



Density functional benchmark studies on structure and energetics of 3d transition metal mononitrides

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Abstract. We report the results of a benchmarking study on generalized gradient approximation (GGA), meta-GGA, hybrid GGA, and hybrid meta-GGA density functional theory (DFT) methods for 3d transition metal mononitrides (3d-TMNs). The selected DFT functionals are, B97-D, BLYP, BP91, MPW91, PBE96, PW91, M06-L, B3LYP, B97, BHandH, PBE0, M05, M05-2X, M06, M06-2X, M06-HF and TPSSh. The performances of these DFT functionals are assessed by calculating the bond distance, harmonic vibrational frequency and atomization energy of 3d-TMNs. The results are compared with the available experimental and high-level *ab initio* results. The calculated results show that MPW91, M06-L, and B3LYP functionals provide better results than the other functionals that are taken in this study. In general, the functionals with significant Hartree–Fock exchange show poor performance in most of the 3d-TMNs. Hence, these functionals are not recommended for the studies of structure and energetics in 3d-TMNs.

Keywords. Transition metal mononitrides; benchmark study; density functional theory; minnesota functionals; Hartree–Fock exchange.

1. Introduction

Understanding the nature of transition metal—main-group element bond is important in many areas of science, such as organometallic chemistry,¹ surface chemistry,² catalysis,^{3,4} high-temperature chemistry⁵ and astrophysics.⁶ The main group element in particular, nitrogen bonded with transition metals (*i.e.*, transition metal nitrides (TMNs)) display a large number of interesting properties such as high melting point, high hardness, high thermal and electrical conductivity, superconductivity, etc.^{7,8} These properties have received much attention for a wide range of applications such as metal nitrides as refractory materials,⁹ pigments for high magnetic density,¹⁰ hard coatings for cutting tools,¹¹ etc. Recently, TMNs have attracted increasing interest, because of their applications in lithium-ion batteries (electrode materials) and as supercapacitors.¹²

Since TMNs have the aforementioned properties, there are a large number of papers published both experimentally and theoretically on these systems. The experimental studies such as, mass-spectrometric

investigation on ScN, TiN and VN,¹³ near-infrared electronic emission spectra on ScN,¹⁴ electronic spectra on TiN,¹⁵ laser ablation and matrix infrared techniques on MN (M=Sc, Ti, V, Cr, Mn, Fe, Co, Ni)¹⁶ and the resonant two-photon ionization spectroscopy study on VN¹⁷ were performed. In the case of theoretical study, both *ab initio* and density functional theory (DFT) methods were used. The *ab initio* studies such as, Multireference Configuration Interaction (MRCI) calculation on ScN,¹⁸ TiN,¹⁹ VN,¹⁹ CrN,¹⁹ CoN,²⁰ and CuN,²¹ Complete Active Space Self-Consistent Field (CASSCF) calculation on FeN and NiN²² and Coupled Cluster Singles Doubles noniterative Triples (CCSD(T)) calculation on MN (M=Sc, Ti, V, Cr)²³ were performed. From the above theoretical studies, it is understood that the researchers used highly correlated *ab initio* methods to get accurate results. Because it is widely believed that, the highly correlated *ab initio* methods give accurate results. However, these methods are computationally very expensive, and this is due to the complexity of equations and a higher level of excitations. Hence, it is not possible to use these methods to study large molecular systems or elements with a higher atomic number. Thus, one needs to find out an alternate method with the

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accuracy of multireference methods and less computation time. Generally, DFT methods act as an alternative to high cost *ab initio* methods. Because of very moderate overall $O(N^2)$ scaling, they are computationally less expensive. From the literature, it can be noted that the DFT calculations were also performed on 3d Transition metal mononitrides (3d-TMNs). For instance, Daoudi *et al.* have performed both *ab initio* and DFT calculations on ScN.²⁴ They concluded that DFT methods are accurate but yield higher vibrational frequencies. Later, Chaudhari and Lee studied 3d-TMNs using B3LYP method and concluded that binding energies of 3d-metal mononitrides are higher than monocarbides and monoxides.²⁵ Even though plenty of experimental and theoretical studies on 3d-TMNs were reported in the literature, a satisfactory description of their electronic, structural, and elastic properties is still an area of active research.

In the recent past, an enormous amount of exchange-correlation functionals developed within the DFT framework. Because of this, one needs to pay careful attention to the selection of functionals to study a particular atomic or molecular system. It is widely believed that B3LYP yields a better result in organic systems. In the case of inorganic systems, the selection of DFT functionals is a challenging one. Because metals possess near degenerate energy levels, subsequently these methods show difficulty in determining the ground state of a system. Hence, in order to find out suitable DFT functional, one needs to perform a benchmark study of DFT functionals on these systems. From the literature survey, it can be understood that no systematic DFT assessment study performed on 3d-TMNs, in particular, using recently developed DFT functionals and Minnesota functionals. Earlier, Wu has investigated the structure and energetic properties of 3d-TMNs using DFT methods. From this investigation, it was concluded that the calculated properties are highly dependent on the DFT functionals.²⁶ But, they selected very few DFT functionals for the study. Apart from this study, no other systematic assessment studies with particular focus on 3d-TMNs were reported in the literature. However, a few other DFT assessment studies were reported in the literature.^{27–31} These studies were assessed DFT functionals for a particular training set, which includes metal dimers, monohydrides, mononitrides, monoxides, and monofluorides. The major problem in using this training set is, it is not always helpful to understand the performance of a functional *i.e.*, how a method works and why.

To identify the best DFT functional for the accurate prediction of the structure and energetic properties of 3d-TMNs, in this study, we systematically assessed the performance of seventeen DFT functionals. The

traditional and recently developed functionals are selected for this study. The selected 3d-TMNs are ScN, TiN, VN, CrN, FeN, CoN, NiN, and CuN. Among the 3d-TMNs, MnN and ZnN are not selected for this study. Because we are performing DFT assessment studies in MnN and ZnN separately. The DFT functionals chosen in this study are shown in Table 1. Our calculated results are compared with the available experimental and previous MRCI results. We hope that this work can provide useful guidance for future experimental studies or the development of new exchange-correlation functionals for the studies in these 3d-TMNs.

2. Computational details

The molecular structure of 3d-TMNs are optimized using seventeen DFT functionals, B97-D,³² BLYP,^{33,34} BP91,^{33,35} MPW91,^{36,37} PBE96,^{38,39} PW91,³⁵ M06-L,⁴⁰ B3LYP,⁴¹ B97,⁴² BHandH,⁴³ PBE0,⁴⁴ M05,⁴⁵ M05-2X,³⁷ M06,²⁸ M06-2X,²⁸ M06-HF⁴⁶ and TPSSH.⁴⁷ The second generation default bases triple zeta valence with polarized basis functions (def2-TZVPP) is used for the calculation. The reliability of the def2-TZVPP basis set for studying the structure and energetic properties of organometallic complexes was tested in an earlier study.^{48–50} One of the main objectives of this study is to identify suitable DFT functional for further studies of large metal nitride systems. Hence, the segmented contraction basis set is more appropriate than the general contraction basis set *i.e.*, correlation consistent (CC) basis set. The CCSD(T) calculations are also performed with def2-TZVPP basis set in late 3d-TMNs (FeN–CuN) due to the lack of experimental or MRCI results. Earlier, 3d-TMNs (ScN–CrN) were well characterized experimentally. Spin-restricted and unrestricted formalisms are employed to calculate the singlet and other spin states, respectively. The harmonic vibrational frequency calculations are performed to identify the minimum energy structure. The atomization energy of 3d-TMNs is also calculated using the following equation.

$$A.E_{(MN)} = E_{(MN)} - (E_{(M)} + E_{(N)}) \quad (1)$$

where $E_{(MN)}$ represents the total energy of metal nitrides, $E_{(M)}$ and $E_{(N)}$ represents the total energy of metal and nitrogen respectively. The atomization energy is also termed as dissociation energy in the literature. The mean deviation values are obtained by comparing DFT results with previous MRCI results as the experimental results are not available for few 3d-TMNs. All the DFT calculations are performed using NWChem 6.0 program.⁵¹

3. Results and Discussion

The 3d-TMNs, ScN, TiN, VN, CrN, FeN, CoN, NiN, and CuN are optimized using the DFT functionals. The

Table 1. DFT functionals selected in this study.

| GGA | Meta-GGA | Hybrid GGA | Hybrid meta-GGA |
|-------|----------|-------------------------|-----------------|
| B97-D | M06-L | B3LYP (20) ^a | M05 (28) |
| BLYP | ... | B97 (19.43) | M05-2X (56) |
| BP91 | ... | BHandH (50) | M06 (27) |
| MPW91 | ... | PBE0 (25) | M06-2X (54) |
| PBE96 | ... | ... | M06-HF (100) |
| PW91 | ... | ... | TPSSh (10) |

^aThe values in parenthesis are Hartree–Fock exchange percentage.

Table 2. The optimized M–N Bond distance (in Å) in 3d Transition metal mononitrides.

| Functionals | ScN | TiN | VN | CrN | FeN | CoN | NiN | CuN |
|-------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|
| B97-D | 1.720 | 1.599 | 1.541 | 1.544 | 1.544 | 1.622 | 1.635 | 1.794 |
| BLYP | 1.686 | 1.620 | 1.559 | 1.549 | 1.535 | 1.625 | 1.631 | 1.783 |
| BP91 | 1.667 | 1.606 | 1.548 | 1.540 | 1.566 | 1.609 | 1.616 | 1.773 |
| MPW91 | 1.727 | 1.655 | 1.591 | 1.616 | 1.585 | 1.648 | 1.663 | 1.851 |
| PBE96 | 1.668 | 1.604 | 1.547 | 1.538 | 1.521 | 1.607 | 1.614 | 1.767 |
| PW91 | 1.669 | 1.604 | 1.546 | 1.537 | 1.579 | 1.606 | 1.614 | 1.767 |
| M06-L | 1.663 | 1.605 | 1.541 | 1.553 | 1.528 | 1.607 | 1.743 | 1.782 |
| TPSSh | 1.659 | 1.560 | 1.539 | 1.546 | 1.564 | 1.614 | 1.622 | 1.792 |
| B97 | 1.703 | 1.550 | 1.529 | 1.540 | 1.597 | 1.624 | 1.640 | 1.813 |
| B3LYP | 1.653 | 1.553 | 1.533 | 1.546 | 1.562 | 1.627 | 1.642 | 1.811 |
| PBE0 | 1.635 | 1.539 | 1.523 | 1.555 | 1.583 | 1.621 | 1.654 | 1.809 |
| M06 | 1.642 | 1.539 | 1.520 | 1.547 | 1.592 | 1.621 | 1.642 | 1.813 |
| M05 | 1.626 | 1.529 | 1.509 | 1.525 | 1.581 | 1.617 | 1.636 | 1.819 |
| M06-2X | 1.627 | 1.526 | 1.498 | 1.609 | 1.743 | 1.818 | 1.886 | 1.922 |
| M05-2X | 1.621 | 1.523 | 1.496 | 1.568 | 1.730 | 1.811 | 1.857 | 1.884 |
| BHandH | 1.621 | 1.521 | 1.561 | 1.755 | 1.738 | 1.763 | 1.824 | 1.868 |
| M06-HF | 1.602 | 1.514 | 1.476 | 1.488 | 1.809 | 1.969 | 2.014 | 2.024 |
| Prev.DFT* | 1.683 | 1.595 | 1.537 | 1.533 | 1.603 | 1.636 | 1.650 | 1.814 |
| MRCI | 1.750 ^a | 1.613 ^c | 1.608 ^c | 1.619 ^c | 1.565 ^f | 1.604 ^g | 1.615 ^f | 1.879 ⁱ |
| expt. | 1.687 ^b | 1.582 ^d | 1.566 ^d | 1.563 ^e | ... | 1.575 ^h | ... | ... |

*Reference²⁵. ^aReference¹⁸. ^bReference¹⁴. ^cReference¹⁹. ^dReference⁵⁹.

^eReference⁶⁰. ^four study CCSD(T)/def2-TZVPP. ^gReference⁵⁷. ^hReference²⁰.

ⁱReference²¹.

DFT functionals that are taken in our study are classified as generalized gradient approximation (GGA), meta-GGA, hybrid GGA and hybrid meta-GGA functionals. The key ingredients in these functionals are density, the gradient of density, kinetic energy density, and HF exchange. For example, GGA has density and gradient of density, meta-GGA has kinetic energy density along with density and gradient of density. The hybrid functionals include a fraction of HF exchange along with density and gradient of density. The difference between the hybrid and hybrid meta-GGA functionals is, in the former case, the starting point is the GGA method. In the latter case, the starting point is a meta-GGA method. The selected DFT functionals are listed in Table 1. Like the previous assessment study by Zhao *et al.*,²⁷ we do

not force the molecular orbitals to have electronic states that agree with experimental results. We calculated the electronic energies of molecular orbitals, with different multiplicities for each molecular orbital to confirm the lowest-energy electronic configuration for each method. The optimized bond distance and the harmonic vibrational frequency along with available experimental and previous theoretical results are given in Table 2 and Table 3, respectively. The calculated atomization energy along with available experimental and previous theoretical results is given in Table 4. The hybrid functionals are listed in the increasing order of HF exchange percentage in the tables and figure. This will help us to understand the performance of functionals as a function of HF exchange percentage.

Table 3. The calculated harmonic vibrational frequencies (in cm^{-1}) of 3d Transition metal mononitrides.

| M–N/Functionals | ScN | TiN | VN | CrN | FeN | CoN | NiN | CuN |
|-----------------|------------------|-------------------|-------------------|-------------------|------------------|------------------|------------------|------------------|
| B97-D | 1043 | 1048 | 1125 | 948 | 940 | 834 | 782 | 571 |
| BLYP | 897 | 1027 | 1103 | 1026 | 1041 | 831 | 802 | 598 |
| BP91 | 939 | 1059 | 1131 | 1028 | 914 | 863 | 829 | 608 |
| MPW91 | 849 | 913 | 956 | 720 | 834 | 770 | 726 | 508 |
| PBE96 | 927 | 1061 | 1135 | 1044 | 1065 | 870 | 835 | 616 |
| PW91 | 926 | 1062 | 1126 | 1045 | 866 | 870 | 835 | 617 |
| M06-L | 944 | 1050 | 1088 | 911 | 966 | 854 | 664 | 597 |
| TPSSh | 952 | 1137 | 1117 | 910 | 827 | 776 | 744 | 590 |
| B97 | 934 | 1166 | 1137 | 892 | 746 | 731 | 679 | 558 |
| B3LYP | 951 | 1152 | 1115 | 862 | 822 | 711 | 646 | 559 |
| PBE0 | 988 | 1190 | 1142 | 747 | 776 | 675 | 542 | 564 |
| M06 | 968 | 1174 | 1134 | 768 | 768 | 741 | 679 | 563 |
| M05 | 985 | 1199 | 1177 | 879 | 870 | 830 | 770 | 552 |
| M06-2X | 1001 | 1245 | 1246 | 527 | 579 | 476 | 514 | 471 |
| M05-2X | 1041 | 1259 | 1212 | 494 | 616 | 499 | 527 | 521 |
| BHandH | 1013 | 1228 | 588 | 504 | 636 | 515 | 545 | 508 |
| M06-HF | 1086 | 1288 | 1851 | 462 | 606 | 455 | 476 | 414 |
| Prev.DFT* | 951 | 1040 | 1107 | 845 | 746 | 700 | 645 | 565 |
| MRCI | 807 ^a | 1024 ^c | 974 ^c | 854 ^c | 869 ^g | 862 ⁱ | 842 ^g | 524 ^k |
| expt. | 795 ^b | 1039 ^d | 1033 ^e | 1050 ^f | 935 ^h | 826 ^j | 832 ^j | ... |

*Reference²⁵. ^aReference¹⁸. ^bReference¹⁴. ^cReference¹⁹. ^dReference¹⁵.
^eReference⁶¹. ^fReference⁵⁴. ^gour study CCSD(T)/def2-TZVPP.
^hReference⁵⁵. ⁱReference⁵⁷. ^jReference¹⁶. ^kReference²¹.

Table 4. The calculated atomization energies (in eV) of 3d Transition metal mononitrides.

| M–N/Functionals | ScN | TiN | VN | CrN | FeN | CoN | NiN | CuN |
|-----------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|
| B97-D | 3.90 | 5.18 | 5.06 | 4.27 | 7.11 | 3.13 | 3.32 | 2.13 |
| BLYP | 4.96 | 5.43 | 6.04 | 4.73 | 7.36 | 3.49 | 3.37 | 2.33 |
| BP91 | 5.13 | 5.62 | 6.20 | 4.35 | 6.58 | 3.50 | 3.35 | 2.23 |
| MPW91 | 2.95 | 3.37 | 4.44 | 2.40 | 4.57 | 2.09 | 2.00 | 1.29 |
| PBE96 | 5.25 | 3.31 | 6.36 | 4.61 | 7.22 | 3.70 | 3.56 | 2.40 |
| PW91 | 5.27 | 5.77 | 6.36 | 4.62 | 6.89 | 3.69 | 3.53 | 4.78 |
| M06-L | 4.82 | 4.95 | 4.88 | 3.83 | 5.76 | 2.62 | 2.22 | 2.14 |
| TPSSh | 4.43 | 5.11 | 5.41 | 3.59 | 5.10 | 2.80 | 3.17 | 1.99 |
| B97 | 3.58 | 12.60 | 4.82 | 3.53 | 4.80 | 2.52 | 2.37 | 3.77 |
| B3LYP | 4.13 | 4.93 | 4.94 | 3.50 | 4.73 | 2.48 | 2.28 | 1.82 |
| PBE0 | 5.75 | 5.52 | 4.87 | 3.00 | 3.90 | 2.30 | 2.07 | 1.72 |
| M06 | 6.37 | 5.13 | 4.47 | 3.10 | 4.54 | 2.26 | 2.10 | 1.63 |
| M05 | 6.64 | 5.30 | 4.65 | 3.42 | 4.80 | 2.46 | 2.32 | 1.63 |
| M06-2X | 3.23 | 12.00 | 3.77 | 2.79 | 2.76 | 1.54 | 1.42 | 1.33 |
| M05-2X | 3.36 | 5.86 | 3.62 | 2.68 | 2.86 | 1.80 | 1.72 | 1.57 |
| BHandH | 2.25 | 10.10 | 2.80 | 1.52 | 1.43 | 0.99 | 0.96 | 0.96 |
| M06-HF | 2.29 | 17.70 | 3.28 | 2.30 | 4.04 | 1.09 | 1.08 | 0.92 |
| MRCI | 4.56 ^a | 4.18 ^c | 3.74 ^c | 2.75 ^c | 2.67 ^e | 1.61 ^f | 2.07 ^e | 1.08 ^g |
| expt. | 4.86 ^b | 5.33 ^b | 5.03 ^b | 3.90 ^d | ... | ... | ... | ... |

^aReference⁶². ^bReference¹³. ^cReference¹⁹. ^dReference⁶³. ^eour study CCSD(T)/def2-TZVPP. ^fReference⁵⁷. ^gReference²¹.

3.1 ScN

The ground electronic state of ScN is $^1\Sigma^+$.¹⁴ All the functionals that are taken in this study predict $^1\Sigma^+$ state to be the ground state of ScN, except B97-D, and B97 functionals. These functionals predict $^3\Sigma^+$ state to be the ground state of ScN molecule. In the case of bond distance, our calculations show that the Sc–N bond distance predicted by BLYP (GGA) functional is in excellent agreement with the experimental value (Table 2). The difference between the experimental and the calculated bond distance is 0.001 Å. The other DFT functionals either slightly underestimate or overestimate the Sc–N bond distance. In general, the GGA functionals show good performance *i.e.*, accurately predict the Sc–N bond distance. Among the hybrid functionals, both TPSSh and B3LYP functionals show better performance than other hybrid functionals considered in this study. The difference between experimental and theoretical (TPSSh, B3LYP) result is less than 0.03 Å. But, this difference is not significant. Further, it can be noted that, if the fraction of HF exchange percentage increases in the functionals, deviation from the experimental bond distance also increases (Table 2). These functionals predict shorter bond distance than the other studied functionals. In the case of vibrational frequency, MPW91 (GGA) functional gives a better result than the other functionals considered in this study. The difference between the experimental and calculated (MPW91) vibrational frequency is 54 cm^{-1} . Our calculations give much better result than the previous DFT study (Table 3). Earlier Chaudhari and Lee calculated the vibrational frequency (951 cm^{-1}) of ScN using DFT method.²⁵ They used B3LYP functional with all electron 6-311+G* basis set in their calculations. In our study, B3LYP functional with def2-TZVPP basis set gives 951 cm^{-1} . This indicates that the vibrational frequency of ScN is already converged in the 6-311+G* basis set and the def2-TZVPP does not improve it any further. Hence, the selection of functional is really important in this case. In our study, MPW91 functional predicts the vibrational frequency (849 cm^{-1}) of ScN. This is close to the experimental value (795 cm^{-1}). In general, GGA functionals show better performance than the hybrid functionals in the case of vibrational frequency also. More recently, Li *et al.*, have assessed the performance of eight DFT functionals in Sc₂ and ScN dimer.⁵² They concluded that PW91 functional with 6-311+G(d) basis set show good performance in bond distance and vibrational frequency. Our calculation result is consistent with this recent study. The atomization energy calculated by the GGA functional BLYP and meta-GGA functional M06-L is in very close agreement with the experimental result

(Table 4). The difference between the experimental and the theoretical (BLYP, and M06-L) result is around 0.1 eV. Among the hybrid functionals, TPSSh (hybrid meta-GGA) gives good performance (4.43 eV). However, the difference between the experimental and TPSSh result is about 0.4 eV. In summary, BLYP shows good performance *i.e.*, this GGA functional accurately predicts the bond distance and atomization energy of ScN molecule. In general, both GGA and hybrid functionals show good performance in the calculation of bond distance. Among the selected functionals, the vibrational frequency calculated by MPW91 is close to the experimental value. But, the difference between experimental and theoretical result is quite large (54 cm^{-1}).

3.2 TiN

The ground electronic state of TiN is $^2\Sigma^+$.¹⁹ All the DFT functionals that are taken in this study successfully predict $^2\Sigma^+$ state to be the ground state of TiN molecule. The Ti–N bond distance calculated by the GGA functionals is in agreement with the experimental bond distance (Table 2). In particular, the Ti–N bond distance calculated by B97-D functional is in very close agreement with the experimental result. The difference between the experimental and theoretical (B97-D) Ti–N bond distance is 0.02 Å. In general, most of the GGA functionals perform well in the calculation of bond distance. Among the hybrid functionals, TPSSh, B97 and B3LYP show better performance than the other hybrid functionals. The difference between the experimental and the theoretical (TPSSh, B97, B3LYP) result is 0.03 Å. It is slightly higher than the GGA functional (B97-D) result. Similar to the ScN case, in this case also if the fraction of HF exchange percentage increases in the functionals, deviation from the experimental bond distance also increases (Table 2). In the case of vibrational frequency, earlier Douglas *et al.*, have obtained the vibrational frequency of TiN (1039 cm^{-1}) experimentally.¹⁵ In our study, the vibrational frequency calculated by the B97-D (GGA) and M06-L (Meta-GGA) functionals is in very close agreement with the experimental result (Table 3). The difference between experimental and theoretical result is $\sim 10 \text{ cm}^{-1}$. The hybrid functionals significantly overestimate the vibrational frequency of TiN, which is more than 100 cm^{-1} . The atomization energy calculated by M05 and BLYP functional is in very close agreement with the experimental result (Table 4). The difference between experimental and theoretical (M05 and BLYP) result is less than 0.1 eV. BP91, PW91, PBE0 functionals slightly overestimate, and B97-D, M06-L,

TPSSH, B3LYP, M06 functionals slightly underestimate the atomization energy. Most of the hybrid functionals overestimate the atomization energy. In particular, B97, M06-2X, BHandH and M06-HF show poor performance, because the atomization energy calculated by these functionals is not reasonable. In summary, B97-D and M06-L show good performance in the calculation of bond distance, vibrational frequency and atomization energy in TiN molecule. Our calculation result is consistent with the previous study in Ti₂ dimer. Earlier we found that M06-L functional showed good performance in the case of Ti₂ dimer also.⁵³ Hence, these functionals are recommended for the studies in TiN molecule.

3.3 VN

The ground electronic state of VN is $^3\Delta$.¹⁹ All the DFT functionals that are taken in this study successfully predict $^3\Delta$ state to be the ground state of the VN molecule. The V–N bond distance calculated by BLYP (GGA) and BHandH (hybrid GGA) functionals is in very close agreement with the experimental bond distance (Table 2). The difference between experimental and theoretical results is about 0.01 Å. In general, most of the local and hybrid functionals show good performance in the calculation of bond distance. In this case, also, functionals with a fraction of HF exchange underestimates V–N bond distance. The vibrational frequency calculated by BLYP (GGA) and M06-L (meta-GGA) functionals is in agreement with the experimental result (Table 3). But, the difference between experimental and theoretical results is ~ 60 cm⁻¹. Except for these two functionals, all the other local and hybrid functionals show significant deviation from the experimental value. This is consistent with the previous DFT study on V₂ dimer.⁵³ In that case, also all the DFT functionals give large deviation from the experimental result. However, in the earlier study, smaller basis set was used for the calculation. Further, in our study, the hybrid meta-GGA functionals with high HF exchange percentage M06-2X (54%), M05-2X (56%) and M06-HF (100%) give large deviation from the experimental vibrational frequency. The atomization energy calculated by the B97-D (GGA), M06-L (meta-GGA) and B3LYP, PBE0 (hybrid GGA) functionals is in very close agreement with the experimental result (Table 4). The difference between experimental and theoretical (M06-L, B3LYP and PBE0) result is less than 0.2 eV. Apart from B97-D and M06-L functionals, all the other GGA functionals overestimate the atomization energy. In the case of hybrid functionals, most of the functionals reasonably predict atomization energy, except the functionals with high HF exchange percentage. For instance, M06-2X

gives 3.77 eV, M05-2X gives 3.62 eV, and M06-HF gives 3.28 eV whereas, the experimental atomization energy is 5.03 eV.¹³ The recent resonant two-photon ionization spectroscopy study gives the bond dissociation energy to be 5.00 eV.¹⁷ In summary, BLYP (GGA), and M06-L (meta-GGA) functionals show reasonable performance than hybrid functionals in the bond distance, and vibrational frequency calculation. In the case of atomization energy, GGA functionals B97-D, M06-L and hybrid GGA functionals B3LYP and PBE0 show good performance. In addition, the functionals with high HF exchange percentage M05-2X, M06-2X and M06-HF show poor performance in VN molecule. Those functionals are not recommended for the studies in VN. This result is contradictory to an earlier study in V₂ dimer.⁵³ In the V₂ dimer, the functionals with high HF exchange percentage M05-2X, M06-2X, show good performance in the calculation of atomization energy. This contradiction is due to the substitution of main group element in the place of a transition metal. This substitution significantly affects the performance of functionals. Another reason is the difference in the size of the basis set used in the calculation. Because, earlier study used 6-31G(d) basis set, but in the present study def2-TZVPP basis set is used in the calculation.

3.4 CrN

The ground electronic state of CrN is $^4\Sigma^-$.¹⁹ All the functionals that are taken in this study successfully predict $^4\Sigma^-$ state to be the ground state of CrN molecule. The Cr–N bond distance calculated by M06-L, PBE0, and M05-2X functionals is in very close agreement with the experimental result (Table 2). The difference between the experimental and the theoretical (M06-L, PBE0 and M05-2X) bond distance is 0.01 Å. In general, most of the GGA and hybrid functionals show good performance in the calculation of bond distance, except BHandH. The double hybrid BHandH functional overestimates the Cr–N bond distance. The difference is about 0.2 Å (Table 2). Earlier Andrews and Chertihin have obtained the vibrational frequency (1050 cm⁻¹) of CrN molecule experimentally.⁵⁴ The GGA functionals that are taken in this study give better performance than the hybrid functionals. In particular, the vibrational frequency calculated by the BLYP, BP91, PBE96, and PW91 is in very close agreement with the experimental result (Table 3). The difference between experimental and theoretical (BLYP, BP91, PBE96, PW91) result is less than 25 cm⁻¹. All the hybrid functionals underestimate the vibrational frequency. This indicates that mixing the exact exchange cannot give improved results in the vibrational frequency of

the CrN molecule. The atomization energy calculated by the M06-L (meta-GGA) coincides very well with the experimental result. All the other functionals either underestimate or overestimate the atomization energy. More precisely, GGA functionals overestimate and hybrid functionals underestimate the atomization energy. In general, the Minnesota functionals with significant HF exchange give large deviation from the experimental atomization energy (Table 4). In summary, the meta-GGA M06-L functional performs well in the calculation of bond distance and atomization energy. This functional is recommended for the calculation of bond distance and atomization energy. In the case of vibrational frequency, most of the GGA functionals perform well. These functionals are recommended for the calculation of vibrational frequency.

3.5 FeN

The ground electronic state of FeN is $^4\Phi$.²⁶ All the functionals that are taken in this study successfully predict $^4\Phi$ state to be the ground state of FeN molecule. In this case, no experimental bond distance and atomization energy are available in the literature. Hence our calculated results are compared with previous MRCI result. The Fe–N bond distance calculated by the BP91 (GGA), TPSSh (hybrid meta-GGA) and B3LYP (hybrid GGA) functionals is in very close agreement with the MRCI value (Table 2). The difference between previous MRCI and our theoretical bond distance is ~ 0.01 Å. The bond distance calculated by the hybrid GGA (M06-2X, M05-2X, and M06-HF) or hybrid meta-GGA (BHandH) functionals give deviated result from the MRCI value. The difference between the MRCI and the above-mentioned functionals is ~ 0.2 Å. Earlier Chaudhari and Lee predicted Fe–N bond distance to be 1.603 Å using B3LYP/6-311+G*.²⁵ Our calculation using B3LYP/def2-TZVPP method yields 1.562 Å, which coincides very well with the MRCI bond distance (1.565 Å). This suggests that the use of higher basis set in the calculation improves the result in this case. The vibrational frequency calculated by B97-D functional is 940 cm^{-1} . This value coincides very well with the experimental value (935 cm^{-1}).⁵⁵ All the other functionals either underestimate or overestimate the vibrational frequency. In particular, the vibrational frequency calculated by the Minnesota (hybrid) functionals underestimates significantly. This indicates that the inclusion of HF exchange cannot improve the vibrational frequency result. From Table 3, it can be seen that both BP91 and M06-L show decent performance in the calculation of vibrational frequency. The atomization energy calculated by M06-2X functional is

2.76 eV, which is in agreement with our CCSD(T) value (2.67 eV).⁵⁵ All the other DFT functionals, *i.e.*, all GGA and a few hybrid functionals significantly overestimate the atomization energy (Table 4). In summary, BP91, TPSSh and B3LYP show good performance in the case of bond distance. The functionals with significant HF exchange give some deviation from the experimental result. Further, B97-D functional gives good performance in the vibrational frequency calculation. While considering the atomization energy, M06-2X functional performs well. All the other GGA and a few hybrid functionals significantly overestimate the atomization energy. These functionals are not recommended for the calculation of atomization energy.

3.6 CoN

The ground electronic state of CoN is $^5\Delta$.²⁰ All the functionals that are taken in this study predict $^5\Delta$ state to be the ground state of CoN molecule. In the case of Co–N bond distance, all the GGA and a few hybrid functionals show decent performance. The hybrid GGA or hybrid meta-GGA functionals such as M06-2X, M05-2X, BHandH and M06-HF show deviation (~ 0.2 Å) from the experimental bond distance (Table 2). Further, our calculation result is consistent with the previous DFT result. For instance, the Co–N bond distance calculated by B3LYP/6-311+G* is 1.636 Å.²⁵ In our study, the Co–N bond distance calculated by B3LYP/def2-TZVPP is 1.627 Å. Earlier, Yin *et al.*, have also used DFT method (BPW91/modified LANL2DZ/6-311+G(d)) to obtain Co–N bond distance (1.617 Å).⁵⁶ It coincides well with the experimental Co–N bond distance (1.575 Å).²⁰ This indicates that the usage of a larger basis set in the calculation will provide the accurate result in this molecule. The experimental vibrational frequency of CoN was obtained by Andrews (826 cm^{-1}).¹⁶ In our study, B97-D, BLYP, M06-L and M05 functionals show good performance in the vibrational frequency calculation. The difference between the experimental and theoretical results is less than 30 cm^{-1} . The experimental atomization energy of CoN is not available in the literature. Hence, the performance of our DFT calculations is assessed by comparing with previous MRCI result. Earlier Gobbo and Borin performed MRCI study on CoN and obtained the atomization energy of 1.61 eV.⁵⁷ The functionals MPW91, M06-2X, and M05-2X perform well. The difference between the result of all these above functionals and MRCI calculation is <0.5 eV. All the GGA functionals significantly overestimate the atomization energy except MPW91 functional. However, the result of all the hybrid functionals (including Minnesota functionals)

is consistent with previous MRCI result. In summary, the GGA and hybrid functionals that are taken in this study show decent performance in the calculation of bond distance. A few GGA functionals namely BP91, PBE96, and PW91 yield lesser deviation in the bond distance and vibrational frequency. The hybrid functionals show better performance than the local functionals in atomization energy calculation. These functionals are recommended for the calculation of atomization energy in CoN molecule.

3.7 NiN

The ground electronic state of NiN is $4\Sigma^-$.²⁶ All the functionals that are taken in this study predict $4\Sigma^-$ state to be the ground state of NiN molecule. Earlier MRCI study predicted 2Π state to be the ground state, and the bond distance to be 1.82 Å for NiN.²² Our calculated result is not in agreement with this previous MRCI result. However, our calculated results are in agreement with our CCSD(T) and previous DFT results. The experimental Ni–N bond distance of NiN molecule is not available in the literature. Hence, our DFT results are compared with the previous DFT and CCSD(T) results. Our calculations show that the bond distance calculated by BP91, PBE96, PW91 and TPSSh functionals are in excellent agreement with the CCSD(T) result. The difference between CCSD(T) and above-mentioned functionals is 0.01 Å. The functional M06-L shows the second best performance. The difference between CCSD(T) and our above functionals result is 0.1 Å. The experimental vibrational frequency of NiN molecule is 832 cm^{-1} .¹⁶ The vibrational frequency calculated by the local functionals with the contribution of 0% HF exchange (BLYP, BP91, PBE96, PW91) is in close agreement with the experimental result. The difference between the experimental and the above-mentioned functionals is less than 30 cm^{-1} . The hybrid functionals significantly underestimate the vibrational frequency in this molecule. Among the selected hybrid functionals, TPSSh gives less deviation than the other hybrid functionals. However, most of the pure functionals considered in this study show better performance than TPSSh functional. This suggests that the mixing of exact exchange cannot improve the vibrational frequency values in this molecule. Our study shows that the GGA functionals give large deviation and hence overestimates the atomization energy except for MPW91 and M06-L. The hybrid functionals such as B97, B3LYP, PBE0, M06, M05, and M05-2X, give less deviation *i.e.*, <0.5 eV. This indicates that the hybrid functionals with the fraction of HF exchange perform well in this case. In summary, the hybrid B97, B3LYP, PBE0, M06 and

M05 functionals show good performance in predicting bond distance and atomization energy. Most of the GGA functionals give good performance in the case of vibrational frequency. Likewise, the hybrid functionals show good performance in the case of atomization energy. Our calculated result is not consistent with the previous study in Ni₂ dimer. A recent study shows BHandH functional perform well in the atomization energy calculation in Ni₂ dimer.⁵³ This is due to the use of lower basis set for the calculation in the earlier study.

3.8 CuN

The ground electronic state of CuN is $3\Sigma^-$.⁵⁸ All the functionals that are taken in this study successfully predict $3\Sigma^-$ state to be the ground state of CuN molecule. The experimental structure and energetic parameters of CuN molecule are not available in the literature. Hence, the performance of the selected DFT functionals is assessed by comparing our theoretical results with previous MRCI result. Recently, Zhang and Liu predicted Cu–N bond distance (1.879 Å) of CuN molecule using MRCI+Q method.²¹ Our calculations show that the hybrid functionals such as B97, B3LYP, PBE0, M06, M05, M06-2X, M05-2X, and BHandH predict Cu–N bond distance accurately (Table 3). This indicates that the mixing of exact exchange in hybrid functionals improves the result in this molecule. In general, most of the GGA and hybrid functionals show decent performance in the calculation of bond distance. Zhang and Liu have also calculated the vibrational frequency of CuN (524 cm^{-1}) using MRCI+Q method.²¹ Our calculations show that the functionals MPW91, M05, M05-2X, and BHandH perform well. The difference between the MRCI and the above functionals is less than 30 cm^{-1} . All the other GGA and hybrid functionals underestimate the vibrational frequency of CuN. The atomization energy calculated by the MRCI method is 1.08 eV.²¹ The functionals MPW91, M06-2X, BHandH and M06-HF accurately predict atomization energy. In general, the hybrid and hybrid meta-GGA functionals show good performance in the calculation of atomization energy. In summary, the GGA and hybrid functionals show good performance in the bond distance calculation. The hybrid functionals also show good performance in the case of vibrational frequency and atomization energy. Hence, these functionals are recommended for the calculation of bond distance, vibrational frequency and atomization energy. Further, the MPW91 functional also show good performance in bond length, vibrational frequency and atomization energy. One may use MPW91 functional to get the structural and energetic properties

of larger molecular systems, because of its lesser computational cost.

3.9 General performance

In order to understand the general performance of the selected DFT functionals, the mean unsigned deviation (MUSD) error of bond distance, vibrational frequency

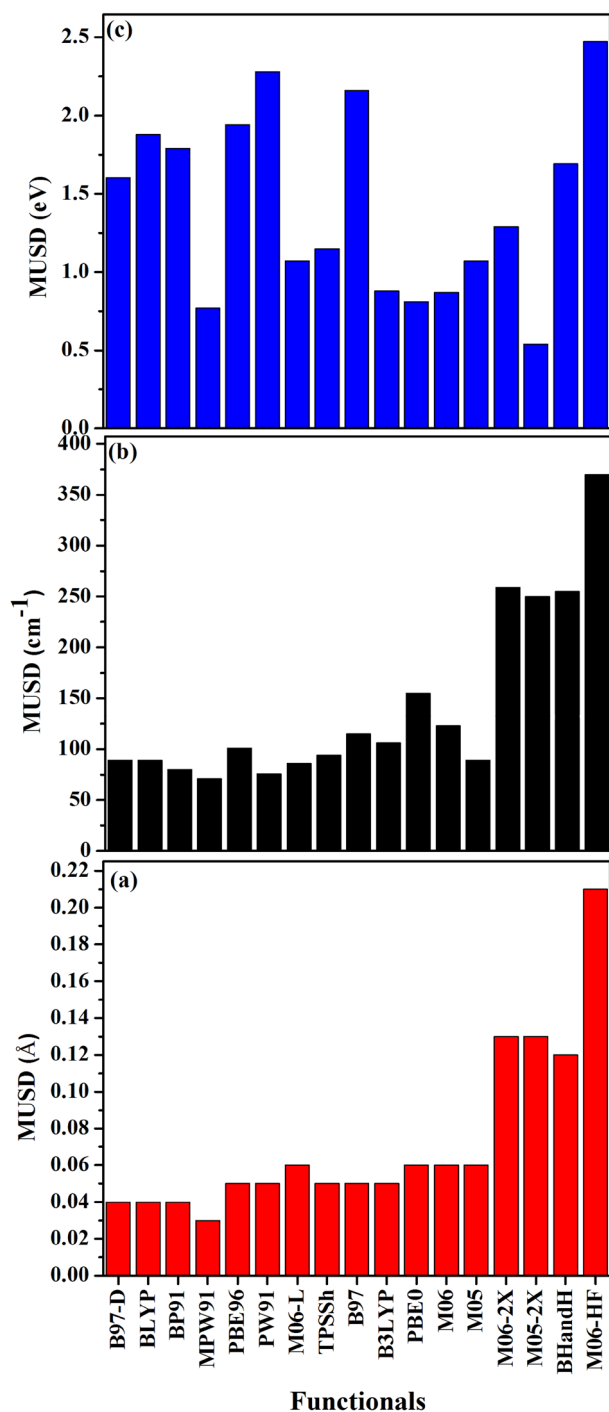


Figure 1. Mean Unsigned Deviation (MUSD) errors of (a) bond distance, (b) vibrational frequency and (c) atomization energy of 3d Transition metal mononitrides.

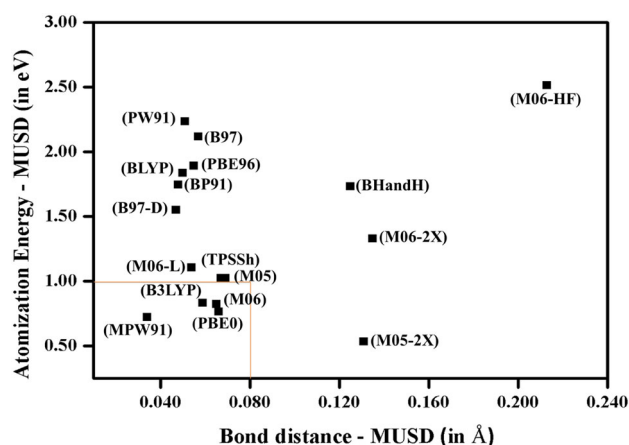
and atomization energy were calculated and are shown in Figure 1. The general performance means the average performance of the functional for all the 3d-TMNs. That is, the errors are averaged over the set of 3d-TMNs. The MUSD value means the difference between our calculated results and previous MRCI result. Because, experimental results are available for a few 3d-TMNs. In the case of FeN and NiN limited experimental or MRCI data are available. In these two cases, CCSD(T)/def2-TZVPP calculations were performed to obtain the bond length, vibrational frequency and atomization energy values.

From Figure 1, it can be seen that the DFT functionals give the MUSD value which ranges from 0.03 to 0.21 Å for bond distance. Among the DFT functionals that are taken in this study, MPW91 gives less deviation from the MRCI result. In general, all local functionals and a few hybrid functionals such as TPSSH, B97, B3LYP, PBE0, M06, and M05 give good performance in the case of bond distance. The Minnesota functionals such as M06-2X, M05-2X, and M06-HF along with double hybrid BHandH functional give slightly higher deviation from MRCI result. This indicates that the incorporation of significant HF exchange (>50%) in the DFT exchange-correlation potential yields a large error in the bond distance. From Table 2, it can be noted that the deviation from experimental bond distance gradually increases as the HF exchange percentage increases. Further, the functionals such as M06-2X and M05-2X are high-nonlocality functionals with the inclusion of the double the amount of nonlocal exchange. These functionals are parameterized for nonmetals. The precursor of these functionals is M06 and M05 functionals, respectively. The M06 and M05 functionals are parameterized for metals. Earlier studies mentioned that M06 and M05 functionals are good for metals and nonmetals.^{40,64} Generally, if the functional is parameterized for a particular system (e.g., transition metals or main group elements) or data set, it yields less error in similar systems. In our study, the Minnesota functionals such as M06-2X and M05-2X show good performance in CuN molecule. In addition, these functionals overestimate metal–nitrogen bond distance in FeN, CoN, and NiN molecules (late 3d-TMNs) and underestimate in ScN, TiN, and VN (early 3d-TMNs). Apart from these two functionals, M06-HF (100% HF exchange) also gives poor performance. The reason is that this functional is parameterized for main group elements and yields a large error in 3d-TMNs. Our result is consistent with the previous study by Zhao *et al.*⁴⁶ Further, the advantage of M06-HF is, it eliminates long range self-interaction error, which plays a major role in the accurate prediction of charge transfer excitation energies.

Table 5. The DFT functional which performed best for the bond distance, vibrational frequency and atomization energy for 3d Transition metal mononitrides.

| Parameters | 1 | 2 | 3 | 4 | 5 |
|-----------------------|--------|-------|------|-------|-------|
| Bond distance | MPW91 | B97-D | BLYP | BP91 | PBE96 |
| Vibrational Frequency | MPW91 | PW91 | BP91 | M06-L | B97-D |
| Atomization Energy | M05-2X | MPW91 | PBE0 | M06 | B3LYP |

In the case of vibrational frequency, our calculations give the MUSD error ranging from 71 to 370 cm^{-1} . Even the smallest deviation (71 cm^{-1}) is a significant error in the vibrational frequency. In general, most of the GGA functionals give less deviation than hybrid functionals. Among the hybrid functionals, M05 (hybrid meta-GGA) yields less deviation (Figure 1). But, the deviation is slightly higher than the deviation obtained by the GGA functionals. All the other hybrid functionals show a large deviation from the MRCI result. The MUSD error of atomization energy ranges from 0.54 to 2.47 eV. The smallest deviation (0.54 eV) is obtained by M05-2X functional. It must be noted that this functional gives large deviation in the metal–nitrogen bond distance calculation. Generally, the local functionals considered in this study give large deviation except MPW91 functional. This is due to the fact that the GGA functionals have difficulty in determining the metal atom energy.⁵³ GGA functionals are unable to predict the metal atom energy accurately because metals possess near degenerate energy levels. In the present study, the MPW91 functional gives better performance (slightly higher than 0.77 eV) in the atomization energy. The MPW91 functional is the modified form of PW91 functional. The exchange part of the PW91 functional is modified by Adamo *et al.*, to enhance the behavior of exchange functional in low density and large gradient regions in a system.³⁶ Further, GGA and meta-GGA exchange and correlation holes are short ranged, whereas hybrid functionals have long ranged exchange hole. This accounts for strong non-dynamical correlation in transition metal containing compounds. In addition, the magnitude of correlation energy in exchange-correlation energy is generally less than 10% of the exchange energy. Hence, the exchange energy is to be more accurate than the correlation energy. Further, the best performance of an exchange functional is obtained when it is combined with the same correlation functional for example, the exchange functional PW yield better results when it is combined with its correlation part, *i.e.*, PWPW. However, some exceptional cases like B3LYP are also available. In Figure 1, it can be seen that the PW91 functional predicts the MUSD of atomization energy

**Figure 2.** Structure vs Energetics MUSD errors of 3d Transition metal mononitrides.

to be 2 eV. This value is significantly reduced while using MPW91 functional. Among the hybrid functionals, B3LYP, PBE0, M05-2X, and M06 give small deviation (slightly higher than 0.80 eV) from MRCI result.

While considering the Minnesota functionals, a few functionals give good performance in 3d-TMNs. The mean deviation values vary from 0.06 Å (M06-L, M06, M05) to 0.21 Å (M06-HF) for bond distance, from 86 cm^{-1} (M06-L) to 370 cm^{-1} (M06-HF) for vibrational frequency and from 0.54 eV (M05-2X) to 2.47 eV (M06-HF) for atomization energy. Among the recently developed Minnesota functionals, M06-L (meta-GGA functional) performs well for the structural and energetic properties of 3d-TMNs. This is consistent with previous study by Zhao *et al.*²⁸ Earlier, Zhao *et al.*, mentioned that M06 and M06-L functionals are good for transition metal containing compounds. They have studied TM atomization energies, TM-ligand bond energies, and reaction energies from TMRE48 data set. They concluded that M06 and M06-L functionals give 0.26 eV as Mean Absolute Deviation error for energies. In the present study, it is interesting to see that the MUSD of M05-2X is 0.54 eV. Even though this functional has double amount of exact exchange, it produces a good result in this study. As earlier studies

mentioned that the functionals with a high amount of HF exchange percentage affects the accuracy of the calculated atomization energies.^{64,65} In our study, M05-2X shows good performance because it gives minimum deviation in most of the 3d-TMNs. Further, the functionals such as M06 and M06-L give slightly higher deviation. The main objective in the present study is to find out suitable DFT functional for studying 3d-TMNs. Earlier studies used an extensive data set, which contains more than 40 transition metal containing complexes. The errors are averaged over a set of transition metal containing complexes. This is the reason for the performance of M05-2X functional. Recently, Wang *et al.*, presented an improved version of M06-L (revM06-L) functional.³¹ This revM06-L functional could reduce the error in the bond distance, vibrational frequency and atomization energy values. The best performed functionals for the bond distance, vibrational frequency and atomization energy of 3d-TMNs are listed in Table 5. Figure 2 shows MUSD of structure versus energetic values of 3d-TMNs. From this figure, it is identified that MPW91, B3LYP and PBE0 functionals perform well for both structure and energetic properties of 3d-TMNs. These functionals show best average performance when the errors are averaged over a set of 3d-TMNs. It is interesting to see that these functionals have no HF exchange or smaller. Overall, the GGA functionals are good for the calculation of bond distance and vibrational frequency, and hybrid functionals are good for the calculation of atomization energy.

4. Conclusions

The performance of seventeen DFT functionals in the structure and energetic properties were investigated by calculating the bond distance, vibrational frequency and atomization energy of 3d-TMNs. The calculated results show that, both GGA and hybrid functionals that are taken for this study perform well for the structural properties in 3d-TMNs. In the case of vibrational frequency, GGA functionals show good performance in all the 3d-TMNs except ScN and VN. The vibrational frequency calculated by GGA functionals is close to experimental result in these two cases. But, the difference between experimental and theoretical result is large. In the case of energetics, the GGA functionals perform well in ScN, TiN, VN, and CrN, and the hybrid functionals perform well in FeN, CoN, NiN, and CuN. This coincides well with the previous study.²⁹ Among the recently developed Minnesota functionals, M06-L performs well for both structure and energetics of all 3d-TMNs. From the structure versus

energetics MUSD (Figure 2), it is evident that MPW91, B3LYP and PBE0 functionals are the best-performing functionals in the 3d-TMNs. In general, the functionals with significant Hartree–Fock exchange show poor performance in most of the 3d-TMNs. Similarly, none of the functionals showed good performance for both the structure and energetic properties in each 3d-TMN. Therefore, the search continues for a functional which accurately predicts the structure and energy parameters of transition metal nitrides.

Our study provides a generalized overview of the performance of traditional as well as recently developed DFT functionals for 3d-TMNs. We believe that this work can provide useful guidance for further experimental and theoretical studies in these 3d-TMNs.

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