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Application of the NDDO method to transition metal compounds

Christine Nieke and Joachim Reinhold

Sektion Chemie, Karl-Marx-Universität, Liebigstr. 18, DDR-7010 Leipzig,
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The NDDO method has been extended to include elements with *d*-orbitals. A parametrization for the first-row transition metals is given, which has been worked out to describe structural properties of transition metal complexes. Applications of the method to the Jahn–Teller distortions of tetrachloro complexes are presented. The NDDO results are compared with those from CNDO and INDO calculations. It turns out that the NDDO method seems to be the most sensitive among the ZDO procedures.

Key words: NDDO calculations—transition metal compounds—Jahn–Teller distortions

1. Introduction

In computational quantum chemistry two calculational strategies are currently applied: the semiempirical procedures and the *ab initio* approach. For systems containing only elements of the lower rows of the periodic table well-balanced semiempirical methods have been worked out. In recent time, however, more and more *ab initio* calculations have appeared, the accuracy of which is becoming higher and higher. For systems containing elements of the higher rows including transition metals the situation is much more complicated. No semiempirical "standard" procedures could be found. We are referring to the various extensions of the CNDO/INDO method of Pople et al. [1] for transition metal compounds [2–14], which were successful in those cases for which they had been worked out, but quickly ran into trouble if applied to different systems. On the other hand, *ab initio* calculations published recently show that rather high computational effort is required to get calculated values which are quantitatively comparable to experimental data. For instance, even a recent high-level calculation with large basis sets including polarization functions for the ferrocene could not satisfactorily reproduce the metal-ring distance [15]. Consequently, both *ab initio* and semiempirical treatments retain their importance, especially if qualitative problems are under study. See e.g. the successful work of R. Hoffmann.

Two ways are possible to reduce the gap between semiempirical and *ab initio* methods. The latter can be simplified and made more handable for larger systems by introducing pseudopotentials. This way is expected to be the most promising for the next future. Indeed, pseudopotentials for practically the whole periodic table are now available [16]. On the other hand, more sophisticated semiempirical methods should be studied. For organic molecules it has been shown [17–19] that the NDDO method originally proposed by Pople et al. [1] is able to yield qualitatively better results than the CNDO or INDO methods. But up to now – as far as we know – no attempt has been made to include transition metals into the NDDO procedure.

We have prepared a NDDO program which includes atoms with *d*-orbitals (transition metals or main group elements with arbitrary principal quantum number). Closed-shell and spin-polarized open-shell (UHF) calculations can be carried out. A geometry optimization is possible using a Quasi-Newton procedure [20] with numerically formed gradients.

In this paper we are discussing some problems concerning the choice of the one-electron terms, giving a simple parametrization for the first-row transition metals. Applications of the method to the Jahn–Teller distortions of the tetrachloro complexes are presented. Compressions or elongations, respectively, of the regular tetrahedron for both the tetragonal and the trigonal distortions are examined.

2. Method and parametrization

In the NDDO approximation the differential overlap is neglected only for atomic orbitals on different atoms, e.g. all one-center charge distributions are retained. The matrix elements of the Hartree–Fock operator at this level of approximation are [1]

$$F_{\mu\nu} = H_{\mu\nu} + \sum_{\lambda,\delta}^{A} P_{\lambda\delta}[\langle\mu\nu|\lambda\delta\rangle - \tfrac{1}{2}\langle\mu\lambda|\nu\delta\rangle] \tag{1}$$

$$F_{\mu\rho} = H_{\mu\rho} - \tfrac{1}{2}\sum_{\nu}^{A}\sum_{\sigma}^{B} P_{\nu\sigma}\langle\mu\nu|\rho\sigma\rangle \tag{2}$$

where μ, ν, λ and δ are centered on atom A, and ρ and σ on atom B. In the open-shell case one has

$$F^{\alpha}_{\mu\nu} = H_{\mu\nu} + \sum_{\lambda,\delta}^{A} [P_{\lambda\delta}\langle\mu\nu|\lambda\delta\rangle - P^{\alpha}_{\lambda\delta}\langle\mu\lambda|\nu\delta\rangle] \tag{3}$$

$$F^{\alpha}_{\mu\rho} = H_{\mu\rho} - \sum_{\nu}^{A} \sum_{\sigma}^{B} P^{\alpha}_{\nu\sigma} \langle \mu\nu | \rho\sigma \rangle \tag{4}$$

and corresponding expressions for $F^{\beta}_{\mu\nu}$ and $F^{\beta}_{\mu\rho}$.

A very large number of different two-center two-electron integrals occur due to the high quantum numbers we admit. Therefore, the use of explicit integral formulas as given by Roothaan [21] and realized by Birner et al. [22] is not possible for us. We employed a recurrence algorithm proposed by Harris [23] relating the electron interaction integrals to overlap and nuclear attraction integrals by the Fourier transform technique.

Regarding the one-electron and one-center two-electron elements there are some uncertainties. As there is only little experience we decided to choose these terms as similar as possible to the corresponding terms in a common CNDO procedure [3]. Moreover, this has the advantage, that if we compare CNDO, INDO, and NDDO results we can be sure that the deviation are not caused by one-electron parts but can be traced back to the different treatments of electronic interaction.

The following points should be noted:

(a) All one-center two-electron integrals are calculated exactly from atomic orbitals. This differs from most INDO modifications that include spectroscopic parameters.

(b) The one-center core matrix elements $H_{\mu\nu}$ in (1) and (3) are written as

$$H_{\mu\nu} = U_{\mu\nu} - \sum_{B(\neq A)} \langle \mu | V_B | \nu \rangle \tag{5}$$

where $U_{\mu\nu}$ is the one-center one-electron part, and $\langle \mu | V_B | \nu \rangle$ describes the interaction of a charge distribution $\chi_\mu \chi_\nu$ on atom A and the core of atom B. For $\mu \neq \nu$ one has $U_{\mu\nu} = 0$. The $U_{\mu\mu}$ are calculated using the formulas given by Clack et al. [3] including the orbital electronegativity parameters $(I_\mu + A_\mu)/2$. For the calculation of the two-center core attraction terms we use

$$\begin{aligned} \langle \mu | V_B | \nu \rangle = & -P^B_{ss} (\mu\nu | s^B s^B) - P^B_{pp} \sum_{m=-1}^{1} (\mu\nu | p^B_m p^B_m) \\ & - P^B_{dd} \sum_{m=-2}^{2} (\mu\nu | d^B_m d^B_m), \end{aligned} \tag{6}$$

due to the Goeppert–Mayer–Sklar approximation [24]. The $P_{\mu\mu}$ in (6) represent fixed occupation numbers of the neutral atom.

(c) A NDDO consistent calculation of the diatomic core matrix elements $H_{\mu\rho}$ appearing in Eqs. (2) and (4) would be the Ruedenberg approximation [25]:

$$H_{\mu\rho} = \frac{1}{2} \left(\sum_{\nu}^{A} K^{\mathrm{Rued}}_{\mu} S_{\nu\rho} H_{\mu\nu} + \sum_{\sigma}^{B} K^{\mathrm{Rued}}_{\rho} S_{\mu\sigma} H_{\rho\sigma} \right). \tag{7}$$

But there are only little experiences in fitting the parameters K_μ and K_ρ, even for the second-row elements. Therefore, we approximate the $H_{\mu\rho}$ simply by

$$H_{\mu\rho} = \beta_{\mu\rho} S_{\mu\rho} = \tfrac{1}{2}(\beta_\mu + \beta_\rho) S_{\mu\rho} \tag{8}$$

as is common in CNDO and INDO methods.

Consequently, for each atom we have the following parameters: the orbital exponents ζ_μ, the orbital electronegativities $(I_\mu + A_\mu)/2$, the bonding parameters β_μ corresponding to the parameter set used in the CNDO method. For main group elements we apply standard CNDO parameter values [26]. A first set of NDDO parameters for transition metals was adjusted to fullfil the following criterions. The parameters should

- be as similar as possible to published CNDO parameters [3, 5],
- smoothly change over the first-row transition metals,
- well reproduce the experimental bond lengths of sample compounds, in our case the tetrachloro complexes,
- yield positively charged metals in the sample compounds,
- well influence the convergency of the SCF iteration procedure.

It turned out, that the bonding parameters β_μ as well as the $(I_\mu + A_\mu)/2$ have only little influence concerning the criterions. So we use the $(I_\mu + A_\mu)/2$ of Clack et al. [3] and an extrapolated set of bonding parameters β_μ based on the values given by Serafini et al. [5]. The orbital exponents ζ_μ, however, are very sensitive parameters. The exponent ζ_p strongly influences the p-orbital density and by this the metal charge. This was already described by Serafini et al. [5]. The trial calculations showed, that the rapidity of the SCF iteration procedure or the

Table 1. NDDO parameters for the first-row transition metals, orbital densities and charges of the central metals, calculated as well as experimental bond lengths (in Å) of MCl_4 (M = Ti, V) and $[MCl_4]^{2-}$ (M = Mn, Fe, Co, Ni, Cu)

	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
ζ_s	1.33	1.40	1.47	1.54	1.60	1.65	1.70	1.74	1.77
ζ_p	0.462	0.475	0.487	0.500	0.512	0.525	0.538	0.550	0.562
ζ_d	2.07	2.19	2.31	2.43	2.55	2.67	2.79	2.91	3.03
$-(I_s + A_s)/2$	3.657	3.770	3.822	3.909	3.983	4.120	4.170	4.306	4.567
$-(I_p + A_p)/2$	0.558	0.690	0.777	0.876	0.975	1.062	1.160	1.260	1.347
$-(I_d + A_d)/2$	3.709	4.140	4.475	4.822	5.157	5.504	5.839	6.182	6.520
$-\beta_s$	3.0	9.0	14.0	18.0	21.0	23.0	24.3	25.0	25.5
$-\beta_p$	11.0	12.0	13.0	14.0	15.0	16.0	17.0	18.0	19.0
$-\beta_d$	9.0	15.0	20.0	24.0	27.0	29.0	30.3	31.0	31.5
P_s		0.57	0.64		0.69	0.71	0.73	0.74	0.76
P_p		0.35	0.38		0.74	0.80	0.85	0.91	0.97
P_d		1.96	3.20		5.33	6.32	7.28	8.22	9.15
q_M		1.12	0.78		0.24	0.17	0.14	0.13	0.12
R_{cal}		2.19	2.14		2.27	2.25	2.23	2.24	2.23
R_{exp}		2.19	2.14		2.33	2.27	2.25	2.27	2.22
		(27)	(28)		(29)	(29)	(30)	(31)	(32)

convergency behaviour in general mainly depends on the ζ_d value. Therefore, the variation intervals for both ζ_p and ζ_d are rather small. It follows that only the exponent ζ_s remains to fit the experimental bond length. Indeed, the potential curve depending on the metal-ligand distance is strongly influenced by the ζ_s value, so that it was possible to find out suitable exponents ζ_s.

The final results of our parametrization are collected in Table 1. The table also shows the orbital densities and the charges of the central metals and a comparison between mean experimental and calculated bond lengths, where we assumed regular tetrahedral molecular structures. The orbital exponents for scandium have been extrapolated.

3. Application to the Jahn–Teller distortion of tetrahedral complexes

In a tetrahedral ligand field the *d*-orbitals of the central metal split into t_2 and *e* levels (Fig. 1). The splitting parameter is relatively small ($\frac{4}{9}$ of the octahedral value), so that almost all tetrahedral complexes have high-spin configurations. From the Jahn–Teller theorem [33] it follows that only the d^0, d^2, d^5, and d^7 electronic configurations can maintain regular tetrahedral symmetry. All other systems should undergo distortions resulting in equilibrium geometries of lower symmetry. For a tetrahedral system with a partially filled t_2 level a tetragonal or a trigonal distortion can arise (Figs. 1 and 2). A system with a partially filled *e* level can be stabilized only by the tetragonal distortion.

Figure 1 exhibits the two possible tetragonal distortions, a compressed tetrahedron and an elongated tetrahedron. In both cases the t_2 and *e* levels split up, but the d_{xz} and d_{yz} orbitals remain degenerate. With respect to d_{xy}, the d_{xz} and d_{yz} orbitals should be stabilized in the compressed tetrahedron and destabilized

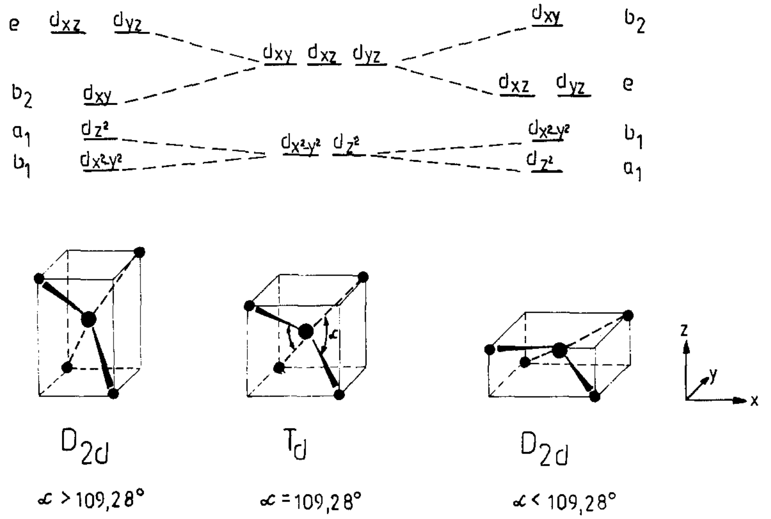

Fig. 1. Tetragonal Jahn–Teller distortion of a tetrahedron

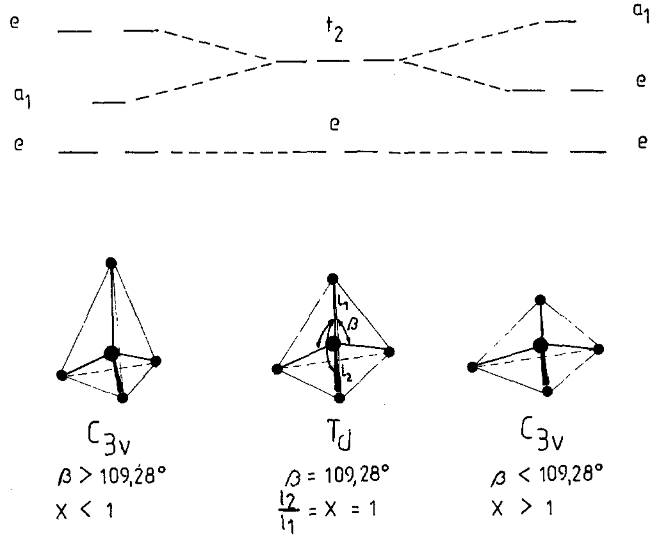

Fig. 2. Trigonal Jahn–Teller distortion of a tetrahedron

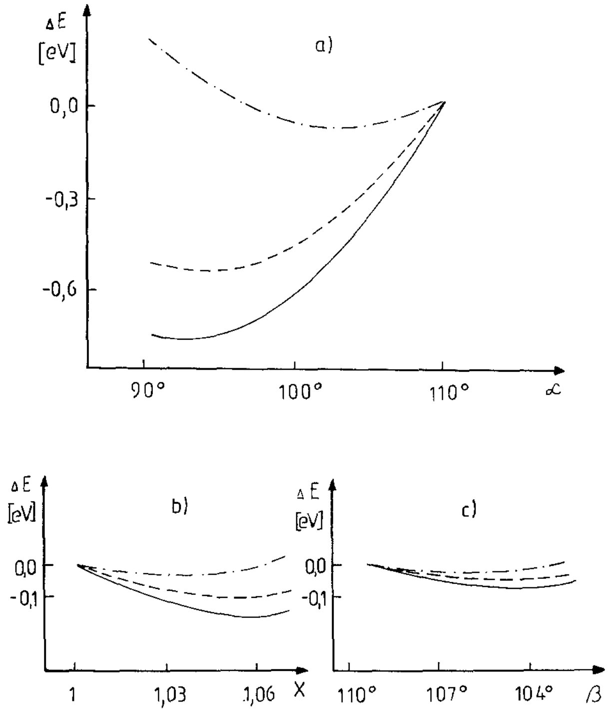

Fig. 3. $[CrCl_4]^{2-}$. Dependence of the total energy on the distortion parameters. **a** α; **b** X; **c** β. —— NDDO --- INDO -·- CNDO

in the elongated one, respectively. The trigonal distortion (Fig. 2) cannot be described by a single distortion parameter. We consider the bond angle between one bond and one of the other three and the ratio of one bond length to one of the other three. In reality both cases will overlap. The single d_{z^2} orbital will be stabilized by the elongation and destabilized by the compression.

The systems under study are the high-spin complex ions $[MCl_4]^{2-}$ with M = Cr(II), Fe(II), Ni(II) and Cu(II). Using the equilibrium metal-ligand bond lengths of Table 1 we varied the angle α (see Fig. 1) of the tetragonal distortion and the parameters β and X (see Fig. 2) of the trigonal distortion of the tetrahedron. The Figs. 3–6 show the total energy curves depending on the distortion parameters. Additionally, CNDO as well as INDO potential curves are presented using the same parameters as for the NDDO calculations to be able to compare the methods concerning their different consideration of electronic interaction.

$[CrCl_4]^{2-}$

The $[CrCl_4]^{2-}$ ion is a hypothetical molecule, the real Cr(II) complex is the octahedral $[CrCl_6]^{4-}$. The d^4 electronic configuration can be stabilized by a tetragonal or a trigonal compression (see Figs. 1 and 2). For both cases the CNDO method gives minima near the regular tetrahedron, as it could be expected by the theory, but which do not exist experimentally (Fig. 3). All CNDO minima and the INDO and NDDO minima for the trigonal compression are relatively flat. Only the INDO and the NDDO method predict such a "strong" tetragonal compression that planar structures would result, which in reality leads to octahedral complexes by adding another two ligands.

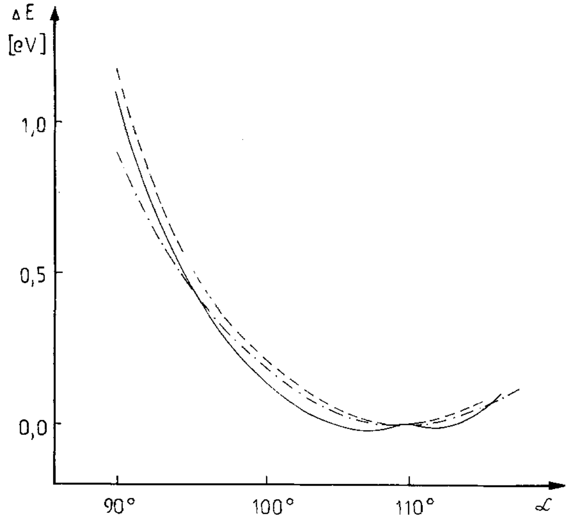

Fig. 4. $[FeCl_4]^{2-}$. Dependence of the total energy on the distortion angle α —— NDDO - - - INDO — · — CNDO

$[\mathrm{FeCl}_4]^{2-}$

The experimental structure of the $[\mathrm{FeCl}_4]^{2-}$ is a regular tetrahedron [34] that is reproduced by the CNDO and INDO calculations (Fig. 4). Due to the Jahn–Teller theorem, however, the tetrahedron should be distorted (see Fig. 1). Indeed, the NDDO calculations yield two small minima for a slightly compressed or elongated tetrahedron, respectively. But these minima are very flat, so that the experiments result in a regular tetrahedron.

$[\mathrm{NiCl}_4]^{2-}$

The d^8 system could be stabilized by a tetragonal or a trigonal elongation, compression will not arise due to electronic configuration (see Figs. 1 and 2). Indeed, for the tetragonal case all methods give an energy minimum for $\alpha > 109.28°$ (Fig. 5). Again, the NDDO minimum is the deepest, it is located at around 115° which is in good agreement with one of the experimental bond angles (114.5° [31]). For the trigonal case we restricted ourselves to the NDDO method. From the calculations follows, that the $[\mathrm{NiCl}_4]^{2-}$ ion should undergo a tetragonal as well as a trigonal distortion. This corresponds to the experimental fact that the bond lengths vary (2.256–2.283 Å [31]) and the bond angles 114.5° and 107.8° can not be realized in regular D_{2d} or C_{3v} symmetry, respectively.

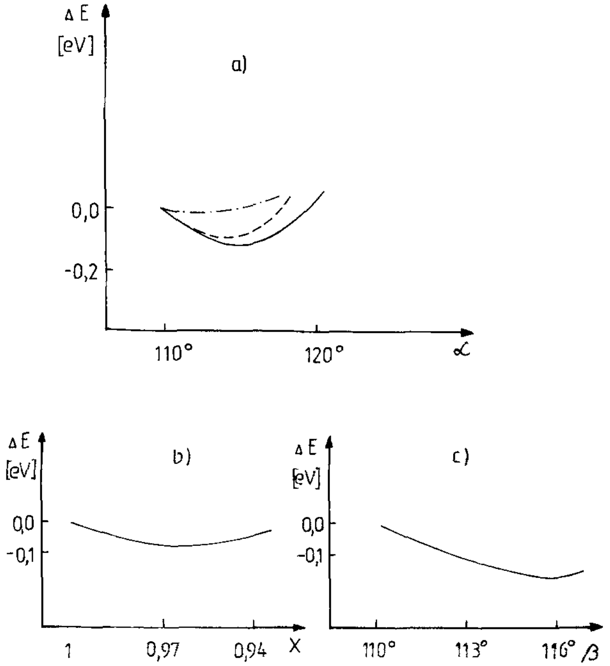

Fig. 5. a–c. $[\mathrm{NiCl}_4]^{2-}$. Dependence of the total energy on the distortion parameters. **a** α; **b** X; **c** β.
—— NDDO - - - INDO -·- CNDO

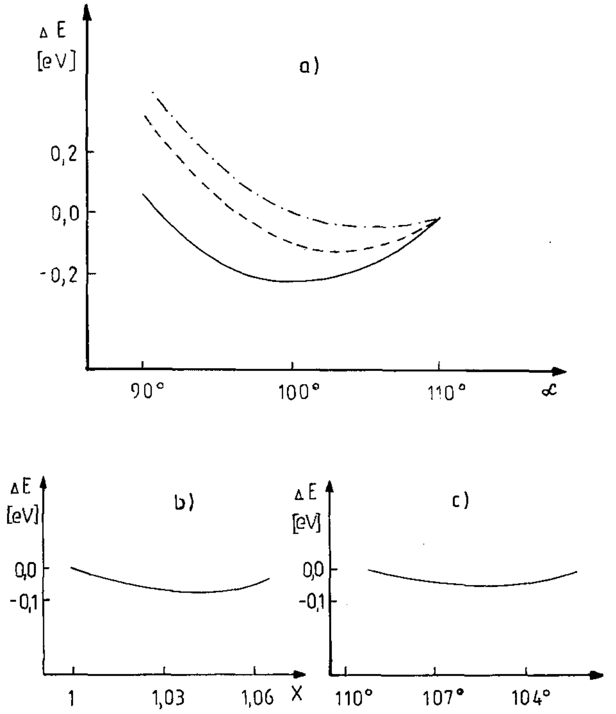

Fig. 6 a–c. $[CuCl_4]^{2-}$. Dependence of the total energy on the distortion parameters. **a** α; **b** X; **c** β.
—— NDDO - - - INDO -·- CNDO

$[CuCl_4]^{2-}$

The d^9 electronic configuration could be stabilized by a tetragonal or a trigonal compression like the d^4 system. The experimental structures for the $[CuCl_4]^{2-}$ ion are the compressed tetrahedron [32] or in the solid state planar arrangements. As for the d^4 system the CNDO method gives only a weakly distorted tetrahedron. The INDO and NDDO results, however, differ from the d^4 case. Now, a tetragonal compression is predicted, the trigonal compression being negligible (Fig. 6). Again, the NDDO minimum is the deepest and at best reproduce the experimental bond angles (101.5°, 102.9°, 123.3°, 124.9° [32]). Moreover, looking at the relative energies of square planar and regular tetrahedral structures, only the NDDO method seems to indicate that also planar arrangements can exist.

4. Conclusions

The application of the three semiempirical methods CNDO, INDO and NDDO to structural problems of the tetrachloro complexes of the first-row transition metals shows that the NDDO method has some advantage. The extent of the calculated distortions increases in the series CNDO, INDO, NDDO. The main structural properties are correctly described even by the CNDO method which is in agreement with the work of Pelikan et al. [35]. Due to the consideration of the directed character of the orbitals for the calculation of electron interaction integrals the NDDO method, however, seems to be more sensitive for special problems. The advantages of the method should be most apparent in treatments of metal–metal interactions.

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