An investigation of density functionals: The first-row transition metal dimer calculations

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The performance of different density functional theory (DFT) methods was investigated in the calculations of the bond length and the binding energy of the first-low transition metal dimers. The 4s–3d interconfigurational energies and 4s and 3d ionization potentials were also calculated for the first-row transition metal atoms. In general, the hybrid DFT method, B3LYP, yields the bond lengths that are too short compared to the experimental ones. In contrast, the optimized bond lengths by nonhybrid DFT methods such as BOP or PW91 are in good agreement with the experiment. It was also found that nonhybrid DFT methods overestimate the binding energies, because they have a tendency to overestimate the electron configurations that contain the atomic and molecular orbitals in a higher angular momentum open shell. The hybrid DFT method yields more accurate binding energies, but it estimates rather poor energy gaps between states whose spin multiplicity is quite different. © 2000 American Institute of Physics. [S0021-9606(00)31002-9]

I. INTRODUCTION

The difficulties in the theoretical treatment of transition metal systems result from the near-degeneracy effects from the formation of d bonds, the strong dynamical correlation effects from the tightly packed electrons in the d shell, and the non-negligible relativistic effects. To properly describe the d bonds of these systems in the ab initio method, a heavy computational effort is required: a multireference based theory with a large active space and an extended basis set.

A transition metal dimer is theoretically one of the most interesting electronic systems, because it has various kinds of spin configurations that are comprised of the orbitals with different angular momenta in a limited energy region. Even though a dimer consists of only one metallic bond, ab initio molecular orbital (MO) methods can barely reproduce the equilibrium geometries that have been accepted as being less sensitive to the level of calculations. Thus, the transition metal dimer is a challenging system that is of growing theoretical interest.

Density functional theory (DFT) is drawing the attention of theoretical chemists, because it can accurately estimate the chemical properties of a wide variety of systems. DFT is comparable or sometimes superior to high-level ab initio MO methods as a means of describing the coordinate bonds of transition metal complexes, and is a standard tool for the investigation of the chemical reactions of these complexes. For the first-row transition metal dimers, various DFT calculations have also been carried out, and it has been reported for some systems that DFT gives accurate properties when compared with the results of conventional ab initio MO methods. However, little is known about the applicability of DFT to the metallic bonds of transition metal systems because no studies on DFT have ever tried to comprehensively discuss the chemical bonds of the dimers.

In this paper, we compare various DFT methods by calculating the equilibrium geometries and the atomization energies of the first-row transition metal dimers and evaluate the description of the electron configurations of the dimers that each method produces. We then explore the features of the functionals in detail by calculating the 4s–3d interconfigurational energies and 4s and 3d ionization potentials of the atoms for various dimer electron configurations and try to find out how applicable these functionals are to the determination of different electronic states.

II. COMPUTATIONAL DETAILS

The energy calculations reported here were carried out by the unrestricted Kohn–Sham approach; the second-order Møller–Plesset (MP2) approach was used as a comparison. The Hartree–Fock (HF) calculation was also applied to the interconfigurational energies and ionization potentials of the atoms. The Wachters Gaussian basis functions were employed in all cases. We have studied the performance of several DFT approaches, including the Becke 1988 (B88) exchange9 (B null), the B88 exchange+the OP correlation10 (BOP), the B88 exchange+the Lee–Yang–Parr correlation11 (BLYP), the Perdew–Wang 1991 exchange-correlation (PW91), and the hybrid B3LYP13 as the functionals in the Kohn–Sham equation. For the calculations of the atoms, we also evaluated the HF exchange+the B88-corrected OP functional (HOP), for comparison. The 96-point Euler–Maclaurin quadrature14,15 and the 16×32-point Gauss–Legendre quadrature were used in the numerical integrations for radial and angular grids, respectively. Relativistic corrections (RC) were included by a relativistic scheme by eliminating small components (RESC). Only the one electron term is implemented in
TABLE I. Equilibrium distances of the dimers of the first-row transition metals in Angstrom. The relativistic correction and the zero-point vibration correction are incorporated. The underlined results correspond to those of the ground states of each dimer. Conventional high-level *ab initio* MO results are also given for a comparison.

<table>
<thead>
<tr>
<th>Dimer</th>
<th>State</th>
<th>Exp</th>
<th>BOP</th>
<th>B3LYP</th>
<th>B-null</th>
<th>PW91</th>
<th>MP2</th>
<th>High-level <em>ab initio</em> MO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sc₂</td>
<td>5S⁺</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2.74 (MRSDQCI)</td>
</tr>
<tr>
<td>Ti₂</td>
<td>3∆</td>
<td>1.94</td>
<td>1.925</td>
<td>1.880</td>
<td>1.989</td>
<td>1.896</td>
<td>no conv.⁺</td>
<td>2.587 (MRSDQCI)</td>
</tr>
<tr>
<td>V₂</td>
<td>5S⁺</td>
<td></td>
<td>2.426</td>
<td>2.321</td>
<td>2.474</td>
<td>2.386</td>
<td>no conv.⁺</td>
<td>2.587 (MRSDQCI)</td>
</tr>
<tr>
<td>Cr₂</td>
<td>1S⁺</td>
<td>1.679</td>
<td>1.608</td>
<td>1.562</td>
<td>1.593</td>
<td>1.632</td>
<td>no conv.⁺</td>
<td>1.713 (CASPT2)</td>
</tr>
<tr>
<td>Mn₂</td>
<td>1S⁺</td>
<td>3.4</td>
<td>unbound⁻</td>
<td>unbound⁻</td>
<td>unbound⁻</td>
<td>unbound⁻</td>
<td>unbound⁻</td>
<td>2.06 (FE-CI)</td>
</tr>
<tr>
<td>Fe₂</td>
<td>2∆</td>
<td>2.02</td>
<td>2.032</td>
<td>1.989</td>
<td>2.077</td>
<td>2.010</td>
<td>1.817</td>
<td>2.06 (FE-CI)</td>
</tr>
<tr>
<td>Co₂</td>
<td>5∆</td>
<td></td>
<td>no conv.⁺</td>
<td>2.661</td>
<td>no conv.⁺</td>
<td>no conv.⁺</td>
<td>2.512</td>
<td>2.06 (FE-CI)</td>
</tr>
<tr>
<td>Ni₂</td>
<td>3S⁻</td>
<td>2.155</td>
<td>2.133</td>
<td>2.076</td>
<td>2.181</td>
<td>2.104</td>
<td>1.745</td>
<td>2.528 (CASPT2)</td>
</tr>
<tr>
<td>Cu₂</td>
<td>1S⁻</td>
<td>2.219</td>
<td>2.267</td>
<td>2.265</td>
<td>2.321</td>
<td>2.233</td>
<td>2.241</td>
<td>2.715 (CASPT2)</td>
</tr>
</tbody>
</table>

Mean absolute Δ⁺ | 0.033  | 0.164  | 0.128  | 0.042  | 0.212  | 0.161  |
Max Δ⁺ | −0.071 | 0.541  | 0.532  | −0.086 | 0.497  | 0.645  |

RES Wei, because it has already been confirmed that the relativistic correction to the two-electron term is not significant in the calculations of molecular valence properties. Calculated atomization energies were also corrected by the zero-point vibrational energies.

III. TRANSITION HYDROGEN DIMERS

The calculated equilibrium geometries and atomization energies of the first-row transition metal dimers are shown in Tables I and II. (Refs. 18–29). The atomization energy calculations used the correct asymptote as the dissociation limit for each dimer state. Although we calculated all the low-lying electronic states that have already been proposed for every dimer, we showed only the ones that are assigned as the ground state in at least one method, in the tables for simplicity.

All DFT methods as well as conventional high-level *ab initio* MO calculations predict the 5S⁻ state (3dσ₁d3dπ₁d4sσ₁d4sσ₁d) to be the ground state of the scandum dimer Sc₂. The experimental bond distance is not avail-

TABLE II. Atomization energies of the dimers of the first-row transition metals in eV. The relativistic correction and the zero-point vibration correction are incorporated. The underlined results correspond to those of the ground states of each dimer. Conventional high-level *ab initio* MO results are also given for a comparison.

<table>
<thead>
<tr>
<th>Dimer</th>
<th>State</th>
<th>Dissociation limit</th>
<th>Exp</th>
<th>BOP</th>
<th>B3LYP</th>
<th>B-null</th>
<th>PW91</th>
<th>MP2</th>
<th>High-level <em>ab initio</em> MO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sc₂</td>
<td>5S⁺</td>
<td>3D⁻ 4F</td>
<td>1.04±0.22</td>
<td>1.92</td>
<td>1.36</td>
<td>1.35</td>
<td>2.30</td>
<td>2.00</td>
<td>0.59 (MRSDQCI)</td>
</tr>
<tr>
<td>Ti₂</td>
<td>3∆</td>
<td>3F⁻ 4F</td>
<td>1.54±0.19</td>
<td>2.79</td>
<td>1.77</td>
<td>0.43</td>
<td>2.98</td>
<td>unbound⁻</td>
<td>0.94 (ACPF)</td>
</tr>
<tr>
<td>V₂</td>
<td>5S⁻</td>
<td>4D⁻ 6D</td>
<td>2.75</td>
<td>3.38</td>
<td>1.45</td>
<td>0.26</td>
<td>3.40</td>
<td>unbound⁻</td>
<td>1.58 (CASPT2)</td>
</tr>
<tr>
<td>Cr₂</td>
<td>5S⁻</td>
<td>3S⁻ 5S</td>
<td>1.53±0.06</td>
<td>1.56</td>
<td>−1.53</td>
<td>−2.46</td>
<td>1.32</td>
<td>unbound⁻</td>
<td>3.17 (FE-CI)</td>
</tr>
<tr>
<td>Mn₂</td>
<td>5S⁻</td>
<td>5S⁻ 6S</td>
<td>0.3±0.3</td>
<td>2.49</td>
<td>0.98</td>
<td>1.49</td>
<td>2.95</td>
<td>0.31</td>
<td>0.81 (SDCI)</td>
</tr>
<tr>
<td>Fe₂</td>
<td>2∆</td>
<td>2F⁻ 4F</td>
<td>1.15±0.09</td>
<td>2.45</td>
<td>0.42</td>
<td>1.30</td>
<td>2.72</td>
<td>1.73</td>
<td>1.80 (CASPT2)</td>
</tr>
<tr>
<td>Co₂</td>
<td>5∆</td>
<td>4F⁻ 4F</td>
<td></td>
<td>2.45</td>
<td>0.42</td>
<td>1.30</td>
<td>2.72</td>
<td>1.73</td>
<td>1.80 (CASPT2)</td>
</tr>
<tr>
<td>Ni₂</td>
<td>3S⁻</td>
<td>3D⁻ 3D</td>
<td>2.04</td>
<td>2.67</td>
<td>1.48</td>
<td>1.86</td>
<td>2.92</td>
<td>−2.28</td>
<td>1.78 (CASPT2)</td>
</tr>
<tr>
<td>Cu₂</td>
<td>1S⁻</td>
<td>2S⁻ 2S</td>
<td>2.06±0.03</td>
<td>2.16</td>
<td>2.03</td>
<td>1.61</td>
<td>2.41</td>
<td>1.99</td>
<td>1.97 (CASPT2)</td>
</tr>
</tbody>
</table>

Mean absolute Δ⁺ | 0.65  | 0.69  | 1.02  | 0.86  | 0.92  | 0.497  |
Max Δ⁺ | −3.06 | −3.99 | −1.80 | −2.75 | (1.93) |
The theoretical description of the chromium dimer \( \text{Cr}_2 \) has been the subject of controversy over the last few decades. The molecule has a short bond distance due to the sextuple bond, which stems from the \( 3d\sigma_2^2 3d\pi_1^2 3d\delta_1^2 4s\sigma_2^2 \) configuration of the ground state \( \left( \Sigma^+ \right) \). Even for high-level \textit{ab initio} MO calculations, it is difficult to obtain accurate properties for \( \text{Cr}_2 \) unless a large basis set and numerous configuration state functions are incorporated. For example, Scuseria reported that the singlets, doubles, and triples coupled cluster \( \text{CCSD(T)} \) method with a large basis \( 10s8p3d2f \) gives a bond distance \( r = 1.679 \, \text{Å} \) and the atomization energy \( D_e = 1.53 \pm 0.06 \, \text{eV} \) of 1.604 Å and 0.5 eV, respectively. Andersson \textit{et al.} also calculated these properties by the complete active space second-order perturbation (CASPT2)+RC method that includes \( 3s3p \) correlation effects with an atomic natural orbital \( 8s7p6d4f \) basis. \textit{CASPT2} gives a more accurate bond distance \( 1.713 \, \text{Å} \) and atomization energy \( 1.583 \, \text{eV} \). All DFT methods tend to underestimate the bond distance, giving values close to the \( \text{CCSD(T)} \) result, and MP2 does not predict a bound state for \( \text{Cr}_2 \). As supported by the above-mentioned argu-
ment for V₂, BOP and PW91 give atomization energies in excellent agreement with the experimental value, while the B3LYP and B-null functionals do not even give positive values, probably because of the significant difference in spin multiplicity between the molecule (1Σ⁺) and the dissociation limit (7S⁺+7S). Applying the approximate spin projection scheme of Noodleman³⁴ to the hybrid B3P86 method, Edgecombe and Becke³ suggested that the short bond length and low dissociation energy calculated by the hybrid method are attributable to the spin contamination in the Cr₂ antiferromagnetic broken-symmetry state of the spin-unrestricted Kohn–Sham calculations. Since the Kohn–Sham orbital of Cr₂ that is obtained in this calculation is, however, correctly assigned to the 3d nonbonding state (3dσ₂⁴3dπ₃⁴3dδ₁⁴4sδ₁⁴4sσ₂⁴) configuration of the ground state, we cannot bring ourself to accept that the erroneous result of B3LYP comes from the limitation of single-configurational methods.

In the manganese dimer Mn₂, there is one doubly occupied 4s orbital on each atom, and, therefore, the 4s electrons do not influence the 3d–3d bonding. Bauschlicher³⁵ calculated Mn₂ at three bond lengths, 5.5, 6.0, and 6.5 a.u. by using the complete active space self-consistent field (CASSCF) method, and found that the ground state 1Σ⁺ is very multiconfigurational in character and repulsive at all three bond lengths. In order to account for the van der Waals bonding, it is necessary to incorporate a very large basis set with multiple sets of polarization functions and to make extensive use of a correlation that accurately accounts for the 4s–4p near-degeneracy. The tables show that a bound state is not given by any of the methods, although the long bond distance (3.4 Å)³⁵ and the very small dissociation energy (0.3 ± 0.5 eV)³⁶ are reported by experiments. The Mn₂ molecule is a unique first-row transition metal dimer in which the chemical bond is formed without involving the 4s–4s coupling. The weak bond of Mn₂, therefore, justifies the argument that the 3d–3d bonding is negligibly weaker than the 4s–4s one.

Conventional high-level ab initio calculations suggest that two states (in particular) are expected to be the ground state of the iron dimer Fe₂: the 3d–3d bonding 7Δ_u (3dσ₂³3dπ₂³3dπ₂³3dδ₁³4sδ₁³4sσ₂³) and 3d–3d nonbonding 7Σ⁺_u states (3dσ₂³3dπ₂³3dπ₂³3dδ₁³4sδ₁³4sσ₂³). Noro et al.³⁶ calculated the bond length and the atomization energy of the 7Δ_u state to be 2.06 Å and 1.57 eV, respectively, by using the full-external CI (FE-Cl) method with a Slater-type basis (10s9p5d2f). These values are close to the experimental results (r_e = 2.02 Å³⁷ and D_e = 1.15 ± 0.09 eV³⁸). We should note that the atomic ground state 3D + 3D is postulated as the dissociation limit in the calculation of the atomization energy, whereas the ground state of Fe₂, 7Δ_u, smoothly dissociates to the 5F + 5F state that may lead to the calculated energy of 3.17 eV. The calculated bond lengths in Table I also clearly indicate that the 7Δ_u state is the ground state. Compared with the experimental data, the BOP and PW91 functionals give accurate bond distances and very high atomization energies. Since B3LYP and MP2 underestimate the atomization energies for the 7Δ_u state, the high atomization energies of BOP and PW91 may be attributable to the error of the exchange functional. BOP, B-null and PW91 do not yield a convergent 7Σ⁺_u state, probably because of the quasidegeneracy of the state with the 7Δ_u state. On the other hand, B3LYP and MP2 lead to the unfavorable result that the 7Σ⁺_u state is the ground state. These methods give more accurate atomization energies and worse bond lengths for this state than those for the 7Δ_u state.

Experimental information is limited for the cobalt dimer Co₂; even the bond length and the atomization energy are not known. As far as we know, there has been no experimental investigation on the electron configuration of the ground state. Theoretical calculations predict two candidates: the 5Δ_u state (3dσ₂³3dπ₂³3dπ₂³3dδ₁³4sδ₁³4sσ₂³) and 5Σ⁺_g state (3dσ₂³3dπ₂³3dπ₂³3dδ₁³4sδ₁³4sδ₁³4sσ₂³). By SDCI cal-

FIG. 1. The 4s–4p interconfigurational energies for the first-row transition metal atoms, △E=4s[4s3d²]−4s[4s3d⁰³] - Exp.
The ground state of the copper dimer Cu$_2$ ($^1\Sigma_g^+$) is clearly described by the $4s - 4s$ bonding of two Cu atoms as $3d\sigma_g^2 3d\delta_g^2 3d\pi_g^2 3d\delta_u^2 3d\delta_g^2 4s\sigma_g^2$. In contrast to the Mn$_2$ molecule, Cu$_2$ is a unique first-row transition metal dimer in which the chemical bond is formed by only the $4s - 4s$ coupling. By comparing CASPT2 with CASSCF, Pou-Amérgio et al. 38 suggest that the 3d dynamical correlation effects have to be taken into account to properly describe the bonding. If only the $4s$ dynamical correlation is taken into account, CASPT2 gives only about 60% of the experimental value $(2.06 \pm 0.03$ eV$^2$). It should, however, be noted that since the CASSCF method tends to excessively stabilize dissociated states, a large part of dynamical correlation is frequently required to recover the dissociation energies. Highly accurate bond distances and atomization energies are obtained by almost all methods in Tables I and II, except for B-null. We can see from the results that the $4s - 4s$ bonding is correctly described by all DFT methods, provided that the correlation effect is taken into account.

Let us summarize the major points that have become apparent for the ground state of transition metal dimers in this section.

1. The BOP and PW91 functionals tend to overestimate the atomization energies, and they become more accurate as the number of 3d electrons increases (from Sc$_2$ to Cr$_2$ and from Fe$_2$ to Cu$_2$).

2. The B3LYP functional gives an extremely low estimate for the atomization energies of V$_2$ and Cr$_2$, probably due to the different spin multiplicity between the dimers and the dissociation limits.

3. In contrast, the MP2 method gives no bound state for almost all the first half-row dimers, Ti$_2$, V$_2$, and Cr$_2$.

4. The calculated and experimental dissociation energy of Mn$_2$ may support the argument that the $3d - 3d$ bonding is negligibly weaker than the $4s - 4s$ one. By the Mulliken population analysis of Fe$_2$, 39 Co$_2$, 37 Ni$_2$, 40 and Cu$_2$, 41 Shim et al. also suggest that the chemical bond is almost entirely due to the $4s\sigma_g$ molecular orbital, because this is the only orbital with an appreciable overlap population.

5. Comparing the result of BOP with that of B-null, it is found that the OP correlation functional shortens the bond lengths and increases the atomization energies.

### Table IV. Calculated 4s ionization energies from the 4s$^2$3d$^{10}$ configuration for all the first-row transition metal atoms and from the 4s$^1$3d$^{10}$ configuration for Cr, Ni, and Cu atoms employing the Wachters $t^f$ basis set [14s,11p,6d,3f]/(8s,6p,4d,1f) in eV. The relativistic effect is taken into account.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Neutral state</th>
<th>Cationic state</th>
<th>Exp$^a$</th>
<th>BOP</th>
<th>B-null</th>
<th>B3LYP</th>
<th>PW91</th>
<th>HF</th>
<th>HOP</th>
<th>MP2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sc(4s$^2$3d$^1$)</td>
<td>2$^D$</td>
<td>3$^D$</td>
<td>6.56</td>
<td>6.32</td>
<td>5.64</td>
<td>6.51</td>
<td>6.48</td>
<td>5.39</td>
<td>6.07</td>
<td>6.32</td>
</tr>
<tr>
<td>Ti(4s$^2$3d$^1$)</td>
<td>2$^F$</td>
<td>3$^F$</td>
<td>6.83</td>
<td>6.62</td>
<td>5.81</td>
<td>6.79</td>
<td>6.72</td>
<td>5.56</td>
<td>6.52</td>
<td>6.53</td>
</tr>
<tr>
<td>V(4s$^2$3d$^1$)</td>
<td>2$^F$</td>
<td>3$^F$</td>
<td>7.06</td>
<td>6.63</td>
<td>5.75</td>
<td>6.77</td>
<td>6.70</td>
<td>5.40</td>
<td>6.24</td>
<td>6.50</td>
</tr>
<tr>
<td>Cr(4s$^2$3d$^1$)</td>
<td>2$^D$</td>
<td>3$^D$</td>
<td>7.28</td>
<td>7.14</td>
<td>6.18</td>
<td>7.30</td>
<td>7.14</td>
<td>5.89</td>
<td>6.79</td>
<td>6.90</td>
</tr>
<tr>
<td>Mn(4s$^2$3d$^1$)</td>
<td>2$^S$</td>
<td>3$^S$</td>
<td>7.43</td>
<td>7.34</td>
<td>6.30</td>
<td>7.51</td>
<td>7.29</td>
<td>6.02</td>
<td>6.97</td>
<td>7.03</td>
</tr>
<tr>
<td>Fe(4s$^2$3d$^1$)</td>
<td>2$^D$</td>
<td>3$^D$</td>
<td>7.90</td>
<td>7.86</td>
<td>6.92</td>
<td>7.97</td>
<td>7.88</td>
<td>6.44</td>
<td>7.30</td>
<td>7.50</td>
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<td>Co(4s$^2$3d$^1$)</td>
<td>2$^F$</td>
<td>3$^F$</td>
<td>8.28</td>
<td>8.31</td>
<td>7.45</td>
<td>8.39</td>
<td>8.37</td>
<td>6.79</td>
<td>7.60</td>
<td>7.90</td>
</tr>
<tr>
<td>Ni(4s$^2$3d$^1$)</td>
<td>2$^F$</td>
<td>3$^F$</td>
<td>8.67</td>
<td>8.75</td>
<td>7.95</td>
<td>8.80</td>
<td>8.85</td>
<td>7.14</td>
<td>7.91</td>
<td>8.29</td>
</tr>
<tr>
<td>Cu(4s$^2$3d$^{10}$)</td>
<td>2$^S$</td>
<td>3$^S$</td>
<td>7.72</td>
<td>8.26</td>
<td>7.91</td>
<td>8.18</td>
<td>8.50</td>
<td>6.60</td>
<td>6.90</td>
<td>7.49</td>
</tr>
</tbody>
</table>

The mean absolute deviation

- The experimental data are given in Ref. 43.

- The experimental data are given in Ref. 43.

- The experimental data are given in Ref. 43.
IV. TRANSITION METAL ATOMS

In this section, we investigate the 4s–3d interconfigurational energies and 4s and 3d ionization potentials for the first-row transition metal atom \(^{42}\) in order to make sure of the characteristics of each functional. The experimental results are weighted averages of energies of the spin–orbit states for the pertinent electron configuration,\(^{42,43}\) while the spin–orbit coupling is not taken into account in the calculations.

A. The 4s–3d interconfigurational energies

The calculated interconfigurational energies, from the \(4s^23d^{n-2}\) to the \(4s^13d^n\) configurations, are shown in Table III and Fig. 1. Figure 1 illustrates that B-null generally underestimates the interconfigurational energies, whereas HF slightly underestimates them in the first half-row atoms (up to Cr) and overestimates them in the second half-row atoms. The MP2 method gives highly accurate interconfigurational energies for atoms, Sc through Fe, but severely underestimates those of Co, Ni, and Cu atoms. Comparing the BOP results with those of HOP, we can see that the OP correlation functional does not necessarily improve the B-null interconfigurational energies, because it may bring the HF results close to the exact ones by recovering a part of the correlation effect.

The important point to note is that the calculated atomization energies of the dimers for BOP, PW91, and B3LYP functionals in Table II seem to be associated with the results of the interconfigurational energies. These functionals also overestimate the atomization energies of the first half-row dimers, although B3LYP underestimates those of \(V_2\) and \(Cr_2\) for reasons mentioned in the previous section. However, for the second half-row dimers, B3LYP slightly underestimates the atomization energies, while BOP and PW91 overestimate them. We should also notice from the experimental values that the discrepancies in the calculated atomization energies of BOP and PW91 increase as the interconfigurational energies of the constituent atoms increase.

The HF behavior has already been explained by the pairing scheme\(^ {44,45}\). In the first half-row atoms, the transition of a 4s electron to the 3d shell breaks the strong 4s opposite-spin pair, where the correlation effect is very large, and no additional strong pair 4s–3d pair is formed. On the other hand, the transition of a 4s electron to the 3d shell in the second half-row atoms also breaks the strong 4s opposite-spin pair, but in this case it forms a new strong 3d opposite-spin pair where the correlation effect is larger than that of the 4s pair because of the more localized character of the 3d shell. The low interconfigurational energies that were calculated by MP2 may be due to the overestimation of the correlation effect between the 3d opposite-spin pairs.

The underestimation of the 4s–3d interconfigurational energies by the DFT calculations has been an object of study for a long time. Since Harris and Jones\(^ {46}\) pointed out that there is an absolute error of about 1 eV in the local spin density (LSD) results, which unduly favors the 3d-rich configuration, a considerable number of studies have been done on this topic from the viewpoints of the self-interaction correction (SIC)\(^ {47}\) in the central-field approximation scheme.\(^ {48,49}\) By comparison with the systematically higher HF interconfigurational energies for the second half-row atoms, it seems reasonable to suppose that the self-interaction error (SIE) is responsible for this situation. Actually, the exact HF exchange has frequently been adopted to get rid of SIE\(^ {44}\) while the calculated results are only slightly improved.
from the HF ones by combining with conventional correlation functionals just like HOP. It has, however, been shown that the variational SIC-LSD scheme gives almost the same interconfigurational energies as those of the uncorrected one.\textsuperscript{47} Harrison\textsuperscript{48} pointed out that this error may be due to the neglect of the multipolar terms that are compensated by corresponding terms in the HF exchange. He then introduced a modified SIC scheme that spherically averages the contributions from the atomic orbitals in the same shell to regain the unitary transformation invariance. The high angular momentum orbitals are overstabilized by omitting the multipolar terms. The interconfigurational energies obtained by this scheme seem to be in much better agreement with experiments.\textsuperscript{49} Since it is, however, obvious that the central-field approximation is applicable only to atomic orbitals, it remains an unsettled question how to deal with molecular systems.

The above line of reasoning leads to a conclusion that the neglected multipolar terms in DFT may cause the overstabilization of the 4s\textsuperscript{2}3d\textsuperscript{n−1} configuration. The overestimation of the atomization energies may also be explained in the same way, because all dimers, other than Cr\textsubscript{2} and Cu\textsubscript{2} molecules, contain open-shell 3d orbitals. Since the omission of the multipolar terms unduly favors the configurations that include the orbitals with high angular momentum, BOP, B-null, and PW91 erroneously predict the electron configurations of Co\textsubscript{2} to occupy not the 3d\textalpha\textsubscript{u} and 3d\textpi\textsubscript{g} \textsubscript{g} orbitals, but the 3d\textpi\textsubscript{u} and 3d\textdelta\textsubscript{g} orbitals. For the Ni\textsubscript{2} molecule, BOP and PW91 incorrectly predict the \pi\textsubscript{g} hole ground state instead of the \delta\textsubscript{g} hole ground state. Because the dimers further overstabilize the configurations that contain high angular momentum orbitals, the atomization energies are overestimated in DFT calculations. In contrast, by combining the exchange functional with the HF exchange that prefers the low angular momentum orbitals, B3LYP slightly underestimates the dissociation energies of the second half-row dimers.

**B. The 4s and 3d ionization potentials**

Table IV and Fig. 2 summarize the 4s ionization potentials of the 4s\textsuperscript{2}3d\textsuperscript{n−1} configuration of all atoms and those of the 4s\textsuperscript{1}3d\textsuperscript{n−1} configuration of Cr, Ni, and Cu. The analysis of the calculated 4s ionization energies may be a useful tool for judging the validity of the description of a chemical bond that is formed by the donation and the back-donation of electrons in the 4s orbital. Since the metallic bonds of the transition metal dimers are especially dominated by the 4s−4s bonding, the accuracies in the 4s ionization energies of atoms may affect the calculated atomization energies of the dimers. Figure 2 illustrates that the BOP, PW91, B3LYP, and MP2 results are in excellent agreement with the experimental ones. The HF method greatly underestimates (by over 1.3 eV) the 4s ionization energies, because this process breaks the strong 4s opposite-spin pair with the large correlation effect. The HOP method seems to give insufficient correlation effects. On the other hand, BOP and PW91 give accurate results because the 4s ionization process is essentially unaffected by the neglect of the multipolar terms. The B3LYP functional also predicts values close to the exact ones, probably due to the small differences in spin multiplicity.

The calculated 3d ionization potentials of the 4s\textsuperscript{2}3d\textsuperscript{n−2} configuration for all the first-row transition metal atoms and those of the 4s\textsuperscript{1}3d\textsuperscript{n−1} configuration for Cr, Ni, and Cu atoms are shown in Table V and Fig. 3. It may be useful for discussing the 3d bonding that is significant in, for example, transition metal complexes. The neglect of multipolar terms in DFT methods is anticipated to affect the results of these energies, because the ionization process of these atoms generally results in the exclusion of an electron in a less-stabilized 3d orbital with low angular momentum. The BOP, PW91, and B3LYP results are in fair agreement with the

<table>
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<tr>
<th>Atom</th>
<th>Neutral state</th>
<th>Cationic state</th>
<th>Exp. \textsuperscript{a}</th>
<th>BOP</th>
<th>B-null</th>
<th>B3LYP</th>
<th>PW91</th>
<th>HF</th>
<th>HOP</th>
<th>MP2</th>
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<td>Sc(4s\textsuperscript{2}3d\textsuperscript{1})</td>
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<td>3F</td>
<td>···</td>
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<td>8F</td>
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The mean absolute deviation

The max deviation

\textsuperscript{a}The experimental data are given in Ref. 43.
experimental values; they slightly overestimate the 3d ionization energies with the errors that decrease as the number of 3d electrons increases (from Sc to Cr atoms and from Fe to Cu atoms). Compared with the HOP results, the accurate 3d ionization energies of BOP may be due to the differences between those of B-null and HF.

V. CONCLUSIONS

In this paper, we calculated the equilibrium geometries and the atomization energies for the first-row transition metal dimers in order to explore the characteristics and the applicabilities of various kind of density functionals. For further analysis, we evaluated the 4s–3d interconfigurational energies and 4s and 3d ionization potentials of the atoms.

We first calculated the equilibrium bond lengths and the atomization energies of the first-row transition metal dimers. In spite of the very simple structures of the dimer, it is difficult to reproduce these values, because the dimers have different characteristic electron configurations for each ground state. The following features were evident from the calculated results for the dimers. (1) The BOP and PW91 functionals overestimate the atomization energies, and the errors tend to decrease as the number of 3d electrons increases (from Sc2 to Cr2 and from Fe2 to Cu2). (2) The hybrid B3LYP functional considerably underestimates the atomization energy of V2 and Cr2 because of the large differences in spin multiplicity between the molecules and the dissociation limits. (3) The MP2 method gives no bound state for almost all of the first half-row dimers. (4) The Mn2 results support the argument that the 3d–3d bonding is negligibly weaker than the 4s–4s one. (5) The OP correlation functional makes the bond lengths shorter and increases the atomization energies.

To determine the origins of the above features, we calculated the 4s–3d interconfigurational energies and 4s and 3d ionization energies of the atoms. As a result, we found that the calculated atomization energies of the dimers are closely related to the 4s–3d interconfigurational energies of the constituent atoms. The BOP and PW91 functionals underestimate the interconfigurational energies, probably because the omission of the multipolar terms in DFT causes the overstabilization of the configurations that contain orbitals in a high angular momentum shell that is not fully occupied. These functionals overestimate the atomization energies because the dimers appear to show a remarkable tendency to prefer the configurations with high angular momentum orbitals. In contrast, the HF exchange strongly favors orbitals with low angular momenta for the second half-row transition metals (as explained by the pairing scheme). Hence, the methods that use the HF exchange, for example, B3LYP and MP2, slightly underestimate the atomization energies of the second half-row dimers. The highly accurate 4s and 3d ionization potentials calculated by BOP, PW91, and B3LYP functionals supported that these functionals correctly reproduce the chemical properties of the transition metal complexes.2

In summary, the applicabilities of density functionals are as follows.

1) The pure density functionals, BOP and PW91, scarcely depend upon the spin configurations of the calculated systems, but tend to overstabilize the electron configurations that contain the orbitals in a high angular momentum shell that is not fully occupied.
(2) The hybrid density functional (B3LYP) generally gives more accurate atomization energies than those of the pure functionals, even if high angular momentum orbitals are present in the configuration. However, B3LYP gives an erroneous energy gap between the configurations of fairly different spin multiplicity, probably due to the unbalance of the exchange and correlation functionals.

(3) The OP correlation functional leads to the better results than those of the exchange-only case, in general, although it may not always bring the KS results close to the exact values because of the errors contained in the exchange functional.

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2 T. Ziegler, V. Tschinke, and A. Becke, J. Am. Chem. Soc. 109, 1351 (1987), and references therein.