatrix} \mathbf{X}_n \\ \mathbf{Y}_n \end{pmatrix} = \omega_n \begin{pmatrix} \mathbf{X}_n \\ \mathbf{Y}_n \end{pmatrix}. \tag{29}$$

At the GOEP stationary point of the RPA energy functional, the density of the physical system derived from Eq. 25 takes the following expression

$$\rho^{\mathrm{RPA}}(\mathbf{x}) = \sum_i \phi_i(\mathbf{x})\phi_i^*(\mathbf{x}) + \sum_{ij} D_{ij}^{\mathrm{RPA}}\phi_j(\mathbf{x})\phi_i^*(\mathbf{x}) + \sum_{ab} D_{ab}^{\mathrm{RPA}}\phi_b(\mathbf{x})\phi_a^*(\mathbf{x}). \tag{30}$$

Here we define D_{ij}^{RPA} and D_{ab}^{RPA} as the occupied-occupied and virtual-virtual blocks of the RPA density matrix:

$$\begin{aligned}
D_{ij}^{\mathrm{RPA}} &= -\frac{1}{2}\sum_a\left\{\sum_{n>0}[(Y_n)_{ai}(Y_n)_{aj} + (X_n)_{ai}(X_n)_{aj}] - \delta_{ij}\right\}; \\
D_{ab}^{\mathrm{RPA}} &= \frac{1}{2}\sum_i\left\{\sum_{n>0}[(Y_n)_{ai}(Y_n)_{bi} + (X_n)_{ai}(X_n)_{bi}] - \delta_{ab}\right\}.
\end{aligned} \tag{31}$$

The first term in Eq. 30 is the density of the reference non-interaction system. The latter two terms originate from the external potential dependence of the RPA correlation energy. It is worth noting that the density of the physical system does not have any contribution from the occupied-virtual block.

III. DENSITY OF MP2

Here we discuss the MP2 correlation energy functional. In order to keep the total energy invariant with respect to orbital rotations within each subspace (occupied or virtual), we need to start from the Hylleraas function representation of the MP2 energy[8]. The Hylleraas function can be expanded by orbitals and the Fock operator,

$$E_c^{\mathrm{MP2}} = \frac{1}{4}\sum_{ijab} t_{ab}^{ij}\langle ij||ab\rangle + t_{ab}^{ij*}\langle ab||ij\rangle + \sum_{ij} D_{ij}^{\mathrm{MP2}} F_{ij} + \sum_{ab} D_{ab}^{\mathrm{MP2}} F_{ab} \tag{32}$$

where $i, j, k, \cdots$ represent occupied orbitals and $a, b, c, \cdots$ represent virtual orbitals. In Eq. 32, F is the Fock operator, t is the MP2 wavefunction amplitude, and D is the MP2 density block. If the orbitals diagonalize the occupied and virtual subspaces of F, namely

$$\begin{aligned} F_{ij} &= \delta_{ij} F_{ii} = \varepsilon_i, \\ F_{ab} &= \delta_{ab} F_{aa} = \varepsilon_a \end{aligned} \tag{33}$$

the wavefunction amplitude t is then

$$t_{ab}^{ij} = -\frac{\langle ij||ab\rangle}{\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j} \tag{34}$$

And the MP2 density blocks are

$$\begin{aligned} D_{ij}^{\mathrm{MP2}} &= -\frac{1}{2}\sum_{kab} t_{ab}^{ik} t_{ab}^{jk*} \\ D_{ab}^{\mathrm{MP2}} &= \frac{1}{2}\sum_{ijc} t_{ac}^{ij*} t_{bc}^{ij} \end{aligned} \tag{35}$$

The total energy of MP2 is

$$E^{\mathrm{tot}} = E^{\mathrm{HF}} + E_c^{\mathrm{MP2}} \tag{36}$$

Note that the wavefunction amplitudes t always obey the condition that $\partial E^{\mathrm{tot}}/\partial t_{ab}^{ij} = 0$. At the SCF solution, the electron density is further expanded as

$$\rho^{\mathrm{MP2}}(\mathbf{x}) = \sum_i \phi_i(\mathbf{x})\phi_i^*(\mathbf{x}) + \sum_{ij} D_{ij}^{\mathrm{MP2}} \phi_j(\mathbf{x})\phi_i^*(\mathbf{x}) + \sum_{ab} D_{ab}^{\mathrm{MP2}} \phi_b(\mathbf{x})\phi_a^*(\mathbf{x}) \tag{37}$$

The first term in Eq. 37 is the non-interacting reference density. Notice that the non-interacting reference density is not the density of the physical system for MP2 functional.

IV. DENSITY OF PP-RPA

Here we discuss the RPA correlation energy functional in the particle-particle channel, denoted as pp-RPA. The eigenvalue equation for pp-RPA is

$$\omega_n = \begin{pmatrix} \mathbf{X}_n^\dagger & \mathbf{Y}_n^\dagger \end{pmatrix} \begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^\dagger & \mathbf{C} \end{pmatrix} \begin{pmatrix} \mathbf{X}_n \\ \mathbf{Y}_n \end{pmatrix} \tag{38}$$

where

$$\begin{aligned} A_{ab,cd} &= h_{ac}\delta_{bd} + h_{bd}\delta_{ac} + \frac{1}{2}\langle ab||cd\rangle \\ B_{ab,ij} &= \frac{1}{2}\langle ab||ij\rangle \\ C_{ij,kl} &= -h_{ik}\delta_{jl} - h_{jl}\delta_{ik} + \frac{1}{2}\langle ij||kl\rangle \end{aligned} \tag{39}$$

The pp-RPA correlation energy [9] is

$$E_c = \sum_n \omega_n^{N+2} - \mathrm{Tr}\mathbf{A} \tag{40}$$

The eigenvalue part is

$$\begin{aligned}\omega_n &= \mathbf{X}_n^\dagger \mathbf{A}\mathbf{X}_n + \mathbf{X}_n^\dagger \mathbf{B}\mathbf{Y}_n + \mathbf{Y}_n^\dagger \mathbf{B}^\dagger \mathbf{X}_n + \mathbf{Y}_n^\dagger \mathbf{C}\mathbf{Y}_n \\ &= \sum_{a>b,c>d} (X_n)^*_{ab} A_{ab,cd} (X_n)_{cd} + \sum_{a>b,i>j} (X_n)^*_{ab} B_{ab,ij} (Y_n)_{ij} \\ &+ (Y_n)^*_{ij} B_{ij,ab} (X_n)_{ab} + \sum_{i>j,k>l} (Y_n)^*_{ij} C_{ij,kl} (Y_n)_{kl}\end{aligned} \tag{41}$$

The corresponding derivative is

$$part1 = \sum_{a>b,c>d} (X_n)^*_{ab} (\phi_a^* \phi_c \delta_{bd} + \phi_b^* \phi_d \delta_{ac}) (X_n)_{cd} - \sum_{i>j,k>l} (Y_n)^*_{ij} (\phi_i^* \phi_k \delta_{jl} + \phi_j^* \phi_l \delta_{ik}) (Y_n)_{kl} \tag{42}$$

The trace part is

$$\mathrm{Tr}\mathbf{A} = \sum_{a>b} F_{aa} + F_{bb} + \langle ab||ab\rangle + \text{spin } \beta \text{ channel} + \sum_{a\bar{b}} F_{aa} + F_{\bar{b}\bar{b}} + \langle a\bar{b}|a\bar{b}\rangle \tag{43}$$

The corresponding derivative is

$$part2 = \sum_{a>b} (\phi_a \phi_a^* + \phi_b \phi_b^*) + \text{spin } \beta \text{ channel} + \sum_{a\bar{b}} (\phi_a \phi_a^* + \phi_{\bar{b}} \phi_{\bar{b}}^*) \tag{44}$$

And plus the reference density part $\rho_s^{\mathrm{ref}}(\mathbf{x}) = \sum_i^{\mathrm{occ}} \phi_i(\mathbf{x}) \phi_i^*(\mathbf{x})$.

V. ORIGINAL DATA

All calculations were performed in the QM^{4}D package[10]. We here list all data mentioned in the main text. The notation for RPA is different from the main text because here we calculate the dipoles with both ph- and pp-RPA. Here, ph or pp@X (where X is the functional of the chosen reference density functional) refer to the ph- or pp-RPA density of the physical system calculated with our GOEP method. In addition, the MP2 column refers to the MP2 density calculated with the couple perturbed Hartree Fock equation, while the GOEP-MP2 column refers to our GOEP calculations with MP2. In the Supplementary Materials, We only reported the dipole moments with the density of the physical system, not the noninteracting reference density. Some elements are left blank because imaginary eigenvalues were observed while performing the GOEP calculations The experimental reference data are from CCCBDB[11].

We first tested the basis set convergence with water molecule (Fig. 1). Diffusion basis functions are important, or the dipole moment can be highly overestimated. Def2-TZVPD can be considered as converged (within 0.02 Debye), which was used for all the calculations in the main text.

TABLE I. Dipole moments of H_2O calculated with different functionals.

Mol.	Ref.	Basis Set	HF	PBE	B3LYP	MP2	GOEP-MP2	ph@HF	ph@PBE	ph@B3LYP	pp@HF	pp@PBE	pp@B3LYP
H_2O	1.855	Def2-SVP	2.127	1.929	1.976	2.040	2.025	2.020	1.932	1.960	2.076	1.994	2.011
		Def2-TZVP	2.151	2.020	2.065	2.103	2.093	2.089	2.019	2.041	2.132	2.083	2.082
		Def2-SVPD	2.027	1.828	1.888	1.890	1.861	1.902	1.807	1.837	1.944	1.864	1.885
		Def2-TZVPD	1.977	1.789	1.848	1.864	1.838	1.886	1.800	1.827	1.915	1.838	1.858
		Def2-TZVPPD	1.977	1.790	1.849	1.845	1.819	1.861	1.767	1.796	1.904	1.833	1.845

TABLE II. Dipole moments of HF calculated with different functionals.

Mol.	Ref.	Basis Set	HF	PBE	B3LYP	MP2	GOEP-MP2	ph@HF	ph@PBE	ph@B3LYP	pp@HF	pp@B3LYP
HF	1.82	Def2-SVP	1.987	1.788	1.838	1.887	1.875	1.878	1.797	1.822	1.927	1.862
		Def2-TZVP	2.016	1.875	1.921	1.941	1.932	1.940	1.869	1.891	1.983	1.923
		Def2-SVPD	1.962	1.771	1.828	1.829	1.805	1.842	1.755	1.782	1.880	1.836
		Def2-TZVPD	1.921	1.740	1.796	1.806	1.786	1.827	1.746	1.771	1.857	1.805
		Def2-TZVPPD	1.924	1.745	1.800	1.795	1.775	1.811	1.725	1.751	1.850	1.802

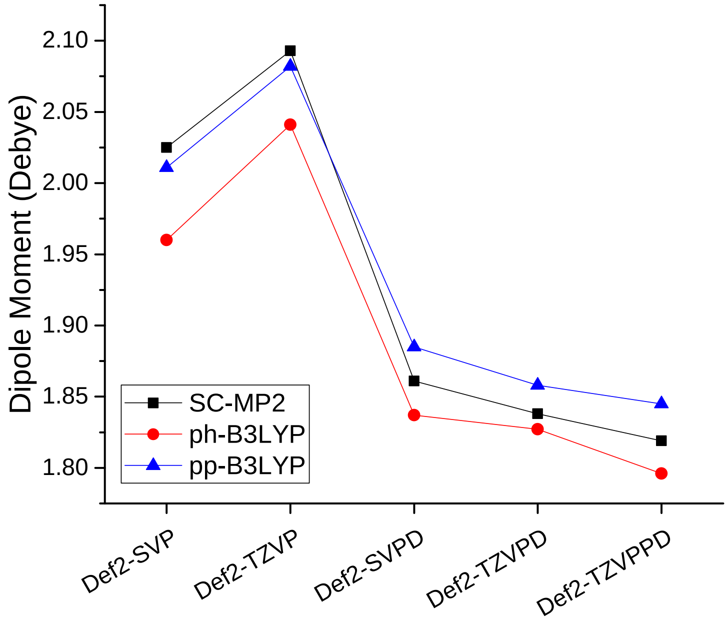

FIG. 1. Basis set convergence test with H_2O.

TABLE III. Dipole moments of HCl calculated with different functionals.

Mol.	Ref.	Basis Set	HF	B3LYP	MP2	GOEP-MP2	ph@HF	ph@B3LYP	pp@HF	pp@B3LYP
HCl	1.08	Def2-SVP	1.407	1.299	1.355	1.344	1.287	1.230	1.370	1.336
		Def2-TZVP	1.292	1.230	1.282	1.272	1.231	1.200	1.282	1.278
		Def2-SVPD	1.230	1.121	1.156	1.135	1.116		1.172	1.159
		Def2-TZVPD	1.181	1.087	1.125	1.113	1.100	1.064	1.141	1.136
		Def2-TZVPPD	1.182	1.087	1.101	1.088	1.069	1.026	1.125	1.115

TABLE IV. Dipole moments of H_2S calculated with different functionals.

Mol.	Ref.	Basis Set	HF	B3LYP	MP2	GOEP-MP2	ph@HF	ph@B3LYP	pp@HF	pp@B3LYP
H_2S	0.97	Def2-SVP	1.329	1.241	1.302	1.283	1.193	1.134	1.302	1.274
		Def2-TZVP	1.170	1.115	1.185	1.179	1.119	1.099	1.175	1.185
		Def2-SVPD	1.127	1.008	1.041	1.015	0.981		1.056	1.067
		Def2-TZVPD	1.073	0.971	1.019	1.005	0.986	0.954	1.034	1.019
		Def2-TZVPPD	1.072	0.968	0.989	0.970	0.942	0.900	1.011	

TABLE V. Dipole moments of NH_3 calculated with different functionals.

Mol.	Ref.	Basis Set	HF	B3LYP	MP2	GOEP-MP2	ph@HF	ph@B3LYP	pp@HF	pp@B3LYP
NH_3	1.47	Def2-SVP	1.806	1.702	1.763	1.747	1.731	1.686	1.780	1.744
		Def2-TZVP	1.778	1.727	1.761	1.755	1.745	1.713	1.776	1.752
		Def2-SVPD	1.669	1.569	1.584	1.558	1.584	1.536	1.614	1.579
		Def2-TZVPD	1.630	1.527	1.552	1.529	1.564	1.520	1.586	1.553
		Def2-TZVPPD	1.633	1.533	1.539	1.517	1.547	1.496	1.580	

TABLE VI. Dipole moments of CO calculated with different functionals. For C and O atoms, Def2-TZVPD and Def2-TZVPPD are same.

Mol.	Ref.	Basis Set	HF	B3LYP	MP2	GOEP-MP2	ph@HF	ph@B3LYP	pp@HF	pp@B3LYP
CO	0.122	Def2-SVP	0.233	0.218	0.405	0.418	0.116	0.206	0.128	
		Def2-TZVP	0.262	0.097	0.305	0.334	0.048		0.052	0.189
		Def2-SVPD	0.238	0.113	0.322	0.343			0.077	0.205
		Def2-TZVPD	0.261	0.091	0.293	0.323	0.039	0.124	0.043	

TABLE VII. Dipole moments of LiF calculated with different functionals.

Mol.	Ref.	Basis Set	HF	PBE	B3LYP	MP2	GOEP-MP2	ph@HF	ph@PBE	ph@B3LYP	pp@HF	pp@PBE	pp@B3LYP
LiF	6.284	Def2-SVP	6.363	5.454	5.663	5.840	5.846	6.075	5.762	5.881	6.098	5.890	5.950
		Def2-TZVP	6.592	6.012	6.164	6.337	6.278	6.441		6.326	6.441	6.377	6.515
		Def2-SVPD	6.528	6.161	6.260	6.388	6.338	6.426	6.318	6.360	6.430	6.315	6.340
		Def2-TZVPD	6.484	6.123	6.220	6.338	6.287	6.387		6.316	6.386	6.355	6.300
		Def2-TZVPPD	6.485	6.122	6.220	6.337	6.283	6.385		6.310	6.385	6.459	6.312

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