

Advanced Initial-Guess Algorithm for Self-Consistent-Field Calculations on Organometallic Systems

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Abstract

Based upon ligand-field theory, an algorithm to create high-quality initial-guess wavefunctions for organometallic systems leads to the ground-state 88% of the time for HF and 92% for DFT. In contrast, calculations starting from a Hückel guess were successful only 14% and 9% of the time, and a traditional AO overlap guess only 39% and 42%. The SCF convergence is also achieved in fewer iteration starting from the advanced guess - on average, in 9 iterations. When several states lie very close in energy, the algorithm also warns the user, making it easy to explore each one.

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1 Introduction

Current quantum mechanical (QM) software is notoriously inadequate for calculations involving transition metals. Although these systems can be quite large, their *size* is not the major hindrance to performing Hartree-Fock (HF) or Density-Functional Theory (DFT) calculations; Jaguar [1] [2], whose algorithms are extremely fast, has been used routinely for organic molecules with just as many basis functions as would be required for realistic studies of transition-metal (TM) systems [3] [4] [5] [6]. The real difficulty lies in getting these systems, which have a high density of low-lying states, to converge at all [7]. The quality of the initial-guess wavefunction (IG) used for *ab initio* Self-Consistent Field (SCF) calculations is crucial for TM-containing systems. A poor IG can result in failure to converge, more iterations to reach convergence, or converge to the wrong state. Although existing software generates trial orbitals and occupations automatically, they are designed with organic systems in mind.

Because the development of QM techniques has traditionally focused on achieving optimal performance for organic compounds, no electronic-structure program has an algorithm that generates IGs that reflect reasonable assumptions about organometallics. Several programs, including Gaussian [8] [9], compute a Hückel guess for *ab initio* calculations on TM-containing systems, but this algorithm has serious limitations. For instance, it generally assigns too much electronic charge to the metal, doubly occupying valence *d* orbitals of the metal in preference to filling ligand orbitals. Jaguar's tra-

ditional algorithm [2] computes guess orbitals by diagonalizing the overlap matrix between the valence atomic orbitals (AOs). The best bonding orbitals, those with largest overlap, are occupied first. While this algorithm is an improvement over the Hückel guess in regard to organometallics [7], it often fails to match the more accurate guess most chemists would be capable of making.

For inorganic systems, “organic” guess wavefunctions are somewhat random, violating well-understood rules of inorganic chemistry. User modification of these incorrect choices is generally difficult, non-intuitive, time-consuming, and error-prone. The consequent dubious reliability of QM on systems containing transition metals has been a major hurdle to widespread application to such cases, including the biochemistry of metalloproteins and other important biochemistry and materials science problems. Inorganic chemists have developed general rules and concepts to help describe the differences between TM complexes and organic compounds, including, for example, oxidation states, the 18-electron rule, and back bonding in organometallic systems [10]. The primary focus of this paper is improvement of the guess wavefunction used for SCF calculations on organometallic systems. Due to the advances described here, Jaguar 3.5 [1] now includes several improvements when generating transition metal initial guesses which lead to more reliable ground-state convergence.

2 Method

We found the following features critical to the production of a high-quality initial guess for organometallics:

- conceptually separating the molecule into metal and ligand fragments, then allowing the user to assign formal charges and spins to the metal and ligands based upon chemical intuition, and requiring the initial guess to agree with this assignment;*
- estimating the ligand-field splitting of the nonbonding d orbitals of the TM by assigning a penalty for metal d orbitals having large overlap with occupied ligand orbitals and a bonus for metal d orbitals having large overlap with unoccupied ligand orbitals;
- including the effects of the unoccupied metal s orbital on the ligand orbitals; and
- for highly unsaturated cases, estimating the d - d repulsion of the metal orbitals.

We incorporated each of these effects by building effective Hamiltonians based upon the modified AO-overlap matrix. The penalties and bonuses

* A full description of the input section appears in the Jaguar User's Guide version 3.5. A simple example, for $[Fe^{II}H]^+$ (which is a ground state pentet), would be:

```
&atomic
atom      formal  multip
Fe        +2      5
H         -1      1
&
```

depend on the sum of the squares of the relevant overlap matrix elements. Diagonalization of the effective Hamiltonian (while maintaining formal charges and spins on the fragments) provides a new wavefunction, which in turn yields a new overlap matrix for the next step.

We tested the algorithm by performing HF and B3LYP [11] DFT calculations on a suite of organometallics. All calculations used the LACVP** basis set, which is based upon Hay-Wadt effective core potentials [12]. The suite consisted of 80 molecules $[M^{II}H]^+$, $[M^I CO]^+$, $[M^I CH_2]^+$, $[M^{III}(CH_3)_2]^+$, and $[M^I(CO)_2]^+$, where M is a first- or second-row metal in the range Sc-Ni or Y-Pd, and the 8 molecules $[M^{III}H]^+$, where M is a third-row atom in the range La-Pt. We used the ground state geometries and spin states of each molecule as determined from high levels of theory [13] [14] [15] [16] [17]. This suite provides an excellent standardized test of IG algorithm performance since the compounds' high degree of unsaturation leads to many low-lying excited states. Successful performance on these cases suggests that our new algorithm holds great promise for other difficult problems involving transition metals. The test suite also provides a means of testing *d-d* repulsion, an often subtle effect that is particularly important for cases with weak ligand fields. It should be noted that the algorithm is completely general and, although the test suite doesn't include them, the algorithm is appropriate for higher-coordinate systems, bimetallic systems, and systems with chelating ligands.

3 Results

In this section, we present test set results for each of three major stages of our research, showing the improvement of each addition to the algorithm. For comparison, we have also included results obtained using a Hückel guess as generated by the Gaussian program [8] [9], and using the traditional AO overlap initial guess from Jaguar [2]. In Table 1 and the following discussion, “ground state” refers to the lowest-energy state for that particular level of theory, not necessarily the true ground state. For a few cases, HF and DFT disagree on the ground state, making a 100% success rate impossible to achieve.

3.1 Performance of Traditional Initial-Guess Algorithms

The limitations both of the Hückel guess and unmodified AO overlap guess are clearly exposed by our test set, as shown in Table 1. For Hückel, convergence is often slow, and most of the jobs fail to converge or converge to excited states. In fact, only 11% of the HF and DFT energy calculations on these molecules successfully converge to the ground state. The AO overlap case almost always converges but converges to an excited state much of the time (59%). As demonstrated below, this performance can be improved dramatically with a better guess wavefunction and without changing other SCF convergence options.

3.2 Formal Charge and Oxidation State Information

Although ligand formal charges and TM oxidation states provide only a rough description of charge distribution, it is desirable to have the IG agree with the charge assignment a chemist would make. The Hückel guess is inadequate for these purposes: for $[Fe(H_2O)_6]^{+2}$, it yields a Mulliken charge of -1.5 on the iron and distributes a charge of +3.5 over the water ligands – clearly a bad description of the system. AO overlap is somewhat better, assigning a Mulliken charge of -0.8 to the iron, but since it calculates orbital occupation entirely according to overlap, it cannot correctly account for the electrostatics in a inorganic molecule at even the most basic level.

Our new algorithm allows users to employ their chemical intuition to input formal charges and oxidation states, which are then incorporated into the IG generated by the program. The user simply specifies the spin on the metal and on each ligand, and any formal charges on each fragment. Once the program knows how many electrons should be assigned to the metal and how many to the ligands, it generates an IG using the procedure outlined in Section 3.3 through Section 3.5. This ability to specify a particular metal oxidation state will also help researchers to more easily examine excited states.

3.3 Stage 1: Preliminary Assessment of Ligand-Field Effects

The energies of the metal d orbitals in an organometallic complex are primarily dependent upon two things: the splitting due to the ligand field (LF), and the intrinsic repulsions between the d electrons in the bare metal.

The LF, largely determined by the overlap between orbitals on the ligands and the metal, dominates the energetic ordering of the d orbitals in the complex. The d - d repulsion is important for cases involving ligands with weak field strengths.

To the first-order approximation made in the initial guess, the LF splitting is not affected by the occupation of the metal d orbitals; in contrast, the d - d repulsion is intrinsically dependent on the metal d orbital occupation. Since the description of the metal d orbitals is actually altered to account for the LF, we first perform this step, then incorporate the d - d repulsion, as in Section 3.5. A preliminary estimate of the LF splitting can be evaluated by the sum of the squares of each metal d orbital’s overlap with the ligand orbitals.[†] (In this stage, the ligand orbitals used are the AOs; in Section 3.4, the ligand orbitals will have been “pre-treated” before this step.)

Here, the ligand orbital occupations are not considered, but rather, *all* overlaps between ligand orbitals and metal d orbitals are applied as penalties when occupying the metal d orbitals. The metal-ligand repulsion properly predicts that the σ orbital is most unstable in $[M^{II}H]^+$. Overall, however, it is obvious that this stage of our work did not show any real improvement for these test cases. Shown in Table 1, only 74 of these HF and DFT jobs converged to the ground state, compared to 71 for the standard AO default shown earlier. Clearly a more sophisticated approach is required.

[†]Accessible in Jaguar 3.5 with the `iguess=23` input flag.

3.4 Stage 2: The Effect of Dative Bonding

For Stage 1, the ligand AOs were not adjusted before computing the effect of each on the metal d orbital occupations. Further, the ligand-metal overlaps were included as penalties in the effective Hamiltonian whether or not the ligand orbitals were occupied. In the next stage of our work, we addressed both of these limitations.

We first form an effective Hamiltonian that includes a bonus for the ligand AOs having high overlap with the metal s orbital. Upon diagonalization, the ligand AOs mix with each other but are not allowed to directly mix with the metal orbitals. The bonus enhances hybridization between ligand orbitals on the same atom center based upon the overlap with the metal s orbital, and the orbital energies are thereby stabilized. The resultant ligand “molecular orbitals” are reoccupied according to energy ordering; the number of electrons on each ligand is determined by the user’s formal charges, as described in Section 3.2. With the ligand orbital occupations thus determined, we compute the metal’s Hamiltonian, with a penalty to metal d orbitals for overlap with *occupied* ligand orbitals, and a bonus for overlap with *unoccupied* ones.

Results from this stage of our work[‡] are shown in Table 1. The metal-empty-ligand-orbital bonus properly lowers the energy of the π orbitals setting the stage for π back bonding in $[M^I CO]^+$ and $[M^I(CO)_2]^+$ and π covalent bonding in $[M^I CH_2]^+$. Although ten of the 48 $[M^I H]^+$ cases still converge to an excited state, on the whole, this stage of our work shows

[‡]Accessible in Jaguar 3.5 with the `iguess=25` input flag.

tremendous progress. Of all the test cases, 80%, correctly converge to the ground state using the IG algorithm at this stage, compared to 40% for the unmodified AO guess.

3.5 Stage 3: Intrinsic Metal d - d Repulsions

The repulsions between electrons in different metal d orbitals can affect the orbital energies. For instance, for a metal with two d electrons, a configuration with one electron in a d_{xy} orbital and one in a $d_{x^2-y^2}$ orbital, where both orbitals are in the xy plane, is less favorable than a configuration with one d_{xy} electron and one d_{z^2} electron.

The splittings due to d - d repulsions are well-known for various metal atoms in various oxidation states [18]; for cases where the metal d orbitals change little from the AOs during the procedure described in Section 3.4, the known values could be adequate to account for the effect. Since that is not always the case, it is more effective to compute the exact Coulomb repulsions between the new orbitals for different configurations. The configuration with the lowest energy (orbital energies + Coulomb repulsions) determines the final orbital occupation.[§] Including d - d repulsion helps address some limitations of the earlier stages: for example, d - d repulsion allows the software to distinguish between the $\pi^2\delta^1$ and $\pi^1\delta^2$ states in NbH^+ .

Although the techniques described here provide excellent results for the majority of cases, the predicted configuration energies are sometimes so close

[§]Accessible in Jaguar v3.5 with the `iguess=30` input flag.

that it is still difficult to guess which configuration should be used. To address this problem, the program reports cases where the configuration energies are too close to call. The program will either stop and suggest to the user several reasonable occupations (within 0.5 mHartree), or warn the user that there are near-degeneracies (5 mHartree), but continue with the calculation. Thus it informs the user of potential problems and provides a means to obtain reliable results. For the results in Table 1, when the program stopped we completed all suggested occupations and include the best results here; for the cases where the program only provided a warning, we let it run and accepted the results.

For our final algorithm, results are excellent, with 90% successfully converging to the ground state, a reversal of Hückel’s 11% performance ratio. In this stage, ground state convergence took 9 iterations on average, compared to 12 for the Hückel guess. Also, for the few cases that converged to the excited state, the excited state energies were 9.84 mHartree for HF and 8.24 mHartree for DFT on average, much lower-lying than those resulting from the Hückel guess. It is also important to note that for the 2 $[M(CH_3)_2]^+$ cases (M=Co,Ni) that failed to converge for either HF or DFT in Stage 2 and 3, the IG determined the correct occupation. The new guesses for these 2 cases are easily converged to the ground-state by setting a non-default value for the virtual orbital level shift.

4 Discussion and Conclusion

Our new algorithm generates initial-guess wavefunctions that reflect the true chemistry of organometallics. Including ligand-field theory in the effective Hamiltonian leads to excellent orbital occupations and a reasonable description of the orbital shapes. This improvement leads to faster and far more reliable ground-state SCF convergence. For our test set of 88 organometallic molecules, the initial-guess wavefunctions produced by Jaguar’s new algorithm led to ground state convergence 88% of the time for HF and 92% for DFT. Only 14% and 9% of the calculations starting from a Hückel guess were able to converge to the ground state, and from a traditional AO overlap initial guess only 39% and 42%. The SCF calculation also converges quickly starting from the high-quality guess, on average 9 iterations. For cases where reasonable initial-guess wavefunctions are very close in energy, the program also informs the user of the choices, making each one easy to explore. Therefore the user will ultimately find the correct solution, where other software would simply compute the wrong state with no warning.

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Table 1: Number of cases where SCF, starting from various initial guesses, converged to the ground state, an excited state or failed to converge, the ratio of successful cases in the total suite and the average number of iterations for the successful cases to reach convergence. $M = Sc - Ni, Y - Pd$, and, for $[M^{II}H]^+$ only, $La - Pt$.

| | Initial Guess | | | | | | | | | | | | | | |
|-----------------------|----------------|----------------|----------------|------------|----|---|---------|----|---|---------|----|---|---------|---|---|
| | Hückel | | | AO overlap | | | Stage 1 | | | Stage 2 | | | Stage 3 | | |
| | G ^a | E ^b | F ^c | G | E | F | G | E | F | G | E | F | G | E | F |
| HF: | | | | | | | | | | | | | | | |
| $[M^{II}H]^+$ | 6 | 17 | 1 | 9 | 15 | 0 | 14 | 10 | 0 | 14 | 10 | 0 | 20 | 4 | 0 |
| $[M^I CH_2]^+$ | 3 | 13 | 0 | 8 | 8 | 0 | 3 | 13 | 0 | 13 | 3 | 0 | 15 | 1 | 0 |
| $[M^{III}(CH_3)_2]^+$ | 2 | 13 | 1 | 9 | 7 | 0 | 8 | 6 | 2 | 12 | 2 | 2 | 12 | 2 | 2 |
| $[M^I CO]^+$ | 0 | 12 | 4 | 7 | 8 | 1 | 7 | 9 | 0 | 15 | 1 | 0 | 15 | 1 | 0 |
| $[M^I(CO)_2]^+$ | 1 | 15 | 0 | 1 | 15 | 0 | 5 | 11 | 0 | 15 | 1 | 0 | 15 | 1 | 0 |
| Total | 12 | 70 | 6 | 34 | 53 | 1 | 37 | 49 | 2 | 69 | 17 | 2 | 77 | 9 | 2 |
| Success Rate | 13.6% | | | 38.6% | | | 42.0% | | | 78.4% | | | 87.5% | | |
| Average Iters | 12.33 | | | 9.74 | | | 9.69 | | | 8.76 | | | 9.24 | | |
| DFT: | | | | | | | | | | | | | | | |
| $[M^{II}H]^+$ | 3 | 20 | 1 | 11 | 13 | 0 | 14 | 9 | 1 | 14 | 9 | 1 | 21 | 3 | 0 |
| $[M^I CH_2]^+$ | 3 | 12 | 1 | 8 | 8 | 0 | 3 | 13 | 0 | 13 | 3 | 0 | 15 | 1 | 0 |
| $[M^{III}(CH_3)_2]^+$ | 2 | 13 | 1 | 12 | 4 | 0 | 8 | 6 | 2 | 13 | 1 | 2 | 14 | 0 | 2 |
| $[M^I CO]^+$ | 0 | 9 | 7 | 6 | 10 | 0 | 7 | 9 | 0 | 16 | 0 | 0 | 16 | 0 | 0 |
| $[M^I(CO)_2]^+$ | 0 | 15 | 1 | 0 | 16 | 0 | 5 | 11 | 0 | 15 | 1 | 0 | 15 | 1 | 0 |
| Total | 8 | 69 | 11 | 37 | 51 | 0 | 37 | 48 | 3 | 71 | 14 | 3 | 81 | 5 | 2 |
| Success Rate | 9.1% | | | 42.0% | | | 42.0% | | | 80.7% | | | 92.0% | | |
| Average Iters | 11.36 | | | 8.61 | | | 8.67 | | | 8.54 | | | 8.74 | | |

^a ground state

^b excited state

^c failed to converge