

## Comparative assessment of density functional methods for 3d transition-metal chemistry

Yan Zhao and Donald G. Truhlar<sup>a)</sup>

*Departments of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455-0431  
and Supercomputing Institute, University of Minnesota, Minneapolis, Minnesota 55455-0431*

(Received 13 February 2006; accepted 13 April 2006; published online 12 June 2006)

In the present study, we comparatively assessed the newly developed M05 functional against a data set of reaction energies for transition-metal chemistry. The functionals to which we compare are BLYP, B3LYP, B97-2, MPWLYP1M, TPSS, and TPSSh. We draw the following conclusions: (1) TPSS gives the best performance for calculating the binding energies of three transition-metal dimers ( $\text{Sc}_2$ ,  $\text{Ni}_2$ , and  $\text{V}_2$ ) that have severe multireference character, (2) B97-2 gives the best performance for calculating the binding energies of the nine metal-ligand diatomics (three monohydrides, three monoxide, and three monofluorides), and (3) M05 gives the overall best performance for all 18 data in the assessment, and it has a mean unsigned error 55% lower than the popular B3LYP functional. Since the M05 functional also gives good performance for main-group thermochemistry, for noncovalent chemistry, and for calculating barrier heights, M05 can be applied to a wide range of problems where nonhybrid functionals or functionals designed for kinetics fail.  
© 2006 American Institute of Physics. [DOI: [10.1063/1.2202732](https://doi.org/10.1063/1.2202732)]

### I. INTRODUCTION

Transition-metal chemistry underlies a number of catalytic processes in chemical and biological systems, and the 2005 Nobel Prize in chemistry was awarded for pioneering work in metathesis in which transition-metal chemistry plays a key role. However, an accurate theoretical description of systems involving transition metals is a highly demanding computational task due to the strong multireference character of their electronic wave function and the nondynamical electron correlation in these systems. Density functional theory<sup>1-58</sup> (DFT) has had considerable success<sup>4,13</sup> in treating transition-metal systems due to its excellent performance-to-cost ratio and due to the fact that DFT exchange functionals based on local ingredients (e.g., spin density, density gradient, and kinetic energy density) contain a certain amount of nondynamical correlation.<sup>14,22</sup> However, one notable failure of the local DFT methods is the underestimation of reaction barrier heights. This seems to be correctable only by admixing Hartree-Fock exchange, which makes the functional nonlocal.

The DFT methods on the first three rungs of “Jacob’s ladder”<sup>23</sup> have no nonlocal character and are not suitable for calculating barrier heights; they give a mean unsigned error greater than 7 kcal/mol on a recent barrier height database.<sup>42</sup> Recently several DFT methods on the fourth rung have been developed for kinetics, for example, MPW1K,<sup>21</sup> BB1K,<sup>34</sup> MPWB1K,<sup>36</sup> BMK,<sup>35</sup> and PWB6K.<sup>42</sup> These functionals have a large percentage of Hartree-Fock exchange (more than 40%), and they can accurately predict barrier heights with mean unsigned errors of about 1.4 kcal/mol.<sup>34-36,39,42</sup> However, a large amount of nondynamical correlation is lost in these functionals due to the replacement of local exchange

by the large amount of Hartree-Fock exchange, and they fail badly for many transition-metal systems.<sup>41,53,55</sup> Recently we developed a functional, M05,<sup>54,58</sup> which has been shown to give good performance for both kinetics and transition-metal systems.

More recently, Furche and Perdew<sup>57</sup> investigated the performance of the BP86, PBE,<sup>11</sup> TPSS,<sup>28</sup> TPSSh,<sup>29</sup> and B3LYP (Ref. 9) DFT functionals for bond energies, structures, dipole moments, and harmonic frequencies of 3d transition-metal compounds; the methods were assessed by comparison with experiments. They also compiled a reference energetic data set for 3d transition-metal thermochemistry with data selected based on diversity and on the quality of the experimental data. In the present article, we assess the M05 functional against this reference data set. We also present results for three other functionals that were not tested in Furche and Perdew’s paper: in particular, we include the BLYP,<sup>2,3</sup> B97-2,<sup>25</sup> and MPWLYP1M<sup>53</sup> functionals because of their encouragingly good performance in previous assessments.<sup>41,53</sup>

Section II describes the computational methods. Section III presents results and discussion, and Sec. IV has concluding remarks.

### II. COMPUTATIONAL METHODS

All calculations are performed self-consistently using a locally modified version of the GAUSSIAN03 program.<sup>59</sup> We tested the newly developed functional M05,<sup>54,58</sup> which is a hybrid (H) meta (M) generalized gradient approximation (GGA) functional, because of its good performance for transition-metal systems and main-group systems. MGGA functionals, such as TPSS, are semilocal (a special case of local) HMGGA functionals, such as M05 and TPSSh, are nonlocal. We also tested one GGA functional, namely, BLYP. BLYP gives good performance<sup>41</sup> for calculating the bond en-

<sup>a)</sup>Electronic mail: truhlar@umn.edu

TABLE I. Binding energies (in kcal/mol) and mean errors with the QZVP basis sets.

| Molecule   | TPSS <sup>a</sup> | B3LYP <sup>a</sup>    | TPSSh <sup>a</sup>    | M05                    | BLYP      | MPWLYP1M  | B97-2                                  | Reference data <sup>a</sup> |
|--|-------------------|-----------------------|-----------------------|------------------------|-----------|-----------|--|-----------------------------|
| Sc <sub>2</sub>  | 32.4              | 11.6                  | 24.6                  | 18.0                   | 27.3      | 23.6      | 17.7                                   | 39.8                        |
| V <sub>2</sub>   | 64.4              | 27.0                  | 39.6                  | 53.2                   | 77.6      | 70.1      | 45.1                                   | 64.6                        |
| Ni <sub>2</sub>  | 57.8              | 40.2                  | 44.3                  | 34.5                   | 58.6      | 52.2      | 43.7                                   | 49.7                        |
| CrH  | 57.4              | 54.9                  | 55.9                  | 56.3                   | 57.3      | 57.8      | 55.0                                   | 45.7                        |
| MnH  | 52.3              | 39.4                  | 50.9                  | 38.9                   | 39.9      | 38.9      | 30.8                                   | 32.3                        |
| CoH  | 64.3              | 61.6                  | 62.9                  | 58.1                   | 61.6      | 61.1      | 61.7                                   | 46.6                        |
| TiO  | 173.9             | 164.7                 | 165.5                 | 155.8                  | 178.9     | 177.9     | 160.6                                  | 158.8                       |
| MnO  | 120.1             | 93.8                  | 106.5                 | 78.4                   | 119.4     | 113.3     | 85.4                                   | 91.1                        |
| CuO  | 73.0              | 63.3                  | 66.8                  | 62.3                   | 774.9     | 73.2      | 65.4                                   | 63.7                        |
| ScF  | 151.4             | 143.0                 | 146.5                 | 146.8                  | 146.9     | 146.3     | 139.2                                  | 143.0                       |
| CrF  | 117.8             | 113.7                 | 113.9                 | 115.5                  | 120.4     | 120.6     | 114.5                                  | 105.1                       |
| CuF  | 99.4              | 93.1                  | 95.9                  | 95.6                   | 98.7      | 98.5      | 97.6                                   | 102.5                       |
| Fe <sub>2</sub> Cl <sub>4</sub> → 2FeCl <sub>2</sub>     | 25.2              | 3.7                   | 14.3                  | 25.0                   | 23.5      | 20.4      | 9.0                                    | 35.0                        |
| CoCl <sub>4</sub> → CoCl <sub>2</sub> + ½Cl <sub>2</sub> | 17.0              | 6.7                   | 11.8                  | 16.6                   | 26.6      | 24.2      | 15.9                                   | 16.7                        |
| Fe(CO) <sub>5</sub> → Fe(CO) <sub>4</sub> + CO           | 46.6              | 36.9                  | 45.7                  | 36.2                   | 37.6      | 38.8      | 39.7                                   | 42.2                        |
| Ni(CO) <sub>4</sub> → Ni(CO) <sub>3</sub> + CO           | 28.9              | 19.6                  | 26.9                  | 17.6                   | 21.7      | 22.3      | 20.5                                   | 24.9                        |
| ½CrBz <sub>2</sub> → ½Cr + Bz                            | 38.7              | 13.4                  | 32.2                  | 31.1                   | 23.0      | 22.7      | 22.8                                   | 31.8                        |
| ½FeCp <sub>2</sub> → ½Fe + Cp                            | 94.8              | 67.9                  | 88.0                  | 79.1                   | 78.4      | 76.8      | 75.2                                   | 80.1                        |
| X <sup>b</sup>   | 0                 | 20                    | 10                    | 28                     | 0         | 5         | 21                                     |                             |
| Maximum absolute error                                   | 29.0(MnO)         | 37.6(V <sub>2</sub> ) | 25.0(V <sub>2</sub> ) | 21.8(Sc <sub>2</sub> ) | 28.3(TiO) | 22.2(MnO) | 26.0(Fe <sub>2</sub> Cl <sub>4</sub> ) |                             |
| MSE  | 7.8               | -6.6                  | 1.3                   | -3.0                   | 5.5       | 3.6       | -4.1                                   |                             |
| MUE  | 10.2              | 12.0                  | 9.7                   | 7.8                    | 10.6      | 9.5       | 8.3                                    |                             |

<sup>a</sup>The reference data and the results for TPSS, B3LYP, and TPSSh are taken from Furche and Perdew's paper (Ref. 57).

<sup>b</sup>X denotes the percentage of Hartree-Fock exchange in each functional.

ergies of transition-metal dimers when it is employed with an effective core potential. We also tested two hybrid GGAs, namely, MPWLYP1M<sup>53</sup> and B97-2,<sup>25</sup> both of which show good performance<sup>53</sup> for calculating the energetics of transition-metal systems when employed with a triple-zeta-quality basis set.

We tested these four functionals for the Furche-Perdew data set of 18 data, which consists of the dissociation energies ( $D_e$ ) of three transition-metal dimers (Sc<sub>2</sub>, V<sub>2</sub>, and Ni<sub>2</sub>),  $D_e$  of three monohydrides (CrH, MnH, and CoH),  $D_e$  of three monoxides (TiO, MnO, and CuO),  $D_e$  of three monofluorides (ScF, CrF, and CuF), four nondissociative reaction energies, and two  $D_e$  values for the transition-metal complexes with  $\pi$ -bound ligands [ferrocene (FeCp<sub>2</sub>) and bis(benzene)chromium (CrBz<sub>2</sub>)].

For all four functionals, we employed a quadruple-zeta-quality basis set, QZVP, developed by Weigend *et al.*,<sup>60</sup> and TPSS/QZVP geometries. For the purpose of comparison, we also present results for the M05 functional as obtained with the 6-311+G\* basis set both with the TPSS/QZVP geometries and also with geometries consistently optimized at the M05/6-311+G\* level. There are various motivations for looking at accuracies attained with a variety of basis sets. Although one can argue that the results obtained with the largest basis set provide the purest test of the functional itself, one can also argue that averaging errors over two or more basis sets tests the robustness of predictions in a practical context where one cannot always afford the largest basis set. [This aspect is well appreciated in wave function theory (WFT) studies. It is only a small comfort that full configuration interaction is an excellent method (it is exact) for a complete basis set because one cannot afford a complete ba-

sis set; therefore one values methods that give useful results even for a medium-quality basis set.] Finally we mention that the combination of a density functional and a basis set can be the basis of a model chemistry,<sup>61</sup> and understanding the quality of the predictions of a model chemistry provides essential guidance for practical computational chemistry.

### III. RESULTS AND DISCUSSION

In this section, we gauge the quality of the results by calculating mean unsigned error (MUE) and mean signed error (MSE).

Table I presents results obtained with the QZVP basis set. For the binding energies of the tested transition-metal dimers, the TPSS MGGA shows best performance, followed by the MPWLYP1M HGGA. The other hybrid functionals, M05, B97-2, and B3LYP, underbind all three dimers. The Sc<sub>2</sub> dimer is a difficult case, and all tested functionals underbind this dimer. In a previous paper, we have shown that non-dynamical correlation is important in the Ni<sub>2</sub> and V<sub>2</sub> dimers; both have large  $B_1$  diagnostic values.<sup>53</sup>

For calculating the binding energies of the monohydrides, monoxides, and monofluorides, the hybrid functionals give better performances than the pure ones. In particular, B97-2, M05, and B3LYP predict more accurate binding energies than TPSS and BLYP for these compounds.

Four of the remaining six data in Table I are more general reaction energies, that is, energies of reaction more general than just bond dissociations. The semilocal functionals (TPSS and BLYP) and hybrid functionals (TPSSh, MPWLYP1M, TPSSh, B97-2, and M05) give similar performance for these final six data.

TABLE II. Effects of basis set and geometries.

| Molecules   | M05/6-311+G**//<br>M05/6-311+G* | M05/6-311+G**//<br>TPSS/QZVP | M05/QZVP//<br>TPSS/QZVP | Reference<br>data |
|---|---------------------------------|------------------------------|-------------------------|-------------------|
| Sc <sub>2</sub>   | 15.6                            | 15.5                         | 18.0                    | 39.8              |
| V <sub>2</sub>  | 50.7                            | 49.7                         | 53.2                    | 64.6              |
| Ni <sub>2</sub>   | 47.1                            | 42.0                         | 34.5                    | 49.7              |
| CrH   | 55.4                            | 55.1                         | 56.3                    | 45.7              |
| MnH   | 38.1                            | 37.7                         | 38.9                    | 32.3              |
| CoH   | 60.2                            | 60.1                         | 58.1                    | 46.6              |
| TiO   | 156.2                           | 156.0                        | 155.8                   | 158.8             |
| MnO   | 78.0                            | 78.0                         | 78.4                    | 91.1              |
| CuO   | 62.6                            | 61.9                         | 62.3                    | 63.7              |
| ScF   | 147.0                           | 147.0                        | 146.8                   | 143.0             |
| CrF   | 116.6                           | 116.2                        | 115.5                   | 105.1             |
| CuF   | 97.3                            | 97.0                         | 95.6                    | 102.5             |
| Fe <sub>2</sub> Cl <sub>4</sub> → 2FeCl <sub>2</sub>                  | 24.0                            | 23.4                         | 25.0                    | 35.0              |
| CoCl <sub>3</sub> → CoCl <sub>2</sub> + $\frac{1}{2}$ Cl <sub>2</sub> | 21.5                            | 21.0                         | 16.6                    | 16.7              |
| Fe(CO) <sub>5</sub> → Fe(CO) <sub>4</sub> + CO                        | 36.8                            | 36.9                         | 36.2                    | 42.2              |
| Ni(CO) <sub>4</sub> → Ni(CO) <sub>3</sub> + CO                        | 18.6                            | 18.4                         | 17.6                    | 24.9              |
| $\frac{1}{2}$ CrBz <sub>2</sub> → $\frac{1}{2}$ Cr + Bz               | 30.8                            | 30.2                         | 31.1                    | 31.8              |
| $\frac{1}{2}$ FeCp <sub>2</sub> → $\frac{1}{2}$ Fe + Cp               | 78.3                            | 78.1                         | 79.1                    | 80.1              |
| MSE   | -2.2                            | -2.7                         | -3.0                    |                   |
| MUE   | 7.6                             | 8.0                          | 7.8                     |                   |

When we consider the average errors for the full set of data, an encouraging result is that the M05 functional gives the lowest MUE (7.8 kcal/mol) and lowest maximum error, although there is 28% Hartree-Fock exchange in the M05 functional. Note that M05 also gives good performance for thermochemistry and kinetics for main-group compounds.<sup>54,58</sup> The good performance of B97-2 on the data set of Table I is consistent with our previous findings.<sup>41,53</sup>

The effects of geometry and basis sets are shown in Table II. Decreasing basis set size from QZVP to 6-311+G\*, the MUE for the M05 functional only increases from 7.8 to 8.0 kcal/mol, although there are some large differences for individual cases (e.g., V<sub>2</sub> and Ni<sub>2</sub>). The M05/6-311+G\* calculation with the consistently optimized geometries gives a MUE of 7.6 kcal/mol; the largest difference (5.1 kcal/mol) occurs for the Ni<sub>2</sub> dimer. We recalculated the binding energy of Ni<sub>2</sub> at the M05/QZVP//M05/QZVP level of theory, and we obtained a  $D_e$  of 44.8 kcal/mol for the Ni<sub>2</sub> dimer. If we use this  $D_e$  to calculate MUE for the M05/QZVP method, we obtain a MUE of 7.3 kcal/mol. The results in Table II confirm that the comparative study in Table I, based on TPSS/QZVP geometries, gives meaningful trends.

A few added comments on the nature of the present comparison are in order. In our previous systematic studies of transition metals, with Schultz *et al.*,<sup>41,53</sup> special care was taken to include only the experimental data that we judged most accurate. We were hesitant to include Sc<sub>2</sub> for that reason. Within the constraints of using reliable data, though, we tried for broad diversity. Since both unspecified experimental errors and the diversity and representativeness of our data set were questioned by Furche and Perdew,<sup>57</sup> in the present test we used their data set, with no substitutions, to provide a test of functionals against an alternative standard. Furthermore we used the same basis set that Furche and Perdew selected

for testing TPSS, the functional that they recommend. It is encouraging that two functionals (M05 and MPWLYP1M) that we proposed prior to the publication of this new reference set of benchmark reaction energies both have smaller mean unsigned errors and maximum absolute errors than TPSS, as does B97-2.

Although the present study employed very large basis sets, one of the advantages of DFT is that one can often obtain very useful results with smaller polarized, augmented triple-zeta and even polarized, augmented double-zeta basis sets, and we refer the interested reader to previous studies for quantitative tests of the quality attainable with such practically important basis sets.

The seven functionals tested in this study have now been applied to a broad set of databases. Table III compares their performance very broadly over six recently studied databases.

- 3dRE18 is the 3d transition-metal reaction energy set<sup>57</sup> of 18 data. The errors are from Table I.
- MBE30 is the set of 30 metal bond energies for metal-metal<sup>41</sup> and metal-ligand bonds.<sup>53</sup> The error shown is the average mean unsigned error.<sup>53,54</sup>
- MGT135 is the set of 135 main-group thermochemistry data based on bond energies, ionization potentials, and electron affinities.<sup>62</sup> The error shown is the total mean unsigned error for the MG3S basis set with QCISD/MG3 geometries.<sup>36,42</sup>
- NCBE31 is the set of 31 noncovalent binding energies including hydrogen bonding, charge transfer complexes, dipole interactions, weak interactions, and  $\pi \cdots \pi$  stacking.<sup>42</sup> The error shown is the mean unsigned error.<sup>42</sup>

TABLE III. Mean unsigned errors (kcal/mol) across multiple databases.

| Functional | 3dRE18            | MBE30             | MGT135             | NCBE31           | HTK57            | NHTBH38          | Average <sup>a</sup> |
|------------|-------------------|-------------------|--------------------|------------------|------------------|------------------|----------------------|
| M05        | 7.8 <sup>b</sup>  | 6.5 <sup>c</sup>  | 1.0 <sup>c</sup>   | 0.5 <sup>c</sup> | 1.4 <sup>c</sup> | 2.1 <sup>b</sup> | 3.2                  |
| B97-2      | 8.3 <sup>b</sup>  | 7.6 <sup>d</sup>  | 1.0 <sup>e,f</sup> | 1.2 <sup>f</sup> | 2.2 <sup>c</sup> | 2.2 <sup>g</sup> | 3.7                  |
| MPWLYM1M   | 9.5 <sup>b</sup>  | 6.1 <sup>d</sup>  | 1.6 <sup>b</sup>   | 1.2 <sup>b</sup> | 4.8 <sup>b</sup> | 8.4 <sup>b</sup> | 5.3                  |
| TPSSh      | 9.7 <sup>h</sup>  | 9.5 <sup>d</sup>  | 1.4 <sup>f</sup>   | 1.1 <sup>f</sup> | 4.3 <sup>c</sup> | 6.9 <sup>g</sup> | 5.5                  |
| TPSS       | 10.2 <sup>h</sup> | 7.4 <sup>d</sup>  | 1.4 <sup>f</sup>   | 1.2 <sup>f</sup> | 5.1 <sup>c</sup> | 9.0 <sup>g</sup> | 5.7                  |
| B3LYP      | 12.0 <sup>h</sup> | 12.6 <sup>d</sup> | 1.4 <sup>e,f</sup> | 1.1 <sup>f</sup> | 3.1 <sup>c</sup> | 4.6 <sup>g</sup> | 5.8                  |
| BLYP       | 10.6 <sup>b</sup> | 6.6 <sup>d</sup>  | 1.9 <sup>f</sup>   | 1.6 <sup>f</sup> | 4.9 <sup>c</sup> | 9.1 <sup>g</sup> | 5.8                  |

<sup>a</sup>Average of six previous columns.<sup>b</sup>Present work.<sup>c</sup>Reference 54.<sup>d</sup>Reference 53.<sup>e</sup>Reference 36.<sup>f</sup>Reference 42.<sup>g</sup>Reference 39.<sup>h</sup>Reference 57.

- HTK57 is the set of 57 hydrogen transfer kinetics data consisting of 38 barrier heights and 19 energies of reaction.<sup>38</sup> The error shown is the average mean unsigned error.
- NHTBH38 is the set of 38 non-hydrogen-transfer barrier heights for heavy atom transfer, nucleophilic substitution, association, and unimolecular reaction.<sup>39</sup> The error shown is the mean unsigned error.<sup>39</sup>

The final column of Table III is based on all 310 data and is obtained by taking the unweighted average of the six previous columns. Table III shows that M05 has the best performance over a broad assortment of energetic data.

#### IV. CONCLUDING REMARKS

In the present study, we comparatively assessed the newly developed M05 functional against a data set for transition-metal chemistry. We draw the following conclusions.

- For the three transition-metal dimers (Sc<sub>2</sub>, Ni<sub>2</sub>, and V<sub>2</sub>) that have severe multireference character, TPSS gives the best performance for calculating the binding energies.
- B97-2 gives the best performance for calculating the binding energies of the nine transition-ligand diatomics (three monohydrides, three monoxides, and three monofluorides)
- M05 gives the overall best performance for all species, and it has a MUE 55% lower than the popular B3LYP functional.

Since the M05 functional also gives good performance for main-group thermochemistry, for noncovalent chemistry, and for calculating barrier heights,<sup>54,58</sup> M05 can be applied to a wide range of problems where nonhybrid functionals fail. For example, to calculate barrier heights involving transition-metal compounds and organic molecules, as in catalysis, M05 is the best choice because the nonhybrid functionals seriously underestimate<sup>39</sup> barrier heights, and the functionals designed for kinetics (BB1K, MPWB1K, BMK,...) fail<sup>41,53,55</sup> badly for some bond energies involving transition-metal compounds.

#### ACKNOWLEDGMENTS

The authors are grateful to Nathan Schultz for many helpful discussions. This work was supported in part by the U.S. Department of Energy, Office of Basic Energy Sciences and in part by the Office of Naval Research under Grant No. N00012-05-01-0538.

#### APPENDIX: ATOMIC ENERGIES

Transition-metal chemistry is complicated by the large number of low-lying electronic states, and DFT methods do not always predict the same ground states for the atoms as higher-level calculations or as are observed experimentally. In this paper, we do not force the atoms to have electronic configurations that agree with experimental results, but rather we always chose the atomic references to be the ones with the lowest energies for each method. We calculated the atomic energies with several different guesses for each atom to ensure that we had found the lowest-energy electronic configuration for each method. This leads to another complication, namely, that the optimal DFT determinant for an open-shell system is not necessarily an eigenfunction of  $\hat{S}^2$ , where  $S$  is total electron spin and a caret denotes an operator. The determinant is, however, an eigenfunction of  $\hat{S}_z$  with eigenvalue  $M_s\hbar$ . Thus, when one say, for example, that one has a “quartet” state, it simply means that  $M_s=3/2$ , not that the expectation value of  $\hat{S}^2$  is 3.75 [which is the value of  $S(S+1)$  when  $S=3/2$ ]. Furthermore, the optimized orbitals do not necessarily transform as pure spherical harmonics, that is, they may be hybrid orbitals rather than pure  $s$ ,  $p$ , or  $d$  orbitals. This is further complicated by the fact that the calculations are carried out with  $O_h$  symmetry, not with the full  $O(3)$  group. When the optimum orbitals are hybrid orbitals, the solution to the DFT equations is said to break symmetry. When no symmetry breaking occurs, the predicted atomic ground states may be  $Ns^2(N-1)d^{n-2}$ ,  $Ns^1(N-1)d^{n-1}$ , or  $(N-1)d^n$  pure states, where  $N$  is the highest principal quantum number of the atom and  $n$  is the number of electrons beyond the previous rare gas number. When symmetry breaking occurs, a nominal configuration is assigned by analyzing the DFT density matrix by natural atomic orbital analysis.<sup>63,64</sup> Note that the natural atomic orbital analysis employs symmetry averaging to obtain pure  $s$ ,  $p$ , and  $d$  orbitals.<sup>63</sup>

TABLE IV. Predicted raw energies (hartree) and ground-state configurations for 3d transition metals with the QZVP basis set. All calculations are performed with the GAUSSIAN 03 program (Ref. 59).

| Atom | M05          |                    | BLYP         |                    | MPWLYP1M     |                    | B97-2        |                    | Experimental configuration |
|------|--------------|--------------------|--------------|--------------------|--------------|--------------------|--------------|--------------------|----------------------------|
|      | Energy       | Configuration      | Energy       | Configuration      | Energy       | Configuration      | Energy       | Configuration      |                            |
| Sc   | -760.643 54  | $3d^1 4s^2(^2D)$   | -760.643 32  | $3d^1 4s^2(^2D)$   | -760.653 68  | $3d^1 4s^2(^2D)$   | -760.712 48  | $3d^1 4s^2(^2D)$   | $3d^1 4s^2(^2D)$           |
| Ti   | -849.364 75  | $3d^2 4s^2(^3F)$   | -849.387 83  | $3d^2 4s^1.8(3)$   | -849.393 20  | $3d^2 4s^1.8(3)$   | -849.463 07  | $3d^2 4s^1.8(3)$   | $3d^2 4s^2(^3F)$           |
| V    | -943.913 91  | $3d^3 4s^1.6(4)$   | -943.953 27  | $3d^3 4s^1(^6D)$   | -943.959 19  | $3d^3 4s^1(^6D)$   | -944.043 52  | $3d^3 4s^1.7(4)$   | $3d^3 4s^2(^4F)$           |
| Cr   | -1044.448 84 | $3d^5 4s^1(^7S)$   | -1044.490 52 | $3d^5 4s^1(^7S)$   | -1044.497 07 | $3d^5 4s^1(^7S)$   | -1044.608 08 | $3d^5 4s^1(^7S)$   | $3d^5 4s^1(^7S)$           |
| Mn   | -1151.030 98 | $3d^5 4s^2(^6S)$   | -1151.041 83 | $3d^5 4s^2(^6S)$   | -1151.053 93 | $3d^5 4s^2(^6S)$   | -1151.211 76 | $3d^5 4s^2(^6S)$   | $3d^5 4s^2(^6S)$           |
| Fe   | -1263.710 60 | $3d^6 4s^2(^5D)$   | -1263.756 72 | $3d^6 4s^1.4(5)$   | -1263.764 37 | $3d^6 4s^1.5(5)$   | -1263.932 88 | $3d^6 4s^2(^5D)$   | $3d^6 4s^2(^5D)$           |
| Co   | -1382.763 48 | $3d^7 4s^1.5(4)$   | -1382.839 92 | $3d^7 4s^1.2(4)$   | -1382.846 12 | $3d^7 4s^1.2(4)$   | -1383.035 32 | $3d^7 4s^1.6(4)$   | $3d^7 4s^2(^4F)$           |
| Ni   | -1508.338 23 | $3d^9 4s^1(^3D)$   | -1508.411 38 | $3d^8 4s^1.2(3)$   | -1508.417 42 | $3d^8 4s^1.2(3)$   | -1508.646 32 | $3d^9 4s^1(^3D)$   | $3d^8 4s^2(^3F)$           |
| Cu   | -1640.570 99 | $3d^{10} s^1(^1S)$ | -1640.635 08 | $3d^{10} s^1(^2S)$ | -1640.641 75 | $3d^{10} s^1(^2S)$ | -1640.921 37 | $3d^{10} s^1(^2S)$ | $3d^{10} s^1(^2S)$         |

We can make this clearer by discussing calculations on the  $M_s=3/2$  ground state of vanadium atom. When we use the double-zeta-quality or triple-zeta-quality basis sets of our previous work,<sup>41</sup> we obtain essentially pure-symmetry orbitals in  $O_h$  symmetry for both the BLYP and B97-2 functionals. Natural atomic orbital analysis shows that the nominal configuration is a  $4s^1 3d^4$  state with the BLYP functional and a  $4s^2 3d^3$  state with the B97-2 functional. Note that the latter arise from  $4s^1 3d^3$  in the  $\alpha$  manifold and  $4s$  in the  $\beta$  manifold. When the B97-2 calculation is repeated with the larger QZVP basis set used in the present paper, the highest-energy occupied  $\alpha$  orbital and the highest-energy occupied  $\beta$  orbital break symmetry even in the  $O_h$  symmetry group, and the nominal configuration is found by natural atomic orbital analysis to be  $4s^{1.7} 3d^{3.3}$ . Note that this arises from  $4s^{0.7} 3d^{3.3}$  in the  $\alpha$  manifold and  $4s$  in the  $\beta$  manifold.

The predicted raw atomic energies and ground-state configurations with the QZVP basis set are summarized in Table IV. We also give the term symbol for the atomic ground state in those cases where DFT method predicts a pure state for that atom. In other cases we just give the nominal multiplicity, assigning it (as explained above) as  $2M_s+1$ .

The results with the QZVP basis set may be summarized as follows: All tested DFT methods predict a pure ground state for Sc, Cr, Mn, and Cu. For Ti, only M05 predicts a pure ground state,  $3d^2 4s^2(^3F)$ , which agrees with the experimental results. M05 and B97-2 predict a mixed state for V, whereas BLYP and MPWLYP1M predict a  $3d^4 4s^1$  state for V, which is not the experimental ground state for V. M05 and B97-2 predict a pure ground state for Fe, whereas BLYP and MPWLYP1M predict a mixed state. All four tested DFT methods predict a mixed ground state for Co. M05 and B97-2 predict a pure  $3d^9 4s^1$  ground state for Ni, whereas BLYP and MPWLYP1M predict a mixed ground state for Ni.

<sup>1</sup> P. Hohenberg and W. Kohn, Phys. Rev. **136**, 864 (1964).<sup>2</sup> A. D. Becke, Phys. Rev. A **38**, 3098 (1988).<sup>3</sup> C. Lee, W. Yang, and R. G. Parr, Phys. Rev. B **37**, 785 (1988).<sup>4</sup> T. Ziegler, Chem. Rev. (Washington, D.C.) **91**, 651 (1991).<sup>5</sup> J. P. Perdew, in *Electronic Structure of Solids '91*, edited by P. Ziesche and H. Eschig (Akademie, Berlin, 1991), p. 11.<sup>6</sup> J. P. Perdew and Y. Wang, Phys. Rev. B **45**, 13244 (1992).<sup>7</sup> A. D. Becke, J. Chem. Phys. **98**, 1372 (1993).<sup>8</sup> A. D. Becke, J. Chem. Phys. **98**, 5648 (1993).<sup>9</sup> P. J. Stephens, F. J. Devlin, C. F. Chabalowski, and M. J. Frisch, J. Phys.Chem. **98**, 11623 (1994).<sup>10</sup> A. D. Becke, J. Chem. Phys. **104**, 1040 (1996).<sup>11</sup> J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).<sup>12</sup> J. P. Perdew, M. Ernzerhof, and K. Burke, J. Chem. Phys. **105**, 9982 (1996).<sup>13</sup> A. Berces and T. Ziegler, Top. Curr. Chem. **182**, 41 (1996).<sup>14</sup> O. V. Gritsenko, P. R. T. Schipper, and E. J. Baerends, J. Chem. Phys. **107**, 5007 (1997).<sup>15</sup> A. D. Becke, J. Chem. Phys. **107**, 8554 (1997).<sup>16</sup> C. Adamo and V. Barone, Chem. Phys. Lett. **274**, 242 (1997).<sup>17</sup> C. Adamo and V. Barone, J. Chem. Phys. **108**, 664 (1998).<sup>18</sup> H. L. Schmider and A. D. Becke, J. Chem. Phys. **108**, 9624 (1998).<sup>19</sup> A. D. Becke, J. Chem. Phys. **109**, 2092 (1998).<sup>20</sup> C. Adamo, M. Ernzerhof, and G. E. Scuseria, J. Chem. Phys. **112**, 2643 (2000).<sup>21</sup> B. J. Lynch, P. L. Fast, M. Harris, and D. G. Truhlar, J. Phys. Chem. A **104**, 4811 (2000).<sup>22</sup> N. C. Handy and A. J. Cohen, Mol. Phys. **99**, 403 (2001).<sup>23</sup> J. P. Perdew and K. Schmidt, in *Density Functional Theory and Its Applications to Materials*, edited by V. Van-Doren, C. V. Alsenoy, and P. Geerlings (American Institute of Physics, New York, 2001), p. 1.<sup>24</sup> B. J. Lynch and D. G. Truhlar, J. Phys. Chem. A **105**, 2936 (2001).<sup>25</sup> P. J. Wilson, T. J. Bradley, and D. J. Tozer, J. Chem. Phys. **115**, 9233 (2001).<sup>26</sup> J. Baker and P. Pulay, J. Chem. Phys. **117**, 1441 (2002).<sup>27</sup> A. D. Becke, J. Chem. Phys. **119**, 2972 (2003).<sup>28</sup> J. Tao, J. P. Perdew, V. N. Staroverov, and G. E. Scuseria, Phys. Rev. Lett. **91**, 146401 (2003).<sup>29</sup> V. N. Staroverov, G. E. Scuseria, J. Tao, and J. P. Perdew, J. Chem. Phys. **119**, 12129 (2003).<sup>30</sup> V. N. Staroverov, G. E. Scuseria, J. Tao, and J. P. Perdew, Phys. Rev. B **69**, 75102 (2004).<sup>31</sup> J. P. Perdew, J. Tao, V. N. Staroverov, and G. E. Scuseria, J. Chem. Phys. **120**, 6898 (2004).<sup>32</sup> Y. Zhao, J. Pu, B. J. Lynch, and D. G. Truhlar, Phys. Chem. Chem. Phys. **6**, 673 (2004).<sup>33</sup> X. Chu and A. Dalgarno, J. Chem. Phys. **121**, 4083 (2004).<sup>34</sup> Y. Zhao, B. J. Lynch, and D. G. Truhlar, J. Phys. Chem. A **108**, 2715 (2004).<sup>35</sup> A. D. Boese and J. M. L. Martin, J. Chem. Phys. **121**, 3405 (2004).<sup>36</sup> Y. Zhao and D. G. Truhlar, J. Phys. Chem. A **108**, 6908 (2004).<sup>37</sup> S. Andersson and M. Gruning, J. Phys. Chem. A **108**, 7621 (2004).<sup>38</sup> Y. Zhao, B. J. Lynch, and D. G. Truhlar, Phys. Chem. Chem. Phys. **7**, 43 (2005).<sup>39</sup> Y. Zhao, N. González-García, and D. G. Truhlar, J. Phys. Chem. A **109**, 2012 (2005).<sup>40</sup> Y. Zhao and D. G. Truhlar, J. Chem. Theory Comput. **1**, 415 (2005).<sup>41</sup> N. Schultz, Y. Zhao, and D. G. Truhlar, J. Phys. Chem. A **109**, 4388 (2005).<sup>42</sup> Y. Zhao and D. G. Truhlar, J. Phys. Chem. A **109**, 5656 (2005).<sup>43</sup> M. C. Holthausen, J. Comput. Chem. **26**, 1505 (2005).<sup>44</sup> Y. Zhao and D. G. Truhlar, J. Phys. Chem. A **109**, 6624 (2005).<sup>45</sup> Y. Zhao and D. G. Truhlar, Phys. Chem. Chem. Phys. **7**, 2701 (2005).

- <sup>46</sup> A. D. Becke, *J. Chem. Phys.* **122**, 64101 (2005).
- <sup>47</sup> B. Zhou and E. A. Carter, *J. Chem. Phys.* **122**, 184108 (2005).
- <sup>48</sup> C.-Y. Ren, *J. Chem. Phys.* **122**, 244109 (2005).
- <sup>49</sup> J. P. Perdew, A. Ruzsinszky, J. Tao, V. N. Staroverov, G. E. Scuseria, and G. I. Csonka, *J. Chem. Phys.* **123**, 62201 (2005).
- <sup>50</sup> E. Ruiz, A. Rodríguez-Forteza, J. Tercero, T. Cauchy, and C. Massobrio, *J. Chem. Phys.* **123**, 74102 (2005).
- <sup>51</sup> R. M. Dickson and A. D. Becke, *J. Chem. Phys.* **123**, 111101 (2005).
- <sup>52</sup> T. W. Keal and D. J. Tozer, *J. Chem. Phys.* **123**, 121103 (2005).
- <sup>53</sup> N. Schultz, Y. Zhao, and D. G. Truhlar, *J. Phys. Chem. A* **109**, 11127 (2005).
- <sup>54</sup> Y. Zhao, N. E. Schultz, and D. G. Truhlar, *J. Chem. Phys.* **123**, 161103 (2005); note that in this communication we interchanged  $c_{C\alpha\beta,i}$  and  $c_{C\sigma\sigma,i}$  in Table I. In addition, “reduced density  $x_\sigma$ ” before Eq. (1) should read “reduced density gradient  $x_\sigma$ .”
- <sup>55</sup> M. M. Quintal, A. Karton, M. A. Iron, A. D. Boese, and J. M. L. Martin, *J. Phys. Chem. A* **110**, 709 (2006).
- <sup>56</sup> M. J. G. Peach, T. Helgaker, P. Saek, T. W. Keal, O. B. Lutnæs, D. J. Tozer, and N. C. Handy, *Phys. Chem. Chem. Phys.* **8**, 558 (2006).
- <sup>57</sup> F. Furche and J. P. Perdew, *J. Chem. Phys.* **124**, 044103 (2006).
- <sup>58</sup> Y. Zhao, N. E. Schultz, and D. G. Truhlar, *J. Chem. Theory Comput.* **2**, 364 (2006).
- <sup>59</sup> M. J. Frisch, G. W. Trucks, H. B. Schlegel *et al.*, GAUSSIAN 03, Gaussian, Inc., Pittsburgh, PA, 2003.
- <sup>60</sup> F. Weigend, F. Furche, and R. Ahlrichs, *J. Chem. Phys.* **119**, 12753 (2003).
- <sup>61</sup> J. A. Pople, *Rev. Mod. Phys.* **71**, 1267 (1999).
- <sup>62</sup> B. J. Lynch, Y. Zhao, and D. G. Truhlar, *J. Phys. Chem. A* **107**, 1384 (2003).
- <sup>63</sup> A. E. Reed, R. B. Weinstock, and F. Weinhold, *J. Chem. Phys.* **83**, 735 (1985).
- <sup>64</sup> A. E. Reed and F. Weinhold, *J. Am. Chem. Soc.* **108**, 3586 (1986).