

Extension of the PM3 Method on s,p,d Basis. Test Calculations on Organochromium Compounds

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A model for estimation of the two-electron interaction in molecules is proposed. It is based on the bipolar expansion of the Ohno potential which is considered as a universal effective potential of the two-electron interaction. It allows to estimate efficiently the two-electron fockian terms taking into implicit account the dynamic electron correlation. The formulas obtained do not depend explicitly on the orbital quantum number of the basis AO's, and this approach may be used to extend the semiempirical NDDO-type methods to the s,p,d basis. In this work, this approach was applied to the semiempirical PM3 model, and the test calculations were performed on organochromium compounds, taking into explicit account the chromium d orbitals. The calculated thermodynamic, structural, and electron properties of above 30 organochromium compounds of different classes (sandwich complexes, carbonyls, nitrosyls, and mixed derivatives) stay in good agreement with the experimental data.

Advances in theory of semiempirical quantum chemical methods of MNDO type (MNDO, AM1, PM3)^{1–3} are well-known now. However, the taking into explicit account the transition metal d AO's to treat the structure and reactivity of the organometal compounds (OMC) is an actually unresolved problem in the framework of these methods. One of the questions consists of the semiempirical estimation of two-center, two-electron integrals over the Slater's s,p,d basis. Such a semiempirical procedure must not be the ordinary method of their approximation but must keep track of the dynamic electron correlation and the sufficient noncompleteness of the basis set. Within the MNDO-type methods the "point charge model"⁴ is used for the estimation of the two-center, two-electron integrals. The continuous electron distribution of the atom is presented by a set of separate point charges provided that the long-distance multipole moments of the atom are kept. Unfortunately, this approach cannot be simply extended to the arbitrary basis set (s,p,d,f,...). Recently, McCourt et al.⁵ have applied the operator technique to generate the point charges in the more comprehensive case of s,p,d distributions. Unfortunately, the resulting integral expressions are too cumbersome and, moreover, are of the form of series with sign-alternating high-order terms which may cause instability of the algorithm.

In 1992, Thiel and Voityuk^{6,7} have proposed the modification of the point charge scheme to treat the hypervalent compounds with s,p,d basis (the MNDO/d method). Within the MNDO/d the small multipole moments of third and fourth order induced by the p,d and d,d electron distributions are ignored, and only the monopole, dipole, and quadrupole moments are taken into account. To preserve the rotational invariance of this procedure, additional relations have been imposed on the corresponding two-electron integrals. Unfortunately, the atom parameters of the transition metal atoms have not been reported so far for this method. It is doubtful that the point charge model is convenient to describe the complex electron distributions of transition metal atoms because of the large number of energetically near-valence states. The energy difference between these states is often of the order of the terms ignored in the point charge model or of the errors arising in going from the continuous electron distributions to the discrete charges.

Moreover, this approach does not eliminate the problem of the extension to other basis sets (e.g., of s,p,d,f AO's), and it generates a large number of atom parameters.

Therefore, the point charge scheme is not employed in this work, and we suggest the use of another electron interaction model. It is not surprising that the dynamic electron correlation somewhat decreases the interaction between the electrons moving in the molecule. In other words, the interaction potential of correlated electrons is distinguished from the Coulomb interaction, and it is less in magnitude. This decrease may be represented as an increase of the effective interelectron distance, and the interaction of correlated electrons may be described by an effective interelectron potential. The ratio of this effective potential to the Coulomb potential is referred to here as a correlation function.

Recently, this approach was used by Filatov, Zilberberg, and Zhidomirov in the NDDO/MC method⁸ and its modifications. The Heaviside function was suggested as a correlation function. However, this choice is not correct enough as a physical model. This correlation function is not continuous, and moreover, it requires numerical methods to compute the molecular integrals.

The semiempirical Ohno formula corresponding to the Ohno potential

$$(r_{12}^2 + a^2)^{-1/2} \quad (1)$$

seems to be more promising as effective interelectron potential because it is continuous and has the proper asymptotic behavior in both the long- and short-range limits. Moreover, the series expansion in terms of the pair products of spherical functions centered on two different atoms (bipolar expansion) may be made in the case of the Ohno potential, which is important in elaborating on the efficient calculation method.

Thus, in this work we use a new approach for the estimation of two-electron integrals based on the above model. This approach consists of the following:

1. The Ohno potential is a universal semiempirical potential describing the interaction of correlated electrons in the molecule. (The parameter a takes into account the dynamic electron correlation and, perhaps, the basis noncompleteness.) Thus, all two-electron Coulomb integrals should be replaced by the

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corresponding ones with the Ohno potential

$$(\mu\nu, \lambda\sigma) = \int \chi_\mu^A \chi_\nu^A (r_{12}^2 + a^2)^{-1/2} \chi_\lambda^B \chi_\sigma^B d\tau_1 d\tau_2 \quad (2)$$

where χ_μ^A is an AO μ centered on atom A. In accordance with the NDDO approximation, the AO's μ and ν are occupied by electron 1 and λ and σ by electron 2.

2. The Ohno potential may be exactly expanded in terms of pair products of spherical functions centered on two different atoms (bipolar expansion):

$$1/(r_{12}^2 + a^2)^{1/2} = \sum_{l_1=0}^{\infty} \sum_{l_2=0}^{\infty} \sum_{m=0}^{\min(l_1, l_2)} B_{l_1 l_2 m}(r_1, r_2; R, a) \times P_{l_1}^m(\cos \vartheta_1) P_{l_2}^m(\cos \vartheta_2) \cos m\Delta\varphi \quad (3)$$

where R is an internuclear distance between atoms A and B, $P_l^m(\cos \vartheta)$ is an associated Legendre function, and $B_{l_1 l_2 m}(r_1, r_2; R, a)$ is a coefficient independent of the spherical coordinates ϑ and φ (bipolar coefficient).

It should be noted that radial and spherical variables are totally separated in (3). Therefore, it reduces the multiple integration in (2) to the double integration over r_1 and r_2 .

The expressions for the bipolar coefficients are known in the case of the Coulomb potential.⁹ The bipolar coefficients of the Ohno potential have been found by us with a spherical function differentiation technique.¹⁰ The exact and general expressions for the bipolar coefficients were given in refs 11 and 12 for all practically important cases. In the special case when the internuclear separation between two atoms is large, we have

$$B_{l_1 l_2 m}(r_1, r_2; R, a) = \sum_{u=l_1}^{\infty} \sum_{v=l_2}^{\infty} \frac{(-1)^v r_1^u r_2^v}{(\sqrt{R^2 + a^2})^{u+v+1}} \times \sum_{w=m}^u \sum_{\tau=\tau_{\min}}^{[(w-m)/2]} \sum_{j=\tau_{\min}}^{\tau} \sum_{p=0}^{[(v+w+2j)/2]} \frac{(-1)^{p+w+\tau} q(w, p, \tau) (u+v+2j-2p)! \left[\frac{a}{\sqrt{R^2 + a^2}} \right]^{2j}}{(v+w+2j+2p)! (u+w)!} \times P_{u+v+2j}^{2p} \left(\frac{R}{\sqrt{R^2 + a^2}} \right) g_{l_1 l_2}^m(u, v, w, \tau, j, p) \quad (4)$$

where $\tau_{\min} = \max(0, [(w-v+1)/2])$. The asterisk by the summation over τ means that the sum is equal to zero when the lower limit exceeds the upper one. The factor $g_{l_1 l_2}^m(u, v, w, \tau, j, p)$ is given in refs 11 and 12.

3. On the basis of this exact expression, the various level approximations may be derived in a successive manner. The first-level approximation is used in this work to demonstrate the general features of a new approach. It may be obtained if we drop all terms except the first one in summation by u and v in (3):

$$B_{l_1 l_2 m}(r_1, r_2; R, a) = \frac{(-1)^{l_2+m} (l_1 + l_2)! r_1^{l_1} r_2^{l_2}}{(l_1 + m)! (l_2 + m)! (\sqrt{R^2 + a^2})^{l_1+l_2+1}} b_{l_1 l_2 m} \left(\frac{R}{\sqrt{R^2 + a^2}} \right) \quad (5)$$

$b_{l_1 l_2 m}(s)$ is the polynomial of degree $l_1 + l_2 - 2m$ in the variable

$$R/(R + a)^{1/2}:$$

$$b_{l_1 l_2 m}(s) = \sum_{k=0}^{l_1+l_2-2m} c_k s^k \quad (6)$$

The coefficients c_k are tabulated in ref 13 for all practically important cases.

4. The integration of this approximate expression over radial variables gives the approximate formula for the estimation of the two-electron, two-center integrals:

$$N_\mu N_\nu N_\lambda N_\sigma \sum_{l_1, l_2=0}^{\infty} \sum_{m=-\min(l_1, l_2)}^{\min(l_1, l_2)} \mathbf{a}_{l_1}^m(\mu, \nu) \mathbf{a}_{l_2}^m(\lambda, \sigma) S_{l_1 l_2 m}(R, a) \quad (7)$$

where

$$S_{l_1 l_2 m}(R, a) = \frac{(-1)^{n_\mu+n_\nu+n_\lambda+n_\sigma} (l_1 + l_2)! b_{l_1 l_2 m}(R/(R^2 + a^2)^{1/2})}{(l_1 + m)! (l_2 + m)! (R^2 + a^2)^{(l_1+l_2+1)/2}} \times \frac{(n_\mu + n_\nu + l_1 + 1)! (n_\lambda + n_\sigma + l_2 + 1)!}{(\xi_\mu + \xi_\nu)^{n_\mu+n_\nu+l_1+1} (\xi_\lambda + \xi_\sigma)^{n_\lambda+n_\sigma+l_2+1}} \quad (8)$$

N_χ is the scaling factor of the Slater AO χ , n_χ and ξ_χ are its principal quantum number and exponent, and $\mathbf{a}_l^m(\mu, \nu)$ are coefficients arising after integration over spherical variables (given in ref 14).

This formula has the advantage of not being dependent on the azimuthal quantum number of the basis AO's. Thus, it may be simply extended to the basis set including arbitrary sort of AO's, e.g., of the d AO's. Moreover, it is simple to use and tolerate small changes of parameters.

This approach was applied within the framework of the semiempirical PM3 method, and test calculations with a modified scheme were performed on different chromium compounds. The two-center, two-electron integrals of the Cr-X atom pairs were calculated from (4)–(6) while the remaining ones have been calculated by the standard point charge scheme. Such an approach requires that optimized parameters and calculation results of the PM3 method remain in force. This approach may be substantiated also if one takes into consideration that the point charge scheme is the special case of general formulas obtained by integration of bipolar coefficients of the Ohno potential. If one does this integration exactly, the results of both methods will coincide.

To estimate the one-center integrals, one can also use the spherical function expansion of the Ohno potential:

$$(r_{12}^2 + a^2)^{-1/2} = \sum_{l=0}^{\infty} B_l(r_1, r_2; a) P_l(\cos \alpha) \quad (9)$$

where α is the angle between radius vectors r_1 and r_2 of two electrons, centered on the same nuclei; r_1 and r_2 are modulus of these vectors. The coefficients $B_l(r_1, r_2, a)$ may be derived from the formulas of the bipolar coefficients given in setting $R \rightarrow 0$ or may be found by projection:

$$B_l(r_1, r_2; a) = (l + 1/2) \int_{-1}^1 \frac{P_l(\cos \alpha)}{(r_1^2 + r_2^2 + a^2 - 2r_1 r_2 \cos \alpha)^{1/2}} d(\cos \alpha) \quad (10)$$

TABLE 1: Optimized Parameters of Chromium (U_i , β_i in eV; ξ_i , ρ_i in au; α , a_i , b_i , c_i in Å)^a

electronic parameters		parameters ρ		core parameters	
U_s	-54.609 100	ρ_0	0.358 068	α	2.141 592
U_p	-48.614 895	ρ_1	0.278 337	a_1	0.405 102
U_d	-63.059 256	ρ_2	0.468 645	b_1	1.232 127
ξ_s	2.346 223	ρ_3	0.493 151	c_1	1.337 580
ξ_p	2.001 782	ρ_4	0.412 857	a_2	-0.245 384
ξ_d	1.726 696			b_2	1.536 090
β_s	-11.651 621			c_2	1.674 196
β_p	-11.882 753				
β_d	-11.906 074				

^a $\Delta H_A(\text{Cr}) = 95.0$ kcal/mol, $E_{\text{isol}}(\text{Cr}) = -219.445\,123$ eV.

Furthermore, we used the explicit expressions for $B(r_1, r_2, a)$ obtained from (6) by straightforward integration.

With (2) the one-center, two-electron integral may be written as

$$(\mu\nu, \lambda\sigma) = N_\mu N_\nu N_\lambda N_\sigma \sum_{l=0}^{\infty} \sum_{m=-l}^l \frac{(l-|m|)!}{(l+|m|)!} a_{l_1}^m(\mu\nu) a_{l_2}^m(\lambda\sigma) S_l(a) \quad (11)$$

where

$$S_l(a) = \int_0^\infty \int_0^\infty B_l(r_1, r_2; a) r_1^{n_\mu+n_\nu} r_2^{n_\lambda+n_\sigma} \exp(-(\xi_\mu + \xi_\nu)r_1 - (\xi_\lambda + \xi_\sigma)r_2) dr_1 dr_2$$

The calculation of $S_l(a)$ was performed by the numeric five-point Laguerre method in the course of the atom parameter optimization. This approach provides a way of estimating the one-center, two-electron integrals without using the Oleari or Slater–Condon parameters. The choice of the Oleari parameters is often ambiguous for transition metals because it requires a priori setting of the valence state of the atom. We have attempted to rule out the use of the Oleari parameters in this work and obtained the one-center integrals by direct calculations with above formulas. The parameter a in (1) may be chosen in various manners. In this work we have applied the general approach of MNDO-type methods: the additive formula

$$a \equiv a_{l_1 l_2} = \rho_{l_1}^A + \rho_{l_2}^B \quad (12)$$

Unlike the MNDO and PM3 the additive terms were adjustable in this work. Thus, the chromium atom (d element) has altogether 14 adjustable electronic parameters: U_{ss} , U_{pp} , U_{dd} , ξ_s , ξ_p , ξ_d , β_s , β_p , β_d , ρ_0 , ρ_1 , ρ_2 , ρ_3 , ρ_4 , and each s,p atom within the PM3 scheme has 11 electronic parameters. Moreover, each atom without regard to its identity has seven core parameters.

The parameter optimization for chromium atom has been performed by a standard procedure.¹ The heats of formation, ionization potentials, dipole moments, bond lengths, and bond and dihedral angles of four chromium compounds CrO_3 , $\text{Cr}(\text{C}_6\text{H}_6)_2$, $\text{Cr}(\text{CO})_6$, and $\text{Cr}(\text{C}_6\text{H}_6)(\text{CO})_3$ were used as reference properties. The optimized parameters of chromium are given in Table 1. With the parameters obtained, the test calculations on 23 organochromium derivatives have been performed. The results of these calculations are presented in Table 2.

The results shown in Table 2 are sufficient to allow the definite conclusions regarding the features and possibilities of a new approach. The results of the calculations show the structural stability of the chromium complexes with the four-

electron ($\text{Cr}[\text{C}(\text{CH}_2)_3](\text{CO})_3$), five-electron ($\text{Cr}(\text{C}_5\text{H}_5)_2$), six-electron ($\text{Cr}(\text{C}_6\text{H}_6)_2$), and seven-electron ($\text{Cr}(\text{C}_5\text{H}_5)(\text{C}_7\text{H}_7)$) ligands as well as several kinds of carbonyls, isocyanide, and nitrosyl complexes.

The mean absolute error in heats of formation is 14.8 kcal/mol. The maximum error occurs for $\text{Cr}(\text{C}_5\text{H}_5)_2$ in triplet state and the mixed carbonyls. Perhaps this fact may be explained by the large error in the PM3 values of the heat of formation of carbon monoxide (+6.7 kcal/mol). It gives +20.1 kcal/mol for three CO groups. With this correction, the absolute error due to the new model becomes only +3 to +9 kcal/mol. In the case of $\text{Cr}(\text{CO})_6$ the geometry structural distortion mentioned below causes the heat of formation to decrease. The calculation of $\text{Cr}(\text{C}_5\text{H}_5)_2$ in the triplet state is very time-consuming, and this compound could not be chosen as a reference.

With the heats of formation calculated, the mean dissociation enthalpies (the M–L bond energies) may be found. These energies are also presented in Table 2 along with the experimental values. The recommended value 95 kcal/mol was used for the heat of formation of the chromium atom, and the PM3 calculated values were used as the ligand enthalpies.

As may be concluded from Table 2, the calculated M–L bond energies are in good agreement with thermochemical estimation. The mean absolute error is 6.0 kcal/mol. The order of mean bond energies in series $\text{C}_5\text{H}_5\text{—C}_6\text{H}_6\text{—CO}$ is also properly reproduced:



This thermochemical sequence is a fundamental fact in the chemistry of transition metal π -complexes. The reproduction of this sequence seems to be important in the proper description of the OMC dissociation processes. It may be concluded from the comparison of the Cr–CO and Cr–CN bond energies that the last one is stronger. Although the experimental data on the energetic and geometry parameters of isocyanides in the gas phase are absent this conclusion stays in agreement with the fact observed that the M–L lengths in the crystal isocyanide complexes are shorter than those in the crystal carbonyls.

The calculated geometry parameters of a number of chromium compounds are listed in Table 3. As may be concluded from these results, the Cr–C bond lengths of sandwich complexes are adequately reproduced by the PM3 method modified with the new scheme of two-electron integral estimation. The mean absolute error is 0.05 Å. The calculated molecular structures of arene complexes coincide with the experimental data. The ground state of *bis*(benzenechromium) is a conformation with D_{6h} symmetry, and there is a small activation barrier to benzene ring rotation around M–L axes (about 0.7 kcal/mol). That the hydrogen atoms of the benzene fragment have a deviation from the ring plane to the central atom in all calculated sandwich complexes is a well-known experimental fact. A dihedral angle of this deviation is considerably larger than the experimental one (16.5° instead of 3.5°). However, such a deviation has a small effect on the Cr–H distances because the C–H bond length is small, which provides an explanation of the dihedral angle increasing. The most stable conformation of $\text{Cr}(\text{C}_5\text{H}_5)_2$ is the D_{5d} structure, in contrast with the experimental D_{5h} , but the rotation barrier is only 0.2 kcal/mol.

In the case of ligands with large substituents (e.g., $\text{C}_6\text{H}_3\text{—}(\text{CH}_3)_3$) the calculations indicate departures of the carbon atoms with substituents from the benzene ring plane, and the optimized structure is characterized by C_{3v} symmetry.

The calculated geometry of mixed arene–carbonyl complexes is in good agreement with the experimental structure parameters. As may be concluded from Table 3, all carbonyl groups are

TABLE 2: Heats of Formation and Average M–L Bond Energies of Chromium Compounds (kcal/mol)

compound 1	ΔH_f			$D(M-L)$		
	calcd 2	exp ^{15,16} 3	Δ 4	calcd 5	exp ¹⁶ 6	Δ 7
CrO ₃	-52.8	-70.0	17.2			
Cr(C ₅ H ₅) ₂ (singlet)	46.2			74.4		
Cr(C ₅ H ₅) ₂ (triplet)	31.8	59.3	-27.5	81.6	67.8	13.8
Cr(C ₆ H ₆) ₂	49.4	54.1	-4.7	46.3	40.2	6.1
Cr[C ₆ H ₅ -CH ₃] ₂	31.8			45.7		
Cr[C ₆ H ₅ -C ₂ H ₅] ₂	24.8	33.9	-9.1	44.6	37.7	6.9
Cr[C ₆ H ₅ - <i>i</i> -C ₃ H ₇] ₂	10.5			47.8		
Cr[<i>o</i> -C ₆ H ₄ (C ₂ H ₅) ₂] ₂	6.7	6.7	0.0	41.1	39.6	1.5
Cr[<i>o</i> -C ₆ H ₄ (<i>i</i> -C ₃ H ₇) ₂] ₂	-12.9	-22.7	9.8	42.2	41.8	0.4
Cr[C ₆ H ₄ (<i>i</i> -C ₃ H ₇) ₂][C ₆ H ₅ - <i>i</i> -C ₃ H ₇]	-1.7	-5.7	4.0	45.2	42.8	2.4
Cr[1,3,5-C ₆ H ₃ (CH ₃) ₃] ₂	-11.7	9.0	-20.7	48.6	39.1	9.5
Cr[1,2,4-C ₆ H ₃ (CH ₃) ₃] ₂	-0.7	11.0	-11.7	43.8	38.7	5.1
Cr(CO) ₆	-227.7	-217.2	-10.5	34.1	25.6	8.5
Cr(C ₆ H ₆)(CO) ₃	-55.3	-84.2	28.9			
Cr(C ₆ H ₅ -CH ₃)(CO) ₃	-65.9	-91.4	25.5			
Cr[1,3,5-C ₆ H ₃ (CH ₃) ₃](CO) ₃	-87.3	-110.6	23.3			
Cr(C ₆ H ₅ -OCH ₃)(CO) ₃	-94.9					
Cr[C(CH ₃) ₃](CO) ₄	-128.6					
Cr(CNH) ₆	147.4			47.6		
Cr(CN-CH ₃) ₆	126.7			49.1		
Cr(CN-CH ₃) ₃ (CO) ₃	-55.1					
Cr(C ₅ H ₅)(C ₇ H ₇) (singlet)	49.9					
Cr(C ₅ H ₅)(C ₇ H ₇) (triplet)	65.2					
Cr(C ₅ H ₅)(CO) ₄ (doublet)	-117.1					
Cr(CO) ₅ (NO) (doublet)	-195.0					
Cr(CO) ₄ (NO) ₂	-149.0					

TABLE 3: Calculated Geometry Parameters of Chromium Compounds in Comparison with Experimental Values^a

compound	sym group	calcd geometry parameters (experimental values ^{17,18})
CrO ₃	<i>D</i> _{3h}	<i>r</i> _{Cr-O} = 1.47 (1.60)
Cr(C ₅ H ₅) ₂	<i>D</i> _{5d}	<i>r</i> _{Cr-C} = 2.13 (2.17), <i>r</i> _{Cr-Cp} = 1.75 (1.80), <i>r</i> _{C-C} = 1.13 (1.43), <i>r</i> _{C-H} = 1.09, α_{H-C-Cr} = 116.8, ϑ = 10.7 (2.9)
Cr(C ₆ H ₆) ₂	<i>D</i> _{6h}	<i>r</i> _{Cr-C} = 2.17 (2.15), <i>r</i> _{Cr-Bz} = 1.64 (1.61), <i>r</i> _{C-C} = 1.42 (1.42), <i>r</i> _{C-H} = 1.10, α_{H-C-Cr} = 116.3, ϑ = 16.5 (3.5)
Cr(CO) ₆	distorted <i>O</i> _h	<i>r</i> _{Cr-C} = 1.91 (1.98), <i>r</i> _{C-O} = 1.16 (1.16)
Cr(C ₆ H ₆)(CO) ₃	<i>C</i> _{3v}	<i>r</i> _{Cr-C(Bz)} = 2.20 (2.22), <i>r</i> _{Cr-CO} = 1.99 (1.89), <i>r</i> _{C-O} = 1.15 (1.14), <i>r</i> _{C-C} = 1.41 (1.42), <i>r</i> _{C-H} = 1.10, $\alpha_{OC-Cr-CO}$ = 87.1 (87.0), α_{H-C-Cr} = 125.2, ϑ = 7.2

^a *r* = bond length, Å; α = bond angle, deg; ϑ = deviation angle of C–H bonds from ring plane to central atom, deg.

equivalent, the bond angle between these groups is about 90°, and the Cr–C₆H₆ bond length is somewhat increased in comparison with bis(arene) complexes. The C–O bond lengths are also increased relative to carbon monoxide. Unfortunately, the geometry of hexacarbonyl chromium Cr(CO)₆ is not totally symmetric. The molecular symmetry is near to the *O*_h group but is intermediate between *O*_h and *D*_{3d} because of the deviation of axial CO groups from the vertical axis by an angle of about 7°. Because of this deviation, the equatorial ligands are not equivalent. An averaged Cr–CO bond length is 1.91 Å, close to the experimental value 1.98 Å. It may be suggested that a second-order Jahn–Teller distortion is responsible for this situation, and it can be improved by a more careful parameter optimization.

The ionization potentials calculated from Koopmans' theorem and corresponding dipole moments for a number of chromium compounds are given in Table 4. It is easy to see that there is a systematic upward deviation of 1.8 eV in the case of π -complexes while the ionization potentials of carbonyls are decreased by 1.1 eV. These results may be explained by the fact that the one-center integrals of chromium atom were not calibrated against the spectral data. All one-center, two-electron integrals of chromium are found by direct calculation without any preliminary suggestions about the atom valence state. There is no possibility of taking into account the spectral information in the optimization process when using a narrow set of reference compounds. This point applies equally to the dipole moment calculations. Because of large interatomic distances and different electronegativity, small changes of effective atomic charge

TABLE 4: Ionization Potentials and Dipole Moments of Chromium Compounds

compound	IP, eV		compound	μ , D	
	calc	exp ¹⁶		calc	exp ¹⁹
CrO ₃	15.3	18.0	Cr(C ₅ H ₅)	0.02	0.00
Cr(C ₆ H ₆) ₂	7.1	5.5	Cr(C ₆ H ₆) ₂	0.00	0.00
Cr[C ₆ H ₅ -CH ₃] ₂	7.1	5.3	Cr[C ₆ H ₅ -CH ₃] ₂	0.01	0.00
Cr[C ₆ H ₅ -C ₂ H ₅] ₂	7.1	5.3	Cr(C ₆ H ₆)(CO) ₃	2.91	5.08
Cr[C ₆ H ₅ - <i>i</i> -C ₃ H ₇] ₂	7.0	5.2	Cr(C ₆ H ₅ -CH ₃)(CO) ₃	2.62	5.20
Cr(C ₆ H ₆)(CO) ₃	6.3	7.4	Cr(C ₆ H ₅ -OCH ₃)(CO) ₃	2.13	5.26
Cr(C ₆ H ₃ (CH ₃) ₃)(CO) ₃	6.4	7.3	Cr(C ₆ H ₃ (CH ₃) ₃)(CO) ₃	2.04	5.81
Cr(CO) ₆	6.8	8.1	Cr(CO) ₆	0.50	0.00

may result in large deviations of dipole moments. We suggest that these results may be sufficiently improved by a more comprehensive and careful parameter adjustment with a wide set of reference compounds, as has been demonstrated in ref 3.

Close inspection of the performance and convergence questions shows that the SCF convergence with the new integral estimation procedure remains rapid. Only the first SCF calculation requires a large number of iterations (50–100). Further SCF calculations achieve the accuracy goal 10⁻⁵ eV with 10–15 iterations. The two-electron integral calculation is comparable in time to the calculation using the point charge model. The SCF procedure is the most time-consuming process, and the integral calculation time is not a determining factor in computations. The calculation on Cr(C₆H₆)₂ (66 orbitals, 69 geometry parameters) with full geometry optimization requires about 20 min on an IBM 486/50 MHz (starting from the experimental structure).

On the basis of the above results, one may conclude that the new electron interaction model based on the assumption of the universal character of the Ohno potential is valid and that the two-electron integral estimation procedure founded on this model permits a proper description of the thermochemical, electron, and geometry parameters of chromium compounds. The advantages of the approach based on the bipolar expansion technique of the Ohno potential are the possibility of deriving and using various levels of approximations in a successive manner, the independence of the kind of basis AO's (s,p,d,f,...), high performance, and stability in computations. Thus, the new integral estimation procedure presented has a number of important advantages and seems to be very promising in terms of its application in the framework of semiempirical methods based on the NDDO approximation.

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