

LISTb: a *Better* Direct Approach to LIST

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ABSTRACT: Following our recent paper on linear-expansion shooting techniques (LIST) [Wang, Y. A.; Yam, C. Y.; Chen, Y. K.; Chen, G. H. *J. Chem. Phys.* **2011**, *134*, 241103], in which the direct approach (LISTd) and the indirect approach (LISTi) were proposed to accelerate the self-consistent field convergence, we discovered a highly simple solution to cure the linear-dependence problem of LISTd. The resultant method, LISTb, is a *better* direct approach to LIST and muscles similar performances to existing LIST methods. More promisingly, LISTb even outshines the best LIST method, LISTi, for systems involving transition-metal atoms.

The self-consistent field (SCF) method has been widely adopted to solve the Hartree–Fock and Kohn–Sham density-functional theory problems.¹ In the Roothaan–Hall procedure,¹ a usual SCF step involves rendering the input density matrix (D^{in}) into the Fock Hamiltonian matrix, then diagonalizing the Fock matrix to obtain the output density matrix (D^{out}) and generating an initial guess (input) for the next iteration. Writing this into equations,¹ for iteration i and orbital k , one has

$$\left\{ -\frac{1}{2}\nabla^2 + \hat{v}_{\text{eff}}[D^{\text{in}}] \right\} |\psi_{k,i}^{\text{out}}\rangle = \varepsilon_{k,i}^{\text{out}} |\psi_{k,i}^{\text{out}}\rangle \quad (1)$$

and

$$\sum_k^{\text{occ}} f_{k,i} |\psi_{k,i}^{\text{out}}\rangle \langle \psi_{k,i}^{\text{out}}| = D_i^{\text{out}} \quad (2)$$

where \hat{v}_{eff} is the effective potential, $f_{k,i}$ and $\varepsilon_{k,i}$ are the occupation number and the eigenvalue of orbital $\psi_{k,i}$ respectively, and the superscripts “out” and “in” stand for the output and input quantities, respectively. At iteration i , the electronic energy is normally evaluated via the Hohnberg–Kohn–Sham (HKS) energy functional:²

$$E_i^{\text{HKS}}[D_i^{\text{out}}] = \sum_k^{\text{occ}} f_{k,i}^{\text{out}} \varepsilon_{k,i}^{\text{out}} - \langle \hat{v}_{\text{eff}}[D_i^{\text{in}}] D_i^{\text{out}} \rangle + E_{\text{H}}[D_i^{\text{out}}] + E_{\text{XC}}[D_i^{\text{out}}] \quad (3)$$

where E_{H} and E_{XC} are the Hartree and exchange-correlation energies, respectively. However, such a pristine SCF algorithm only works for simple small species and fails in most contemporary quantum chemistry studies. There have been some great efforts in designing more powerful schemes to accelerate the convergence of the SCF process prior to 2011.^{3–13} Logically, such SCF acceleration schemes can be divided into two categories: ones that change the SCF route^{3–8} and ones that do not.^{9–13}

In the first category that involves changing the variational path, Pulay’s direct inversion in the iterative subspace (DIIS) algorithm is the most successful one and is widely used today.^{3,4} However, the standard DIIS algorithm does fail occasionally because the targeted commutativity between the Fock matrix and the density matrix is only a necessary but not a sufficient condition for SCF convergence toward an energy minimum. Alternatively, DIIS can be reformulated as a Krylov subspace accelerated inexact Newton (KAIN) method,⁵

but with limited success in performance improvement.⁶ To incorporate the condition of energy minimization, energy-DIIS (EDIIS) and augmented-Roothaan–Hall energy-DIIS (ADIIS) methods have been developed and have shown their ability in some challenging cases.^{7,8} Nonetheless, their strengths are more prominent in the early stages of SCF processes, whereas DIIS takes over the task of acceleration as the SCF is near the final convergence.⁸

The other technique that accelerates the total energy convergence is to only finesse the energy evaluation formula, which has been systematically investigated in our group.^{9–13} On the basis of the analysis of the difference between the final converged exact energy and the current-iteration HKS energy, the corrected HKS (cHKS) energy functional can be used to improve the evaluation of the total electronic energy.^{9,10}

$$E_i^{\text{cHKS}} = E_i^{\text{HKS}}[D_i^{\text{out}}] + \langle \Delta v_i (D^{\text{b}} - D_i^{\text{out}}) \rangle \quad (4)$$

with $\Delta v_i = (\hat{v}_{\text{eff}}[D_i^{\text{out}}] - \hat{v}_{\text{eff}}[D_i^{\text{in}}])/2$, where D^{b} denotes the best estimate of the final converged exact density matrix based on information currently available (before the convergence is reached).

Recently, two linear-expansion shooting techniques (LIST), namely, the direct approach (LISTd) and the indirect approach (LISTi), have been developed in our group.¹⁴ Within LISTd, we imposed the cHKS energy for any iteration to be equal to the final converged energy (exact up to second-order corrections), given that D^{b} is optimally expressed as a linear expansion of historical output density matrices. The final matrix equation for the LISTd method can be succinctly written as

$$\underbrace{\begin{pmatrix} 0 & -1 & -1 & \cdots & -1 \\ -1 & a_{11} & a_{12} & \cdots & a_{1m} \\ -1 & a_{21} & a_{22} & \cdots & a_{2m} \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ -1 & a_{m1} & a_{m2} & \cdots & a_{mm} \end{pmatrix}}_{\mathbf{A}} \underbrace{\begin{pmatrix} E \\ c_1 \\ c_2 \\ \vdots \\ c_m \end{pmatrix}}_{\mathbf{C}} = \underbrace{\begin{pmatrix} -1 \\ 0 \\ 0 \\ \vdots \\ 0 \end{pmatrix}}_{\mathbf{O}}, \quad (5)$$

with $a_{ij} = E_i^{\text{HKS}}[D_i^{\text{out}}] + \langle \Delta v_i (D_j^{\text{out}} - D_i^{\text{out}}) \rangle$, where E is the current best estimate of the total energy and D_j^{out} is a historical

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output density matrix used to expand D^b via the expansion coefficients $\{c_j\}$:

$$D^b = \sum_{j=1}^m c_j D_j^{\text{out}} \quad (6)$$

with the normalization condition

$$\sum_{j=1}^m c_j = 1 \quad (7)$$

In eq 5, one should note that matrix **A** for LISTd is asymmetric, which will become vitally important later.

Taking an alternative approximation, within LISTi, we imposed the equalization of the cHKS energies expanded in terms of the input and output density matrices, resulting in an almost identical matrix equation except that the matrix elements of **A** are defined as $\langle \Delta v_i (D_j^{\text{out}} - D_j^{\text{in}}) \rangle$. Solving the linear equations for LISTd or LISTi, one has a set of expansion coefficients $\{c_j\}$ to construct the input effective potential for the next iteration

$$\hat{v}_{\text{eff}}[D_{m+1}^{\text{in}}] = \sum_{j=1}^m c_j \hat{v}_{\text{eff}}[D_j^{\text{out}}] \quad (8)$$

Case studies have shown that LISTi is more effective than LISTd, because LISTd suffers from linear-dependence problems near convergence.¹⁴ Hereafter, we introduce a *better* direct approach to the LIST method, LISTb, which is capable of curing the linear-dependence problem rooted in LISTd.

We first start with the key imposition within LISTd:¹⁴

$$\sum_{j=1}^m c_j a_{ij} = E, \quad \forall i \quad (9)$$

Upon introducing an additional set of expansion coefficients $\{c'_i\}$ with $\sum_{i=1}^m c'_i = 1$, we can generalize eq 9 into a double summation form:

$$\sum_{i=1}^m \sum_{j=1}^m c'_i c_j a_{ij} = E \quad (10)$$

Now, interchanging the order of summations on the left-hand side of eq 10, we arrive at

$$\sum_{j=1}^m c_j \left\{ \sum_{i=1}^m c'_i a_{ij} \right\} = E \quad (11)$$

in which we can choose the values of $\{c'_i\}$ properly, such that

$$\sum_{i=1}^m c'_i a_{ij} = E', \quad \forall j \quad (12)$$

After plugging eq 12 back into eq 11, we readily conclude $E = E'$ because of eq 7. Then, eqs 9–12 can be recast in terms of a single expansion over $\{c'_i\}$ instead:

$$\sum_{i=1}^m c'_i a_{ij} = E, \quad \forall j \quad (13)$$

which immediately leads to a matrix equation virtually identical to eq 5:

$$\mathbf{B}\mathbf{C}' = \mathbf{A}^T \mathbf{C}' = \mathbf{O} \quad (14)$$

except that matrix **B** is exactly the transpose of matrix **A** ($b_{ij} = a_{ji}$) and $\mathbf{C}' = (E, c'_1, c'_2, \dots, c'_m)^T$. Of course, this is only meaningful if

matrix **B** differs from matrix **A**, which fortunately is so, as already noted above.

Amazingly, it turns out that this transposition is the key to success here: it avoids the severe linear dependence of LISTd while inheriting the power of LIST. The linear-dependence problem of LISTd stems from the fact that as the calculation approaches the final convergence, the rightmost column of matrix **A** becomes increasingly similar to the column on its left, with an element-wise difference

$$a_{i,m} - a_{i,m-1} = \langle \Delta v_i (D_m^{\text{out}} - D_{m-1}^{\text{out}}) \rangle \quad (15)$$

which is of second order of the density matrix residual error. On the other hand, LISTb will not suffer from the same problem of LISTd, because the difference between two neighboring columns of matrix **B**

$$b_{i,j} - b_{i,j-1} = (E_j^{\text{HKS}} - E_{j-1}^{\text{HKS}}) + \langle (\Delta v_j - \Delta v_{j-1}) D_i^{\text{out}} \rangle - \langle \Delta v_j D_j^{\text{out}} \rangle + \langle \Delta v_{j-1} D_{j-1}^{\text{out}} \rangle \quad (16)$$

is dominated by terms of first order of the density matrix residual error.

According to Cramer's rule,¹⁵ the solution to eq 5 or eq 14, $\{c_i\}$ for LISTd or $\{c'_i\}$ for LISTb, is the quotient of two determinants, with the numerator being the determinant of a matrix with one column replaced by vector **O** and the denominator being the determinant of matrix **A**. For example, $c_m = |\mathbf{A}_m|/|\mathbf{A}|$, where matrix \mathbf{A}_m is simply matrix **A** with its last column replaced by vector **O**. Therefore, in the LISTd scheme, as it approaches the final convergence, the tiny difference between the last two columns, eq 15, in matrix **A** will routinely result in c_{m-1} and c_m of very big, nearly identical magnitude but with opposite signs. In contrast, LISTb has a much bigger difference in the last two columns, eq 16, that avoids the build-up of the linear-dependence problem. Thus, the transpose of matrix **A** of LISTd into matrix **B** of LISTb yields a different, much improved acceleration path. For future reference, we name the above transpose technique "alleviation of linear dependence in asymmetric system via transposition" (ALDAST).

To compare LISTb with other LIST members and DIIS, all LIST methods, including LISTb, LISTd, and LISTi, were implemented in the NWChem 5.0 source code.¹⁶ Within a LIST calculation, the cHKS total electronic energy functionals were evaluated at every iteration.^{9,10} In all calculations, only five Fock and density matrices were used in the linear mixing unless otherwise noted, and no other SCF convergence schemes, such as level shifting or density damping, were invoked. For all calculations, full convergence was defined as the energy difference between two consecutive iterations smaller than 10^{-9} Hartrees.

We chose several molecules to benchmark the performance of our methods. For hydrogen fluoride (HF), the H–F bond length was 0.920 Å. For water (H₂O), the two H–O bond lengths and the H–O–H bond angle were 0.965 Å and 103.75°, respectively. For ethene (C₂H₄), the C–C bond length and all C–H bond lengths were 1.335 and 1.098 Å, respectively, while all H–C–C bond angles were 122.88°. The C–C and C–H bond lengths in benzene (C₆H₆) were all set to 1.396 and 1.097 Å, respectively, and all bond angles were 120°. For the aforementioned four molecules, a local density approximation (LDA) exchange-correlation functional was used in conjunction with the 6-31G basis set.^{17,18} A large water cluster system, (H₂O)₅₁, was also

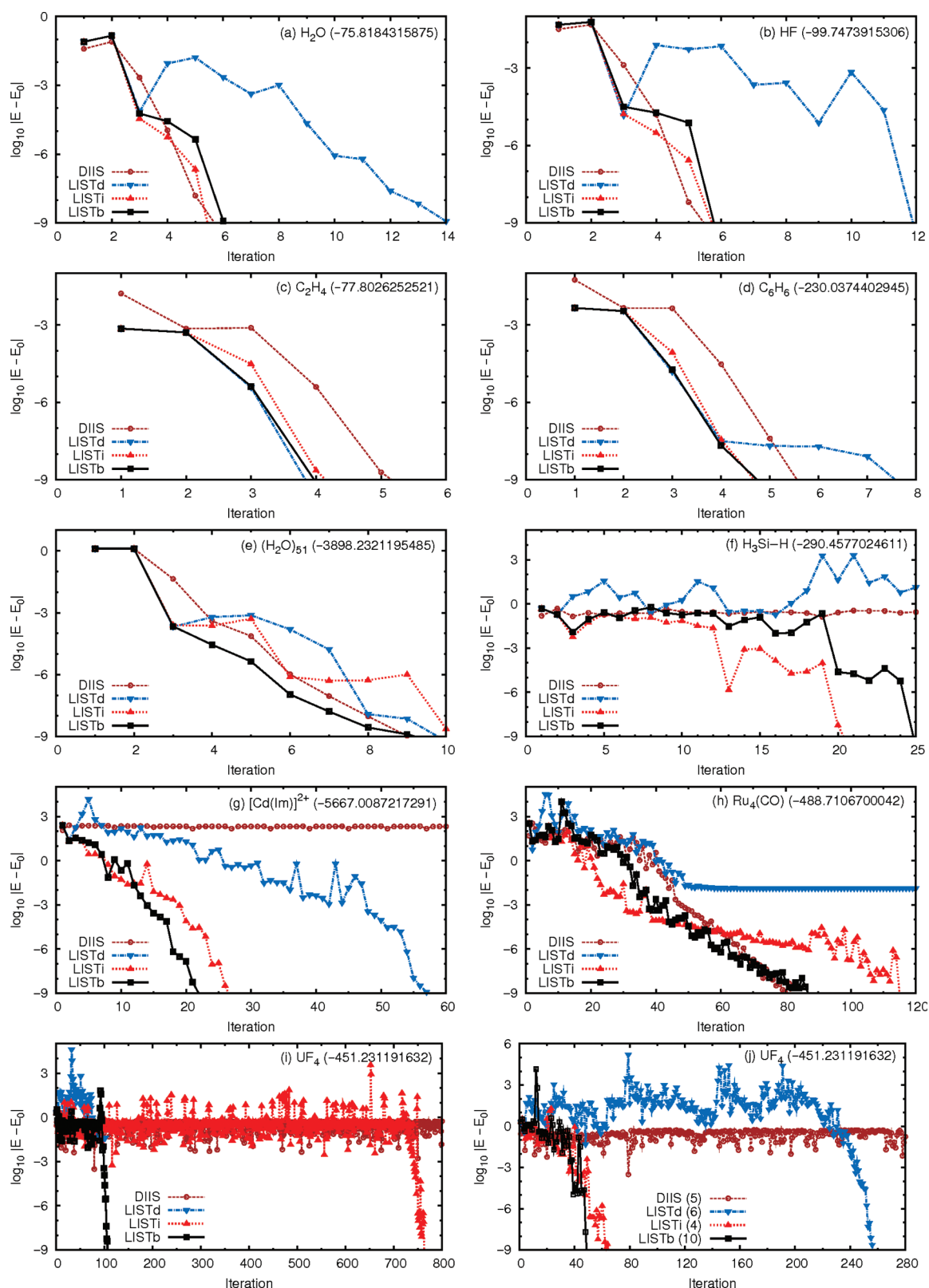


Figure 1. Convergence of the total energy (in Hartrees) for different systems. The final converged energy E_0 (in Hartrees) is in the parentheses in the topright corner of each subfigure. In j, the optimal linear-expansion length of each method is in the parentheses of the legend. In a–i, the linear-expansion length is fixed to 5.

calculated at the B3LYP/6-31G** level of theory,¹⁹ and its geometry can also be found in ref 8.

We have also performed numerical tests on several challenging systems that had been studied elsewhere under similar conditions.^{7–9,13}

A silane (SiH_4) molecule with a much elongated Si–H bond was calculated at the LDA/6-31G* level of theory, under the same conditions as previously studied:^{9,14} the three regular and the elongated Si–H bond lengths were 1.47 and 4.00 Å, respectively, and all four H–Si–H bond angles were 109.28°. A cadmium-imidazole cation ($[\text{Cd}(\text{Im})]^{2+}$)^{8,14} was calculated at the B3LYP/3-21G level of theory¹⁹ using the core Hamiltonian as the very first initial guess. The tetranuclear ruthenium carbonyl cluster $\text{Ru}_4(\text{CO})_8$ and tetrahedral uranium fluoride (UF_4) with a U–F bond length of 1.98 Å⁷ were also calculated at the B3LYP/LanL2DZ level with the core electrons of the transition-metal atoms represented by the LanL2 pseudopotentials.²⁰ For UF_4 , a superposition of atomic densities was utilized as the very first initial guess, different from ref 7.

The performances of different LIST methods and DIIS are compared in Figure 1. For simple molecules around their equilibrium geometries, such as HF and H_2O , LISTb, LISTi, and DIIS demonstrate comparable performances (maybe with a slightly slower pace for LISTb), and all three outpace LISTd by about eight iterations. Cases with more complex π bonding interactions, i.e., C_2H_4 and C_6H_6 , also confirm that LISTb is comparable to LISTd, LISTi, and DIIS: all of them can achieve a similar rate of convergence for SCF calculations, whereas LISTd is only marginally slower than the other three algorithms. For the much bigger system, $(\text{H}_2\text{O})_{51}$, LISTb unequivocally outperforms all other methods, whereas LISTi goes sideways after iteration six but catches up after iteration nine. The silane molecule with a much elongated Si–H bond represents a prototype case of nonequilibrium structures. Both DIIS and LISTd fail in this case, while LISTb and LISTi can converge within 25 iterations with LISTi leading by four iterations.

For molecules containing transition-metal atoms that involve much more complicated bonding interactions, LISTb is the clear winner among all four methods compared in this study. Despite the complete failure of DIIS for $[\text{Cd}(\text{Im})]^{2+}$, all three LIST methods work but at different speeds: LISTb can reach full convergence within only 22 iterations, five and 35 iterations faster than LISTi and LISTd, respectively. In the case of $\text{Ru}_4(\text{CO})$, all four methods converge, but LISTd guides the system toward a different energy of -488.6972714297 Hartrees, higher than the true ground state by about 0.0134 Hartrees. LISTi falls behind eventually even after outperforming others in the first 40 iterations. LISTb begins to lead the race after 50 iterations, while DIIS only catches up after nearly 80 iterations. As for UF_4 , LISTb only takes about 100 iterations to converge, whereas LISTi spends more than 760 iterations and DIIS does not converge for the first 1000 iterations. Again, the LISTd scheme in this case converges to a higher energy of -451.1890747131 Hartrees within 100 iterations.

We also found that the length of the linear expansion of eq 8 does affect the convergence behavior of all methods studied here. Taking $\text{Ru}_4(\text{CO})$ for example, DIIS only converges when the linear-expansion length is 5. For this very reason, we have intentionally presented the results with five expansion Fock matrices in Figure 1a–i. If we choose the fastest convergence rate of each method with its optimal expansion length, Figure 1j shows that, for UF_4 , LISTb and LISTi can reach full convergence within 49 and 65 iterations with 10 and 4 expansion Fock matrices, respectively. Interestingly, LISTd does converge with six expansion Fock matrices, but only after 256 iterations. It is thus desirable to finetune the length of the linear expansion to achieve optimal performance, although five expansion Fock matrices seem to be a good default choice for most systems investigated thus far.

Overall, the above case studies indicate that LISTb rivals LISTi in terms of the robustness and effectiveness of accelerating SCF convergence, especially for species containing transition-metal atoms. Though LISTb shares the same overall matrix equation with LISTd and LISTi, but with the ALDAST technique curing the severe linear-dependence problem faced by LISTd, LISTb delivers a more smooth, much faster SCF convergence path, particularly illustrated by the $\text{Ru}_4(\text{CO})$ and UF_4 calculations. On the basis of the numerical tests reported in this work and previous publication,¹⁴ we now wholeheartedly endorse LISTb and LISTi as the two most powerful implementations of LIST.

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