Perturbative total energy evaluation in self-consistent field Iterations: Tests on molecular systems

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The corrected Hohenberg–Kohn–Sham and corrected Harris total energy functionals recently proposed [B. Zhou and Y. A. Wang, J. Chem. Phys. **128**, 084101 (2008)] have been generalized to the Hartree–Fock method. We have tested the functionals on a few molecular systems and found them to be very useful in accelerating the convergence of the total energy during a self-consistent field process. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3104662]

I. INTRODUCTION

Most quantum mechanical calculations, for example, Hartree–Fock (HF) and density functional theory[1–3] (DFT) methods, are carried out iteratively. Although these methods have lower computational scalings than post-HF methods do, they are still too expensive to deal with systems with thousands of atoms routinely. Searching for algorithms with higher computational efficiency has become an active research area of contemporary theoretical chemistry.[4]

Both HF and DFT methods utilize matrix diagonalization in the self-consistent field (SCF) procedure. The computational cost of matrix diagonalization usually scales as $O(N^3)$, where N is a measure of the size of the system, i.e., the number of basis functions. If N becomes very large, a full HF or DFT calculation will become unaffordable. Additionally, it normally takes many iterations to fully converge the SCF cycle. This further increases the computational cost. So, reducing the number of matrix diagonalizations is an effective way to make calculations of large systems accessible. We will focus on this issue in this paper.

For a given density $\rho(\mathbf{r})$ and external potential $v_{\text{ext}}(\mathbf{r})$, the Kohn–Sham (KS) decomposition of the DFT total electronic energy has four parts,

$$E[\rho] = T_s[\rho] + V_{\text{ext}}[\rho] + E_{\text{H}}[\rho] + E_{\text{xc}}[\rho], \tag{1}$$

where T_s is the kinetic energy, $V_{\text{ext}}=\langle\rho(\mathbf{r})v_{\text{ext}}(\mathbf{r})\rangle$ is the external potential energy, $E_{\text{H}}[\rho]$ is the Hartree energy, and $E_{\text{xc}}[\rho]$ is the exchange-correlation (XC) energy. In each iteration of solving the KS equations, one uses an input density $\rho^{\text{in}}(\mathbf{r})$ to construct the Hartree (v_{H}) and XC (v_{xc}) potentials and obtains the output orbitals $\{\psi_i^{\text{out}}\}$ and their corresponding orbital energies $\{\varepsilon_i^{\text{out}}\}$,

$$\left\{-\tfrac{1}{2}\nabla^2 + v_{\text{ext}}(\mathbf{r}) + v_{\text{H}}[\rho^{\text{in}}](\mathbf{r}) + v_{\text{xc}}[\rho^{\text{in}}](\mathbf{r})\right\}\psi_i^{\text{out}} = \varepsilon_i^{\text{out}}\psi_i^{\text{out}}. \tag{2}$$

The output density $\rho^{\text{out}}(\mathbf{r})$ can then be obtained from the output orbitals,

$$\rho^{\text{out}}(\mathbf{r}) = \sum_i^{\text{occ}} f_i^{\text{out}}|\psi_i^{\text{out}}|^2, \tag{3}$$

where f_i^{out} is the occupation number of ψ_i^{out}. Multiplying the left-hand side of Eq. (2) with the complex conjugate of ψ_i^{out}, integrating over the entire space, and summing over all occupied orbitals, one arrives at

$$\sum_i^{\text{occ}} f_i^{\text{out}}\varepsilon_i^{\text{out}} = \langle\rho^{\text{out}}(\mathbf{r})\{v_{\text{H}}[\rho^{\text{in}}](\mathbf{r}) + v_{\text{xc}}[\rho^{\text{in}}](\mathbf{r})\}\rangle + T_s[\rho^{\text{out}}] + V_{\text{ext}}[\rho^{\text{out}}]. \tag{4}$$

We can then write an approximate DFT total electronic energy during the iterative process as

$$E^{\text{HKS}}[\rho^{\text{in}},\rho^{\text{out}}] = \sum_i^{\text{occ}} f_i^{\text{out}}\varepsilon_i^{\text{out}} + E_{\text{H}}[\rho^{\text{out}}] + E_{\text{xc}}[\rho^{\text{out}}] - \langle\rho^{\text{out}}(\mathbf{r})\{v_{\text{H}}[\rho^{\text{in}}](\mathbf{r}) + v_{\text{xc}}[\rho^{\text{in}}](\mathbf{r})\}\rangle. \tag{5}$$

This is the well-known Hohenberg–Kohn–Sham (HKS) functional,[5] an upper bound of the exact ground-state KS total electronic energy.[6] Alternatively, Harris[7] approximated the total electronic energy based on some consideration from perturbation theory,

$$E^{\text{Harris}}[\rho^{\text{in}},\rho^{\text{out}}] = \sum_i^{\text{occ}} f_i^{\text{out}}\varepsilon_i^{\text{out}} - E_{\text{H}}[\rho^{\text{in}}] + E_{\text{xc}}[\rho^{\text{in}}] - \langle\rho^{\text{in}}(\mathbf{r})v_{\text{xc}}[\rho^{\text{in}}](\mathbf{r})\rangle. \tag{6}$$

The Harris functional can be obtained by replacing all ρ^{out} in Eq. (5) with ρ^{in}, although f_i^{out} and $\varepsilon_i^{\text{out}}$ must come from solving the KS equations. Unlike the HKS functional, the Harris functional is neither an upper bound nor a lower bound of the exact ground-state energy in general.[8–10] Practically, both the HKS and Harris functionals often are about the same quality if self-consistency is not achieved; sometimes the Harris functional yields better results than the HKS functional does due to error cancelation.[11]

When the converged electron density $\rho^{\text{KS}}(\mathbf{r})$ is obtained at the end of the SCF cycle, both the HKS and Harris functionals yield the exact KS total electronic energy $E^{\text{KS}}[\rho^{\text{KS}}]$,

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$$E^{\mathrm{KS}}[\rho^{\mathrm{KS}}] = \sum_{i}^{\mathrm{occ}} f_i^{\mathrm{KS}} \varepsilon_i^{\mathrm{KS}} - E_{\mathrm{H}}[\rho^{\mathrm{KS}}] + E_{\mathrm{xc}}[\rho^{\mathrm{KS}}] - \langle \rho^{\mathrm{KS}}(\mathbf{r}) v_{\mathrm{xc}}[\rho^{\mathrm{KS}}](\mathbf{r}) \rangle, \tag{7}$$

where f_i^{KS} and $\varepsilon_i^{\mathrm{KS}}$ are the occupation number and the energy eigenvalue of the converged ith KS orbital, respectively.

II. PERTURBATION EXPANSIONS OF TOTAL ELECTRONIC ENERGY FUNCTIONALS

We can expand Eqs. (5) and (6) around the converged electron density $\rho^{\mathrm{KS}}(\mathbf{r})$. After some algebraic manipulations, the final results (up to second order in density difference) are as the following:[11]

$$E^{\mathrm{HKS}}[\rho^{\mathrm{in}}, \rho^{\mathrm{out}}] = E^{\mathrm{KS}}[\rho^{\mathrm{KS}}] + \langle \{\rho^{\mathrm{out}}(\mathbf{r}_1) - \rho^{\mathrm{in}}(\mathbf{r}_1)\} C(\mathbf{r}_1, \mathbf{r}_2) \{\rho^{\mathrm{out}}(\mathbf{r}_2) - \rho^{\mathrm{KS}}(\mathbf{r}_2)\} \rangle, \tag{8}$$

$$E^{\mathrm{Harris}}[\rho^{\mathrm{in}}, \rho^{\mathrm{out}}] = E^{\mathrm{KS}}[\rho^{\mathrm{KS}}] + \langle \{\rho^{\mathrm{out}}(\mathbf{r}_1) - \rho^{\mathrm{in}}(\mathbf{r}_1)\} C(\mathbf{r}_1, \mathbf{r}_2) \{\rho^{\mathrm{in}}(\mathbf{r}_2) - \rho^{\mathrm{KS}}(\mathbf{r}_2)\} \rangle, \tag{9}$$

where

$$C(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{2} \left(\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} + \left. \frac{\delta v_{\mathrm{xc}}[\rho(\mathbf{r}_1)]}{\delta \rho(\mathbf{r}_2)} \right|_{\rho^{\mathrm{in}}} \right). \tag{10}$$

Based on this appreciation, we recently proposed the corrected HKS (cHKS) and corrected Harris (cHarris) total electronic energy functionals,[12]

$$E^{\mathrm{cHKS}}[\rho^{\mathrm{in}}, \rho^{\mathrm{out}}] = E^{\mathrm{HKS}}[\rho^{\mathrm{in}}, \rho^{\mathrm{out}}] + \langle \{\rho^{\mathrm{out}}(\mathbf{r}_1) - \rho^{\mathrm{in}}(\mathbf{r}_1)\} C(\mathbf{r}_1, \mathbf{r}_2) \{\rho^{b}(\mathbf{r}_2) - \rho^{\mathrm{out}}(\mathbf{r}_2)\} \rangle, \tag{11}$$

$$E^{\mathrm{cHarris}}[\rho^{\mathrm{in}}, \rho^{\mathrm{out}}] = E^{\mathrm{Harris}}[\rho^{\mathrm{in}}, \rho^{\mathrm{out}}] + \langle \{\rho^{\mathrm{out}}(\mathbf{r}_1) - \rho^{\mathrm{in}}(\mathbf{r}_1)\} C(\mathbf{r}_1, \mathbf{r}_2) \{\rho^{b}(\mathbf{r}_2) - \rho^{\mathrm{in}}(\mathbf{r}_2)\} \rangle, \tag{12}$$

where ρ^b stands for some electron density "better" than ρ^{in} and ρ^{out}. Obviously, the performance of these two functionals is dictated by the choice of ρ^b.

In practice, the functional derivative term in $C(\mathbf{r}_1, \mathbf{r}_2)$ might be difficult to compute since the form of many XC functionals is quite complicated. To avoid this problem, the following finite-difference approximation can then be adopted:[12,13]

$$\left\langle \{\rho^{\mathrm{out}}(\mathbf{r}_1) - \rho^{\mathrm{in}}(\mathbf{r}_1)\} \left(\left. \frac{\delta v_{\mathrm{xc}}[\rho(\mathbf{r}_2)]}{\delta \rho(\mathbf{r}_1)} \right|_{\rho^{\mathrm{in}}} \right) \right\rangle_{\mathbf{r}_1} \approx v_{\mathrm{xc}}[\rho^{\mathrm{out}}(\mathbf{r}_2)] - v_{\mathrm{xc}}[\rho^{\mathrm{in}}(\mathbf{r}_2)], \tag{13}$$

where the integration on the left-hand side is carried out on the variable $\mathbf{r}_1$. Consequently, we can approximate Eqs. (11) and (12) as

$$E^{\mathrm{cHKS}}[\rho^{\mathrm{in}}, \rho^{\mathrm{out}}] = E^{\mathrm{HKS}}[\rho^{\mathrm{in}}, \rho^{\mathrm{out}}] + \tfrac{1}{2} \langle (\rho^b - \rho^{\mathrm{out}})(v_{\mathrm{eff}}^{\mathrm{out}} - v_{\mathrm{eff}}^{\mathrm{in}}) \rangle_{\mathbf{r}_1, \mathbf{r}_2}, \tag{14}$$

$$E^{\mathrm{cHarris}}[\rho^{\mathrm{in}}, \rho^{\mathrm{out}}] = E^{\mathrm{Harris}}[\rho^{\mathrm{in}}, \rho^{\mathrm{out}}] + \tfrac{1}{2} \langle (\rho^b - \rho^{\mathrm{in}})(v_{\mathrm{eff}}^{\mathrm{out}} - v_{\mathrm{eff}}^{\mathrm{in}}) \rangle_{\mathbf{r}_1, \mathbf{r}_2}, \tag{15}$$

where the KS effective potential $v_{\mathrm{eff}} = v_{\mathrm{ext}} + v_{\mathrm{H}} + v_{\mathrm{xc}}$.

In fact, the cHKS and cHarris models are very general and can be employed in other quantum chemistry methods. Specifically, we consider extension of the cHKS and cHarris concepts to the HF method. For simplicity, we only study the closed-shell case with spinless density matrices. The occupation numbers f_i are either 2 or 0 and are the same for ψ_i^{out} and ψ_i^{HF} in the following derivation.

The ordinary HF equation is written as

$$\left[-\frac{1}{2}\nabla^2 + v_{\mathrm{ext}}(\mathbf{r}_1) + 2\sum_{j}^{\mathrm{occ}} \int \frac{\psi_j^*(\mathbf{r}_2)\psi_j(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_2 \right] \psi_i(\mathbf{r}_1) - \sum_{j}^{\mathrm{occ}} \psi_j(\mathbf{r}_1) \int \frac{\psi_j^*(\mathbf{r}_2)\psi_i(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_2 = \varepsilon_i^{\mathrm{HF}} \psi_i(\mathbf{r}_1), \tag{16}$$

where ψ_i and $\varepsilon_i^{\mathrm{HF}}$ are the ith HF orbital and its corresponding orbital energy, respectively. We can construct the HF density matrix $P^{\mathrm{HF}}(\mathbf{r}_1, \mathbf{r}_2)$ from the HF obitals,

$$P^{\mathrm{HF}}(\mathbf{r}_1, \mathbf{r}_2) = 2\sum_{i}^{\mathrm{occ}} \psi_i^*(\mathbf{r}_1)\psi_i(\mathbf{r}_2), \tag{17}$$

whose diagonal elements define the HF density $\rho^{\mathrm{HF}}(\mathbf{r})$. The HF total electronic energy reads

$$E_{\mathrm{HF}} = 2\sum_{i}^{\mathrm{occ}} \varepsilon_i^{\mathrm{HF}} - E_{\mathrm{H}}^{\mathrm{HF}} - E_{\mathrm{HFX}}^{\mathrm{HF}}, \tag{18}$$

where the HF Hartree ($E_{\mathrm{H}}^{\mathrm{HF}}$) and exchange ($E_{\mathrm{HFX}}^{\mathrm{HF}}$) energies are defined as

$$E_{\mathrm{H}}^{\mathrm{HF}} = \tfrac{1}{2} \langle \rho^{\mathrm{HF}}(\mathbf{r}_1) v_{\mathrm{H}}^{\mathrm{HF}}(\mathbf{r}_1) \rangle_{\mathbf{r}_1}, \tag{19}$$

$$E_{\mathrm{HFX}}^{\mathrm{HF}} = \tfrac{1}{2} \langle P^{\mathrm{HF}}(\mathbf{r}_1, \mathbf{r}_2) v_{\mathrm{HFX}}^{\mathrm{HF}}(\mathbf{r}_1, \mathbf{r}_2) \rangle_{\mathbf{r}_1, \mathbf{r}_2}, \tag{20}$$

with

$$v_{\mathrm{H}}^{\mathrm{HF}}(\mathbf{r}_1) = \int \frac{\rho^{\mathrm{HF}}(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_2, \tag{21}$$

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$$v_{\mathrm{HFX}}^{\mathrm{HF}}(\mathbf{r}_1,\mathbf{r}_2) = -\frac{1}{2}\frac{P^{\mathrm{HF}}(\mathbf{r}_2,\mathbf{r}_1)}{|\mathbf{r}_1-\mathbf{r}_2|}. \tag{22}$$

Analogously, one can define the HF versions of the HKS and Harris total electronic energy functionals,

$$E_{\mathrm{HF}}^{\mathrm{HKS}} = 2\sum_{i}^{\mathrm{occ}} \varepsilon_i^{\mathrm{out}} - \langle \rho^{\mathrm{out}} v_{\mathrm{H}}^{\mathrm{in}} \rangle_{\mathbf{r}_1} - \langle P^{\mathrm{out}} v_{\mathrm{HFX}}^{\mathrm{in}} \rangle_{\mathbf{r}_1,\mathbf{r}_2} + E_{\mathrm{H}}^{\mathrm{out}} + E_{\mathrm{HFX}}^{\mathrm{out}}, \tag{23}$$

$$E_{\mathrm{HF}}^{\mathrm{Harris}} = 2\sum_{i}^{\mathrm{occ}} \varepsilon_i^{\mathrm{out}} - E_{\mathrm{H}}^{\mathrm{in}} - E_{\mathrm{HFX}}^{\mathrm{in}}, \tag{24}$$

where the superscripts "in" and "out" denote the input and output quantities, respectively. The difference between the HKS and Harris functionals can be readily shown to be

$$\begin{aligned} E_{\mathrm{HF}}^{\mathrm{HKS}} - E_{\mathrm{HF}}^{\mathrm{Harris}} &= \tfrac{1}{2}\langle (P^{\mathrm{out}} - P^{\mathrm{in}})(v_{\mathrm{HFX}}^{\mathrm{out}} - v_{\mathrm{HFX}}^{\mathrm{in}}) \rangle_{\mathbf{r}_1,\mathbf{r}_2} \\ &\quad + \tfrac{1}{2}\langle (\rho^{\mathrm{out}} - \rho^{\mathrm{in}})(v_{\mathrm{H}}^{\mathrm{out}} - v_{\mathrm{H}}^{\mathrm{in}}) \rangle_{\mathbf{r}_1} \\ &= \tfrac{1}{2}\langle (P^{\mathrm{out}} - P^{\mathrm{in}})(v_{\mathrm{ee}}^{\mathrm{out}} - v_{\mathrm{ee}}^{\mathrm{in}}) \rangle_{\mathbf{r}_1,\mathbf{r}_2}, \end{aligned} \tag{25}$$

where

$$v_{\mathrm{ee}}(\mathbf{r}_1,\mathbf{r}_2) = v_{\mathrm{H}}(\mathbf{r}_1)\delta(\mathbf{r}_2-\mathbf{r}_1) + v_{\mathrm{HFX}}(\mathbf{r}_1,\mathbf{r}_2). \tag{26}$$

Also, the difference between the Harris and HF total electronic energy functionals can be grouped into three parts,

$$E_{\mathrm{HF}}^{\mathrm{Harris}} - E_{\mathrm{HF}} = \underbrace{2\sum_{i}^{\mathrm{occ}} (\varepsilon_i^{\mathrm{out}} - \varepsilon_i^{\mathrm{HF}})}_{①} - \underbrace{(E_{\mathrm{H}}^{\mathrm{in}} - E_{\mathrm{H}}^{\mathrm{HF}})}_{②} - \underbrace{\frac{1}{2}\langle P^{\mathrm{in}} v_{\mathrm{HFX}}^{\mathrm{in}} - P^{\mathrm{HF}} v_{\mathrm{HFX}}^{\mathrm{HF}} \rangle_{\mathbf{r}_1,\mathbf{r}_2}}_{③}, \tag{27}$$

which will be analyzed part by part in turn.

First, we evaluate part 1 in Eq. (27) with orbital perturbation theory. The HF equation for ψ_i^{HF} is

$$\left[-\tfrac{1}{2}\nabla^2 + v_{\mathrm{ext}}(\mathbf{r}_1) + v_{\mathrm{eff}}^{\mathrm{HF}}(\mathbf{r}_1)\right]\psi_i^{\mathrm{HF}} = \varepsilon_i^{\mathrm{HF}}\psi_i^{\mathrm{HF}}, \tag{28}$$

where $v_{\mathrm{eff}}(\mathbf{r}_1)$ is the nonlocal HF effective potential. Let $\delta v_{\mathrm{eff}} = (v_{\mathrm{eff}}^{\mathrm{in}} - v_{\mathrm{eff}}^{\mathrm{HF}})$ be the perturbation in the potential of the system described by Eq. (28). Then, to second order in orbital change, we have

$$\varepsilon_i^{\mathrm{out}} - \varepsilon_i^{\mathrm{HF}} = \sum_{j}^{\mathrm{occ}} \langle \psi_j^{\mathrm{HF}} | \delta v_{\mathrm{eff}} | \psi_j^{\mathrm{HF}} \rangle + \sum_{j\neq i} \frac{|\langle \psi_i^{\mathrm{HF}} | \delta v_{\mathrm{eff}} | \psi_j^{\mathrm{HF}} \rangle|^2}{\varepsilon_i^{\mathrm{HF}} - \varepsilon_j^{\mathrm{HF}}}, \tag{29}$$

and consequently,

$$\sum_{i}^{\mathrm{occ}} (\varepsilon_i^{\mathrm{out}} - \varepsilon_i^{\mathrm{HF}}) = \frac{1}{2}\langle P^{\mathrm{HF}}(v_{\mathrm{ee}}^{\mathrm{in}} - v_{\mathrm{ee}}^{\mathrm{HF}}) \rangle_{\mathbf{r}_1,\mathbf{r}_2} + \sum_{i}^{\mathrm{occ}}\sum_{t}^{\mathrm{vir}} \frac{|\langle \psi_i^{\mathrm{HF}} | \delta v_{\mathrm{eff}} | \psi_t^{\mathrm{HF}} \rangle|^2}{\varepsilon_i^{\mathrm{HF}} - \varepsilon_t^{\mathrm{HF}}}, \tag{30}$$

where in the second term of the right-hand side the summation index t runs over all the virtual orbitals. Similarly, applying this orbital perturbation theory to the HF equation for ψ_i^{out},

$$\left[-\tfrac{1}{2}\nabla^2 + v_{\mathrm{ext}}(\mathbf{r}_1) + v_{\mathrm{eff}}^{\mathrm{in}}(\mathbf{r}_1)\right]\psi_i^{\mathrm{out}} = \varepsilon_i^{\mathrm{out}}\psi_i^{\mathrm{out}}, \tag{31}$$

we have

$$\sum_{i}^{\mathrm{occ}} (\varepsilon_i^{\mathrm{HF}} - \varepsilon_i^{\mathrm{out}}) = \frac{1}{2}\langle P^{\mathrm{out}}(v_{\mathrm{ee}}^{\mathrm{HF}} - v_{\mathrm{ee}}^{\mathrm{in}}) \rangle_{\mathbf{r}_1,\mathbf{r}_2} + \sum_{i}^{\mathrm{occ}}\sum_{t}^{\mathrm{vir}} \frac{|\langle \psi_i^{\mathrm{out}} | \delta v_{\mathrm{eff}} | \psi_t^{\mathrm{out}} \rangle|^2}{\varepsilon_i^{\mathrm{out}} - \varepsilon_t^{\mathrm{out}}}, \tag{32}$$

where the perturbation in the potential is $-\delta v_{\mathrm{eff}} = (v_{\mathrm{eff}}^{\mathrm{HF}} - v_{\mathrm{eff}}^{\mathrm{in}})$. After working out the Taylor expansion of the second-order term of Eq. (32) around the HF quantities, we find that its difference from the second-order term of Eq. (30) only enters in the third order. Hence, we can cancel the second-order terms of Eqs. (30) and (32) and derive a much simpler yet accurate expansion for part 1:

$$① = \tfrac{1}{2}\langle (P^{\mathrm{out}} + P^{\mathrm{HF}})(v_{\mathrm{ee}}^{\mathrm{in}} - v_{\mathrm{ee}}^{\mathrm{HF}}) \rangle_{\mathbf{r}_1,\mathbf{r}_2} + O(\delta^3). \tag{33}$$

It is straightforward to show that parts 2 and 3 can be exactly expanded as

$$\begin{aligned} ② &= \tfrac{1}{2}\langle (\rho^{\mathrm{in}} v_{\mathrm{H}}^{\mathrm{in}} - \rho^{\mathrm{HF}} v_{\mathrm{H}}^{\mathrm{HF}}) \rangle_{\mathbf{r}_1} \\ &= \tfrac{1}{2}\langle (\rho^{\mathrm{in}} v_{\mathrm{H}}^{\mathrm{in}} - \rho^{\mathrm{HF}} v_{\mathrm{H}}^{\mathrm{HF}}) \rangle_{\mathbf{r}_1} + \tfrac{1}{2}\langle (\rho^{\mathrm{HF}} v_{\mathrm{H}}^{\mathrm{in}} - \rho^{\mathrm{in}} v_{\mathrm{H}}^{\mathrm{HF}}) \rangle_{\mathbf{r}_1} \\ &= \tfrac{1}{2}\langle (\rho^{\mathrm{in}} + \rho^{\mathrm{HF}})(v_{\mathrm{H}}^{\mathrm{in}} - v_{\mathrm{H}}^{\mathrm{HF}}) \rangle_{\mathbf{r}_1}, \end{aligned} \tag{34}$$

and

$$\begin{aligned} ③ &= \tfrac{1}{2}\langle P^{\mathrm{in}} v_{\mathrm{HFX}}^{\mathrm{in}} - P^{\mathrm{HF}} v_{\mathrm{HFX}}^{\mathrm{HF}} \rangle_{\mathbf{r}_1,\mathbf{r}_2} \\ &= \tfrac{1}{2}\langle P^{\mathrm{in}} v_{\mathrm{HFX}}^{\mathrm{in}} - P^{\mathrm{HF}} v_{\mathrm{HFX}}^{\mathrm{HF}} \rangle_{\mathbf{r}_1,\mathbf{r}_2} + \tfrac{1}{2}\langle P^{\mathrm{HF}} v_{\mathrm{HFX}}^{\mathrm{in}} - P^{\mathrm{in}} v_{\mathrm{HFX}}^{\mathrm{HF}} \rangle_{\mathbf{r}_1,\mathbf{r}_2} \\ &= \tfrac{1}{2}\langle (P^{\mathrm{in}} + P^{\mathrm{HF}})(v_{\mathrm{HFX}}^{\mathrm{in}} - v_{\mathrm{HFX}}^{\mathrm{HF}}) \rangle_{\mathbf{r}_1,\mathbf{r}_2}, \end{aligned} \tag{35}$$

where the second terms after the second equal signs are zero after interchanging the two integration dummy variables, $\mathbf{r}_1$ and $\mathbf{r}_2$,

$$\left\langle \frac{\rho^{\mathrm{HF}}(\mathbf{r}_1)\rho^{\mathrm{in}}(\mathbf{r}_2)}{|\mathbf{r}_1-\mathbf{r}_2|} \right\rangle_{\mathbf{r}_1,\mathbf{r}_2} - \left\langle \frac{\rho^{\mathrm{in}}(\mathbf{r}_1)\rho^{\mathrm{HF}}(\mathbf{r}_2)}{|\mathbf{r}_1-\mathbf{r}_2|} \right\rangle_{\mathbf{r}_1,\mathbf{r}_2} = \langle (\rho^{\mathrm{HF}} v_{\mathrm{H}}^{\mathrm{in}} - \rho^{\mathrm{in}} v_{\mathrm{H}}^{\mathrm{HF}}) \rangle_{\mathbf{r}_1} = 0, \tag{36}$$

$$\left\langle \frac{P^{\mathrm{in}}(\mathbf{r}_1,\mathbf{r}_2)P^{\mathrm{HF}}(\mathbf{r}_2,\mathbf{r}_1)}{|\mathbf{r}_1-\mathbf{r}_2|} \right\rangle_{\mathbf{r}_1,\mathbf{r}_2} - \left\langle \frac{P^{\mathrm{HF}}(\mathbf{r}_1,\mathbf{r}_2)P^{\mathrm{in}}(\mathbf{r}_2,\mathbf{r}_1)}{|\mathbf{r}_1-\mathbf{r}_2|} \right\rangle_{\mathbf{r}_1,\mathbf{r}_2} = 2\langle P^{\mathrm{HF}} v_{\mathrm{HFX}}^{\mathrm{in}} - P^{\mathrm{in}} v_{\mathrm{HFX}}^{\mathrm{HF}} \rangle_{\mathbf{r}_1,\mathbf{r}_2} = 0. \tag{37}$$

Substituting Eqs. (33)–(35) into Eq. (27), we arrive at

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$$E_{\mathrm{HF}}^{\mathrm{Harris}} - E_{\mathrm{HF}} = \tfrac{1}{2}\langle (P^{\mathrm{out}} + P^{\mathrm{HF}})(v_{\mathrm{ee}}^{\mathrm{in}} - v_{\mathrm{ee}}^{\mathrm{HF}})\rangle_{\mathbf{r}_1,\mathbf{r}_2} - \tfrac{1}{2}\langle (\rho^{\mathrm{in}} + \rho^{\mathrm{HF}})(v_{\mathrm{H}}^{\mathrm{in}} - v_{\mathrm{H}}^{\mathrm{HF}})\rangle_{\mathbf{r}_1} - \tfrac{1}{2}\langle (P^{\mathrm{in}} + P^{\mathrm{HF}})(v_{\mathrm{HFX}}^{\mathrm{in}} - v_{\mathrm{HFX}}^{\mathrm{HF}})\rangle_{\mathbf{r}_1,\mathbf{r}_2} = \tfrac{1}{2}\langle (P^{\mathrm{out}} - P^{\mathrm{in}})(v_{\mathrm{ee}}^{\mathrm{in}} - v_{\mathrm{ee}}^{\mathrm{HF}})\rangle_{\mathbf{r}_1,\mathbf{r}_2} = \tfrac{1}{2}\langle (P^{\mathrm{in}} - P^{\mathrm{HF}})(v_{\mathrm{ee}}^{\mathrm{out}} - v_{\mathrm{ee}}^{\mathrm{in}})\rangle_{\mathbf{r}_1,\mathbf{r}_2} = \tfrac{1}{2}\mathrm{Tr}\{(P^{\mathrm{in}} - P^{\mathrm{HF}})(F^{\mathrm{out}} - F^{\mathrm{in}})\}, \quad (38)$$

where F^{out} and F^{in} are Fock matrices built from output and input HF orbitals, respectively. With the aid of Eqs. (25) and (38), we can easily deduce the difference between the HKS and HF total electronic energy functionals,

$$E_{\mathrm{HF}}^{\mathrm{HKS}} - E_{\mathrm{HF}} = \tfrac{1}{2}\langle (P^{\mathrm{out}} - P^{\mathrm{HF}})(v_{\mathrm{ee}}^{\mathrm{out}} - v_{\mathrm{ee}}^{\mathrm{in}})\rangle_{\mathbf{r}_1,\mathbf{r}_2} = \tfrac{1}{2}\mathrm{Tr}\{(P^{\mathrm{out}} - P^{\mathrm{HF}})(F^{\mathrm{out}} - F^{\mathrm{in}})\}. \quad (39)$$

Therefore, we can define the HF versions of the cHKS and cHarris functionals,

$$E_{\mathrm{HF}}^{\mathrm{cHKS}} = E_{\mathrm{HF}}^{\mathrm{HKS}} + \tfrac{1}{2}\mathrm{Tr}\{(P^{b} - P^{\mathrm{out}})(F^{\mathrm{out}} - F^{\mathrm{in}})\}, \quad (40)$$

$$E_{\mathrm{HF}}^{\mathrm{cHarris}} = E_{\mathrm{HF}}^{\mathrm{Harris}} + \tfrac{1}{2}\mathrm{Tr}\{(P^{b} - P^{\mathrm{in}})(F^{\mathrm{out}} - F^{\mathrm{in}})\}, \quad (41)$$

where P^b denotes some density matrix of better quality than P^{in} and P^{out}. Interestingly, Eqs. (14) and (15) look very similar to the above two equations.

The preceding derivation supersedes Finnis' analysis:[11] Our argument builds upon the general orbital perturbation theory and, as such, apparently can be applied to all levels of quantum chemistry theory.

It is also necessary to mention the connection between our functionals and the energy direct inversion of the iterative subspace (EDIIS) method proposed by Kudin *et al.*[14] The EDIIS energy functional is written as

$$E^{\mathrm{EDIIS}}(\tilde{P}) = \sum_{i=1}^{k} c_i E_0(P_i) - \frac{1}{2}\sum_{i,j=1}^{k} c_i c_j \,\mathrm{Tr}\{(P_i - P_j)(F_i - F_j)\}, \quad (42)$$

where $P_{i,j}$ are density matrices; $\tilde{P} = \Sigma_{i=1}^{k} c_i P_i$ with $c_i \geq 0$ and $\Sigma_i^k c_i = 1$; $F_{i,j}$ are Fock matrices; and $E_0(P_i)$ is the HF energy evaluated with P_i. The quadratic term looks very similar to our second-order correction terms in Eqs. (40) and (41), so the EDIIS method can be viewed as finding an optimal reference zero-order total energy and the corresponding second-order correction term in a linear subspace of the density matrices. The EDIIS scheme arises from an optimization consideration; we propose our functionals based on perturbation theory. In the end, both approaches arrive at similar results.

III. IMPLEMENTATION AND COMPUTATIONAL DETAILS

The NWCHEM 5.0 source code[15] was modified to run all calculations. The cHKS and cHarris total electronic energy functionals were evaluated in each DFT or HF SCF iteration. For the estimation of ρ^b or P^b, we took advantage of the direct inversion of the iterative subspace (DIIS) method,[16] which is readily available in the code. The 6-31G* basis set was used for all calculations. Local density approximation (LDA) exchange functional[17] and the VWN_5 correlation functional[18] were used for all DFT calculations.

We tested our models on four molecular systems: HF, H_2O, CrC, and SiH_4 (with one elongated Si–H bond). In DFT calculations, the H–F bond length was 0.920 Å, the H–O bond length was 0.965 Å, the H–O–H bond angle was 103.75°, the Cr–C bond length was 2.00 Å, the regular Si–H bond length was 1.47 Å, the elongated Si–H bond length was 4.00 Å, and any H–S–iH bond angle was 109.47°. For HF calculations, the H–F bond length was 0.911 Å, the structure of H_2O was the same as above, and the structure of SiH_4 was similar except that the elongated Si–H bond length was 12.0 Å.

To guarantee the convergence, the criterion of the root mean square of the electron density difference was set to be 1×10^{-7} in all DFT calculations for HF, H_2O, and SiH_4, and 1×10^{-8} for CrC. For HF calculations, the convergence threshold of the norm of the orbital gradient was set to be 1×10^{-7}. In all calculations, the default initial guesses were adopted to start the SCF procedure, and DIIS began immediately upon becoming possible and was used throughout the SCF processes. Damping (with 70% of previous density) was employed in the first 20 SCF iterations in some DFT calculations for HF and H_2O to investigate the performance of our models. For the DFT calculations on SiH_4, a 50% damping factor was utilized. For the HF calculations on SiH_4, the damping factor was 40% and 10% before and after the 100th iteration, respectively. In all calculations, level shifting was used (with a parameter of 0.5 a.u.) whenever the gap between the highest occupied molecular orbital and the lowest unoccupied molecular orbital was less than 0.05 hartree.

IV. RESULTS AND DISCUSSIONS

First we present the results for HF and H_2O in Figs. 1 and 2. Both show the same tendency: The cHKS and cHarris energies are virtually identical to each other throughout the entire iteration process. This behavior is reasonable because the difference between the cHKS and cHarris functionals is of third order in the density or density matrix variation (see the analysis in Sec. II). The HKS and Harris energies are roughly of the same quality. The cHKS and cHarris models do improve upon the HKS and Harris energies that come from the current iteration, but they are not better than the HKS and Harris energies that come from the next iteration. Such a behavior is not surprising because the DIIS density or density matrix is designed to minimize the total energy gradient of the SCF process,[16] but is not necessarily optimal for the total energy minimization. It is very difficult to propose a general scheme to achieve fast, smooth convergence for any arbitrary molecular system. Therefore, in most modern quantum chemistry packages, one has to rely on trial and error to choose the best convergence scheme among many options.

For further testing of the performance of our models in DFT calculations with different convergence schemes, we intentionally slowed down the SCF convergence with damp-

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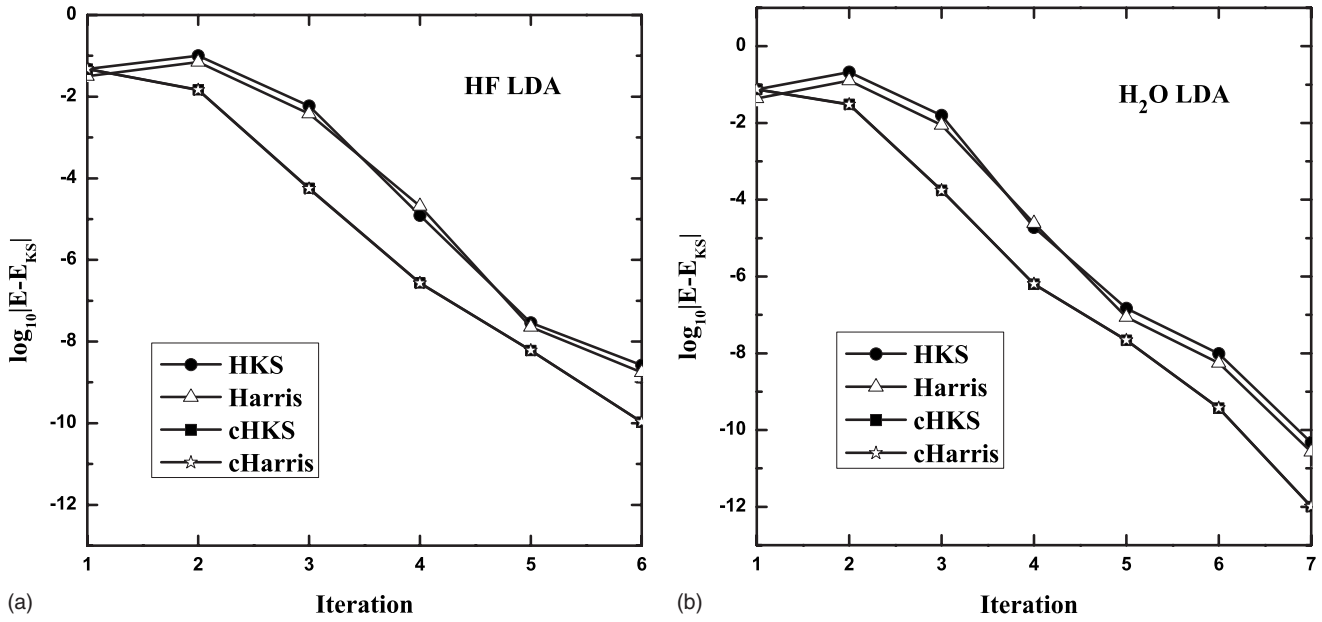

FIG. 1. Convergence of the total energies (in hartree) of HF (left) and H_2O (right) molecules evaluated with the HKS (circles), the Harris (hollow triangles), the cHKS (squares), and the cHarris (hollow stars) functionals during the SCF iterations of KS calculations.

ing (with 70% of previous density) on the same two molecules. (This commonly used procedure is also known as linear mixing or Pratt mixing.) The results are displayed in Fig. 3. It shows that the cHKS and cHarris energies are always together and so are the HKS and Harris energies. Amazingly, the cHKS and cHarris models converge much faster than the HKS and Harris energies do. Our corrected models converge to within 1×10^{-6} hartree only after five SCF iterations, but the HKS and Harris energies do not achieve this kind of accuracy until iteration 15. Of course, a damped DIIS density or density matrix is not optimal for minimizing the total energy gradient, so the HKS and Harris total energies converge very slowly in the above two cases shown in Fig. 3. Even with such "bad" input densities, the perturbative corrections in the cHKS and cHarris models still demonstrate significant improvement.

However, when we performed the same tests on the same molecules using the HF method, we did not observe a similar dramatic improvement. This is because for most molecular systems at their equilibrium geometries, the DIIS method (even with damping) already provides an excellent convergence scheme and our correction models do not show much enhancement (see Fig. 2). On the other hand, if the molecular system is far away from its equilibrium geometry, the damped HF results might possess a similar pattern to the DFT counterparts. A multiatom molecule, SiH_4 with one

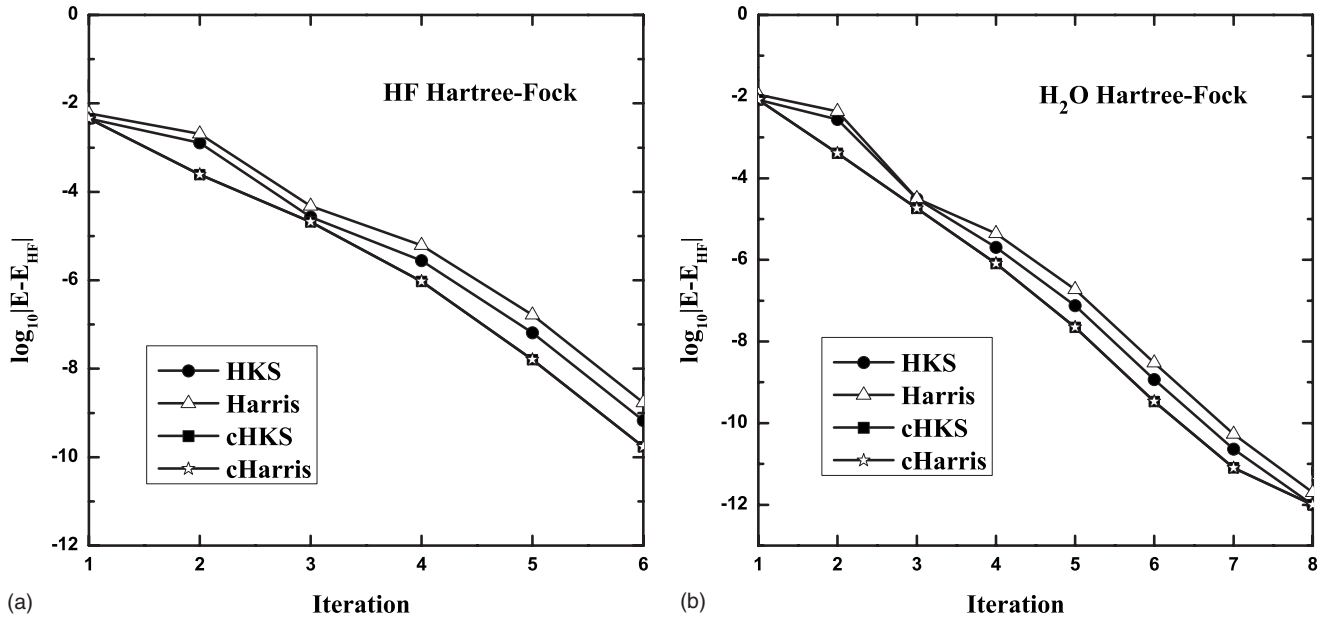

FIG. 2. Convergence of the total energies (in hartree) of HF (left) and H_2O (right) molecules evaluated with the HKS (circles), the Harris (hollow triangles), the cHKS (squares), and the cHarris (hollow stars) functionals during the SCF iterations of HF calculations.

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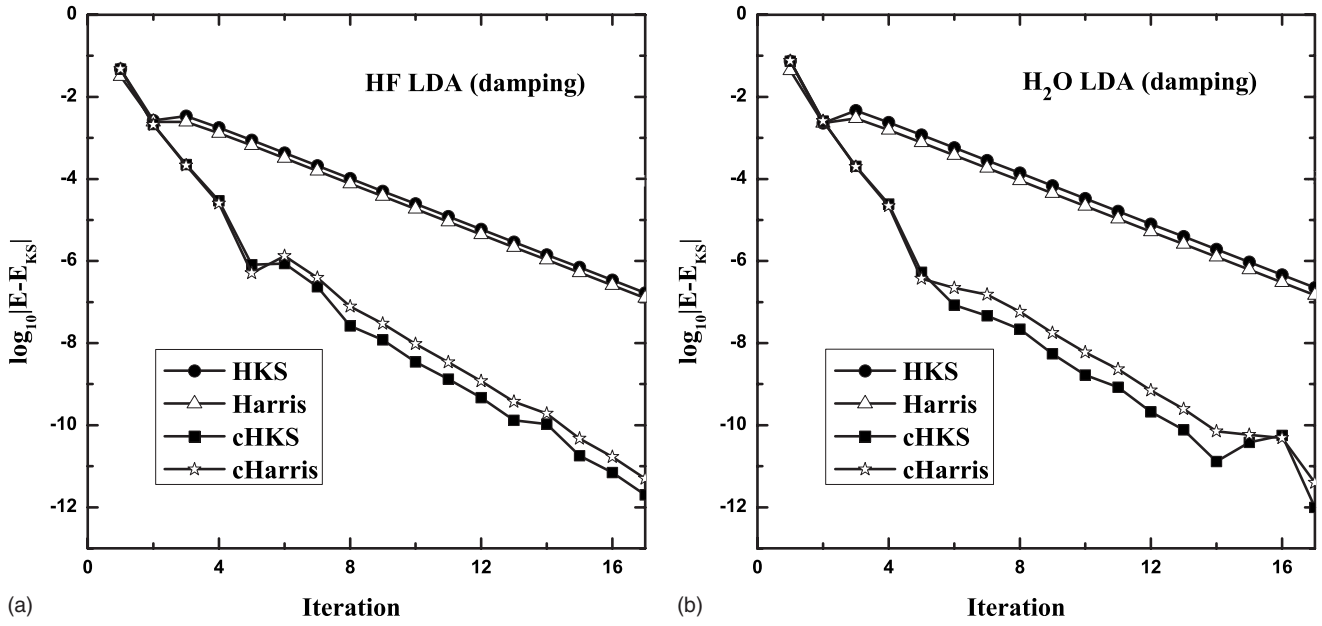

FIG. 3. Convergence of the total energies (in hartree) of HF (left) and H_2O (right) molecules evaluated with the HKS (circles), the Harris (hollow triangles), the cHKS (squares), and the cHarris (hollow stars) functionals during the SCF iterations of KS calculations with damping.

elongated Si–H bond, was then chosen to illustrate this scenario. Figure 4 shows that when one Si–H bond is much elongated, both DFT and HF methods have great difficulty to achieve fast SCF convergence. It takes more than 30 and 140 iterations for the damped DIIS scheme to locate the fast descending path in the DFT and HF calculations, respectively. After the turning point, the cHKS and cHarris models bear a similar fast converging trait to what Fig. 3 exhibits.

To further investigate the performance of our models in different chemical environments, we chose one notoriously difficult case for almost all conventional SCF convergence acceleration methods—the CrC molecule.[19–24] DFT calculations were performed for both singlet and triplet states of CrC without and with damping (with the same damping parameter as before). Because the cHKS model works slightly better than the cHarris model (see Fig. 3), we only show the cHKS results in Fig. 5.

Unlike the cases for HF or H_2O, damping does not affect the convergence of the conventional SCF scheme strongly for CrC. This effect can be observed from the results in Table I. In both cases, damping only slows the complete SCF process (below 1×10^{-12} hartree) by 12 iterations. The cHKS model always uses five to nine fewer iterations than the HKS model does to converge the total energy below 1×10^{-6} hartree. Interestingly, we also found that calculations with different damping parameters pose similar conver-

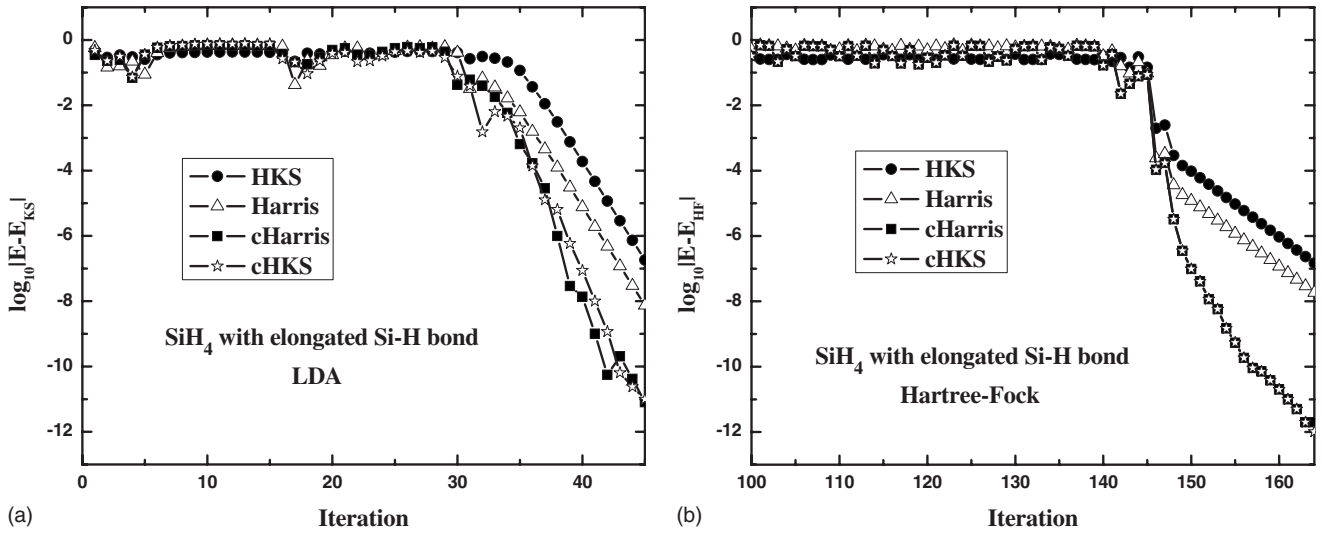

FIG. 4. Convergence of the total energy (in hartree) of a SiH_4 molecule with an elongated Si–H bond, evaluated with the HKS (circles), the Harris (hollow triangles), the cHarris (squares), and the cHKS (hollow stars) functionals during the SCF iterations of a KS calculation (left) and a HF calculation (right). For the KS calculation, the elongated Si–H bond length is 4 Å and the damping factor is 50%. For the HF calculation (only shown the data after 100th iteration), the elongated Si–H bond length is 12 Å, and the damping factors are 40% and 10% before and after the 100th iteration, respectively. The HF data of first 140 iterations behave very similarly.

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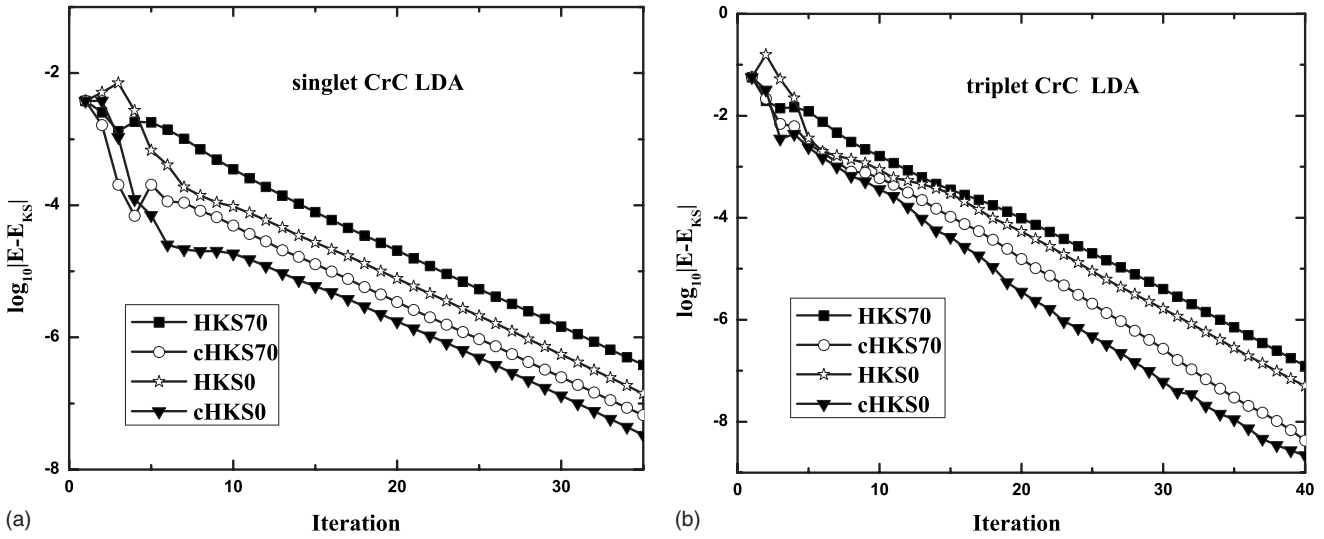

FIG. 5. Convergence of the total energies (in hartree) of singlet (left) and triple (right) CrC molecules during the SCF iterations of KS calculations. "HKS70" and "cHKS70" denote the HKS and cHKS energies with 70% damping, respectively. "HKS0" and "cHKS0" denote the HKS and cHKS energies without damping, respectively.

gence behavior. This supports our conclusion regarding the damping calculations for HF and H_2O: Whatever input densities are given, perturbative corrections always deliver improvement, sometimes quite substantial. Except for the first several iterations, the cHKS model always produces an energy higher than the converged one, which seems to suggest that the cHKS functional converges from above without much oscillation. This is different from the behavior of the Harris and cHarris models, whose convergence oscillates with iteration and is much less uniform.

V. CONCLUSION

In summary, we have generalized the cHKS and cHarris functionals to the HF method and have done case studies on several molecules. Numerical evidence shows that the performance of such perturbative correction models is greatly affected by the choice of the estimation of the density or density matrix. Even when the quality of such estimation is not good for those commonly implemented convergence schemes for DFT or HF methods, our perturbative correction models accelerate the convergence of the total energy drastically. For the difficult cases of the conventional SCF acceleration schemes, our perturbative correction models still deliver very promising results. Given the fact that no convergence acceleration method, including DIIS, level shifting, or damping, performs universally well for all molecular systems, our perturbative correction models thus offer powerful alternatives to obtain an accurate enough value of the total energy without completely converging the wave function.

TABLE I. Convergence of the SCF process of DFT calculations on CrC.

Molecular state	Damping	Energy model	Iterations[a]	Iterations[b]
^{1}CrC	No	HKS	28	73
		cHKS	23	
	Yes	HKS	32	85
		cHKS	25	
^{3}CrC	No	HKS	32	78
		cHKS	23	
	Yes	HKS	35	91
		cHKS	27	

[a]Number of iterations to converge the total energy within 1×10^{-6} hartree.
[b]Number of iterations to converge the total energy within 1×10^{-12} hartree.

ACKNOWLEDGMENTS

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