A Comparison of Mesquac- and "Full" AB Initio MO-Wavefunctions

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The quality of wavefunctions for complex systems derived by either "full" ab initio MO-SCF calculations or within the MESQUAC-MO framework [1] is investigated comparing chemically interesting quantities as atomic and overlap populations and the character of the chemical bond. A direct relation between the results of both methods is shown to exist, allowing an extrapolation of the much less time consuming MESQUAC computations to the "full" MO SCF level. Hydrate complexes of main group and transition metal ions have been chosen for some practical applications.

Introduction

It has been shown recently [1] that the use of mixed electrostatic-quantum chemical (MESQUAC) MO calculations yields very satisfactory stabilization energies for rather large chemical systems like hydrated cations with one, two or three hydration shells. The application of this theoretical concept to transition metal ion hydrates [2, 3] also led to good energy values, some difficulties were encountered, however, in reproducing the absorption spectrum of a hydrated ion like Ti(III) [2]. By enlarging the part of the system which is described by a "full" ab initio treatment within the MESQUAC formalism, essentially satisfactory values have been obtained, however, even for the electronic spectrum. Since the electronic spectrum is much more sensitive to the quality of the wavefunction of the system than the stabilization energy, the difficulties encountered gave the reason for a more systematic investigation of the question, to which extent "full" ab initio and MESQUAC wavefunctions agree with each other, or if one can extrapolate, at least, from a MESQUAC function to the composition of the "regular" function obtained by the usual MO-SCF procedure.

Method

The general procedure of the MESQUAC MO calculation has been outlined in detail in (1) and (2). This procedure was followed also in the work presented here, including the charge transfer correction [1]. Ion metal hydrates have been employed for the comparison of the wavefunctions of MESQUAC and full MO SCF calculations. Due to the rather large systems, a minimal Gaussian basis set was used [4]. The calculations were performed in part on the CDC Cyber 74 of the Technical University of Vienna (MESQUAC modification of the program [5]), in part on the CDC 3300 of the University of Innsbruck (program MESQUAC 200).

For the comparison of the wave functions, "chemically relevant" properties, being derived from the composition of the total wavefunction or the one particle functions, have been used. Such properties are atomic and overlap populations (after Mulliken). A correct description of the "character" of the chemical bond (i.e. ionic and covalent contribution) is also quite important for the estimation of the wave function's quality. Unfortunately, there is no simple common concept to convert the rather qualitative terms of "ionicity" or "covalency" of a bond into quantities available from MO calculations of a complex compound (as it may be done in VB calculations by calculating the contribution of ionic structures to the total wave functions). We have tried, therefore, to establish such a quantitative measure for the covalent bond character also for MO calculations. The concept is based on the evaluation of the composition of the one particle functions (MO's), in the case of the hydrated ions on the composition of these functions by basis functions assigned to the central ion and the ligand, respectively, leading to a quantitative measure for the covalency of the metal-ligand bond. The quantity thus derived will be named "covalency

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parameter (CP)" in the text, and its evaluation will be outlined briefly in the following.

We first restrict ourselves to the "valence orbitals", excluding MO's describing the low lying inner core electrons, since these MO's are composed almost completely by functions of the respective atoms only. Taking now the coefficients of the metal functions and the functions of the atom being the coordinative center of the ligand in each of these valence MO's, we renormalize these coefficients neglecting contributions by other atoms. If the composition of this renormalized MO is 1 : 1 (metal functions: ligand atom functions), it is considered to be 100% "covalent", if the composition is 1 : 0 (0 : 1), it is considered to be 100% "ionic". Consequently, a ratio of either 15 : 85 or 85 : 15 corresponds to a 30% covalent character of the bond. If n denotes now the number of valence shell MO's and N_i the occupation number of the i-th MO, we evaluate the covalency parameter CP for the metal-ligand binding in total, given in percent, from

$$\mathrm{CP} = \left(\frac{\sum_i^n N_i c_i}{\sum_i^n N_i} \right) \cdot \frac{1}{100} ,$$

where c_i means the percentual covalent character of the i-th valence MO and $N_i * 100$ corresponds to the maximal possible covalency of the molecule, concerning the metal-ligand-bonds.

Results and Discussion

1. Gross Populations

In Table 1, the gross population for the mono- and tetrahydrates of alkali and alkaline earth cations, derived from the usual ab initio procedure, are compared to those of the MESQUAC calculations for the tetrahydrate, where three ligands have been considered as electrostatic perturbation. As for the charge distribution in the ligand molecule, MESQUAC leads to almost the same distribution as the "full" calculation of the tetrahydrate, giving thus a remarkable improvement compared to the calculation of the monohydrate, but without extending the computation time significantly over that of the monohydrate. The charge transfer to the cation, however, is underestimated strongly by the MESQUAC method, the densities obtained are related, however, to those of the complete MO calculation by

$$q_{\mathrm{SCF}} = 4.754 * q_{\mathrm{MES}} - 0.019 \; (R = 0.98)$$

in a statistically significant way, allowing thus a good estimation by extrapolation.

Table 1. Gross charge densities: a) Tetrahydrate ... ab initio MO SCF, b) Tetrahydrate ... MESQUAC MO SCF, c) Monohydrate ... ab initio MO SCF.

Ion		metal	O	H
	a	2.0397	8.5207	0.7347
Li^+	b	2.0105	8.5349	0.7275
	c	2.0137	8.5829	0.7071
	a	10.0750	8.4866	0.7473
Na^+	b	10.0198	8.5004	0.7399
	c	10.0252	8.5236	0.7256
	a	18.3199	8.4144	0.7528
K^+	b	18.0850	8.4245	0.7452
	c	18.0957	8.4324	0.7359
	a	2.0089	8.7902	0.6038
Be^{2+}	b	2.0027	8.8105	0.5934
	c	2.0035	8.9307	0.5329
	a	10.1297	8.6704	0.6486
Mg^{2+}	b	10.0353	8.6950	0.6349
	c	10.0447	8.7514	0.6019
	a	18.5242	8.5213	0.6869
Ca^{2+}	b	18.1018	8.5271	0.6856
	c	18.1356	8.5832	0.6407

2. Overlap Populations

The total overlap populations between the metal ion and the oxygen atom (i.e. the coordinative center of the ligand) have been evaluated. The values obtained after "full" and MESQUAC MO procedure are listed in Table 2. The values differ, but they are related again by a significant linear correlation

$$p_{\mathrm{SCF}} = 4.10 * p_{\mathrm{MES}} \; (R = 0.99)$$

which indicates the possibility of extrapolation in the case of larger systems, for which only

Table 2. Mulliken overlap populations: a) MESQUAC MO SCF results, b) ab initio MO SCF results.

Ion	a	b
Li(I)	0.004	0.015
Na(I)	0.009	0.035
K(I)	0.047	0.194
Mg(II)	0.012	0.042
Ga(II)	0.069	0.276

MESQUAC calculations can be performed due to computational limitations.

The values for the overlap populations seem to be of some interest, since they also represent a measure for the "covalency" of the metal-ligand bond and thus have some relation to the discussion of the following chapter. Apparently the bond between Li, Na and Mg ions and water is a rather ionic one, whereas for the larger ions of K and Ca covalent contributions to the bond seem to increase quite remarkably.

3. *The "Covalency Parameter"*

Evaluating the above introduced "covalency parameter" CP for the hydrate complexes leads, similar to the previous data, to a linear relation between MESQUAC and full MO-SCF data (Table 3):

$$CP_{SCF} = 2.66 * CP_{MES} - 0.72 \; (R = 0.99) .$$

Again we have the possibility of extrapolation, which has been used in the case of the hydrates $M^{2+}(H_2O)_6$ of some first row transition metals, which are also included in Table 3. In order to test the reliability of the extrapolation, the hydrate of Zn^{2+} has been included also in the "full" ab initio calculations, and an additional calculation series was performed for the $Cr(CO)_6$ complex, for which the full calculation leads to a CP value of 11.3, the extrapolation from the MESQUAC calculation to 10.9.

Table 3. Covalency parameter "CP" *.

Ion	$CP_{ab\ initio}$	$CP_{MESQUAC}$	$CP_{extrapolated}$
Li(I)	0.2	0.2	0.0
Na(I)	0.4	0.4	0.3
K(I)	1.7	0.9	1.7
Mg(II)	0.9	0.6	0.9
Ca(II)	2.6	1.5	3.3
Zn(II)	11.2	4.4	11.0
Fe(II)	—	3.7	9.1
Mn(II)	—	3.9	9.7
Co(II)	—	9.9	25.6
Ni(II)	—	20.6	54.1

* Li(I)-Ca(II) ... tetrahydrates, Zn(II)-Ni(II) ... hexahydrates.

The degree of "covalency" of the hydrate complexes of alkali and alkaline earth metal ions reflected by CP is in full agreement with that predicted by the overlap populations. For the transition elements, a strong increase of the covalent character of the metal-ligand bond is indicated, culminating at the hydrate complex of Ni(II) ion and decreasing strongly again at the closed-shell ion Zn(II).

Conclusion

Summarizing the results of our comparison of full ab initio and MESQUAC MO results, one can conclude that the MESQUAC wave functions give, besides good stabilisation energies, also a good representation of the charge distribution and thus the polarization of the ligand in the complexes. Charge transfer from the ligand to the metal ion, overlap populations and the character of the metal-ligand bond are reflected correctly only in a qualitative sense, but the simple linear relations between MESQUAC and ab initio data in all cases allow a satisfactory extrapolation of the MESQUAC values in a quantitative sense, leading thus to approximately the same information as the full ab initio procedure, but within a small fraction of their computation time.

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