

Robust and Reliable Multilevel Minimization of the Kohn–Sham Energy

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Abstract: Kohn–Sham density-functional calculations are used in many branches of science to obtain information about the electronic structure of molecular systems and materials. Conventional algorithms for minimization of the Kohn–Sham energy have certain deficiencies, however, that may cause divergence or, worse, convergence to unphysical saddle points. We here present a three-level hierarchical minimization strategy which is both more efficient and robust than the conventional algorithms and which does not suffer from the flaws of these algorithms. Using the three-level minimization strategy, the molecular density is built up in a hierarchical fashion in accordance with chemical insight: First, the molecular density is composed by a superposition of atomic densities; next, bonds are formed by performing a simple valence-shell optimization; finally, the molecular description is refined by an optimization in the full molecular basis. Importantly, the density matrix generated at each of the two lower levels in this hierarchy is transferred to the next without loss of information. Examples demonstrate the efficacy and robustness of the proposed scheme.

1. Introduction

A common trend in many fields of science is the increased use of atomistic models for predictions and rationalizations. In particular, theoretical and experimental studies of molecular properties and interactions rigorously based on the laws of quantum mechanics are making important contributions to advances in many branches of science. Kohn–Sham (KS) density-functional theory^{1,2} currently represents the best compromise between cost and accuracy in describing the electronic structure of molecules and materials. Indeed, thousands of KS calculations are carried out every day, not only in the fields of chemistry and physics but also in related fields such as molecular biology and medicine, to obtain information of the electronic structure of molecules and materials. As ever more complex calculations are being

attempted, it becomes paramount to use algorithms that locate the KS energy minimum reliably and efficiently.³

In KS theory, the electronic energy is minimized with respect to variations in the one-electron density matrix. The efficiency and reliability of this minimization depends not only on the optimization algorithm itself but also on the quality of the starting density matrix. Usually, this matrix is obtained by diagonalizing the one-electron Hamiltonian (HCOE) or the Hückel Hamiltonian. Starting density matrices have also been obtained by carrying out an initial molecular calculation in a minimal basis, followed by projection of the obtained density matrix onto the full basis. Recently, van Lenthe et al. demonstrated that a starting density matrix constructed as a superposition of atomic density matrices constitutes the best available approach to date.⁴

Here, we propose a new strategy for the optimization of the KS energy, where the minimization is carried at three

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levels of description, of increasing cost and complexity. First, the molecule is formed from separate atoms, by a simple superposition of atomic densities. Next, chemical bonds are formed in a valence-shell description, using a small subset of the full molecular basis. This second level constitutes the crux of our proposed scheme—it allows all the essential elements of molecular bonding to be approximated accurately, at a cost much smaller than that of a full-basis optimization. Finally, and importantly, the information obtained about the system at this second level is transferred—without loss of information—to the third level, where the description is refined in the full molecular basis. Notably, this full-basis optimization begins either inside or close to the local region—the difficult global optimization is essentially completed at the first and second levels, providing a high-quality starting guess for the expensive final refinement.

The proposed three-level method can in principle be combined with any existing method for the minimization of the KS energy from a given starting guess. We here use the augmented Roothaan–Hall (ARH) method,⁵ which was recently shown to possess several advantages over the traditional minimization schemes.

In the traditional KS optimization scheme, each iteration consists of two steps: first, a Roothaan–Hall (RH) step, where the KS matrix (the energy gradient) is constructed from the current approximate density matrix and then diagonalized to yield a new density matrix; second, an averaging step, where the density matrix for the next RH iteration is determined as a combination of the new and old density matrices using Pulay’s method of direct inversion in the iterative subspace (DIIS).⁶ Although successful, this traditional two-step RH/DIIS scheme occasionally fails—in particular, for the larger and more complicated electronic systems often studied by KS theory nowadays. Since only gradient information is used in the RH/DIIS scheme, the optimization may sometimes diverge or converge to a saddle point rather than the ground-state minimum. Whereas divergence is an obvious failure, saddle-point convergence is more pernicious in that it typically leaves the user unaware that the provided solution does not properly represent the electronic ground state.

In the ARH algorithm, the two separate RH and DIIS steps are merged into a single, concerted minimization step that fully exploits the second-derivative (Hessian) information available from the current and previous iterations. At each ARH iteration, a local quadratic model of the KS energy is constructed that is exact (within the quasi-Newton approximation) in the directions of the old density matrices and approximate (but accurate) in the remaining directions. The new density matrix is then obtained by applying the trust-region minimization method to this quadratic model, thereby ensuring that the energy is lowered at each iteration and that a minimum is obtained.⁷ Therefore, the ARH method does not suffer from the deficiencies of the RH/DIIS method.⁵

Combining the ARH method with the three-level (3L) method introduced in this paper, we arrive at a highly efficient and robust strategy for KS energy optimizations. Following the introduction of the 3L scheme in Section 2, we demonstrate the efficacy and robustness of the combined

ARH-3L method in Section 3, where comparisons are also made with traditional methods. Section 4 contains some final remarks.

2. The Three-Level Optimization of the KS Energy

The optimization of the KS energy presented here is carried out at three consecutive levels, where the density matrix obtained at one level is used as starting guess at the next level. The three optimization levels are as follows: separate atomic optimizations, a valence-basis molecular optimization, and a full-basis molecular optimization. The cost of the optimization is dominated by the full-basis optimization, which is typically an order of magnitude higher than that of the valence-basis optimization, while the cost of the atomic optimizations is negligible. In the following sections, we describe each optimization level in greater detail.

2.1. Atom-in-a-Molecule Density Matrix. To generate an atom-in-a-molecule density matrix, we first carry out a separate canonical ensemble KS optimization for each atom *P* in the molecule, in an atomic-orbital (AO) basis $|\chi^P\rangle$ consisting of local atom-centered functions. In a canonical ensemble KS calculation, fractional occupation numbers are assigned to the highest occupied AOs if they are not fully occupied to ensure that a spherical symmetric atomic density matrix is obtained.

The eigenvectors of the atomic KS eigenvalue problem are next partitioned as $\mathbf{C}^P = (\mathbf{C}_o^P, \mathbf{C}_u^P)$, where \mathbf{C}_o^P contains the (possibly fractionally) occupied AOs and \mathbf{C}_u^P the unoccupied ones. (In our notation, subscripts ‘o’ and ‘u’ denote ‘occupied’, and ‘unoccupied’, respectively.) In the $|\chi^P\rangle$ basis, the atom-optimized AOs are then given by

$$|\xi_o^P, \xi_u^P\rangle = |\chi^P\rangle (\mathbf{C}_o^P, \mathbf{C}_u^P) \quad (1)$$

and the corresponding spherically symmetric atomic density matrix basis becomes

$$\mathbf{D}^P = \begin{pmatrix} \mathbf{D}_o^P & \mathbf{0} \\ \mathbf{0} & \mathbf{0} \end{pmatrix} \quad (2)$$

where the diagonal matrix \mathbf{D}_o^P contains the (fractional) occupation numbers of the occupied atomic orbitals \mathbf{C}_o^P . For an oxygen atom with electronic structure $(1s^2 2s^2 2p^4)$ the occupied atom-optimized AOs are $(\xi_{1s} \xi_{2s} \xi_{2px} \xi_{2py} \xi_{2pz})$ with occupation numbers $(2, 2, 4/3, 4/3, 4/3)$.

To prepare for the subsequent molecular calculation, we now set up a full atomic (denoted by subscript ‘A’) basis consisting of the atom-optimized AOs

$$|\xi_A\rangle = |\xi_{Ao}, \xi_{Au}\rangle \quad (3)$$

where the sets of occupied and unoccupied atomic orbitals are given by

$$|\xi_{Ao}\rangle = |\xi_o^P, \xi_o^Q, \dots\rangle \quad (4)$$

$$|\xi_{Au}\rangle = |\xi_u^P, \xi_u^Q, \dots\rangle \quad (5)$$

Likewise, we generate a molecular density matrix as the superposition of atomic density matrices

$$\mathbf{D}_A = \begin{pmatrix} \mathbf{D}_{Ao} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} \end{pmatrix} \quad (6)$$

whose occupied part is the superposition (direct sum) of the occupied atomic density matrices

$$\mathbf{D}_{Ao} = \mathbf{D}_o^P \oplus \mathbf{D}_o^Q \oplus \dots \quad (7)$$

The resulting atom-in-a-molecule density matrix \mathbf{D}_A satisfies the symmetry and trace conditions of a valid KS density matrix but not the idempotency condition. However, this lack of idempotency does not matter as the density matrix will only be used to construct a KS matrix, from which an idempotent density matrix is obtained from the KS eigenvectors in agreement with the Aufbau principle.

2.2. Valence-Basis Molecular Optimization. In the ATOMS scheme advocated by van Lenthe et al.,⁴ a full-basis molecular calculation is now carried out in the full atomic orbital basis $|\chi\rangle = |\chi^P, \chi^Q, \dots\rangle$, using the full-basis atom-in-a-molecule density matrix \mathbf{D}_A , eq (6), transformed from the $|\zeta_A\rangle$ basis to the $|\chi\rangle$ as a starting guess. We instead first perform a molecular calculation in the smaller atom-optimized AO occupied basis $|\zeta_{Ao}\rangle \subset |\zeta_A\rangle$, using \mathbf{D}_{Ao} of eq (7) as a starting guess. The purpose of this valence-basis calculation is to incorporate the essential features of bonding into the density matrix at low cost, before the expensive final refinement of the molecular density matrix in the full atomic orbital basis.

The valence-basis optimization is carried out in the usual manner, by treating the occupied atomic basis functions $|\zeta_{Ao}\rangle$ as a generally contracted basis with contraction coefficients obtained by multiplying \mathbf{C}_{Ao}^P on the $|\chi^P\rangle$ atomic contraction coefficients. The occupied atom-optimized AO basis $|\zeta_{Ao}\rangle$ contains core as well as valence atomic orbitals—for a first-row atom, for example, it contains the atomic orbitals $(\zeta_{1s}\zeta_{2s}\zeta_{2px}\zeta_{2py}\zeta_{2pz})$. Since the 1s core orbitals are reasonably well described by the ζ_{1s} atomic orbitals and change little upon bond formation, they may be omitted from the valence-basis optimization, but this has not been done in the calculations reported here.

The valence-basis calculation may be carried out using any standard KS optimization scheme. We use the ARH algorithm with \mathbf{D}_{Ao} as the starting density matrix. At convergence, the optimization returns a density matrix $\mathbf{D}_{Vo}^{\Delta o}$ in the $|\zeta_{Ao}\rangle$ basis that satisfies the Fock/KS eigenvalue equation

$$\mathbf{F}^{Ao}(\mathbf{D}_{Vo}^{\Delta o})\mathbf{C}_V = \mathbf{S}^{Ao}\mathbf{C}_V\epsilon_V \quad (8)$$

providing us with a valence optimized molecular basis as a linear combination of the occupied atom-optimized AOs

$$|\zeta_V\rangle = |\zeta_{Vo}, \zeta_{Vu}\rangle = |\zeta_{Ao}\rangle(\mathbf{C}_{Vo}, \mathbf{C}_{Vu}) \quad (9)$$

where the \mathbf{S}^{Ao} and \mathbf{F}^{Ao} are the overlap and Kohn–Sham matrices in the occupied atom-optimized AO basis. We have here partitioned the orbitals as $\mathbf{C}_V = (\mathbf{C}_{Vo}, \mathbf{C}_{Vu})$, where \mathbf{C}_{Vo} and \mathbf{C}_{Vu} contain the occupied and virtual orbitals, respectively. (We use ‘V’ to denote ‘valence’, in contrast to ‘A’ for ‘atomic’.) In this valence basis $|\zeta_V\rangle$, the molecular density matrix becomes

$$\mathbf{D}_V = \begin{pmatrix} \mathbf{I} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} \end{pmatrix} \quad (10)$$

where \mathbf{I} is a unit matrix of the dimension of $|\zeta_{Vo}\rangle$.

In the course of the valence-basis optimization, chemical bonds are formed between neighboring atoms, providing us with a set of local occupied and virtual orbitals with contributions only from neighboring atoms involved in the bond formation. For high locality, diffuse basis functions may be omitted from the optimization of the atomic orbitals.

Returning to the full atom-optimized AO basis eq (3), we see that our atomic and valence-basis KS optimizations have provided us with the following partitioning of the basis

$$|\zeta_F\rangle = |\zeta_V, \zeta_{Au}\rangle = |\zeta_{Vo}, \zeta_{Vu}, \zeta_{Au}\rangle \quad (11)$$

which, apart from being local, has a definite orbital occupancy associated with each orbital. It may therefore be useful to express the results of a full-basis KS optimization (discussed below) in the $|\zeta_F\rangle$ basis (or in its orthogonalized counterpart), rather than in the atomic-orbital basis, as is usually done. Likewise, it may be useful to express KS response-function calculations and correlated calculations in this basis, as discussed in a forthcoming paper.

2.3. Full-Basis Molecular Optimization. At the beginning of the full-basis optimization, we have a density matrix \mathbf{D}_V [eq (10)] that represents the KS energy minimum in the molecular valence basis $|\zeta_V\rangle$ but not yet in the full basis $|\zeta_F\rangle \supset |\zeta_V\rangle$. In the full basis, the corresponding density matrix is given by

$$\mathbf{D}_F^F = \begin{pmatrix} \mathbf{D}_V & \mathbf{0} \\ \mathbf{0} & \mathbf{0} \end{pmatrix} \quad (12)$$

which (like \mathbf{D}_V in the valence basis) satisfies the symmetry, trace, and idempotency conditions. The molecular valence basis optimized density matrix \mathbf{D}_V is thus transferred to the full basis $|\zeta_F\rangle$ without loss of information. Our final calculation is carried out in the $|\zeta_F\rangle$ basis using \mathbf{D}_F^F as the starting guess for an ARH optimization in this basis.

3. Illustrative Results

To illustrate the performance of the ARH-3L method, we present in Section 3.1 calculations on a Rh complex [(4-dimethylaminopyridine-*N*)dicarbonylchlororhodium [Rh(C₇N₂H₁₀)(CO)₂Cl]] at the B3LYP(VWN3)/3–21G level of theory^{8–10} and on a model of vitamin B12, at the BP86/AhlrichsVDZ^{11,12} level. The valence- and full-basis optimizations are carried out using the ARH method. In Section 3.2, ARH-3L optimizations are compared with optimizations using the RH/DIIS algorithm without RH level shifting. Most electronic-structure programs use a RH/DIIS algorithm with some level shifting in the initial RH iterations and possibly with other modifications so as to accelerate convergence.

In ref 4, van Lenthe et al. demonstrated the usefulness of their ATOMS approach by carrying out B3LYP calculations on 23 transition-metal complexes—in Section 3.3, we compare their results with those of the ARH-3L method.

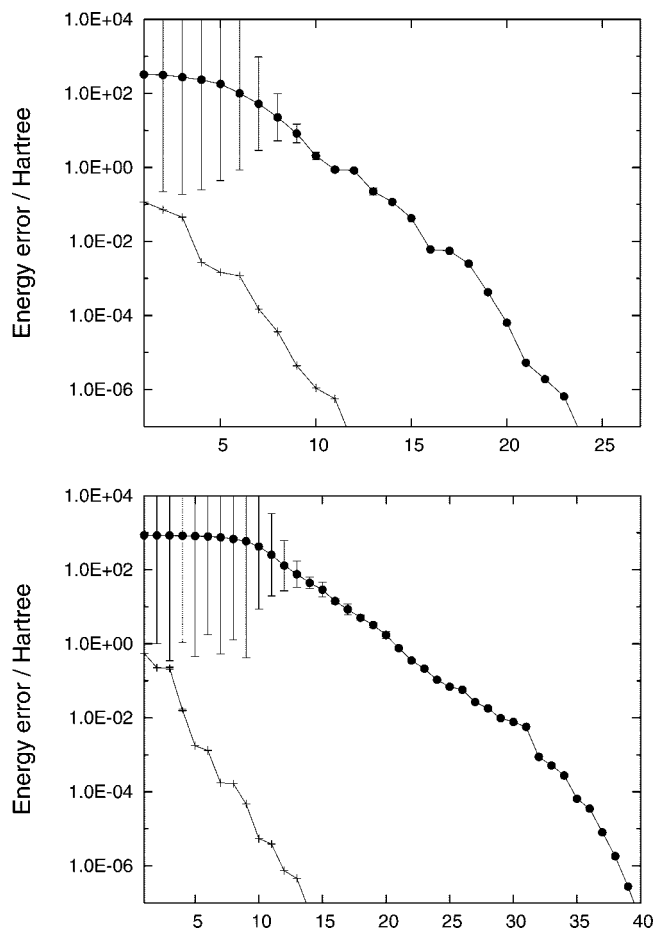


Figure 1. The convergence of calculations on the Rh complex (upper panel) and B12 (lower panel) using the ARH-3L method (plus signs) and ARH with a HCore initial guess of the density matrix (full circles). The level shifts at each iteration are displayed as error bars.

All calculations have been carried out with a development version of the Dalton program package.¹³ For molecular geometries, see the Supporting Information.

3.1. Convergence of ARH-3L Calculations. In Figures 1 and 2, the convergence of the ARH-3L calculations on the Rh complex (upper panel) and B12 (lower panel) is compared to the convergence obtained using other optimization strategies, by plotting the energy at each full-basis iteration relative to the converged full-basis energy. In Figure 1, the convergence of ARH-3L calculations is compared with that of ARH calculations with a one-electron Hamiltonian (HCore) starting guess. The error bars represent the magnitudes of the level shifts, plotted on a relative scale. Because of the poor HCore starting guess, large shifts (up to 3.2 for the Rh complex and 42.4 for B12) are imposed in the global region (first 5–15 iterations) of the ARH optimization. These shifts decrease as the optimizations approach the local region, where no shifts are needed. By contrast, hardly any level shifts are needed in the ARH-3L optimizations, indicating that these optimizations begin close to the local region, bypassing the difficult global and semiglobal regions.

Although ARH calculations with HCore starting guesses provide useful insight into the performance of the ARH-3L method, better guesses are usually used in electronic-structure

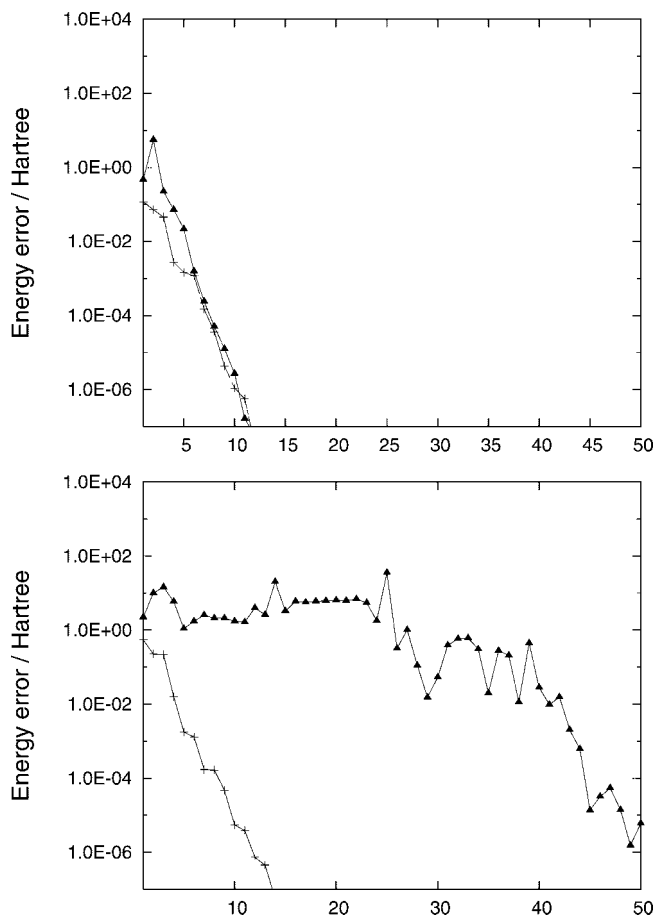


Figure 2. The convergence of calculations on the Rh complex (upper panel) and B12 (lower panel) using the ARH-3L method (plus signs) and RH/DIIS (full triangles) with ATOMS starting density matrix.

programs. In Figure 2, we compare ARH-3L optimizations of the Rh complex (upper panel) and of B12 (lower panel) with optimizations using the plain RH/DIIS algorithm with an ATOMS starting density matrix and without level shifting in the initial iterations.

For the Rh complex, our plain RH/DIIS implementation converges in about the same number of iterations, as does the ARH-3L method. In the more difficult B12 case, the superiority of the ARH-3L method becomes more pronounced; the RH/DIIS method requires significantly more iterations than the ARH-3L method to reach convergence.

3.2. Robustness and Reliability of the ARH Algorithm. To demonstrate the robustness of the ARH algorithm, we here compare the convergence of the full-basis ARH method with that observed with the RH/DIIS implementation for the two test molecules, using the HCore starting guess—see Figure 3. For both molecules, the ARH convergence is smooth and fast, while the convergence using RH/DIIS is more erratic. For the Rh complex, the optimizations require about the same number of iterations. For B12, on the other hand, the RH/DIIS method fails, whereas the ARH method shows its typical robust global convergence.

Because of the good starting density matrices in the ARH-3L method, it might be thought that the choice of optimization algorithm matters little. This is not the case, as demonstrated by calculations on an imidazolecadmium(2+)

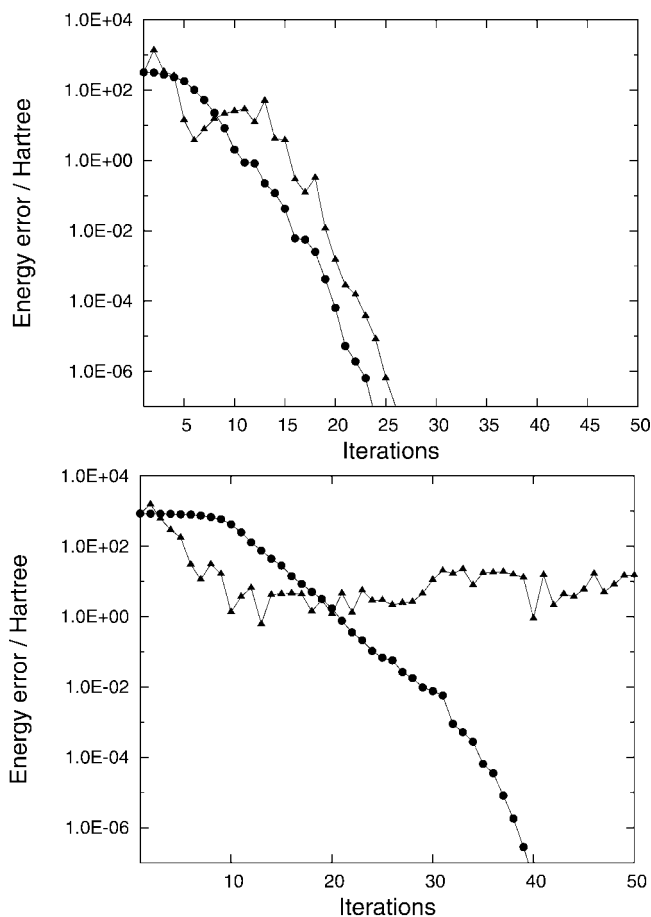


Figure 3. The convergence of calculations on the Rh complex (upper panel) and B12 (lower panel) with the HCore starting density matrix using the ARH method (full circles) and the RH/DIIS method (full triangles).

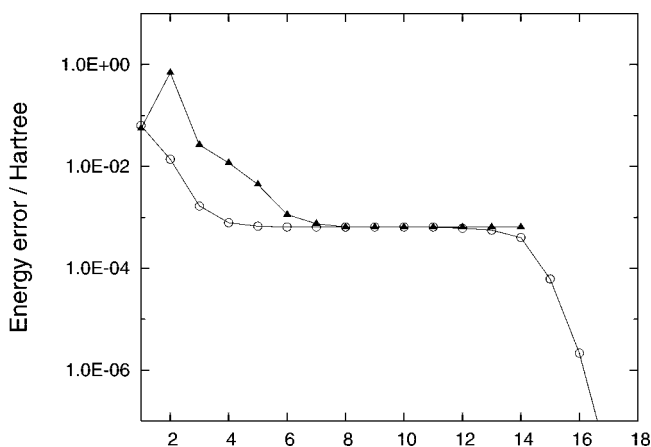


Figure 4. Convergence of full-basis B3LYP(VWN3)/3-21G calculations of imidazolecadmium(2+) using the ARH-3L (open circles) and RH/DIIS (full triangles) methods. Both calculations start from a valence-basis optimized density matrix.

complex, whose full-basis ARH-3L convergence is displayed in Figure 4. The horizontal plateau in Figure 4 arises as the optimization converges toward a saddle point. Close to the saddle point, the ARH algorithm detects a negative Hessian eigenvalue, upon which the optimization turns toward the minimum and converges quickly. From the same starting

Table 1. Statistics for Calculations on a Test Set of 23 Transition-Metal Complexes^{4a}

	ΔE (Hartrees)		num. of iter. (%)			
	max.	mean	best	mean	worst	fail
HCore	159.63	159.63	291	291	291	22
MINGUESS	2.03	1.57	88	117	175	1
ATOMS	1.93	0.46	100	100	100	0
ARH-3L	0.20	0.06	42	78	94	0

^a The HCore, MINGUESS, and ATOMS results are taken from ref 4. In addition, results are given for the ARH-3L algorithm. ΔE is the energy difference between the initial and final iterations. The number of iterations is given in percent relative to the ATOMS calculation. The final column contains the number of optimizations that did not converge.

guess, the RH/DIIS calculation converges (very tightly, with a gradient norm less than 10^{-6}) to the same saddle point in few iterations, without recognizing that a saddle point instead of a minimum has been reached. Moreover, several standard programs also converge to this saddle point.⁵ To avoid saddle-point convergence, it is therefore important to use the ARH algorithm, even with very good starting density matrices.

3.3. Comparison of ARH-3L and ATOMS Starting Density Matrices. We now consider the 23 transition-metal complexes studied by van Lenthe et al., using the RH/DIIS algorithm with the ATOMS starting guess and a predefined level shift in the first iterations.⁴ For comparison, van Lenthe et al. reported MINGUESS calculations, where the starting guess was obtained in a preliminary STO-3G calculation and then projected onto the full TZVP basis¹⁴ as well as calculations with the HCore starting guess. The results of van Lenthe et al. are summarized in Table 1, which contains information on ΔE (the energy in the first iteration relative to the converged energy) and the number of iterations in the optimizations (in percent relative to the ATOMS calculations in the same table). We have augmented the table by including results obtained with the ARH-3L method.

The results in Table 1 demonstrate the superiority of the ARH-3L valence-basis starting guess, whose energy on average is only 0.06 hartree above the converged result, compared with 1.93 hartree for the ATOMS starting guess.

The MINGUESS calculations are not an improvement on the ATOMS calculations because of the errors introduced in the projection onto the TZVP basis. The loss of information that arises when the molecular STO-3G density matrix is projected onto the full basis is thus very significant. In the ARH-3L method, the molecular valence-basis density matrix is transferred to the full basis without loss of information.

On average, the ARH-3L calculations use 22% fewer iterations than do the ATOMS calculations—in the best case, 58% fewer iterations are needed. The ARH-3L method thus converges significantly faster than previous methods, already for these small systems.

4. The Three-Level Approach Summarized

We have presented a novel ARH-3L optimization scheme for the KS energy, consisting of three levels:

1) Atomic canonical-ensemble optimizations in the $|\chi^p\rangle$ atomic basis, giving a spherically symmetric atomic density matrix. Superposition of atomic density matrices is used as the starting guess in the valence-basis molecular optimization.

2) A valence-basis molecular ARH optimization in the $|\zeta_{\text{AO}}\rangle$ basis, giving a valence-basis starting guess for the full-basis molecular optimization

3) A full-basis molecular ARH optimization of the KS energy

In the three-level ARH-3L method, information about the molecular system is built up gradually, exploiting chemical insight. Because of the high quality of the valence- and full-basis starting guesses, these minimizations begin close to the local region, bypassing almost entirely the difficult global region. The cost of the first two ARH-3L levels, where the global optimization is carried out, is insignificant compared with that of the third level.

The ARH-3L algorithm is highly cost-effective, requiring significantly fewer iterations than other algorithms, even for the small systems considered here. Bearing in mind that a large proportion of the CPU time allocated to quantum-chemical simulations is actually spent optimizing KS energies, this translates into considerable savings of computational resources. Furthermore, the ARH-3L method exhibits reliable convergence, also when standard methods fail. Last but not least, whereas the traditional methods may converge to saddle points, the ARH-3L method is designed to avoid such points. For both efficiency and reliability, we recommend its use in molecular KS calculations.

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Supporting Information Available: Atomic coordinates. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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