Starting SCF Calculations by Superposition of Atomic Densities

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Abstract: We describe the procedure to start an SCF calculation of the general type from a sum of atomic electron densities, as implemented in GAMESS-UK. Although the procedure is well known for closed-shell calculations and was already suggested when the Direct SCF procedure was proposed, the general procedure is less obvious. For instance, there is no need to converge the corresponding closed-shell Hartree–Fock calculation when dealing with an open-shell species. We describe the various choices and illustrate them with test calculations, showing that the procedure is easier, and on average better, than starting from a converged minimal basis calculation and much better than using a bare nucleus Hamiltonian.

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Introduction

Any quantum chemical calculation requires properly defined one-electron orbitals. These orbitals are in general determined through an iterative Hartree–Fock (HF) or Density Functional (DFT) procedure. This procedure requires an initial set of orbitals. The quality of these orbitals has a huge influence on the subsequent convergence of the iterative procedure, and thus on its efficiency. It may even determine whether the procedure converges at all. Nevertheless, remarkably few publications have been devoted to this subject.[1–3] For multiconfiguration self-consistent field (MCSCF) or configuration interaction (CI) calculations more ways have been suggested to generate orbitals, for example, refs. 4–9. Part of the reason for this is that there is no theoretical way to guarantee convergence to any state, not even to the ground state. Nevertheless, quite a few approaches are in use in quantum-chemical program packages. Probably the oldest is diagonalizing the one-electron (core) Hamiltonian matrix. Slightly more involved are attempts to generate a reasonable approximation to the Fock matrix based on extended Hückel or more advanced semiempirical Hamiltonians. The latter is the most frequently used approach in *ab initio* program packages, like Gaussian,[10] (Gaussian Inc., http://www.gaussian.com), PQS (Parallel Quantum Systems, PQS: http://www.pqs-chem.com/), MOLCAS (Lund University, MOLCAS: http://www.teokem.lu.se/molcas/),[11] Turbomole (Lehrstuhl fur Theoretische Chemie, University of Kahrlsruhe, Turbomole; http://www.chem-bio.uni-karlsruhe.de/TheoChem/turbomole/),[12] GAMESS(US) (Gordon Research Group, GAMESS, http://www.msg.ameslab.gov/GAMESS/GAMESS.html, 2005),[13] Spartan (Wavefunction Inc., SPARTAN: http://www.wavefun.com/), and Dalton (DALTON, a molecular electronic structure program, release 2.0, 2005: http://www.kjemi.uio.no/software/dalton/). A method always available is restoring the orbitals from a previous calculation, in, for example, a smaller basis, often with projection.

We follow the lead of Faegri and Almlöf[14,15] as originally implemented in DISCO. The idea is that a molecule is to a very good approximation a collection of atoms, so that the molecular electron density may be obtained by simply adding the densities of all the constituting atoms. We describe here the procedure as currently implemented in GAMESS-UK (CFS Ltd., GAMESS-UK; http://

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www.cfs.dl.ac.uk/, 2005)[16] and in its original form in NWChem (Pacific Northwest National Laboratory, Washington; NWChem: http://www.emsl.pnl.gov/docs/nwchem/).[17] We do generate orbitals, without the requirement to first complete a closed-shell type HF or DFT calculation, so that an open-shell single or multi-configuration calculation may be started straight away.

The above approach can be extended in a number of ways. In particular, the charge on an atom may be specified, keeping the atomic configuration of the neutral atom, for instance for partially ionic substances. The electronic configuration of the atoms may be changed in the sense that the orbital occupations or the spin state of the atom may be specified, for example, providing an atomic SCF on an ion. For special purposes, orbitals instead of densities may be generated in the atomic SCF, which are then used, for example, in a valence bond (VB) calculation[18] to generate the atomic structures. Also, one can completely specify the initial wave function in unrestricted HF (UHF) calculations by assigning specific spin-orbital occupations. An approach akin to the present scheme is the fragment (orbital) approach, already employed in the predecessor of ADF [Science Computing & Modelling, Amsterdam Density Functional (ADF): http://www.scm-.com/],[19] the (Amsterdam) Hartree–Fock Slater program, and more recently, in NWChem (Pacific Northwest National Laboratory, Washington, NWChem, http://www.cmsl.pnl.gov/docs/nwchem/).[17] Atomic densities from approximate atomic orbitals are employed in MOLPRO (Werner and Knowles, MOLPRO quantum chemistry package: http://www.molpro.net/)[20] and Jaguar (Schrodinger Inc. Jaguar: http://www.schrodinger.com/), while Qchem (Q-chem Inc., Q-chem: http://www.q-chem.com/)[21] uses predetermined atomic orbitals for selected basis sets. The Gaussian03 (Gaussian Inc., GAUSSIAN, http://www.gaussian.com) program uses the Harris functional[22] unless atoms heavier than Xe are present, which is essentially the same approach.

Procedure

For each unique atom a restricted open-shell HF calculation is performed. For this purpose the atomic SCF program, originally by Roos et al. (Roos, B.; Salez, C.; Veillard, A.; Clementi, E. ATOMSCF, IBM Research Laboratory, San Jose, CA,1968; Revised by K. Faegri et al. for use in Disco; Revised by J. H. van Lenthe, R. Zwaans, and H. J. J. van Dam for use in GAMESS-UK and NWChem) has been included in GAMESS-UK. The basis set as used in GAMESS-UK is translated to the atomic framework, as there is only one spherical harmonic orbital in each contracted shell. If two atoms are described by different basis sets, they are deemed to be different for the atomic program. When using pseudopotentials or ZORA relativistic corrections[23] the one-center integrals of these atoms are explicitly calculated for the entire molecule and subsequently added into the atomic SCF. The same could be done for DFT, but we have observed no favorable effect, so the default is not to include an exchange correlation potential for the atom. The ZORA operator depends explicitly on the density in ways not foreseen or even known at the time the atomic SCF program was conceived. Rather than writing special atomic routines for these cases, we let the molecular code produce these corrections and iterate over the atomic startup procedure until converged. In general, only a few inexpensive iterations are required because of the atomic block-diagonal and restricted form of the density matrix.

The calculation of the one-center integrals requires only minor modifications to the corresponding integral drivers and adds little to the computational cost of a calculation. From the molecular integrals, those involving the pure harmonic functions are selected, that is, the d_{xy}, and the f_{xyz}. We only calculate ground-state atoms, so the restriction of the atomic SCF program to *f*-functions is not a constraint. As an atomic SCF is an exceptionally cheap process, no discernible time is spend calculating the atomic wave functions. The atomic SCF converges routinely regardless of basis set, as the orbital occupations for each symmetry are precisely defined.

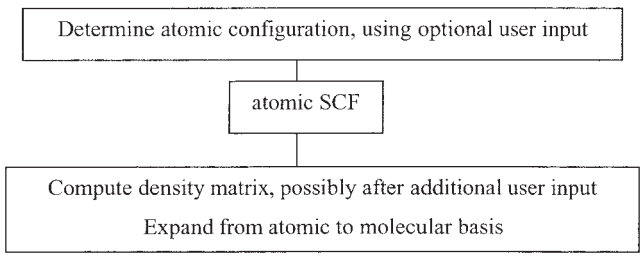
In the original version of the code, the open-shell exchange part of the Fock operator is totally ignored.[24] This amounts to describing an averaged ensemble of spin functions, with the same orbital configuration. This is very reasonable, as atoms in molecules are often combinations of these spin functions, as is obvious from VB calculations.[25] As we have added the spin coupling coefficients for all atoms, real ground-state atoms may also be calculated.

When completed, the density matrix from the atomic SCF is translated to the molecular framework and added into the molecular density matrix for each atom of the treated kind. This results in a block-diagonal nonidempotent density matrix. If one diagonalizes this matrix all the atomic orbitals would be regenerated, with their atomic occupations. Instead, the density matrix is used directly as input to a "closed-shell" Fock matrix builder, including the DFT exchange correlation potential where applicable. The resulting Fock matrix, which may be thought of as the *ab initio* equivalent of the well-known extended Huckel startup matrix or Alpha's matrix in ATMOL[26] is then diagonalized, producing the start-orbitals, which may then be employed in the usual fashion. The advantage of this procedure over first converging a closed-shell calculation is that no artificially charged species, which would result in too diffuse or too compact a wave function, are involved. Although the orbitals are, as will be shown, excellent approximations to the final result, the energy is not, as it is not variational given that the density matrix is not idempotent.

As an aside, the availability of this atomic startup also provides an excellent start for VB calculations, by using the orbitals instead of the density. The resulting orbitals will be those for a spherically symmetric atom, and are thus suited for a classical VB calculation, where the orbitals are fixed in their atomic states. In this case, one might actually prefer to use real ground-state atoms: for modern VB techniques that do include orbital optimisation for the VB wave function, the average spin orbitals are perfectly adequate.

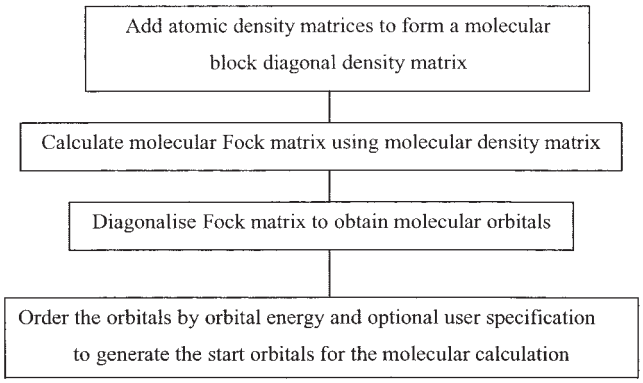
The procedure may be summarized as follows:

For each unique atom:



Scheme 1.

For the molecule:



Scheme 2.

If an operator is used that depends on the density, the atomic part has to be repeated until self-consistency. In the current implementation, the molecular density matrix is also built to allow easy use of the molecular routines. The atomic operator is then extracted from the molecular matrix.

Calculations

Two test sets of molecules were used: for the performance analysis, the G2 test set[27] and a set of transition metal complexes comprising $Ni(PH_3)_2$, $Zn(CH_3)_2$, VF_5, CrF_6, TiF_4, ScF_3, VOF_3, CrO_2F_2, $Fe(CO)_5$, CrO_4^{-2}, $Ni(C_3H_5)_2$, $Co(C_3H_5)(CO)_3$, $Mn(C_5H_5)(CO)_3$, $Mn(CO)_4NO$, $Co(NH_3)_6$, $Fe(C_4H_4)(CO)_3$, $Fe(C_4H_6)(CO)_3$, $Ni(C_5H_5)NO$, $Cr(C_6H_6)(CO)_3$, $Cr(CO)_6$, $Fe(C_2H_4)(CO)_4$, $Mn(CO)_5CN$, $Mn(NO)_3CO$. In the first test a 6-31G* basis set was used in all calculations except for CrO_4^{-2}, where the basis set on oxygen was replaced by 6-31++G**. Alternatively an Ahlrichs TZVP basis[28,29] was used as obtained from the EMSL basis set library. (Basis sets were obtained from the Extensible Computational Chemistry Environment Basis Set Database, V., as developed and distributed by the Molecular Science Computing Facility, Environmental and Molecular Sciences Laboratory which is part of the Pacific Northwest Laboratory, P.O. Box 999, Richland, Washington 99352, and funded by the U.S. Department of Energy. The Pacific Northwest Laboratory is a multiprogram laboratory operated by Battelle Memorial Institute for the U.S. Department of Energy under contract DE-AC06-76RLO 1830. Contact Karen Schuchardt for further information.) All DFT calculations were performed using the B3LYP[30–32] functional. The open-shell HF calculations were done with the restricted open-shell module (ROHF), while the DFT calculations employed UHF. Atomic calculations were not included in the sets.

Three different approaches were tested. The first method, HCORE, corresponds to obtaining the starting orbitals by diagonalizing the one-electron Hamiltonian matrix. The second, hereafter referred to as MINGUESS, obtains the orbitals by first performing a minimal basis SCF calculation, using the standard minimal basis start, and projecting the resulting orbitals onto the actual basis. The final method, hereafter called ATOMS, involves summing the atomic densities as outlined above. As an extension of this approach we tried using ground-state atoms rather than the default treatment of averaging the ensemble of spin functions for the orbital configuration in question.

The standard SCF iteration procedure of GAMESS-UK[16] was used until the tester was below 10^{-5}. Control of the SCF process is achieved through a combination of level shifting[33] and DIIS.[34,35]

With the exception of transition metal species a level shifter[33] of 1.0 was used for the first five SCF iterations, which was reduced to 0.3 in subsequent iterations for Hartree–Fock; in the case of DFT the shifter remained 1.0. For the metal complexes a level shifter of 3.0 was used throughout. In addition, a damping of 1.0 was used for the first two SCF iterations, whereby the Fock matrix was averaged with that from the previous iteration. When a set of orbitals is degenerate, an average occupation is used to build the density matrix.

The DIIS procedure is initiated when the absolute value of the largest occupied—virtual element of the Fock matrix, the "tester"—falls below 0.1. At this point the DIIS data gathering is started, and DIIS is engaged three iterations later, at which point level shifting is terminated. If the energy rises during the iterations, DIIS itself is terminated and level shifting reengaged. DIIS is then engaged again when the above criterion is met. The maximum number of iterations is 50. The calculations were performed within the CHEMSHELL[36] environment.

Results and Discussion

The results of the calculations are listed in Tables 1–3. First-iteration and final-iteration energies and number of iterations are supplied as supplementary material S1. Detailed results and a complete description of the transition metal set and its convergence behavior are supplied as supplementary material S2.

In the tables we provide an analysis of the efficacy of each of the three starting mechanisms in both HF and DFT calculations. The tables include the maximum deviation of the starting energy with respect to the final energy ($E_1 - E_{converged}$), as well as the average deviation over the test set. Characteristics of the SCF iteration process are included under the headings "Best," "Worst," "Average," and "Failures": the first three headings report the number of iterations required compared to that from the ATOMS approach as a percentage. The "Best" and "Worst" column depict the performance of the best and worst performing single case; thus, there is at least one job in the MINGUESS set that takes 50% fewer iterations than ATOMS. The "Average" column gives the average iteration count across all the associated cases with only converged calculations included. The "Failures" column gives the number of jobs that failed to converge at all; note that the two ATOMS cases that did not converge could easily be forced to convergence by applying a level shifter of 1.0. This was not the case for MINGUESS.

ATOMS is seen to outperform HCORE both in terms of the accuracy of the initial energy as well as in the number of cycles required to converge to the final solution. It is comparable but slightly preferable to MINGUESS in number of cycles and initial energy, as discused below. Although the inferior performance of HCORE comes as no surprise, the fact that the initial energy from ATOMS can be even better than when starting on a projected minimal basis result is surprising.

Table 1. The G2 Set of 200 Molecules.

		Total energies $E_1 - E_{converged}$ (a.u.)		SCF iteration characteristics			
		Maximum	Average	%Best	%Average	%Worst	#Failures
HF	HCORE	60.5638	14.4313	−14	36	227	12
	MINGUESS	1.0523	0.2553	−50	5	64	3
	ATOMS	0.2254	0.0564	—	—	—	2
DFT	HCORE	60.5857	12.9535	−21	31	125	24
	MINGUESS	0.9311	0.2197	−36	0	289	4
	ATOMS	0.2162	0.0598	—	—	—	0

The total Deviations in $E_1 - E_{converged}$ (see text) and the relative changes in the number of SCF cycles needed to achieve convergence, compared to the ATOMS method. (ATOMS and MINGUESS failed to converge in the Hartree–Fock calculations on SO and NO^-. MINGUESS also failed for PO^-. Note that though HCORE seems to converge for SO, it is not converging to the groundstate (see supplementary material). For NO^- and PO^- the preceding minimal basis calculation already failed to converge for MINGUESS. The DFT MINGUESS failed to converge in 50 iterations for P_2^+, S_2^+, PH_2^-, and S_2^-).

It should be realized that the first iteration result printed for ATOMS is the first variational result. The orbitals employed to generate the Fock matrix result from a molecular Fock matrix, which was generated from the sum of the atomic density matrices. Although the generation of this Fock matrix is much cheaper then in a normal iteration, the result might be deemed to be beyond a real first iteration result compared to, for example, HCORE. The results do suggest, however, that a correct description of the atoms is more important to the energy than starting with a molecular wave function.

Using ground-state atoms leads to slightly worse convergence behavior, confirming the ideas behind the original atomic start-up.[24]

To illustrate the very poor performance of the HCORE approach, note that in the G2 test set the deviation in the energy of the initial iteration is 13–14 Hartree on average. This is reflected in the large number of calculations that failed to converge using HCORE as a start and in the fact that successful calculations took on average 36% more cycles to converge in HF calculations and 31% more cycles in DFT calculations.

The MINGUESS approach performs far better, giving maximum and average deviations in the energy of the first iteration of about 1.0 Hartree and 0.2 Hartree, respectively, at both the HF and the DFT levels of theory. The number of cycles required for convergence is, on average, the same for MINGUESS and ATOMS; ATOMS has a slight edge, which is due to possible convergence problems in the preceding minimal basis calculation. These cases may be identified by a missing first iteration energy in the more detailed tables (supplementary material). There are some significant differences either way. As an extreme case a reduction of 50% was obtained for the CCH radical at the HF level, using MINGUESS. On the other hand, ATOMS was a factor of 1.6 faster for the NO radical. Although the ATOMS guess assumes neutral atoms ionic systems do not as a rule converge in fewer cycles using MINGUESS. On average, Hartree–Fock G2 calculations based on the MINGUESS approach took 5% more cycles to converge. For DFT there is on average no difference.

The transition metal test set shows more pronounced differences. HCORE fails in the majority of the cases, whereas the MINGUESS requires on average 7% more iterations for the

Table 2. The Test Set of 23 Transition Metal Complexes, Using the 6-31G* Basis.

		Total energies $E_1 - E_{converged}$ (a.u.)		SCF iteration characteristics			
		Maximum	Average	%Best	%Average	%Worst	#Failures
HF	HCORE	220.9982	135.6581	36	88	171	14
	MINGUESS	2.1905	1.3630	−20	6	55	2
	ATOMS	1.7020	0.5419	-	-	-	0
DFT	HCORE	144.2427	94.5866	28	96	155	19
	MINGUESS	2.0714	1.1259	−25	8	42	1
	ATOMS	1.9476	0.4237	-	-	-	0

Deviations in $E_1 - E_{converged}$ (see text) and the relative changes in the number of SCF cycles needed to achieve convergence, compared to the ATOMS method. [For $Mn(CO)_5CN$ and $Mn(NO)_3CO$, the minimal basis Hartree–Fock calculation did not converge. For DFT, this was the case for $Ni(PH_3)_2$.]

Table 3. The Test Set of 23 Transition Metal Complexes, Using the Ahlrichs TZVP Basis.

		Total energies $E_1 - E_{converged}$ (a.u.)		SCF iteration characteristics			
		Maximum	Average	%Best	%Average	%Worst	#Failures
HF	HCORE	160.3708	118.5172	70	90	108	19
	MINGUESS	2.2121	1.5604	−14	16	73	3
	ATOMS	1.7503	0.5522	—	—	—	0
DFT	HCORE	159.6313	159.6313	191	191	191	22
	MINGUESS	2.0343	1.5661	−12	17	75	1
	ATOMS	1.9311	0.4550	—	—	—	0

Deviations in $E_1 - E_{converged}$ (see text) and the relative changes in the number of SCF cycles needed to achieve convergence, compared to the ATOMS method. [For $Mn(CO)_5CN$ and $Mn(NO)_3CO$, the minimal basis Hartree–Fock calculation did not converge. For CrF_6, the MINGUESS calculation that followed it failed. For DFT, the minimal basis calculation failed for $Ni(PH_3)_2$.]

6-31G* basis and 16% for the larger Ahlrichs set. Of course, HCORE would converge much more often if special larger level shifters are employed. For the larger basis, the fact that the ATOMS approach immediately utilizes the bigger basis set where MINGUESS starts from the same wave function as for 6-31G* basis gives ATOMS the edge. In general, the failures of MINGUESS were caused by a failing minimal basis calculation, except for CrF_6. The superior performance of ATOMS may thus be attributed to the fact that the bigger basis is directly used to generate the start avoiding a potentially nonoptimal minimal basis intermediate.

The results up till now required no user intervention. However, if one does know the physical characteristics of the system the atomic startup may easily be adapted to take advantage of these. For instance, if the charges on the atoms are known, they may be used to generate the corresponding charged atomic densities. This is effected by changing the occupation of the outer shells after convergence of the atomic SCF. A calculation on CrF_6, for instance, is accelerated by 27% through specifying that the Chromium atom to should carry a charge of 0.852 and adjusting the Fluorine atoms accordingly. Alternatively, instead of just adjusting the charge of an atom, its atomic configuration may be specified, with the advantage that the corresponding atomic orbitals are generated (although it does not allow for noninteger charges).

Finally, the atomic startup may be used to generate initial density matrices for user-defined spin states. The standard start for an UHF calculation is to use the orbitals obtained from the "closed-shell"-like Fock matrix as described above. One may instead start the UHF on separate alpha and beta density matrices, which may be generated by specifying the spin distributions on the different atoms. An interesting case in point is the ionic material $FeSbO_4$. This material is a selective oxidation catalyst, containing

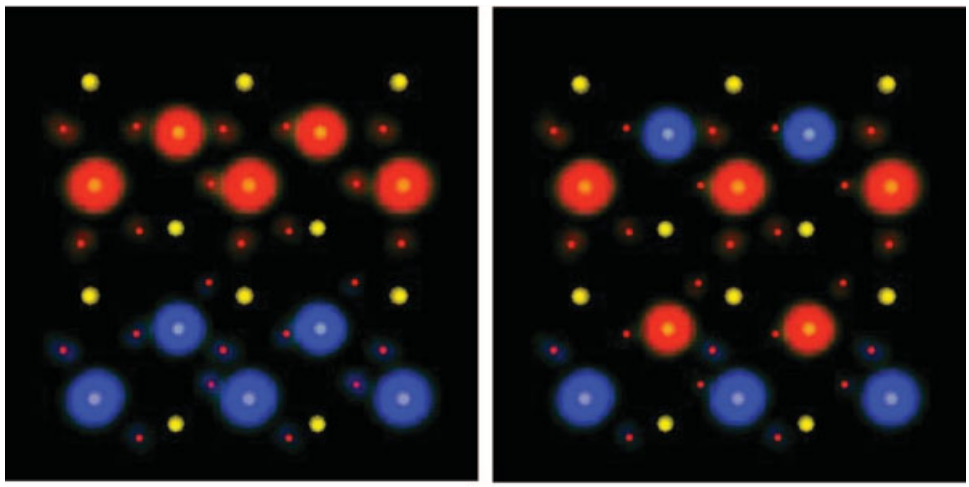


Figure 1. The spin states of the ground state of the $FeSbO_4$ surface for two different spin states with the oxygen and the oxygen and the antimony ions shown as small red and yellow dots. The positive and negative spin densities on the iron ions are shown in red and blue distributions.

antiferromagnetically coupled high spin Fe^{3+} ions in an Sb^{5+} O_4^{2-} environment. One may orient the spins on different iron atoms differently by specifying that a particular atom should have a certain alpha or beta spin density matrix in the startup. By also specifying the atomic configurations of the atoms, to mimic the cluster situation as closely as possible, we were able to selectively calculate a variety of spin distributions.

In Figure 1 we show two of these, which required no more than 32 and 18 iterations, respectively, to converge. The energy difference between the two states is only 1.2 kJ/mol at the HF level and 8.7 kJ/mol employing DFT/BB1K. In the standard approach, the singlet calculation does not even converge. One would need to swap the starting orbitals, but to obtain a desired localised spin state using molecular orbitals is next to impossible.

Conclusion

We describe a procedure to determine starting orbitals for SCF calculations, as implemented in the GAMESS-UK program package. The starting orbitals are obtained from a closed-shell-type Fock matrix generated from a density, which is the sum of the atomic densities. Open-shell calculations may be started directly from these orbitals without first converging a closed-shell calculation. The procedure is more efficient than starting from a bare nucleus Hamiltonian or starting from converged minimal basis calculations. The method offers the possibility for improvement, if the user has a priori knowledge about the electronic wave function of the molecular complex.

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