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On the Calculation of Bonding Energies by the Hartree Fock Slater Method

I. The Transition State Method

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A transition state method has been proposed for the calculation of bonding energies and bond distances within the Hartree Fock Slater Method. Calculations on a number of diatomic molecules and a few transition metal complexes show better agreement with experiment than corresponding Hartree Fock results. The proposed transition state method gives a direct connection between bond orders and bonding energies.

Key words: Bonding energies and bond orders

1. Introduction

The Hartree Fock Slater method has proved itself a powerful tool for the calculation of ionization energies [1], electronic excitation energies [2] and one-electron expectation values [3]. It is shown in this communication that the method is equally useful for the calculation of bonding energies, D_e, and bond distances, R_e. Some promising results have already been presented by Sambe and Felton [4] and by Heijser, Kessel and Baerends [5]. Both groups introduced some approximations in their calculations. Sambe and Felton represented ρ and $\rho^{1/3}$ by a number of auxiliary functions centred on the nuclei, but retained only the $l=0$ components. The higher order terms are all included in the DVM-HFS method by Baerends *et al.* [6]. The problem here is the particular numerical integration scheme used to evaluate all relevant matrix elements. Experience [6] has shown that the Diophantine numerical integration scheme can calculate Hartree Fock Slater matrix elements to a good accuracy with relatively few sample points, whereas the number of points required to evaluate the statistical energy is as much as two orders of magnitude higher. Such numbers of sample points impose a prohibitive computational effort even for the smallest of systems. Thus the Dutch group [5] was forced to use less than the required number of points. Bond distances have also been calculated by the Multiple Scattering method in which the Muffin-tin approximation is applied [7].

We have introduced a transition state method for calculation of bonding energies in Sect. 2. By evaluating some parts of the bonding energy analytically, quite accurate results are obtained using the same number of points necessary for the calculation of Hartree Fock Slater matrix elements, without increasing the computation time significantly. Results from calculations on some diatomic molecules and a few transition metal complexes are shown in Sect. 3.

2. Evaluation of Bonding Energies

2.1. *The Statistical Energy Expression*

The total statistical energy due to an electronic system with the one-electron density $\rho_1(X_1, X_1')$ is given by [8]:

$$\begin{aligned} E_{\mathrm{HFS}} = & \int\limits_{X=X'} f(X_1')\rho_1(X_1, X_1')\,\mathrm{d}X_1 \\ & + \tfrac{1}{2}\int \rho_1(X_1)\rho_1(X_2)/r_{12}\,\mathrm{d}X_1\,\mathrm{d}X_2 \\ & + \tfrac{3}{4}\int \rho_1^{\alpha}(\boldsymbol{r}_1) V_{\mathrm{HFS}}^{\alpha}(\boldsymbol{r}_1)\,\mathrm{d}\boldsymbol{r}_1 \\ & + \tfrac{3}{4}\int \rho_1^{\beta}(\boldsymbol{r}_1) V_{\mathrm{HFS}}^{\beta}(\boldsymbol{r}_1)\,\mathrm{d}\boldsymbol{r}_1 \\ & + \tfrac{1}{2}\sum_{A \neq B}^{\text{nuclei}}\sum Z_A Z_B/|\boldsymbol{R}_A - \boldsymbol{R}_B|. \end{aligned} \tag{2.1}$$

Where $f(X_1)$ is the sum of the operators for the kinetic energy of the electrons and the attraction energy between the electrons and the nuclei. The functions $\rho_1^{\alpha}(\boldsymbol{r}_1)$ and $\rho_1^{\beta}(\boldsymbol{r}_1)$ are the densities of electrons with spin up and spin down respectively, and X_1 is the generalized co-ordinate of an electron at position $\boldsymbol{r}_1$ with the spin co-ordinate s_1. The function $V_{\mathrm{HFS}}^{\alpha}(\boldsymbol{r}_1)$, characteristic for the HFS-method, is given by

$$V_{\mathrm{HFS}}^{\alpha}(\boldsymbol{r}_1) = -3\mathrm{k}[\tfrac{3}{4}\pi\rho^{\alpha}(\boldsymbol{r}_1)]^{1/3}, \tag{2.2}$$

with a similar expression for $V_{\mathrm{HFS}}^{\beta}(\boldsymbol{r}_1)$, where k is the so-called exchange scale factor taken to be 0.7 for the rest of this work [6, 9]. The last term in Eq. (2.1) represents the electrostatic repulsion between the different nuclei Z_A and Z_B.

2.2. *The Hartree-Fock Slater One-Electron Equation*

The one electron HFS equation [8] is derived by writing $\rho_1^{\alpha}(\boldsymbol{r}_1)$ and $\rho_1^{\beta}(\boldsymbol{r}_1)$ in terms of molecular orbitals and the corresponding occupation numbers as

$$\rho_1^{\alpha}(\boldsymbol{r}_1) = \sum_i n_i^{\alpha} u_i^{\alpha}(\boldsymbol{r}_1) u_i^{\alpha}(\boldsymbol{r}_1), \tag{2.3}$$

and require that the total energy shall be stable with respect to any variation in the orbital set $\{u_i^\alpha(\boldsymbol{r}_1)\}$. The system of equations for $u_i^\alpha(\boldsymbol{r}_1)$ has the form

$$h^\alpha(\boldsymbol{r}_1)u_i^\alpha(\boldsymbol{r}_1)=\varepsilon_i^\alpha u_i^\alpha(\boldsymbol{r}_1) \tag{2.4}$$

where

$$h^\alpha(\boldsymbol{r}_1)=f(\boldsymbol{r}_1)+\int\rho_1(X_2)/r_{12}\,\mathrm{d}X_2+V_{\mathrm{HFS}}^\alpha(\boldsymbol{r}_1), \tag{2.5}$$

with a similar equation for orbitals of spin down, $u_i^\beta(\boldsymbol{r}_1)$. The orbital energy ε_i^α can be related to the total energy E_{HFS} [8] by considering the derivative $\mathrm{d}E_{\mathrm{HFS}}/\mathrm{d}n_i^\alpha$ given by

$$\mathrm{d}E_{\mathrm{HFS}}/\mathrm{d}n_i^\alpha=(\delta E_{\mathrm{HFS}}/\delta\rho_1)_{n_i^\alpha}(\delta\rho_1/\delta n_i^\alpha)_{u_j}+(\delta E_{\mathrm{HFS}}/\delta n_i^\alpha)_{u_j}. \tag{2.6}$$

The first term is zero since E_{HFS} is assumed stable to any variation in the orbital set $\{u_i\}$ for a fixed set of occupation numbers, thus

$$(\delta E_{\mathrm{HFS}}/\delta\rho_1)_{n_i^\alpha}=0. \tag{2.6a}$$

The second term of Eq. (2.6) gives after substitution of Eq. (2.3) into Eq. (2.1) and straightforward differentiation

$$(\delta E_{\mathrm{HFS}}/\delta n_i^\alpha)_{u_j}=\varepsilon_i^\alpha. \tag{2.7}$$

The subscript u_j in Eq. (2.7) indicates that the orbital set is fixed. We will use Eq. (2.7) in the next section.

2.3. *The Transition State Method for the Calculation of Bonding Energies*

Consider the molecule $\overline{\mathrm{AB}}$ with a one electron density $\rho_{\overline{\mathrm{AB}}}$, where the subscript $\overline{\mathrm{AB}}$ indicates that the molecule is formed from the two electronic systems A and B with densities ρ_{A} and ρ_{B}. The energies of A, B and $\overline{\mathrm{AB}}$ are defined by the one-electron densities and might be written as $E(\rho_{\mathrm{A}})$, $E(\rho_{\mathrm{B}})$ and $E(\rho_{\overline{\mathrm{AB}}})$ respectively. It is likewise possible to define an energy for the density $\rho_{\mathrm{AB}}=\rho_{\mathrm{A}}+\rho_{\mathrm{B}}$ for any distance between A and B. The energy $E(\rho_{\mathrm{AB}})$ is given by

$$E(\rho_{\mathrm{AB}})=E(\rho_{\mathrm{A}})+E(\rho_{\mathrm{B}})+E_{el}+\Delta E_{ex}^\alpha+\Delta E_{ex}^\beta, \tag{2.8}$$

where

$$\begin{aligned}E_{el}=&\sum_{g\mathrm{A}}\sum_{g\mathrm{B}}Z_{g_{\mathrm{A}}}Z_{g_{\mathrm{B}}}/|\boldsymbol{R}_{g_{\mathrm{A}}}-\boldsymbol{R}_{g_{\mathrm{B}}}|+\int\rho_{\mathrm{A}}(\boldsymbol{r}_1)\rho_{\mathrm{B}}(\boldsymbol{r}_2)/r_{12}\,\mathrm{d}\boldsymbol{r}_1\,\mathrm{d}\boldsymbol{r}_2\\&-\sum_{g\mathrm{A}}\int\rho_{\mathrm{B}}(\boldsymbol{r}_1)Z_{g_{\mathrm{A}}}/|\boldsymbol{r}_1-\boldsymbol{R}_{g_{\mathrm{A}}}|\mathrm{d}\boldsymbol{r}_1-\sum_{g\mathrm{B}}\int\rho_{\mathrm{A}}(\boldsymbol{r}_1)Z_{g_{\mathrm{B}}}/|\boldsymbol{r}_1-\boldsymbol{R}_{g_{\mathrm{B}}}|\,\mathrm{d}\boldsymbol{r}_1\end{aligned} \tag{2.9}$$

is the electrostatic interaction between molecule A and B, and

$$\begin{aligned}\Delta E_{ex}^\alpha=&-\tfrac{3}{4}\int\rho_{\mathrm{A}}^\alpha(\boldsymbol{r}_1)V_{\mathrm{HFS}}^\alpha(\rho_{\mathrm{A}}^\alpha(\boldsymbol{r}_1))\,\mathrm{d}\boldsymbol{r}_1-\tfrac{3}{4}\int\rho_{\mathrm{B}}^\alpha(\boldsymbol{r}_1)V_{\mathrm{HFS}}^\alpha(\rho_{\mathrm{B}}^\alpha(\boldsymbol{r}_1))\,\mathrm{d}\boldsymbol{r}_1\\&+\tfrac{3}{4}\int\rho_{\mathrm{AB}}^\alpha(\boldsymbol{r}_1)V_{\mathrm{HFS}}^\alpha(\rho_{\mathrm{AB}}^\alpha(\boldsymbol{r}_1))\,\mathrm{d}\boldsymbol{r}_1,\end{aligned} \tag{2.10}$$

with a similar expression for ΔE_{ex}^β.

The densities ρ_{AB} and $\rho_{\overline{\mathrm{AB}}}$ can both be expressed in terms of the occupied and virtual orbitals of A and B called $\{u_i\}$ as

$$\rho_{\mathrm{AB}} = \sum_i P^{\alpha}_{ii} u^{\alpha}_i(\boldsymbol{r}_1) u^{\alpha}_i(\boldsymbol{r}_1) + \sum_i P^{\beta}_{ii} u^{\beta}_i(\boldsymbol{r}_1) u^{\beta}_i(\boldsymbol{r}_1) \tag{2.11}$$

and

$$\rho_{\overline{\mathrm{AB}}} = \sum_{ij} (P^{\alpha}_{ii} + \Delta P^{\alpha}_{ij}) u^{\alpha}_i(\boldsymbol{r}_1) u^{\alpha}_j(\boldsymbol{r}_1) + \sum_{ij} (P^{\beta}_{ii} + \Delta P^{\beta}_{ij}) u^{\beta}_i(\boldsymbol{r}_1) u^{\beta}_j(\boldsymbol{r}_1). \tag{2.12}$$

There P_{ii} is the bond order matrix for ρ_{AB} and $P_{ij} \cdot \delta_{ij} + \Delta P_{ij}$ the bond order matrix for $\rho_{\overline{\mathrm{AB}}}$, both with respect to the basis $\{u_i\}$.

It is further expedient to introduce a transition state density ρ_T, the average density of ρ_{AB} and $\rho_{\overline{\mathrm{AB}}}$, given by

$$\rho_T = \sum_{ij} Q^{\alpha}_{ij} u^{\alpha}_i(\boldsymbol{r}_1) u^{\alpha}_j(\boldsymbol{r}_1) + \sum_{ij} Q^{\beta}_{ij} u^{\beta}_i(\boldsymbol{r}_1) u^{\beta}_j(\boldsymbol{r}_1), \tag{2.13}$$

where

$$Q^{\alpha}_{ij} = P^{\alpha}_{ij}\, \delta_{ij} + \tfrac{1}{2} \Delta P^{\alpha}_{ij}. \tag{2.14}$$

Substitution of Eq. (2.13) into Eq. (2.1) and straightforward differentiation gives us the relation

$$(\delta E(\rho_T)/\delta Q^{\alpha}_{ij}) = {}^{\alpha}F^{T}_{ij} \tag{2.15}$$

where

$${}^{\alpha}F^{T}_{ij} = \int u^{\alpha}_i(\boldsymbol{r}_1) h^{\alpha}_T(\boldsymbol{r}_1) u^{\alpha}_j(\boldsymbol{r}_1)\, \mathrm{d}\boldsymbol{r}_1, \tag{2.16}$$

and

$$h^{\alpha}_T(\boldsymbol{r}_1) = f(X_1) + \int \rho_T(\boldsymbol{r}_2)/r_{12}\, \mathrm{d}\boldsymbol{r}_2 + V^{\alpha}_{\mathrm{HFS}}(\rho^{\alpha}_T(\boldsymbol{r}_1)). \tag{2.17}$$

Equation (2.15), which is a generalization of Eq. (2.7), now enables us to calculate the bonding energy $\Delta E = -E(\rho_{\overline{\mathrm{AB}}}) + E(\rho_{\mathrm{A}}) + E(\rho_{\mathrm{B}})$ in the following way. The energies $E(\rho_{\mathrm{AB}})$ and $E(\rho_{\overline{\mathrm{AB}}})$ are expressed as a Taylor expansion in terms of $E(\rho_T)$ and its first and second derivatives with respect to Q_{ij},

$$\begin{aligned} E(\rho_{\mathrm{AB}}) = E(\rho_T) &- \tfrac{1}{2} \sum_{ij} \delta E(\rho_T)/\delta Q_{ij}\, \Delta P_{ij} \\ &+ \tfrac{1}{8} \sum_{kl} \sum_{ij} (\delta^2 E(\rho_T)/\delta Q_{ij}\, \delta Q_{kl})\, \Delta P_{ij}\, \Delta P_{kl} \end{aligned} \tag{2.18}$$

$$\begin{aligned} E(\rho_{\overline{\mathrm{AB}}}) = E(\rho_T) &+ \tfrac{1}{2} \sum_{ij} (\delta E(\rho_T)/\delta Q_{ij})\, \Delta P_{ij} \\ &+ \tfrac{1}{8} \sum_{kl} \sum_{ij} (\delta^2 E(\rho_T)/\delta Q_{ij}\, \delta Q_{kl})\, \Delta P_{ij}\, \Delta P_{kl}, \end{aligned} \tag{2.19}$$

where i, j, k and l runs over orbitals of spin up as well as spin down. The two equations (2.18) and (2.19) give

$$E(\rho_{\overline{\mathrm{AB}}}) - E(\rho_{\mathrm{AB}}) = \sum_{ij} F^{T}_{ij}\, \Delta P_{ij}. \tag{2.20}$$

Finally for the bonding energy one gets from Eq. (2.8)

$$-E(\rho_{\overline{\mathrm{AB}}})+E(\rho_{\mathrm{A}})+E(\rho_{\mathrm{B}})=-E_{el}-\Delta E_{ex}-\sum_{ij}F_{ij}^{T}\,\Delta P_{ij} \tag{2.21}$$

correct to the second order derivatives of $E(\rho_T)$ with regard to Q_{ij}. Here i and j in Eq. (2.21) run over orbitals of spin up and spin down.

The third order derivatives contribute to the bonding energy with the term

$$\sum_{ij}E_{ij}^{(3)}\,\Delta P_{ij}=-\tfrac{1}{24}\sum_{ij}\sum_{kl}\sum_{mn}(\delta^3E_T/\delta Q_{ij}\,\delta Q_{kl}\,\delta Q_{mn})\,\Delta P_{kl}\,\Delta P_{nm}\,\Delta P_{ij}. \tag{2.22}$$

This term can be incorporated into Eq. (2.21) by observing that

$$\begin{aligned}F_{ij}^{\mathrm{AB}}=(\delta E_{\mathrm{AB}}/\delta Q_{ij})=F_{ij}^{T}-\tfrac{1}{2}\sum_{kl}(\delta^2E_T/\delta Q_{ij}\,\delta Q_{kl})\,\Delta P_{kl}\\+\tfrac{1}{8}\sum_{kl}\sum_{mn}(\delta^3E_T/\delta Q_{ij}\,\delta Q_{kl}\,\delta Q_{mn})\,\Delta P_{kl}\,\Delta P_{mn}\end{aligned} \tag{2.23}$$

and

$$\begin{aligned}F_{ij}^{\overline{\mathrm{AB}}}=(\delta E_{\overline{\mathrm{AB}}})/\delta Q_{ij})=F_{ij}^{T}+\tfrac{1}{2}\sum_{kl}(\delta^2E_T/\delta Q_{ij}\,\delta Q_{kl})\,\Delta P_{kl}\\+\tfrac{1}{8}\sum_{kl}\sum_{mn}(\delta^3E_T/\delta Q_{ij}\,\delta Q_{kl}\,\delta Q_{mn})\,\Delta P_{kl}\,\Delta P_{mn}.\end{aligned} \tag{2.24}$$

Thus

$$E_{ij}^{(3)}=\tfrac{1}{3}F_{ij}^{T}-\tfrac{1}{6}F_{ij}^{\mathrm{AB}}-\tfrac{1}{6}{}_{ij}^{\overline{\mathrm{AB}}}. \tag{2.25}$$

Since all even order contributions to the bonding energy are zero one gets the following expression for the bonding energy, correct to the fourth order

$$\Delta E=-E_{el}-\Delta E_{ex}-\sum_{ij}\left\{\tfrac{2}{3}F_{ij}^{T}+\tfrac{1}{6}F_{ij}^{\mathrm{AB}}+\tfrac{1}{6}F_{ij}^{\overline{\mathrm{AB}}}\right\}\Delta P_{ij}, \tag{2.26}$$

where F_{ij}^{T}, F_{ij}^{AB}, $F_{ij}^{\overline{\mathrm{AB}}}$ are the matrix elements over the set $\{u_i\}$ with respect to the Hartree-Fock-Slater operators constructed from the densities ρ_T, ρ_{AB} and $\rho_{\overline{\mathrm{AB}}}$ respectively.

3. Results and Discussion

3.1. Computational Procedure

The HFS one-electron equation is solved in the DVM-HFS method [6] by evaluating all HFS matrix elements in the Diophantine numerical integration scheme [10, 11]. One might attempt to calculate bonding energies from the expression given in Eq. (2.26) by the same numerical method. The result is shown in Table 1 for F_2 as a function of the number of sample points, under ΔE_1. About 100,000 points seem necessary to acquire an accuracy of about 0.01 a.u. An analysis showed that the slow convergence of ΔE_1 as a function of the number of sample points was due to the first term in Eq. (2.26), E_{el}.

Table 1. The entry ΔE_1 is the bonding energy of the F_2 molecule calculated at $R=2.717$ a.u. from numerical integration of all three terms in Eq. (2.26). The entry ΔE_2 is the bonding energy of the same molecule calculated by analytical integration of the first term, E_{el}, of Eq. (2.26). Both ΔE_1 and ΔE_2 are shown as a function of the number of sample points.

	Number of sample points				
	1.000	10.000	20.000	40.000	100.000
ΔE_1 (a.u.)	0.3171	0.2361	0.1474	0.0721	0.1142
ΔE_2 (a.u.)	0.1184	0.1204	0.1210	0.1210	0.1211

This problem was circumvented by calculating E_{el} analytically from a fit (least square) of ρ_A and ρ_B over Slater-type functions placed on the different centres [6]. The calculation of E_{el} then requires the evaluation of two centre Coulomb integrals and electron-nuclei attraction integrals for which efficient programs already exist. The bonding energy in which E_{el} is calculated analytically and the two remaining terms of Eq. (2.26) numerically is shown in Table 1, as ΔE_2. The difference between ΔE_2 calculated at 1,000 points and 100,000 points is now 0.003 a.u.

We are looking for a method which can calculate the statistical bonding energy to an accuracy of ± 0.005 a.u., for the same number of sample points used to obtain molecular orbitals and molecular orbital energies. Such an accuracy is obtained in the case of F_2 where one would use typically 1,000 points (500 points for each first row element) to solve the HFS one electron equation.

Calculations on a number of diatomic molecules (see Sect. 3.2 and Sect. 3.3) with 1,000 points and 10,000 points, and a few transition metal complexes with 2,000 points and 15,000 points, showed in all cases a difference in ΔE_2 less than 0.005 a.u. It thus appears that the method described above gives the required accuracy (± 0.005 a.u.) at least for the sample of compounds discussed in the next two sections.

3.2. Calculation on Diatomic Molecules

The Hartree-Fock energy $E_{HF}(R)$ is the expectation value of an optimal one-determinantal wave function with respect to the exact Hamiltonian.

The statistical energy expression $E_{HFS}(R)$ is on the other hand a model based on some physical assumptions [8]. We found it interesting to compare $E_{HFS}(R)$ with $E_{HF}(R)$ and experimental results, $E_{ex}(R)$. This is done in Table 2 in terms of the spectroscopic constants, R_e, D_e and ω_e. The function $E_{HFS}(R)$ from HFS calculations with an extended (Ext) basis gives in all cases values for D_e, R_e and ω_e in better agreement with experiment than E_{HF} (R) from HF calculation using a similar basis. This is shown in detail for N_2 and the first three states of N_2^+ in Fig. 1.

Experiment, Fig. 1b, reveals a convergence of the two N_2^+ states, X and A, at large inter-atomic distances, and a cross-over of A and B at small distances. Both trends are reproduced by $E_{HFS}(R)$ but not by $E_{HF}(R)$ where, in addition the A state

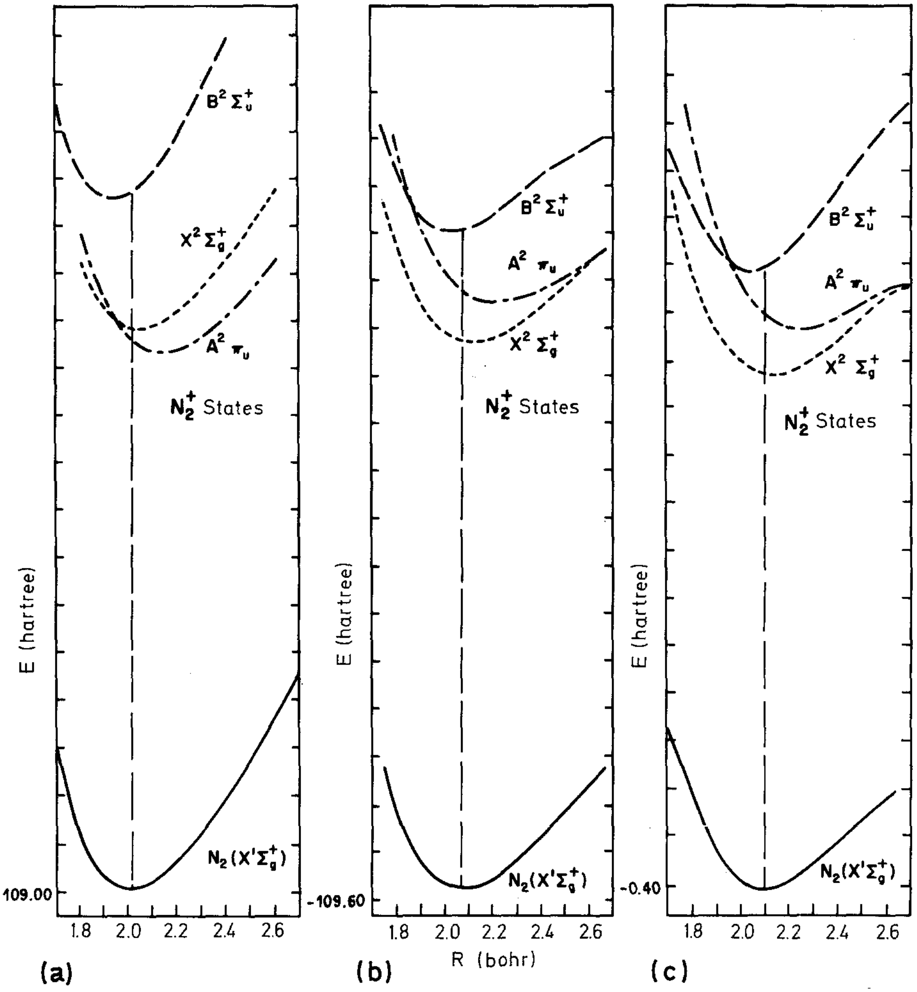

Fig. 1. The energy of N_2 and the first three states of N_2^+ as a function of the inter-atomic distance. Fig. 1a is from HF calculations [12], Fig. 1b from a KKR analysis [12] and Fig. 1c from HFS calculations. The unit at the ordinate is 0.05 a.u.

is placed below *X*. Results from double zeta (DZ) calculations, Table 2, show that basis set effects are important, but it is hoped that these effects are less severe for molecules with longer inter-atomic distances.

3.3. Calculation on Transition Metal Complexes

The three tetrahedral oxo complexes MnO_4^-, CrO_4^{2-} and RuO_4 were chosen as test cases for transition metal complexes, since rather extensive HF calculations have been performed on MnO_4^-. The results from double zeta HFS calculations

Table 2. Calculation of bond distances (R_e), bond energies (D_e) and vibrational frequencies (ω_e) from HFS double zeta-(DZ) and extended (EXT) basis set calculations compared to experiment[a] and results from extended HF calculation[a]. The spectroscopic constants were obtained from a cubic fit of 9 independent calculations around R_e.

	R_e (a.u.)				D_e (ev.)				ω_e (cm^{-1})			
	DZ	EXT	HF	EXP	DZ	EXT	HF	EXP	DZ	EXT	HF	EXP
F_2	2.75	2.61	2.51	2.68	3.04	3.54	−1.63	1.67	890	1207	1257	892
O_2	2.45	2.33	2.18	2.28	2.45	4.14	1.43	5.22	1364	1563	2000	1580
N_2	2.17	2.11	2.01	2.07	9.38	10.86	5.27	9.91	2125	2456	2730	2358
$N_2(+)$-X[b]		2.11	2.04	2.11						2382	2570	2207
$N_2(+)$-A		2.23	2.13	2.22						2084	2312	1902
$N_2(+)$-B		2.04	1.94	2.03						2606	3101	2419
CO	2.24	2.16	2.08	2.13	7.58	9.41	7.89	11.22	1946	2248	2431	2170
NO	2.33	2.19		2.17	4.95	6.42		6.62	1640	1903		1904

[a] Ref. [5]. [b] Ref. [12].

are shown in Table 3. Here R_e is the metal to ligand equilibrium bond distance, ω_e the total symmetric stretching frequency and D_e the energy for the process:

$$M + 4O + ne^- \longrightarrow MO_4^{n-}, \tag{3.1}$$

where a positive value for D_e indicates that MO_4^{n-} is stable with respect to its components. The bonding energy is only known experimentally for RuO_4 where Nikol'skii *et al.* [3] give the value 0.7012 a.u. It is to be expected that D_e should be positive for all three complexes and an estimate based on the known bonding energies of MnO_2 and CrO_3 gives a value around 0.7 a.u. for both CrO_4^{2-} and MnO_4^-.

Table 3. Calculations of bond distances (R_e), the symmetric stretching frequency ω_e and bonding energies D_e for some tetrahedral oxocomplexes in a DZ-basis. A_1^1 is the groundstate corresponding to the configuration $(t_1)^6$ and T_2^1 is the excited state corresponding to the configuration $(t_1)^5(2e)^1$. The transition $A_1^1 \rightarrow T_2^1$ is the first dipole allowed excitation for all three complexes [2]. The spectroscopic constants were obtained from a cubic fit of 5 independent calculations around R_e.

		R (a.u.)		ω_e (cm^{-1})		D_e (a.u.)	
	State	cal	exp	cal	exp	cal	exp
MnO_4^-	A_1^1	3.05	3.08[a]	776	838[b]	0.6033	~0.7[f]
	T_2^1	3.12	—	770	777[c]		
CrO_4^{2-}	A_1^1	3.13	3.14[a]	916	840[b]	0.6429	~0.7
	T_2^1	3.20	—	876	722[d]		
RuO_4	A_1^1	3.25	3.21[a]	851	883[b]	0.7481	0.7012[g]
	T_2^1	3.37		803	782[e]		

[a] Ref. [16]. [b] Ref. [17]. [c] Ref. [18]. [d] Ref. [19]. [e] Ref. [20]. [f] Ref. [14]. [g] Ref. [13].

The HFS method predicts all three complexes, Table 3, to be strongly bonding and thus stable with respect to their components.

A HF calculation of MnO_4^- in a minimal basis set by Dacre *et al.* [14] gave a bonding energy of -0.513 a.u. The authors in Ref. [14] ascribed the large discrepancy to the use of a rather small basis. Johansen [15] has recently carried out a near HF limit calculation on the same complex from which he obtained $D_e = -0.225$, thus the calculated bonding energy still has the wrong sign!

Negative values for D_e were also obtained from near HF limit calculations of ClO_4^- and PO_4^{3-} whereas a large basis set calculation on SO_4^{2-} only gave a small positive bonding energy [15]. All three compounds are assumed to be strongly bonding.

The bonding energies calculated by the HF method is a lower bond to the experimental value, thus the inclusion of configuration interaction (CI) would gradually increase the bonding energy towards the correct value. In the case of MnO_4^- as much as 0.9 a.u. has to be accounted for by CI calculations. The HFS method on the other hand avoids CI calculations by utilizing a model energy functional (the statistical energy expression). It seems, Table 3, that the statistical energy expression is well suited for the calculation of D_e, ω_e and R_e, at least for the complexes treated in this section.

4. Summary

It is hoped that the procedure outlined and applied in the previous sections finally will make it possible to apply the HFS method to problems concerning the structure and reactivity of molecules.

The transition state method presented in Sect. 2 was developed in order to study the weakly bonding interactions between metal fragments and organic molecules as they occur in catalysis and chemisorption. We will show in a forthcoming communication how such interactions can be studied in depth from the last term of Eq. (2.26), where a direct relation is given between bond orders, ΔP_{ij}, and the bonding energy.

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References

1. Baerends, E. J., Ros, P.: Chem. Phys. **2**, 52 (1973)
2. Ziegler, T., Rauk, A., Baerends, E. J.: Theoret. Chim. Acta. (Berl.) in press
3. *Dipole moments:* Baerends, E. J., Ros, P.: Chem. Phys. **8**, 412 (1975)
   Polarizability: Trsic, M., Ziegler, T., Laidlaw, W. G.: Chem. Phys. **15**, 383 (1976)
   Magnetic Circular Dicroism: Ziegler, T., Rauk, A., Baerends, E. J.: Chem. Phys. **16**, 209 (1976)
   Oscillatory Strengths and Circular Dicroism: Rauk, A., Barriel, J. M., Ziegler, T.: Progress in theoretical organic chemistry, Vol. 2. Amsterdam: Elsevier 1976

4. Sambe, H., Felton, R. H.: J. Chem. Phys. **62**, 1122 (1975)
5. Heijser, W., van Kessel, G., Baerends, E. J.: Chem. Phys. **16**, 372 (1976)
6. Baerends, E. J., Ellis, D. E., Ros, P.: Chem. Phys. **2**, 41 (1973)
7. Salahub, D. R., Messmer, R. P., Johnson, K. H.: Mol. Phys. **31**, 521 (1976)
8. Slater, J. C.: Advan. Quantum Chem. **6**, 1 (1972)
9. Gopinathan, M. S., Whitehead, M. G., Bogdanovic, R.: Phys. Rev. A. **1** (1974)
10. Ellis, D. E.: Intern. J. Quantum Chem. **25**, 35 (1968)
11. Conroy, H.: J. Chem. Phys. **47**, 5307 (1967)
12. Cade, P. E., Sales, K. D., Wahl, A. C.: J. Chem. Phys. **44**, 1973 (1966)
13. Nikol'skii, A. B., Rybov, A. N.: Russ. J. Inorg. Chem. **101**, 1 (1965)
14. Dacre, P. D., Elder, M.: Chem. Phys. Letters **11**, 377 (1971)
15. Johansen, H.: Chem. Phys. Letters **17**, 569 (1972)
16. Kalman, A.: J. Chem. Soc. A 1857 (1971)
17. Basile, L. J., Ferraro, J. R., LaBonville, P., Wall, M. C.: Coord. Chem. Rev. **11**, 21 (1973)
18. Johnson, L. W., McGlynn, S. P.: Chem. Phys. Letters **10**, 184 (1971)
19. Johnson, L. W., McGlynn, S. P.: Chem. Phys. Letters **95**, 618 (1973)
20. Foster, S., Felpd, S., Johnson, L. W., Larson, D. B., McGlynn, S. P.: J. Am. Chem. Soc. **95**, 6578 (1973)

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