

## **Decomposition of the interaction energy between metal cations and water or ammonia with inclusion of counterpoise corrections to the interaction energy terms**

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**Summary.** *Ab initio* calculations for complexes of some metal cations ( $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{Be}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Al}^{3+}$ ) with water or ammonia as ligands were performed employing the MINI-1 basis set. The counterpoise-corrected components of the interaction energy were analyzed as a function of the intersystem distance. Results are compared with the corresponding 4-31G and 6-31G\* data for the  $\text{Li}^+$  and  $\text{Be}^{2+}$  complexes. The analysis contributes to both an evaluation of the quantum chemical description and a general understanding of this type of interaction.

**Key words:** Cation complexes — Counterpoise correction — Interaction energy analysis

### **1. Introduction**

A considerable number of recent calculations on weakly bonded chemical systems estimate the basis set superposition error (BSSE) by means of counterpoise (CP) corrections [1]. There is an almost general agreement about the benefits of the CP corrections for calculations performed with basis sets of low and medium size. Calculations with these basis set levels should continue in the foreseeable future at least for systems consisting of large monomeric components or aggregations of numerous small molecules.

Whereas in small chemical systems it is usual for only one specific type of local interaction to dominate, several different types of local interactions often act at the same time in large chemical systems. Frequently, interactions between neutral subunits are accompanied by interactions involving charged constituents. Thus, the attention paid in the last years to the effect of CP corrections to neutral dimers should be supplemented by similar analyses involving this type of

interaction, even if intuition suggests that in the case of metal cation-neutral ligand interactions, the CP corrections should be less important. For complex systems, it is paramount that an unbalanced description of the various local interactions be avoided. Therefore, the introduction of CP corrections solely for neutral-neutral interaction components could be responsible for an erroneous treatment of the interaction phenomena.

Keeping in mind that the principal motivation for studies on the effect of CP corrections has a practical origin, namely the search for methods which are able to provide realistic descriptions of the interaction without excessive use of computational time, it is convenient to combine the analysis of the effect of CP correction on the interaction energy hypersurface  $\Delta E(R)$  with an analysis of the interaction energy *after* CP correction. An interpretation of the set of single numbers (scalars) obtained by the evaluation of  $\Delta E$  at specific points of the  $R$  hypersurface in a model system is a necessary prerequisite for deriving rules and methods for low cost calculations of sufficient reliability. Until now, it has been convenient to use the variational approach at the Hartree-Fock (HF) level leaving further refinements, if necessary, to post-HF calculations [2].

The method for making CP corrections to the separate components of the HF interaction energy proposed by our group a few years ago [3] combines simplicity in the execution with physical plausibility of the results. Thus, it has given valuable suggestions on possible simplifications of the computational scheme. The method may be applied to different decomposition schemes of the HF interaction energy, the most popular is the Kitaura-Morokuma (KM) [4] scheme, and to different versions of the CP procedure. It should be mentioned that there is still a debate on the merits of the "full" CP correction. One of the most recent versions of the "partial" CP correction relies on the use of our CP corrections to the decomposition of  $\Delta E$  [5].

In this paper, we have performed a decomposition of the interaction energy for metal cation-neutral ligand complexes and determined the CP corrections to the various interaction energy components. We limit our analysis to a selected number of metal cations interacting with water and ammonia. The MINI-1 basis set [6], which gives rise to small BSSEs [7, 8], was selected for our analyses. For comparison, calculations employing the 4-31G and 6.31G\* basis sets were also performed. Because of the limited selection of material systems and basis sets, a complete appreciation of all aspects of CP corrections over the whole range of leading variables (chemical composition and basis set) is not intended. However, the results presented here seem to be sufficient to get a fairly accurate description of the cation-ligand interactions, especially when considered together with those reported for a wide variety of other metal-ligand couples in a preceding paper [9].

## 2. Outline of the decomposition method with CP corrections

The formal and computational aspects of the method have been discussed in preceding papers [3, 10–12]. For the sake of convenience, it may be sufficient, therefore, to recall the terminology here.

First, the interaction energy between two monomers  $A$  and  $B$  is split into two parts. One component ( $DEF$ ) corresponds to a shift in the reference energy arising from the deformation of the internal geometry of the monomers, here the ligands, at the equilibrium structure of the dimer; the other component corresponds to an interaction term ( $INT$ ) regarding the deformed monomers:

$$\Delta E(AB; R) = DEF + INT(R). \quad (1)$$

Only the term  $INT$  is subjected to further decomposition and to CP corrections. This approximation, suggested by Umeyama et al. [13], can be applied here without any particular problems because  $DEF$  is quite small with respect to  $INT$  for our ligands (Table 4). The consideration of  $DEF$  may be important, however, if the geometry distortion caused by the cations is indeed large or is artificially increased by the inferiority of the basis set in comparison to the CP correction. In the KM scheme [4], the decomposition of  $\Delta E(AB; R)$  is written without CP corrections:

$$\Delta E(AB; R) = DEF + ES(R) + PL(R) + EX(R) + CT(R) + MIX(R). \quad (2)$$

In this equation, the terms  $ES$ ,  $PL$ ,  $EX$ ,  $CT$ , and  $MIX$  denote the electrostatic, the polarization, the exchange-repulsion, the charge transfer, and the so-called "mixed" rest energy components of the interaction energy, respectively. The CP correction to  $\Delta E(AB; R)$  is represented by  $\Delta^{TOT}$ , and it is obtained with the usual "full" CP procedure, i.e. by calculation of the reference energy of the monomers with the full dimeric basis set at each distance  $R$ :

$$\Delta^{TOT} = DE^{CP}(AB; R) - \Delta E(AB; R). \quad (3)$$

The superscript  $CP$  indicates quantities corrected with the CP procedure.  $\Delta^{TOT}$  is decomposed in the following way:

$$\Delta^{TOT}(R) = \Delta^{EX}(R) + \Delta^{CT}(R) + \Delta^{MIX}(R). \quad (4)$$

There are no corrections for the  $ES$  and  $PL$  terms. Each of the  $\Delta^X$  corrections ( $X = EX, CT, MIX$ ) is obtained by a different enlargement of the basis set for the computation of the monomer reference energies, as described in the papers quoted above. The  $\Delta^X$  terms may be further divided into monomeric contributions:

$$\Delta^X = \Delta_A^X + \Delta_B^X. \quad (5)$$

The relation between corrected and uncorrected energy components is given by:

$$\Delta^X(R) = X^{CP}(R) - X(R). \quad (6)$$

Thus, the final expression of the interaction energy with CP corrections is:

$$\Delta E^{CP}(AB; R) = DEF + ES(R) + PL(R) + EX^{CP}(R) + CT^{CP}(R) + MIX^{CP}(R). \quad (7)$$

### 3. Effect of the CP correction of the SCF description of the cation-ligand interaction

#### 3.1. Stabilization energy and equilibrium geometry

In Table 1, the stabilization energies and the equilibrium distances are listed for twelve  $M^{n+}\cdot L$  complexes ( $M^{n+} = Li^+, Na^+, Be^{2+}, Mg^{2+}, Zn^{2+}$ , and  $Al^{3+}$ ;  $L = H_2O, NH_3$ ) obtained with complete geometry optimization employing the MINI-1 basis set [6] (for the hydrogen basis set and scale factors, see [14]).  $C_{2v}$  and  $C_{3v}$  symmetries, respectively, were found in all cases, in agreement with the geometries determined by optimization with the 4-31G and 6-31G\* basis sets. The stabilization energies compare fairly well with those obtained with more extended calculations [15–25]. The relatively good performance of the MINI-1 basis set in describing these interactions was first exhibited by Sauer and Hobza [8] and confirmed in [9]; it parallels analogous good performances for the description of other non-covalent interactions [7, 26–29].

Table 1 also includes the values found after CP correction. The effect of the correction on both parameters is relatively small, far smaller than that for neutral H-bonded dimers [26–28] and for anion-water dimers [29]. Table 2 compares the differences in  $\Delta E$  ( $\Delta\Delta E = \Delta E^{CP}(R_{eq}^{CP}) - \Delta E(R_{eq})$ ) and in  $R_{eq}$  ( $\Delta R_{eq} = R_{eq}^{CP} - R_{eq}$ ) as well as their relative percentage changes ( $\Delta\Delta E\% = 100 \cdot \Delta\Delta E/\Delta E(R_{eq})$ ;

**Table 1.** Interaction energies and equilibrium distances with and without CP corrections for various cation-water and ammonia complexes using different basis sets<sup>a</sup>

Basis sets	Dimer	$\Delta E(R_{eq})$	$R_{eq}$	$\Delta E^{CP}(R_{eq}^{CP})$	$R_{eq}^{CP}$
MINI-1	$Li^+\cdot OH_2$	-41.83	1.792	-37.93	1.804
	$Na^+\cdot OH_2$	-31.26	2.120	-27.99	2.145
	$Be^{2+}\cdot OH_2$	-127.48	1.553	-121.88	1.565
	$Mg^{2+}\cdot OH_2$	-85.17	1.864	-80.23	1.885
	$Zn^{2+}\cdot OH_2$	-89.62	1.870	-82.51	1.915
	$Al^{3+}\cdot OH_2$	-198.16	1.760	-188.62	1.773
	$Li^+\cdot NH_3$	-46.37	1.904	-42.18	1.926
	$Na^+\cdot NH_3$	-34.31	2.244	-30.78	2.275
	$Be^{2+}\cdot NH_3$	-146.42	1.656	-141.38	1.670
	$Mg^{2+}\cdot NH_3$	-96.27	1.971	-91.29	1.994
	$Zn^{2+}\cdot NH_3$	-106.38	1.934	-98.75	1.985
$Al^{3+}\cdot NH_3$	-227.04	1.929	-220.39	1.939	
4-31G	$Li^+\cdot OH_2$	-47.85	1.816	-45.06	1.826
	$Be^{2+}\cdot OH_2$	-155.22	1.522	-150.98	1.530
	$Li^+\cdot NH_3$	-48.45	1.975	-46.26	1.980
	$Be^{2+}\cdot NH_3$	-173.29	1.635	-169.31	1.643
6-31G*	$Li^+\cdot OH_2$	-39.56	1.858	-37.43	1.863
	$Be^{2+}\cdot OH_2$	-146.88	1.500	-143.89	1.501
	$Li^+\cdot NH_3$	-44.40	2.002	-42.16	1.995
	$Be^{2+}\cdot NH_3$	-170.92	1.622	-167.75	1.624

<sup>a</sup> Energies in kcal/mol, distance in Å

Table 2. Comparison of the changes in  $\Delta E(R_{\text{eq}})$  and in  $R_{\text{eq}}$  produced by CP corrections in dimers of different nature (MINI-1 calculations, values in kcal/mol and Å)

Dimer	$\Delta \Delta E$	$\Delta \Delta E$ (%)	$\Delta R_{\text{eq}}$	$\Delta R_{\text{eq}}$ (%)	Dimer <sup>a</sup>	$\Delta \Delta E$	$\Delta \Delta E$ (%)	$\Delta R_{\text{eq}}$	$\Delta R_{\text{eq}}$ (%)
Li <sup>+</sup> ·OH <sub>2</sub>	3.90	9.3	0.012	0.7	HOH·OH <sub>2</sub>	3.89	46.6	0.16	5.8
Na <sup>+</sup> ·OH <sub>2</sub>	3.28	10.5	0.025	1.2	H <sub>2</sub> NH·OH <sub>2</sub>	2.90	56.7	0.28	9.5
Be <sup>2+</sup> ·OH <sub>2</sub>	5.60	4.4	0.012	0.8	FH·OH <sub>2</sub>	4.68	38.6	0.09	3.4
Mg <sup>2+</sup> ·OH <sub>2</sub>	4.89	5.7	0.031	1.7	HOH·NH <sub>3</sub>	2.45	29.6	0.06	2.1
Zn <sup>2+</sup> ·OH <sub>2</sub>	7.11	7.9	0.045	2.4	H <sub>2</sub> NH·NH <sub>3</sub>	1.93	41.4	0.12	3.9
Al <sup>3+</sup> ·OH <sub>2</sub>	9.54	4.8	0.015	0.9	FH·NH <sub>3</sub>	2.88	20.5	0.03	1.1
Li <sup>+</sup> ·NH <sub>3</sub>	3.75	8.1	0.022	1.2	HOH·FH	3.81	62.7	0.34	12.3
Na <sup>+</sup> ·NH <sub>3</sub>	3.63	10.5	0.031	1.4	H <sub>2</sub> NH·FH	2.64	66.4	0.47	16.1
Be <sup>2+</sup> ·NH <sub>3</sub>	5.04	3.4	0.014	0.8	FH·FH	5.15	59.1	0.20	7.7
Mg <sup>2+</sup> ·NH <sub>3</sub>	4.98	5.1	0.024	1.2	OH <sub>2</sub> ·HCOO <sup>-</sup>	10.85	38.6	0.23	12.3
Zn <sup>2+</sup> ·NH <sub>3</sub>	7.63	7.2	0.051	2.6	OH <sub>2</sub> ·CH <sub>2</sub> COO <sup>-</sup>	10.90	38.6	0.22	11.8
Al <sup>3+</sup> ·NH <sub>3</sub>	6.64	2.9	0.010	0.5	OH <sub>2</sub> ·H <sub>2</sub> PO <sub>4</sub> <sup>-</sup>	12.83	24.2	0.29	15.6

<sup>a</sup> The values for the neutral dimers are taken from [26] and those for the anion-water dimers from [29]

$\Delta R_{\text{eq}} \% = 100 \cdot \Delta R_{\text{eq}} / R_{\text{eq}}$ ) with the corresponding MINI-1 values for some dimers of neutral molecules and anion-water complexes, respectively. The small CP corrections (and presumably the small BSSEs) for the cation complexes also are evident, considering the results for the other basis sets. In Tables 1 and 3, the corresponding 4-31G and 4-31G\* data are given. The enlargement of the basis set to a split valence shell and further improvement by polarization functions do not affect the CP solution for cation-ligand dimers. In particular, the changes of the equilibrium distances are very small. As a consequence, the changes in the *DEF* term due to a revision of the equilibrium distance are practically negligible. Based on these results, it can be concluded that it is sufficient to rescale the interaction energy at  $R_{\text{eq}}$  without recalculating a new equilibrium geometry when cation-water and cation-ammonia interaction potentials are used in conjunction with water-water or similar interaction potentials corrected for the BSSE.

### 3.2. Decomposition of $\Delta E$ and interpretation of the interaction

Table 4 contains the results of the decomposition of  $\Delta E$  at the equilibrium distance with and without CP corrections. As mentioned above, the smallness of the correction to the equilibrium geometry makes the results of the decomposition at  $R_{\text{eq}}^{\text{CP}}$  very similar to those displayed in Table 4. The CP corrections are larger for *CT* and *MIX* than for the *EX* contribution; the correction to this last term is eliminated in the “partial” CP procedure applied in [5]. The main effect of the CP correction is a reduction of the relative weight of the charge transfer component, which was relatively small before correction. The largest part of the total CP correction  $\Delta^{\text{TOT}}$  is due to the extension of the ligand basis set, i.e. of the electron donor, in agreement with the results of H-bonded dimers.

The examination of the  $\Delta E$  components at the equilibrium distance gives valuable, but limited information about the nature of the interaction. It may be better to perform this examination for a larger distance range. Until now, this has only been done in a few cases (see, e.g., [9]). It seems to be important to collect data for a larger set of analyses, especially in view of future parametrizations involving large ligands. Duplication of the analysis over uncorrected and CP corrected values is rather cumbersome, and so it is confined to the examination of the CP corrected values, which have a more regular trend. Each term of the decomposition will be examined separately.

*The electrostatic term, ES.* According to intuition the cation-ligand interaction should be supported mainly by electrostatic interactions. This interaction may be divided into a coulombic interaction between rigid charges, *ES* in the KM terminology, and mutual polarization terms, *PL*. We shall first consider the *ES* term.

The coulombic interaction is formally symmetric in the charges of the two monomers, but it is convenient to consider the asymmetric form which makes use of the molecular electrostatic potential of the ligand:

$$ES = \int \rho_M(\mathbf{r}) V(L; \mathbf{r}) \, d\mathbf{r} \quad (8)$$

Table 3. Comparison of the changes in  $\Delta E(R_{\text{eq}})$  and in  $R_{\text{eq}}$  produced by CP corrections in dimers of different nature (4-31G and 6-31G\* calculations, values in kcal/mol and Å)

Dimer	$\Delta E$	$\Delta \Delta E$ (%)	$\Delta R_{\text{eq}}$	$\Delta R_{\text{eq}}$ (%)	Dimer <sup>a</sup>	$\Delta E$	$\Delta \Delta E$ (%)	$\Delta R_{\text{eq}}$	$\Delta R_{\text{eq}}$ (%)
4-31G									
$\text{Li}^+\cdot\text{OH}_2$	2.79	5.8	0.010	0.6	$\text{HOH}\cdot\text{OH}_2$	1.53	19.7	0.04	1.4
$\text{Be}^{2+}\cdot\text{OH}_2$	4.24	2.7	0.008	0.5	$\text{FH}\cdot\text{OH}_2$	1.89	16.1	0.04	1.5
$\text{Li}^+\cdot\text{NH}_3$	2.19	4.5	0.005	0.3	$\text{HOH}\cdot\text{NH}_3$	1.17	13.1	0.04	1.4
$\text{Be}^{2+}\cdot\text{NH}_3$	3.98	2.3	0.008	0.5	$\text{FH}\cdot\text{NH}_3$	1.59	9.5	0.04	1.4
6-31G*									
$\text{Li}^+\cdot\text{OH}_2$	2.13	5.4	0.005	0.3	$\text{HOH}\cdot\text{OH}_2$	0.97	17.4	0.04	1.3
$\text{Be}^{2+}\cdot\text{OH}_2$	2.99	2.0	0.002	0.1	$\text{FH}\cdot\text{OH}_2$	1.24	13.6	0.03	1.1
$\text{Li}^+\cdot\text{NH}_3$	2.24	5.0	0.007	0.3	$\text{HOH}\cdot\text{NH}_3$	0.66	10.4	0.04	1.3
$\text{Be}^{2+}\cdot\text{NH}_3$	3.17	1.8	0.002	0.1	$\text{FH}\cdot\text{NH}_3$	0.92	7.4	0.03	1.1

<sup>a</sup> The values for the neutral dimers are taken from [26]

Table 4. Decomposition of  $\Delta E$  and of  $\Delta E^{CP}$  at  $R_{eq}$  (values in kcal/mol)

Dimer	DEF	ES	PL	EX <sup>CP</sup>	CT <sup>CP</sup>	MIX <sup>CP</sup>	INT <sup>CP</sup>	EX	CT	MIX	INT
MINI-1 results											
Li <sup>+</sup> ·OH <sub>2</sub>	0.008	-42.271	-4.542	8.568	-1.105	1.337	-37.923	8.300	-3.461	0.042	-41.842
Na <sup>+</sup> ·OH <sub>2</sub>	0.002	-31.181	-2.452	6.408	-1.686	0.961	-27.950	5.734	-3.263	-0.016	-31.267
Be <sup>2+</sup> ·OH <sub>2</sub>	0.260	-106.845	-28.169	23.178	-9.798	-0.490	-122.114	22.960	-12.884	-2.799	-127.737
Mg <sup>2+</sup> ·OH <sub>2</sub>	0.062	-79.250	-15.288	19.141	-5.832	1.010	-80.219	18.236	-7.724	-1.208	-82.234
Zn <sup>2+</sup> ·OH <sub>2</sub>	0.104	-85.105	-15.465	30.892	-9.813	-3.767	-82.258	27.774	-11.936	-5.990	-89.722
Al <sup>3+</sup> ·OH <sub>2</sub>	2.636	-128.934	-43.890	28.048	-37.516	-8.921	-191.213	27.280	-42.095	-13.157	-200.796
Li <sup>+</sup> ·NH <sub>3</sub>	0.324	-51.415	-2.916	12.041	-0.456	0.283	-42.463	11.819	-2.994	-1.192	-46.699
Na <sup>+</sup> ·NH <sub>3</sub>	0.307	-36.987	-1.597	8.676	-1.492	0.353	-31.046	7.975	-3.124	-0.984	-34.716
Be <sup>2+</sup> ·NH <sub>3</sub>	1.751	-133.804	-21.041	30.660	-8.406	-10.500	-143.091	30.443	-11.108	-12.655	-148.165
Mg <sup>2+</sup> ·NH <sub>3</sub>	1.532	-98.249	-11.564	25.971	-4.983	-3.925	-92.751	25.078	-6.765	-6.308	-97.808
Zn <sup>2+</sup> ·NH <sub>3</sub>	1.439	-113.278	-12.395	47.039	-7.641	-13.484	-99.757	43.511	-9.792	-15.862	-107.816
Al <sup>3+</sup> ·NH <sub>3</sub>	4.831	-151.154	-28.880	27.634	-40.246	-32.572	-225.218	26.874	-42.794	-35.965	-231.874
4-31G results											
Li <sup>+</sup> ·OH <sub>2</sub>	0.039	-50.664	-7.073	11.858	-1.676	2.463	-45.090	11.838	-3.508	1.519	-47.886
Be <sup>2+</sup> ·OH <sub>2</sub>	1.258	-134.494	-51.616	39.047	-16.261	11.103	-152.222	39.032	-19.908	10.507	-156.479
Li <sup>+</sup> ·NH <sub>3</sub>	1.708	-55.616	-6.655	14.178	-1.200	0.970	-47.972	14.164	-2.331	-0.071	-50.157
Be <sup>2+</sup> ·NH <sub>3</sub>	4.803	-159.012	-51.980	48.638	-17.245	5.502	-174.093	48.618	-20.734	5.017	-178.090
6-31G*											
Li <sup>+</sup> ·OH <sub>2</sub>	0.083	-39.631	-9.020	9.961	-1.303	2.484	-37.509	9.955	-3.087	2.142	-39.640
Be <sup>2+</sup> ·OH <sub>2</sub>	1.760	-100.578	-81.671	43.519	-21.628	24.709	-145.649	43.495	-24.210	24.328	-148.635
Li <sup>+</sup> ·NH <sub>3</sub>	0.147	-48.026	-9.020	13.229	-0.395	1.902	-42.309	13.227	-2.110	1.381	-44.546
Be <sup>2+</sup> ·NH <sub>3</sub>	0.851	-139.496	-76.641	51.889	-21.629	17.269	-168.597	51.881	-24.253	16.726	-171.783



At large distances,  $ES$  is well represented by  $q_n \cdot V(L; R)$  where  $q_n$  is the formal charge of the cation, while at shorter distances the effect of the mutual penetration of the charge clouds makes  $ES(R)$  more negative than  $q_n \cdot V(L; R)$ . This well-known effect has been called "penetration effect" [30, 31]. It is interpreted as a reduction of the screening of the ligand nuclei by a portion of the ligand electrons when the cation is at small distances. Based on Eq. (8), it may alternatively be viewed as due to the finite size of the cation, which samples a different portion of  $V(L)$  with its specific shape at each distance  $R$ . It is convenient to compare  $q \cdot V(L; R)$  ( $q = 1e$ ) with  $ES(R)/n$ , where  $n$  is the charge of the cation. These values are reported in Table 5. The penetration effect is numerically different for the two ligands, in agreement with the different shape of  $V(\text{H}_2\text{O})$  and  $V(\text{NH}_3)$ , but it is possible to demonstrate a fair parallelism between the entity of the effect and the cation volume in both sets of dimers. A proper use of  $V(L)$  to model  $ES$  in simplified computational methods should consider this effect.

The values of  $ES$  are more negative for the interaction with  $\text{NH}_3$  than with  $\text{H}_2\text{O}$ . This trend is constant for all the cations and depends on the shape of  $V(L)$ . A decomposition of  $V(L)$  into group contributions [32, 33], which is given for both ligands at  $R = 1.8 \text{ \AA}$  in Table 6 (Boys localization [34]) may be a useful tool to exhibit important differences. The ratio  $V(\text{NH}_3)/V(\text{H}_2\text{O})$  regularly decreases

**Table 5.** Values of  $V(L)$  and of the differences  $V(L) - ES(M^{n+} \cdot L)/n$  in kcal/mol (MINI-1 basis set). The  $V(L)$  values refer to the undeformed geometry of the ligand.  $V(L) - ES(M^{n+} \cdot L)/n$  data refer to  $V(L)$  values computed with the ligand geometry optimized at  $R_{\text{eq}}(M^{n+} \cdot L)$

$R$	$V(\text{H}_2\text{O})$	$\text{Li}^+$	$\text{Na}^+$	$\text{Be}^{2+}$	$\text{Mg}^{2+}$	$\text{Zn}^{2+}$	$\text{Al}^{3+}$
1.4	-61.767	7.498	59.931	1.721	19.965	64.309	9.586
1.6	-50.467	2.409	19.789	0.530	6.158	20.935	3.012
1.8	-41.151	0.699	5.789	0.146	1.738	6.178	0.837
2.0	-33.995	0.201	1.491	0.040	0.411	1.503	0.222
2.2	-28.514	0.078	0.339	0.014	0.084	0.331	0.068
2.4	-24.250	0.033	0.069	0.006	0.015	0.064	0.030
2.6	-20.874	0.021	0.013	0.003	0.002	0.010	0.017
2.8	-18.154	0.014	0.003	0.002	0.001	0.000	
3.0	-15.932	0.010	0.003	0.001	0.000	-0.002	
3.2	-14.094	0.006	0.000	0.001	0.000	-0.006	
$R$	$V(\text{NH}_3)$	$\text{Li}^+$	$\text{Na}^+$	$\text{Be}^{2+}$	$\text{Mg}^{2+}$	$\text{Zn}^{2+}$	$\text{Al}^{3+}$
1.4	-83.679	13.226	101.017	3.119	34.959	109.103	17.473
1.6	-67.980	5.287	40.876	1.253	13.868	43.797	6.910
1.8	-54.356	1.912	15.023	0.438	4.939	15.924	2.457
2.0	-43.738	0.630	4.941	0.139	1.556	1.563	0.789
2.2	-35.706	0.198	1.447	0.043	0.434	1.488	0.241
2.4	-29.615	0.067	0.375	0.015	0.111	0.382	0.080
2.6	-24.925	0.028	0.084	0.006	0.028	0.087	0.038
2.8	-21.245	0.014	0.013	0.001	0.010	0.017	0.019
3.0	-18.312	0.007	-0.002	0.000	0.006	0.003	
3.2	-15.937	0.003	-0.005	0.000	0.004	0.002	

**Table 6.** Components of the electrostatic potential  $V(L)$ (MINI-1 results, in kcal/mol)

$R$	$1s_{\text{O}}^{\text{a}}$	$b_{\text{OH}}^{\text{b}}$	$l_{\text{O}}^{\text{c}}$	$1s_{\text{N}}^{\text{d}}$	$b_{\text{NH}}^{\text{e}}$	$l_{\text{N}}^{\text{f}}$
1.4	0.163	20.059	-51.018	0.557	24.869	-158.844
1.6	0.125	14.761	-40.051	0.417	18.033	-122.497
1.8	0.102	11.315	-31.942	0.331	13.635	-95.593
2.0	0.085	8.937	-25.977	0.270	10.659	-75.987
2.2	0.072	7.226	-21.520	0.226	8.561	-61.615
2.4	0.062	5.952	-18.114	0.192	7.028	-50.891
2.6	0.054	4.992	-15.455	0.165	5.875	-42.715
2.8	0.047	4.241	-13.340	0.143	4.987	-36.350
3.0	0.041	3.647	-11.634	0.126	4.288	-31.301
3.2	0.037	3.169	-10.233	0.111	3.728	-27.231

<sup>a</sup> O inner shell contribution

<sup>b</sup> OH bond contribution (multiplicity 2)

<sup>c</sup> O lone pair contribution (multiplicity 2)

<sup>d</sup> N inner shell contribution

<sup>e</sup> NH bond contribution (multiplicity 3)

<sup>f</sup> N lone pair contribution

from 1.35 at  $R = 1.4 \text{ \AA}$  to 1.13 at  $R = 3.2 \text{ \AA}$ . The ratio  $ES(M^{n+} \cdot NH_3) / ES(M^{n+} \cdot OH_2)$  decreases from 1.5 to 1.2 in the same distance range. The differences in these ratios for different cations are, as already mentioned, due to the finite size of the cation. This analysis based on the MINI-1 results seems to be confirmed by the limited number of calculations with more extended basis sets.

It is worth mentioning that the relative strength of the  $ES$  components for the two ligands, which ultimately defines the relative stabilization energy of the two sets of dimers, is in contrast with predictions based on the value of the ligand dipole moment (computed MINI-1 values;  $\mu = 2.25 \text{ D}$  for  $H_2O$  and  $\mu = 2.01 \text{ D}$  for  $NH_3$ ). It has been stated many times that multipolar expansions of molecular interactions cannot be reduced to the lowest expansion term (see, e.g., [32, 33]). The same holds for atomic cation-ligand interactions [35], even if this remark is sometimes forgotten.

The 4-31G basis set overemphasizes the numerical value of the  $ES$  contribution, as occurs in neutral dimers, whereas the 6-31G\* results are in between the MINI-1 and the 4.31G ones, but more similar to the MINI-1 values, again as in neutral dimers. We report the comparison of the  $ES$  values obtained with the three basis sets for the complexes  $Be^{2+} \cdot L$  in Table 7.

*The polarization term, PL.* Whereas the consideration of the electrostatic potential  $V(L; R)$  as a molecular index to model  $ES$  is of common use nowadays, less attention has been paid to a corresponding index,  $P(L; R)$ , referred to the polarization energy (for definition, examples, and a program see [36–39]).

The relatively low polarizability of the cations makes this index a fairly good predictor. It is convenient to compare  $q^2 \cdot P(L; R)$  ( $q = 1e$ ) with  $PL(M^{n+} \cdot L; R) / n^2$ . The results are reported in Table 8. There is no effect comparable to the

**Table 7.** Values of the electrostatic component  $ES$  for the  $Be^{2+}$  complexes with water and ammonia obtained with different basis sets (values in kcal/mol)

$R$	Water			Ammonia		
	MINI-1	4-31G	6-31G*	MINI-1	4-31G	6-31G*
1.4	-126.285	-152.457	-120.584	-177.555	-202.375	-170.897
1.6	-101.497	-123.836	-100.610	-142.572	-165.126	-142.629
1.8	-82.246	-100.424	-82.696	-113.854	-132.794	-116.125
2.0	-67.810	-82.440	-68.375	-92.002	-107.160	-94.258
2.2	-56.854	-68.743	-57.270	-75.616	-87.552	-77.167
2.4	-48.354	-58.169	-48.621	-63.181	-72.622	-64.018
2.6	-41.625	-49.853	-41.781	-53.557	-61.127	-53.854
2.8	-36.206	-43.196	-36.282	-45.962	-52.126	-45.888
3.0	-31.778	-37.784	-31.796	-39.865	-44.957	-39.543
3.2	-28.113	-33.325	-28.090	-34.898	-39.157	-34.413

“penetration effect” found in the  $ES$  term. The  $P(L; R)$  function is in fact more isotropic than the electrostatic potential  $V(L; R)$ .

The analysis of the description of the MINI-1 ligand charge distribution by means of localized orbitals shows a linear response of the shift of the orbital charge centroids with respect to the local electric field generated by the cation. Some deviations from linearity are present for  $Al^{3+}$  complexes at short distances.

**Table 8.** Values of  $P(L)$  and of the differences  $P(L) - PL(M^{n+} \cdot L)/n^2$  (MINI-1 results in kcal/mol). The  $P(L)$  values are computed for the geometry of  $L$  found in the  $Li^+ \cdot L$  complexes

$R$	$P(H_2O)$	$Li^+$	$Na^+$	$Be^{2+}$	$Mg^{2+}$	$Zn^{2+}$	$Al^{3+}$
1.4	-10.169	0.484	4.030	0.350	0.560	3.013	0.230
1.6	-6.538	0.130	1.007	0.155	0.080	0.728	0.180
1.8	-4.346	0.030	0.262	0.059	0.016	0.135	0.173
2.0	-2.988	0.006	0.064	0.013	0.013	0.016	0.166
2.2	-2.117	0.001	0.020	0.000	0.000	0.003	0.148
2.4	-1.540	0.000	0.000	-0.013	-0.008	0.005	0.127
2.6	-1.145	0.000	0.000	-0.016	-0.012	0.009	0.107
2.8	-0.869	0.000	0.000	-0.015	-0.012	0.009	
3.0	-0.671	0.000	0.000	-0.013	-0.013	0.008	
3.2	-0.525	0.000	0.000	-0.013	-0.013	0.008	

$R$	$P(NH_3)$	$Li^+$	$Na^+$	$Be^{2+}$	$Mg^{2+}$	$Zn^{2+}$	$Al^{3+}$
1.4	-8.170	0.166	1.072	0.849	1.169	2.080	1.173
1.6	-5.298	0.062	0.322	0.597	0.698	0.948	0.782
1.8	-3.540	0.021	0.079	0.425	0.447	0.493	0.543
2.0	-2.434	0.008	0.015	0.310	0.310	0.306	0.391
2.2	-1.719	0.003	0.010	0.230	0.227	0.212	0.289
2.4	-1.243	0.002	0.008	0.205	0.202	0.187	0.249
2.6	-0.919	0.001	-0.002	0.134	0.132	0.119	0.167
2.8	-0.692	0.000	-0.002	0.105	0.103	0.092	0.130
3.0	-0.530	0.000	-0.002	0.083	0.082	0.072	
3.2	-0.412	0.000	-0.001	0.066	0.066	0.058	

The ligand lone pair charge distribution is less polarizable than the X–H bonds. This behaviour agrees with that found for other molecular interactions [40, 41].

It is well known that the polarization energy is badly described by minimal basis sets. The modest increment in the number of basis functions provided by the 4-31G and 6-31G\* basis sets is sufficient to produce remarkable numerical changes and also an inversion of the relative values for the two ligands as demonstrated by the  $PL(Be^{2+}\cdot L; R)$  values, which are listed in Table 9 for the three basis sets. It is worth mentioning that the ratio between the 6-31G\* and MINI-1  $PL$  values remains almost constant over a large distance range. This ratio depends on the nature of the ligand (Table 10). Calculations with larger basis sets also show that the 6-31G\* basis set is not of sufficient quality to account properly for this component of the interaction energy (see [27] for further comments), but it seems to be improbable that larger basis sets will change the relative importance of this term with respect to the others for the systems presented here.

**Table 9.** Values of the polarization energy component  $PL$  for the  $Be^{2+}$  complexes with water and ammonia obtained with different basis sets (values in kcal/mol)

R	Water			Ammonia		
	MINI-1	4-31G	6-31G*	MINI-1	4-31G	6-31G*
1.4	-39.285	-66.301	-104.188	-36.077	-77.091	-119.897
1.6	-25.531	-43.823	-64.318	-23.581	-55.400	-80.185
1.8	-17.150	-29.020	-40.801	-15.862	-38.133	-53.376
2.0	-11.898	-19.748	-26.915	-10.977	-26.208	-35.864
2.2	-8.492	-13.877	-18.468	-7.797	-18.349	-24.669
2.4	-6.212	-10.040	-13.115	-5.671	-13.164	-17.448
2.6	-4.643	-7.446	-9.584	-4.211	-9.673	-12.675
2.8	-3.535	-5.600	-7.174	-3.186	-7.261	-9.428
3.0	-2.737	-4.350	-5.480	-2.450	-5.553	-7.158
3.2	-2.151	-3.409	-4.260	-1.913	-4.317	-5.532

**Table 10.** Ratio of the  $PL(6-31G^*)$  and  $PL(MINI-1)$  values for the water and ammonia complexes involving  $Li^+$  and  $Be^{2+}$  compared with the ratio  $P(6-31G^*)/P(MINI-1)$  for the two ligands

R	$Li^+\cdot OH_2$	$Be^{2+}\cdot OH_2$	$Li^+\cdot NH_3$	$Be^{2+}\cdot NH_3$	$P(H_2O)$	$P(NH_3)$
1.4	2.702	2.653	4.131	3.304	2.389	3.448
1.6	2.511	2.519	4.054	3.400	2.343	3.226
1.8	2.349	2.379	3.890	3.365	2.269	3.634
2.0	2.228	2.262	3.712	3.267	2.193	3.583
2.2	2.145	2.175	3.569	3.164	2.129	3.508
2.4	2.088	2.111	3.465	3.077	2.080	3.439
2.6	2.048	2.064	3.395	3.010	2.044	3.381
2.8	2.020	2.029	3.351	2.959	2.013	3.341
3.0	1.997	2.002	3.317	2.922	1.991	3.311
3.2	1.979	1.980	3.296	2.892	1.975	3.289

*The exchange-repulsion term, EX.* The relative weight of the CP corrections to  $EX$  ( $\Delta^{EX}$  in our terminology) increases at larger distances; for the equilibrium distance this ranges from 11.8/8.8% for  $\text{Na}^+$  to 0.7/0.9% for  $\text{Be}^{2+}$  (first value water, second ammonia complex). The  $EX^{CP}$  values are well described by a single exponential function with the regression coefficients  $r = 0.998/1.000$  which are somewhat better than those for the uncorrected values. It should be mentioned that in some cases the uncorrected MINI-1  $EX$  values have a negative sign at large distances which disappears after CP correction (for the occurrence of small negative values in  $EX$ , a fact in apparent contradiction with the picture given by the first-order perturbation theory, see the remarks in [4]). The  $EX^{CP}$  term is constantly larger in the ammonia complexes, which can be understood by considering the ligand charge distribution.

The values of  $EX^{CP}$  considerably increase in passing to the 4-31G and to the 6-31G\* basis sets. As a representative example in Table 11 we report the values of  $EX^{CP}(\text{Be}^{2+}\cdot\text{L})$  obtained with the three basis sets. In the H-bonded dimers we found a different trend [26–28]. The larger equilibrium distances estimated by 4-31G and 6-31G\* calculations are principally due to this increase in  $EX^{CP}$ .

*The charge-transfer term, CT.* The charge-transfer term, before and after the correction, has a peculiar dependence on  $R$ . There is always a local minimum, often followed, at shorter  $R$ , by a local maximum. An example is reported in Fig. 1. We have selected the  $\text{Li}^+$  complexes because after CP correction the decomposition gives positive values at short distances; this unphysical effect is less pronounced in the 6-31G\* calculations. Smaller positive values have been also found for the  $\text{Na}^+$  complexes (0.3 kcal/mol for  $\text{Na}^+\cdot\text{OH}_2$  and 0.8 kcal/mol for  $\text{Na}^+\cdot\text{NH}_3$ , in both cases at  $R = 1.8 \text{ \AA}$  only). Other data, including also a comparison between different basis sets, are reported in Table 12. This trend of  $CT(R)$  for cation-ligand couples has also been noticed with the STO-3G and 3-21G basis sets [40] whereas  $CT(R)$  becomes monotonically more negative for H-bonded dimers going to shorter distances [26–28]. The relatively large

**Table 11.** Values of the exchange-repulsion energy component  $EX^{CP}$  for the  $\text{Be}^{2+}$  complexes with water and ammonia obtained with different basis sets (values in kcal/mol)

$R$	Water			Ammonia		
	MINI-1	4-31G	6-31G*	MINI-1	4-31G	6-31G*
1.4	53.226	68.976	67.850	90.060	121.973	119.302
1.6	17.711	26.726	27.468	40.031	56.041	56.558
1.8	5.212	9.443	10.217	14.885	24.199	25.453
2.0	1.343	2.982	3.408	4.959	9.589	10.603
2.2	0.302	0.835	1.010	1.469	3.439	4.025
2.4	0.057	0.207	0.266	0.386	1.110	1.383
2.6	0.007	0.046	0.062	0.087	0.322	0.429
2.8	0.002	0.010	0.013	0.017	0.084	0.120
3.0	0.000	0.002	0.003	0.001	0.020	0.032
3.2	0.000	0.000	0.000	0.000	0.005	0.008

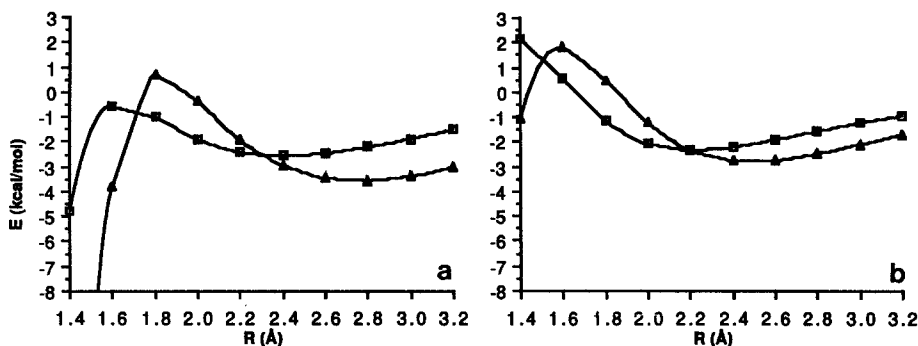


Fig. 1a,b. Values of  $CT^{CP}$  as a function of  $R$  for the complexes  $Li^+ \cdot OH_2$  (■) and  $Li^+ \cdot NH_3$  (▲). a 6-31G\* results; b MINI-1 results

penetration of the cation and the ligand charge cloud illustrates the  $CT$  dependence on the overlap between the virtual orbitals of one partner and the occupied ones of the other. Obviously, there is a distance for which this overlap has a maximum decreasing again at shorter distances. Only in very strong hydrogen bonds did we obtain hints of this behaviour [27]. The numerical experiments described in a recent paper by Latajka and Scheiner [42] document, in our opinion, the same basis set effects described here from a different viewpoint.

The value of the CP correction to the charge-transfer term for a given cation is not significantly affected by the nature of the ligand. Table 4 provides the necessary data to check this statement for the equilibrium distance.  $\Delta^{CT}$  at  $R_{eq}$  represents a sizeable portion of  $\Delta^{TOT}$ . From Table 4 it is apparent that the ratio  $\Delta^{CT}/\Delta^{TOT}$  is in the range of 0.68–0.11 for the water complexes and 0.85–0.06 for the ammonia complexes.

The CP corrections to  $CT$  derive almost completely from the enlargement of the functional space of the electron donor with the empty orbitals of the electron

Table 12. Values of the charge-transfer component  $CT^{CP}$  for the  $Be^{2+}$  complexes with water and ammonia obtained with different basis sets (values in kcal/mol)

$R$	Water			Ammonia		
	MINI-1	4-31G	6-31G*	MINI-1	4-31G	6-31G*
1.4	-2.783	-11.956	-19.830	-0.472	-19.517	-28.401
1.6	-11.711	-19.274	-24.302	-5.521	-15.671	-20.723
1.8	-16.711	-24.211	-26.889	-15.225	-25.289	-29.217
2.0	-17.777	-25.009	-25.840	-21.293	-32.322	-34.470
2.2	-16.399	-23.005	-22.935	-23.435	-35.252	-36.007
2.4	-13.945	-19.576	-19.320	-22.957	-34.895	-35.041
2.6	-11.273	-15.781	-15.580	-21.116	-32.474	-32.536
2.8	-8.819	-12.246	-12.086	-18.776	-29.094	-29.208
3.0	-6.751	-9.232	-9.074	-16.439	-25.518	-25.637
3.2	-5.093	-6.788	-6.636	-14.357	-22.189	-22.244

acceptor. Near the equilibrium distance, the ratio  $\Delta_L^{CT}/\Delta^{CT}$  (Eq. (5)) has values around 0.90.

Contrary to the non-monotonic behaviour of the  $CT$  energy as a function of  $R$  in the cation-ligand complexes,  $\Delta^{CT}(R)$  does decrease monotonically in the MINI-1 calculations. The opposite is true for H-bonded dimers, where the  $CT$  energy changes monotonically and  $\Delta^{CT}(R)$  shows a non-monotonic trend. We cannot give an explanation for this interesting contrast. It may be argued that the limited spatial extent of the virtual space of the atomic cation could be the origin of this behaviour.  $CT(R)$  for cation complexes is particularly sensitive to the local overlap of the cation virtual space with the occupied space of the partner and, on the other hand, the enlargement of the virtual space performed in CP corrected calculations cannot allow for the more complex trend of  $\Delta^{CT}$  with respect to  $R$  found for other polynuclear electron acceptors. One could guess that polynuclear cation complexes will exhibit trends of  $CT^{CP}$  and of  $\Delta^{CT}$  more similar to those found in neutral polyatomic dimers.

In a recent paper [43] it was pointed out that “Morokuma-type” analyses can give positive and unphysical  $CT$  energies. This seems to be supported by the small positive  $CT$  energy values found after CP correction at short distances for the  $\text{Li}^+$  and  $\text{Na}^+$  complexes (see Fig. 1 and the related comments). For all the other complexes we found negative  $CT^{CP}$  values over the whole distance range. Uncorrected  $CT$  values are always negative. Based on our experience with the application of the Kitaura–Morokuma scheme to numerous systems, it can be stated that the occurrence of small positive  $CT$  energy values represents an exceptional behaviour. There are hints that even the small local maxima disappears when employing large basis sets.

The relative importance of the  $CT^{CP}$  terms with respect to  $\Delta E^{CP}(R_{\text{eq}})$  ranges from 1.1% ( $\text{Li}^+\cdot\text{NH}_3$ ) to 19.6% ( $\text{Al}^{3+}\cdot\text{OH}_2$ ) in our calculations as data in Table 5 show. The decomposition of the interaction energy based on natural bond analysis [43] gives more emphasis to the  $CT$  terms. A comparison with this alternative decomposition method will be done on another occasion.

*The remainder, MIX.* The CP corrections to  $MIX$  represent a considerable portion (20–30%) of the total correction  $\Delta^{TOT}$ . The  $MIX$  terms at  $R_{\text{eq}}$  are generally negative. There is a shift to more positive values after correction. The smallness of some values of  $MIX$  at  $R_{\text{eq}}$  makes the examination of  $\Delta^{MIX}/MIX$  ratios meaningless (Table 4). The values of  $MIX^{CP}$  are loosely linked to the corresponding values of  $CT^{CP}$  within the whole distance range. The  $MIX$  term is generally larger for cations with a higher charge. For a given charge, cations with smaller radii have the higher  $MIX$  values. The  $MIX$  values are more negative in ammonia complexes.  $MIX^{CP}$  and  $\Delta^{MIX}$  rapidly decrease as  $R$  increases.

#### 4. Comments and conclusions

The analysis of cation-ligand interactions presented here completes the picture of non-covalent interactions presented in preceding papers. The application of

the Kitaura–Morokuma decomposition accompanied by CP corrections to the energy components shows that the description of the cation–ligand interaction obtained with basis sets with different natures is congruent. The comparison of this analysis with those performed for a wide variety of other dimers [26–29] demonstrates changes in the nature of the interaction which are in agreement with chemical intuition and with conclusions from analyses performed with other theoretical tools.

The attention has been focussed on the MINI-1 basis set here. The results confirm the data provided by Sauer and Hobza [8] and supplement the picture of cation–ligand interactions discussed in the preceding paper [9]. The MINI-1 basis set describes these interactions in a relatively satisfactory manner. It may be recommended, therefore, for similar calculations involving ligands of larger size, when the size of the basis set becomes an important factor in the computations. Also, the decomposition of  $\Delta E(R)$  is relatively well balanced in comparison with those obtained with better basis sets. The main shortcoming, shared with all small basis sets, concerns the *PL* contribution to the interaction energy. The correction to the BSSE has no essential effect on the equilibrium distance and is of limited importance for  $\Delta E(R)$  of the cation complexes, again comparable with the results provided by larger basis sets. However, the introduction of CP corrections may be advantageous in the interpretation of  $\Delta E$  and in the modelling of the interaction. Thus, simpler computational schemes for larger ligands, which are not based on supermolecule calculations, seem to be readily derivable. The CP correction reduces the absolute value of  $\Delta E(R)$ . The MINI-1 stabilization energies for cation–ligand interactions are in general smaller than the values obtained with better basis at the HF level, due to the relatively bad description of *PL*. It is not possible, however, to suppose that BSSEs and the bad description of *PL* compensate each other, because the errors are of different magnitude and exhibit a different distance dependence.

A last comment regards the justification of using the Hartree–Fock one-determinant description for these cation–ligand interactions. The examination of the experimental ionization potentials of cations and ligands suggests a  $M^{(n-1)+} \cdot L^+$  state in some dimers, perhaps preferred at large distances (see, e.g., [18]). We have performed some test calculations using MC SCF and CI descriptions of the lowest electronic states, and it seems that the crossing (or the avoided crossing) of the potential energy surfaces occurs, in general, at relatively large values of  $R$ . Near the equilibrium distance, there is a modest contribution of other configurations to the dominant one. The  $Al^{3+} \cdot L$  dimers could be a possible exception. This point will be considered in a separate investigation [44]. Additionally, it should be mentioned that Mulliken’s population analysis is of little help for this problem. It often indicates a large electron transfer to the metal cation which does not correspond to the description of the electronic distribution given by the same wave function. A clear demonstration of this artefact may be found in a preceding paper on other metal cation interactions [45].



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