I. DERIVATION

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

\[ E_{\psi_{ext}} = T_s[\rho_s^0(r, r')] + J[\rho_s(r)] + \int d\mathbf{r} v_{ext}(\mathbf{r}) \rho_s(\mathbf{r}) + E_{xc}^{DFA}, \]  

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 \( \rho_s^0(\mathbf{r}) \) and \( \rho_s^0(\mathbf{r}, \mathbf{r}') \); \( E_{xc}^{DFA} \) is the exchange-correlation (XC) energy whose exact functional form is unknown, three types of functionals will be discussed below, i.e. \( E_{xc}^{DFA}[\rho_s^0(\mathbf{r})] \), \( E_{xc}^{DFA}[\rho_s^0(\mathbf{r}, \mathbf{r}')] \), and \( E_{xc}^{DFA}[(\phi_{\sigma\tau}(\mathbf{r})) \), \( v_{ext}(\mathbf{r}) \). Here orbitals \( \{\phi_{\sigma\tau}(\mathbf{r})\} \) and orbital energies \( \{\epsilon_{\sigma\tau}\} \) are obtained from the following one-electron Schrödinger equation

\[ \hat{h}_{\sigma}^0 \phi_{\sigma\tau} = (-\frac{1}{2} \nabla^2 + v_{\sigma}^0) \phi_{\sigma\tau} = \epsilon_{\sigma\tau} \phi_{\sigma\tau}. \]  

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

\[ \psi_{\sigma}^s(\mathbf{r}) = v_{ext}(\mathbf{r}) + v_{Hxc}^s(\mathbf{r}). \]  

Here the external potential \( v_{ext}(\mathbf{r}) \) is deliberately separated from the total effective potential \( v_{\sigma}^s(\mathbf{r}) \). \( v_{ext}(\mathbf{r}) \) remains unchanged for a specific system. \( v_{Hxc}^s(\mathbf{r}) \) 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

\[ \frac{\delta E_{\psi_{ext}}}{\delta \psi_{\sigma}^s(\mathbf{r})} = \sum_p \int d\mathbf{r}' \frac{\delta E}{\delta \phi_{\sigma\tau}(\mathbf{r})} \left( \frac{\delta \phi_{\sigma\tau}(\mathbf{r})}{\delta \psi_{\sigma}^s(\mathbf{r}')}) \right) + \text{c.c.} = 0. \]  

In the direct optimization method of Yang and Wu\cite{2, 5}, \( \psi_{\sigma}^s(\mathbf{r}) \) is further selected as \( \psi_{\sigma}^s(\mathbf{r}) = v_0(\mathbf{r}) + \sum b_{\sigma \tau}^t g_t(\mathbf{r}) \), where \( v_0(\mathbf{r}) \) is a fixed reference potential including the external potential, and \( \{b_{\sigma \tau}^t\} \) 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, \( \psi_{\sigma}^s(\mathbf{r}, \mathbf{r}'), \) on the other hand, is a nonlocal potential in space and can be represented in the orbital basis as

\[ \psi_{\sigma}^s(\mathbf{r}, \mathbf{r}') = \sum_{pq} (\mathbf{r}|\phi_{\sigma\tau}) \psi_{\sigma, pq}^s(\phi_{qs}|\mathbf{r}'), \]  

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\cite{4}. When the energy minimum is reached, the derivatives below should be zero,

\[ \frac{\partial E}{\partial \psi_{\sigma, pq}} = 0. \]
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 orbital obey[4]

\[
\left( \frac{\delta E}{\delta \phi_{\rho s}(r)} \right)_O = 0, \tag{7}
\]

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

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

\[
E_{v}^{\text{DFA}}[\rho_s^r(r, r')] = T_s[\rho_s^r(r, r')] + J[\rho_s^r(r)] + \int d\nu_{\text{ext}}(r)\rho_s^r(r) + E_{xc}^{\text{DFA}}[\rho_s^r(r)]. \tag{8}
\]

The g.s. energy is

\[
E_{v}^{\text{DFA}}(N) = \min_{\rho_s^r(r, r')} E_{v}^{\text{DFA}}[\rho_s^r(r, r')], \tag{9}
\]

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

\[
\rho(r) = \frac{\delta E_{v}^{\text{DFA}}(N)}{\delta \nu_{\text{ext}}(r)} = \rho_s(r). \tag{10}
\]

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

\[
E_{v}^{\text{DFA}}[\rho_s^r(r, r')] = T_s[\rho_s^r(r, r')] + J[\rho_s^r(r)] + \int d\nu_{\text{ext}}(r)\rho_s^r(r) + E_{xc}^{\text{DFA}}[\rho_s^r(r, r')]. \tag{11}
\]

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

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

\[
E_{v}^{\text{DFA}}(N) = \min_{\nu_{\text{d}}(r)} E_{v}^{\text{DFA}}[\rho_s^r(r, r')]. \tag{12}
\]

The density of the physical system is

\[
\rho(r) = \frac{\delta E_{v}^{\text{DFA}}(N)}{\delta \nu_{\text{ext}}(r)} = \rho_s(r) + \sum_{\sigma, i} \left[ \int d\mathbf{r}_3 d\mathbf{r}_4 \left( \frac{\delta E_{v}^{\text{DFA}}[\rho_s^r(\mathbf{r}_1, \mathbf{r}_2)]}{\delta \phi_{\rho s}(\mathbf{r}_3)} \right)_O \left( \frac{\delta \phi_{\rho s}(\mathbf{r}_4)}{\delta \nu_{\text{ext}}(\mathbf{r})} \right) + \text{c.c.} \right] \tag{13}
\]

\[
\rho(r) = \rho_s(r) + \sum_{\sigma, i} \left[ \int d\mathbf{r}_3 \left( \frac{\delta E_{v}^{\text{DFA}}[\rho_s^r(\mathbf{r}_1, \mathbf{r}_2)]}{\delta \phi_{\rho s}(\mathbf{r}_3)} \right)_O \left( \frac{\delta \phi_{\rho s}(\mathbf{r}_3)}{\delta \nu_{\text{ext}}(\mathbf{r})} \right) + \text{c.c.} \right] \tag{14}
\]

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

\[
\left( \frac{\delta E_{v}^{\text{DFA}}[\rho_s^r(\mathbf{r}_1, \mathbf{r}_2)]}{\delta \phi_{\rho s}(\mathbf{r}_3)} \right)_O = h_{\text{eff}}^s(\mathbf{r}_3) \phi_{\rho s}(\mathbf{r}_3) = \langle \mathbf{r}_3 | h_{\text{eff}}^s(\mathbf{r}) \phi_{\rho s} | \mathbf{r}_3 \rangle >. \tag{15}
\]

For any hybrid functional, \(h_{\text{eff}}^s\) is just the nonlocal GKS Hamiltonian. \(\left( \frac{\delta E_{v}^{\text{DFA}}[\rho_s^r(\mathbf{r}_1, \mathbf{r}_2)]}{\delta \phi_{\rho s}(\mathbf{r}_3)} \right)_O = \langle \mathbf{r}_3 | (I - P_\sigma) h_{\text{eff}}^s(\mathbf{r}) \phi_{\rho s} | \mathbf{r}_3 \rangle >\), where \(P_\sigma = \sum_i |\phi_{\mathbf{r}_i}\rangle \langle \phi_{\mathbf{r}_i}| [7]\). Using the first-order perturbation theory, we have

\[
\frac{\delta \phi_{\rho s}(\mathbf{r}_3)}{\delta \nu_{\text{ext}}(\mathbf{r})} = \sum_{q \neq i} \phi_{q \sigma}(\mathbf{r}_3) \frac{\phi_{q \sigma}^{*}(\mathbf{r}) \phi_{\rho \sigma}(\mathbf{r})}{\epsilon_{\rho \sigma} - \epsilon_{q \sigma}}. \tag{16}
\]
Thus, the density of the physical system is not the same as the reference density \( \rho \).

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

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

\[
\rho(r) = \frac{\delta E_{\text{DFA}}(N)}{\delta v_{\text{ext}}(r)}
\]

\[
= \rho_s(r) + \sum_{i,\alpha \neq \alpha,} \left[ \langle \phi_{i\sigma} | h_{\text{eff}} | \phi_{\alpha\sigma} \rangle - \frac{\delta v_{\text{ext}}(r)}{\epsilon_{i\sigma} - \epsilon_{\alpha\sigma}} \right] + c.c. \tag{17}
\]

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

\[
E_{\text{DFA}}^v(N) = \min_{v_{\text{ext}}^v(r,r')} E_{\text{DFA}}^v[\rho_s^v(r,r')] = \min_{\phi_{\rho\sigma}(r)} E_{\text{DFA}}^v[\rho_s^v(r,r')],
\]

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

\[
\rho(r) = \frac{\delta E_{\text{DFA}}(N)}{\delta v_{\text{ext}}(r)}
\]

\[
= \rho_s(r) + \sum_i \left[ \int dr_3 dr_4 dr_5 \left( \frac{\delta E_{\text{DFA}}[\rho_s^v(r_1,r_2)]}{\delta \phi_{i\sigma}(r_3)} \right) \frac{\delta \phi_{i\sigma}(r_3)}{\delta v_{\text{ext}}(r_4)} \frac{\delta v_{\text{ext}}(r_3)}{\delta v_{\text{ext}}(r)} + c.c. \right] + \rho_s(r). \tag{19}
\]

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

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

\[
E_{\text{DFA}}^{v_{\text{ext}}}[\{ \phi_{\rho\sigma}(r) \}] = T_s[\rho_s^v(r,r')] + J[\rho_s(r)] + \int dr v_{\text{ext}}(r) \rho_s(r) + E_{\text{xc}}^{\text{DFA}}[\{ \phi_{\rho\sigma}(r) \}, v_{\text{ext}}(r)]. \tag{20}
\]

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

\[
E_{\text{DFA}}^{v_{\text{ext}}}(N) = \min_{v_{\text{ext}}^o(r,r')} E_{\text{DFA}}^{v_{\text{ext}}}[\{ \phi_{\rho\sigma}(r) \}]. \tag{21}
\]

The density of the physical system is

\[
\rho(r) = \frac{\delta E_{\text{DFA}}(N)}{\delta v_{\text{ext}}(r)}
\]

\[
= \rho_s(r) + \sum_{p,\rho \neq \rho,} \left[ \int dr_3 dr_4 \left( \frac{\delta E_{\text{DFA}}[\rho_s^v(r_1,r_2)]}{\delta \phi_{p\sigma}(r_3)} \right) \frac{\delta \phi_{p\sigma}(r_3)}{\delta v_{\text{ext}}(r_4)} \frac{\delta v_{\text{ext}}(r_3)}{\delta v_{\text{ext}}(r)} + c.c. \right] + \rho_s(r). \tag{22}
\]

\[
= \rho_s(r) + \sum_{p,\rho \neq \rho,} \left[ \int dr_3 \left( \frac{\delta E_{\text{DFA}}[\rho_s^v(r_1,r_2)]}{\delta \phi_{p\sigma}(r_3)} \right) \frac{\delta \phi_{p\sigma}(r_3)}{\delta v_{\text{ext}}(r)} + c.c. \right] + \frac{\delta E_{\text{xc}}^{\text{DFA}}[\{ \phi_{\rho\sigma}(r) \}, v_{\text{ext}}(r)]}{\delta v_{\text{ext}}(r)} \tag{23}
\]

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

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

\[
E_{\text{DFA}}^{v_{\text{ext}}}(N) = \min_{v_{\text{ext}}^o(r,r')} E_{\text{DFA}}^{v_{\text{ext}}}[\{ \phi_{\rho\sigma}(r) \}] = \min_{\phi_{\rho\sigma}(r)} E_{\text{DFA}}^{v_{\text{ext}}}[\{ \phi_{\rho\sigma}(r) \}], \tag{24}
\]

GOEP minimizes the total energy (without constraint on the potential being local). The density of the physical
system is
\[ \rho(r) = \frac{\delta E_{v}^{\text{DFA}}(N)}{\delta v_{\text{ext}}(r)} \]
\[ = \rho_{s}(r) + \sum_{\rho_{\sigma}} \left[ \int \frac{d^{3}r_{3}d^{3}r_{4}d^{3}r_{5}}{\rho_{\sigma}^{3}(r_{3})} \left( \frac{\delta E_{v_{\text{ext}}}^{\text{DFA}}[\{\phi_{\rho_{\sigma}}(r)\}]}{\delta v_{\text{ext}}(r_{3})} \frac{\delta v_{\text{ext}}^{\prime}(r_{4}, r_{5})}{\delta v_{\text{ext}}(r)} + \text{c.c.} \right) \right] \]
\[ + \frac{\delta E_{\text{xc}}^{\text{DFA}}[\{\phi_{\rho_{\sigma}}(r)\}, v_{\text{ext}}(r)]}{\delta v_{\text{ext}}(r)} \]
\[ = \rho_{s}(r) + \frac{\delta E_{\text{xc}}^{\text{DFA}}[\{\phi_{\rho_{\sigma}}(r)\}, v_{\text{ext}}(r)]}{\delta v_{\text{ext}}(r)} \] \tag{25}

Therefore, the GOEP/OO reference density \( \rho_{s}(r) \) 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
\[ E_{\text{tot}} = E_{\text{HF}} + E_{c}^{\text{RPA}}. \tag{26} \]

The first term, \( E_{\text{HF}} \), is the HF total energy evaluated with the reference DFA \( \rho_{s}(r', r) \); while the second term is the RPA correlation energy
\[ E_{c}^{\text{RPA}} = \frac{1}{2} \sum_{n > 0} \omega_{n} - \frac{1}{2} \text{Tr} \mathbf{A} \]
\[ = \frac{1}{2} \sum_{n > 0} \sum_{a_{i}, b_{j}} [(X_{n})_{a_{i}a_{j}}^{*} A_{a_{i}b_{j}}(X_{n})_{b_{j}b_{j}} + (X_{n})_{a_{i}a_{j}} A_{a_{i}b_{j}}(X_{n})_{b_{j}b_{j}}] \]
\[ + \frac{1}{2} \sum_{a_{i}} A_{a_{i}a_{i}}, \tag{27} \]

with \( A \) and \( B \) being the RPA matrix components
\[ A_{a_{i}b_{j}} = h_{a_{i}b_{j}} - h_{b_{j}a_{i}} + (a_{i} | b_{j}); \]
\[ B_{a_{i}b_{j}} = (a_{i} | b_{j}). \tag{28} \]

Here \( h \) is the DFA Hamiltonian of the noninteracting reference system. \( X_{n} \) and \( Y_{n} \) are eigenvectors of the RPA matrix
\[ \left( \begin{array}{cc} \mathbf{A} & \mathbf{B} \\ -\mathbf{B}^{\dagger} & -\mathbf{A}^{\dagger} \end{array} \right) \left( \begin{array}{c} X_{n} \\ Y_{n} \end{array} \right) = \omega_{n} \left( \begin{array}{c} X_{n} \\ Y_{n} \end{array} \right). \tag{29} \]

At the GOEP stationary point of the RPA energy functional, the density of the physical system derived from Eq. 25 takes the following expression
\[ \rho^{\text{RPA}}(x) = \sum_{i} \phi_{i}(x) \phi_{i}^{\ast}(x) + \sum_{ij} D_{ij}^{\text{RPA}} \phi_{j}(x) \phi_{i}^{\ast}(x) + \sum_{ab} D_{ab}^{\text{RPA}} \phi_{a}(x) \phi_{b}^{\ast}(x). \tag{30} \]

Here we define \( D_{ij}^{\text{RPA}} \) and \( D_{ab}^{\text{RPA}} \) as the occupied-occupied and virtual-virtual blocks of the RPA density matrix:
\[ D_{ij}^{\text{RPA}} = -\frac{1}{2} \sum_{a} \left\{ \sum_{n > 0} [(Y_{n})_{a_{i}a_{j}}(Y_{n})_{a_{j}} - \delta_{ij}] \right\}; \]
\[ D_{ab}^{\text{RPA}} = \frac{1}{2} \sum_{i} \left\{ \sum_{n > 0} [(Y_{n})_{a_{i}b_{i}}(Y_{n})_{b_{i}} - \delta_{ab}] \right\}. \tag{31} \]

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,

\[
E_{\text{MP2}}^c = \frac{1}{4} \sum_{ijab} t_{ij}^{\ast}(ab) t_{ij}(ab) + \sum_{ij} D_{ij}^\text{MP2} F_{ij} + \sum_{ab} D_{ab}^\text{MP2} F_{ab}
\]  

(32)

where \(i, j, k, \ldots\) represent occupied orbitals and \(a, b, c, \ldots\) 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

\[
F_{ij} = \delta_{ij} F_{ii} = \varepsilon_i, \quad F_{ab} = \delta_{ab} F_{aa} = \varepsilon_a
\]  

(33)

the wavefunction amplitude \(t\) is then

\[
t_{ij}^{\ast} = -\frac{(ij|ab)}{\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j}
\]  

(34)

And the MP2 density blocks are

\[
D_{ij}^\text{MP2} = -\frac{1}{2} \sum_{kab} t_{ik}^{\ast} t_{jk}^{\ast}
\]

\[
D_{ab}^\text{MP2} = \frac{1}{2} \sum_{ijc} t_{ij}^{\ast} t_{ij}
\]  

(35)

The total energy of MP2 is

\[
E_{\text{tot}} = E_{\text{HF}} + E_{\text{MP2}}^c
\]  

(36)

Note that the wavefunction amplitudes \(t\) always obey the condition that \(\partial E_{\text{tot}}/\partial t_{ij}^{\ast} = 0\). At the SCF solution, the electron density is further expanded as

\[
\rho_{\text{MP2}}(\mathbf{x}) = \sum_i \phi_i(\mathbf{x}) \phi_i^{\ast}(\mathbf{x}) + \sum_{ij} D_{ij}^\text{MP2} \phi_j(\mathbf{x}) \phi_i^{\ast}(\mathbf{x}) + \sum_{ab} D_{ab}^\text{MP2} \phi_b(\mathbf{x}) \phi_a^{\ast}(\mathbf{x})
\]  

(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

\[
\omega_n = \begin{pmatrix} X_n & Y_n \end{pmatrix} \begin{pmatrix} A & B \cr B^\dagger & C \end{pmatrix} \begin{pmatrix} X_n \\ Y_n \end{pmatrix}
\]  

(38)

where

\[
A_{ab,cd} = h_{ac} \delta_{bd} + h_{bd} \delta_{ac} + \frac{1}{2} \langle ab|cd \rangle
\]

\[
B_{ab,ij} = \frac{1}{2} \langle ab|ij \rangle
\]

\[
C_{ij,kl} = -h_{ik} \delta_{jl} - h_{jl} \delta_{ik} + \frac{1}{2} \langle ij|kl \rangle
\]  

(39)
The pp-RPA correlation energy \([9]\) is

\[
E_c = \sum_n \omega_n^{N+2} - \text{Tr}A
\]

(40)

The eigenvalue part is

\[
\omega_n = X_n^a A X_n^b + Y_n^a B Y_n^b + Y_n^b C Y_n^a
\]

\[
= \sum_{a>b, c>d} (X_n^a)^* A_{ab,cd} (X_n^c)_{cd} + \sum_{a>b, i>j} (X_n^a)^* B_{ab,ij} (Y_n^i)_{ij}
\]

\[
+ (Y_n^i)_{ij} B_{ij,ab} (X_n^a)_{ab} + \sum_{i>j, k>l} (Y_n^i)^* C_{ijkl} (Y_n^k)_{kl}
\]

(41)

The corresponding derivative is

part 1 = \[
\sum_{a>b, c>d} (X_n^a)^* (\phi_a^* \phi_c \delta_{bd} + \phi_b^* \phi_d \delta_{ac}) (X_n^c)_{cd} - \sum_{i>j, k>l} (Y_n^i)^* (\phi_i^* \phi_k \delta_{jl} + \phi_j^* \phi_l \delta_{ik}) (Y_n^k)_{kl}
\]

(42)

The trace part is

\[
\text{Tr}A = \sum_{a>b} F_{aa} + F_{bb} + (ab||ab) + \text{spin } \beta \text{ channel} + \sum_{ab} F_{aa} + F_{bb} + \langle ab||ab \rangle
\]

(43)

The corresponding derivative is

part 2 = \[
\sum_{a>b} (\phi_a^* \phi_a + \phi_b^* \phi_b) + \text{spin } \beta \text{ channel} + \sum_{ab} (\phi_a^* \phi_a + \phi_b^* \phi_b)
\]

(44)

And plus the reference density part \(\rho_{ref}^s(x) = \sum_i \phi_i(x) \phi_i^*(x)\).

V. ORIGINAL DATA

All calculations were performed in the QM4D 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.

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<td>1.845</td>
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</table>

<table>
<thead>
<tr>
<th>Mol.</th>
<th>Ref.</th>
<th>Basis Set</th>
<th>HF</th>
<th>PBE</th>
<th>B3LYP</th>
<th>MP2</th>
<th>GOEP-MP2</th>
<th>ph@HF</th>
<th>ph@PBE</th>
<th>ph@B3LYP</th>
<th>pp@HF</th>
<th>pp@PBE</th>
<th>pp@B3LYP</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF</td>
<td>1.82</td>
<td>Def2-SVP</td>
<td>1.987</td>
<td>1.788</td>
<td>1.838</td>
<td>1.887</td>
<td>1.875</td>
<td>1.878</td>
<td>1.797</td>
<td>1.822</td>
<td>1.927</td>
<td>1.862</td>
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</tr>
<tr>
<td></td>
<td></td>
<td>Def2-TZVP</td>
<td>2.016</td>
<td>1.875</td>
<td>1.921</td>
<td>1.941</td>
<td>1.932</td>
<td>1.940</td>
<td>1.869</td>
<td>1.891</td>
<td>1.983</td>
<td>1.923</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Def2-SVPD</td>
<td>1.962</td>
<td>1.771</td>
<td>1.828</td>
<td>1.829</td>
<td>1.805</td>
<td>1.842</td>
<td>1.755</td>
<td>1.782</td>
<td>1.880</td>
<td>1.836</td>
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<td>Def2-TZVPD</td>
<td>1.921</td>
<td>1.740</td>
<td>1.796</td>
<td>1.806</td>
<td>1.786</td>
<td>1.827</td>
<td>1.746</td>
<td>1.771</td>
<td>1.857</td>
<td>1.805</td>
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</tr>
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<td>Def2-TZVPPD</td>
<td>1.924</td>
<td>1.745</td>
<td>1.800</td>
<td>1.795</td>
<td>1.775</td>
<td>1.811</td>
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<td>1.751</td>
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</table>
FIG. 1. Basis set convergence test with $\text{H}_2\text{O}$.

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

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

### TABLE IV. Dipole moments of H$_2$S calculated with different functionals.

<table>
<thead>
<tr>
<th>Mol. Ref.</th>
<th>Basis Set</th>
<th>HF</th>
<th>B3LYP</th>
<th>MP2</th>
<th>GOEP-MP2</th>
<th>ph@HF</th>
<th>ph@B3LYP</th>
<th>pp@HF</th>
<th>pp@B3LYP</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$S 0.97</td>
<td>Def2-SVP</td>
<td>1.329</td>
<td>1.241</td>
<td>1.302</td>
<td>1.283</td>
<td>1.193</td>
<td>1.134</td>
<td>1.302</td>
<td>1.274</td>
</tr>
<tr>
<td></td>
<td>Def2-TZVP</td>
<td>1.170</td>
<td>1.115</td>
<td>1.185</td>
<td>1.179</td>
<td>1.119</td>
<td>1.099</td>
<td>1.175</td>
<td>1.185</td>
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<tr>
<td></td>
<td></td>
<td>1.127</td>
<td>1.008</td>
<td>1.041</td>
<td>1.015</td>
<td>0.981</td>
<td>1.056</td>
<td>1.056</td>
<td>1.067</td>
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<tr>
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<td>Def2-TZVPD</td>
<td>1.073</td>
<td>0.971</td>
<td>1.019</td>
<td>1.005</td>
<td>0.986</td>
<td>0.954</td>
<td>1.034</td>
<td>1.019</td>
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<td>Def2-TZVPPD</td>
<td>1.072</td>
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<td>0.989</td>
<td>0.970</td>
<td>0.942</td>
<td>0.900</td>
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</table>

### TABLE V. Dipole moments of NH$_3$ calculated with different functionals.

<table>
<thead>
<tr>
<th>Mol. Ref.</th>
<th>Basis Set</th>
<th>HF</th>
<th>B3LYP</th>
<th>MP2</th>
<th>GOEP-MP2</th>
<th>ph@HF</th>
<th>ph@B3LYP</th>
<th>pp@HF</th>
<th>pp@B3LYP</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH$_3$ 1.47</td>
<td>Def2-SVP</td>
<td>1.806</td>
<td>1.702</td>
<td>1.763</td>
<td>1.747</td>
<td>1.731</td>
<td>1.686</td>
<td>1.780</td>
<td>1.744</td>
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<tr>
<td></td>
<td>Def2-TZVP</td>
<td>1.778</td>
<td>1.727</td>
<td>1.761</td>
<td>1.755</td>
<td>1.745</td>
<td>1.713</td>
<td>1.776</td>
<td>1.752</td>
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<td>1.669</td>
<td>1.569</td>
<td>1.584</td>
<td>1.558</td>
<td>1.584</td>
<td>1.536</td>
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<td>Def2-TZVPD</td>
<td>1.630</td>
<td>1.527</td>
<td>1.552</td>
<td>1.529</td>
<td>1.564</td>
<td>1.520</td>
<td>1.586</td>
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<td>Def2-TZVPPD</td>
<td>1.633</td>
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<td>1.539</td>
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<td>1.547</td>
<td>1.496</td>
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</table>
TABLE VI. Dipole moments of CO calculated with different functionals. For C and O atoms, Def2-TZVPD and Def2-TZVPPD are same.

<table>
<thead>
<tr>
<th>Mol.</th>
<th>Ref.</th>
<th>Basis Set</th>
<th>HF</th>
<th>B3LYP</th>
<th>MP2</th>
<th>GOEP-MP2</th>
<th>ph@HF</th>
<th>ph@B3LYP</th>
<th>pp@HF</th>
<th>pp@B3LYP</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>0.122</td>
<td>Def2-SVP</td>
<td>0.233</td>
<td>0.218</td>
<td>0.405</td>
<td>0.418</td>
<td>0.116</td>
<td>0.206</td>
<td>0.128</td>
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<tr>
<td></td>
<td></td>
<td>Def2-TZVP</td>
<td>0.262</td>
<td>0.097</td>
<td>0.305</td>
<td>0.334</td>
<td>0.048</td>
<td>0.052</td>
<td>0.189</td>
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<tr>
<td></td>
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<td>Def2-SVPD</td>
<td>0.238</td>
<td>0.113</td>
<td>0.322</td>
<td>0.343</td>
<td>0.189</td>
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<td></td>
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<tr>
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<td></td>
<td>Def2-TZVPD</td>
<td>0.261</td>
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<td>0.293</td>
<td>0.323</td>
<td>0.039</td>
<td>0.124</td>
<td>0.043</td>
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</table>

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

<table>
<thead>
<tr>
<th>Mol.</th>
<th>Ref.</th>
<th>Basis Set</th>
<th>HF</th>
<th>B3LYP</th>
<th>MP2</th>
<th>GOEP-MP2</th>
<th>ph@HF</th>
<th>ph@PBE</th>
<th>ph@B3LYP</th>
<th>pp@HF</th>
<th>pp@PBE</th>
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<tbody>
<tr>
<td>LiF</td>
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<td>5.663</td>
<td>5.840</td>
<td>5.846</td>
<td>5.762</td>
<td>5.881</td>
<td>6.098</td>
<td>5.990</td>
<td>5.950</td>
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</table>