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Pseudopotential Calculations on Ion-Molecule Complexes

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Pseudopotential calculations on some cation-molecule complexes - Li^+, Na^+, K^+/H_2O, H_2CO - are presented. Despite a rather crude approximation of Coulomb and exchange potentials a reasonably correct description of binding energies and intermolecular distances is obtained. The inclusion of core polarization by a classical approximation does not change the calculated values very much, nevertheless the errors are reduced somewhat.

Key words: Ion-molecule complexes - Pseudopotentials - Intermolecular interaction - Core polarization energies

1. Introduction

Computational efforts to calculate the electronic structure of molecules increase tremendously with the number of electrons in a system. This difficulty has long been a serious obstacle for the investigation of molecules and molecular complexes containing heavy atoms by quantum mechanical methods. Several techniques have been proposed in the past [1-4] which make use of the well-established fact that "inner-shell" or "core"-orbitals do not change shape appreciably on molecule or complex formation. A few recent calculations using pseudopotential methods are mentioned here as representative examples. Kleiner and McWeeny [1] performed "valence-electrons-only" calculations on the molecules H_2CO and NaCl. They applied a modification of a formalism developed by Öhrn and McWeeny [2] making use of semi-empirical projection operators whose parameters were fitted on atomic term values. Bonifacic and Huzinaga [3] reported pseudopotential calculations on the atoms Li through Ne. They too used empirical projection operators but in conjunction with local potential terms. Chang *et al.* [4] calculated atomic states for atoms of the 1st and 2nd row. The parameters of their potential were fitted to reproduce Rydberg series of the corresponding atoms.

Here we present a simple formalism, containing no empirical parameters, which allows us to replace effects of inner-shell electrons by a non-local potential. The theoretical background of pseudopotential calculations is outlined briefly and applied to some simple cation-molecule complexes. Finally, an estimation of the correction brought about by core polarization of the cations' inner shell electrons is presented. The results obtained are compared with Hartree-Fock-Roothaan (HFR) calculations using essentially the same basis sets.

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2. Method of Calculation

In conventional HFR theory [5] the n orbitals describing a closed shell system with $2n$ electrons are obtained from a set of n coupled pseudo-eigenvalue equations:

$$h_F | \psi_i \rangle = \epsilon_i | \psi_i \rangle, \qquad i = 1, \ldots, n \tag{1}$$

h_F here denotes the Hartree-Fock operator, which consists of two groups of terms, one operating on single electrons and a sum of interaction terms, usually called Coulomb and exchange operators, which couple $| \psi_i \rangle$ with the other one-electron orbitals:

$$h_F = \left\{ -\tfrac{1}{2}\nabla_i^2 - \sum_k \frac{Z_k}{|r_{ik}|} \right\} + \sum_j^n (2J_j - K_j) \tag{2}$$

Lagrangian multipliers ϵ_i, enter the theory in order to maintain mutual orthogonality of the orbitals $| \psi_i \rangle$:

$$\langle \psi_i | \psi_j \rangle = \delta_{ij} \tag{3}$$

Without this restrictive condition the valence electrons would collapse into the core. An attempt to vary valence orbitals independently of core orbitals necessarily violates this condition. It has been shown however [6-9], that variational collapse can be prevented by an operator which annihilates all core components contaminating a trial orbital $| \psi_v^p \rangle$, usually called pseudo-orbital.

Applying this operator it can be shown [6–9], that the HFR equations (1) are now valid in a modified form:

$$| h_F + V_R | \psi_v^p \rangle = \epsilon_v | \psi_v^p \rangle \tag{4}$$

The operator V_R is called pseudopotential, it performs a weighted projection of an arbitrary function onto the core space $\{| \psi_c \rangle\}$:

$$V_R = \sum_c | \psi_c \rangle (\epsilon_v - \epsilon_c) \langle \psi_c | \tag{5}$$

During the variational procedure $| \psi_v^p \rangle$ converges to a valence orbital, which might well be contaminated with components of core functions. The valence pseudo-orbitals, of course, do form an orthogonal set. Optimization of valence pseudo-orbitals in (4), on the other hand, violates the orthogonality conditions between valence and core functions. Consequently, the core orbitals have to be reoptimized and thereby a certain restriction in the variability of pseudo-orbitals is introduced.

Several approximations have now to be introduced in order to make the restricted variation computationally more efficient than the full HFR optimization of all orbitals. The main simplifications are the following:

1. Core and valence functions are in general expanded in a finite basis set and therefore represent only approximate eigenfunctions of the operator h_F. Even in case eigenfunctions were available they could not be transferred from one problem to another without losing this property. The reference core functions used here to describe the inner shells of the alkali-cations Li^+, Na^+ and K^+ were taken from calculations on the isolated ions with basis sets described in Table 1.
2. In actual calculations only approximate numerical values for the core orbital energies, ϵ_c, are available. Here we have chosen the free cations as reference states

Table 1. Basis set definition[a]

Molecule/ion	Basis set
H_2O[b]	O: (9,5) [2,2] H: (4) [2]
H_2CO[c]	C/O: (5,3) [3,2] H: (2) [2]
Li^+	Li: (9,1) [3,1][d]; (4) [3][e]
Na^+	Na: (12,6,1) [5,3,1][f]; (5) [4][e]
K^+	K: (17,11) [9,6][g]; (7) [4][e]

[a] The notation X:$(\alpha,\beta,\gamma,\ldots)$ [a,b,c,...] means, that α *s*-type, β *p*-type, γ *d*-type, ... orbitals were placed at atom X and contracted to a *s*-type, *b* *p*-type, *c* *d*-type, ... orbitals respectively.

[b] Orbital exponents and contraction coefficients were taken from Refs. [12] and [13].

[c] Orbital exponents and contraction coefficients were taken from Ref. [16].

[d] Orbital exponents and contraction coefficients were taken from Refs. [12] and [13].

[e] Truncated sets used in the pseudopotential calculation.

[f] Orbital exponents and contraction coefficients were taken from Ref. [14].

[g] Orbital exponents and contraction coefficients were taken from Ref. [15].

and accordingly the energy values ϵ_c were taken directly from HFR calculations of the isolated ions.

3. The calculations can be simplified considerably in case equal ϵ_v values are applied for all valence orbitals. As has been shown by Schwarz [10], the individual ϵ_c and ϵ_v values can vary appreciably in the general case and the assumption of equal valence state energies ϵ_v is not well justified. The orbital energy differences $|\epsilon_c - \epsilon_v|$, however, were found to be roughly constant [10]. In the concrete examples discussed later, the valence state orbitals under consideration either do not overlap appreciably with the core functions or correspond to ϵ_v values, which in absolute value are rather small compared to the ϵ_c's of the alkaline cations. Consequently, the approximation $|\epsilon_c - \epsilon_v| \sim |\epsilon_c|$ is valid to a reasonable degree of accuracy and was applied here.
4. Great numerical complications arise in case the influence of Coulomb and exchange core electron potentials on valence electrons is taken into account rigorously. Substantial simplification is achieved, however, by replacing these terms by an effective local potential. In the following calculations that part of the Hartree-Fock operator (Eq. (2)) which describes the interaction of the nucleus and the core electrons with the valence electron is replaced by a simple effective potential:

$$-\frac{Z_k}{|r_{ik}|} + \sum_c (2J_c - K_c) \sim -\frac{Z_k - n_c}{|r_{ik}|} \qquad (6)$$

Here n_c represents the total number of core electrons and the summation index "*c*"

Table 2. Molecular geometries

H_2O	R_{OH}: 1.80[a]	α_{HOH}: 104.5°
H_2CO	R_{CO}: 2.32 R_{CH}: 2.00	α_{HCH}: 126°

[a] Atomic units are used throughout this paper.
1 a.l.u. = 0.5291 Å, 1 a.e.u. = 627.5 kcal/mol.

runs over all core orbitals. In most cases Eq. (6) will be rather a very crude approximation and leads to a reduction of an attractive contribution. Alkali cation-molecule complexes, however, are characterized by weak mutual penetration of the considerably populated orbitals. Consequently, the assumption of complete screening of the alkali nucleus by the core electrons is not an unrealistic assumption for the particular examples we are studying here.

5. Finally, the two-electron part of the HF operator (h_F) was approximated by pseudovalence orbitals instead of exact HF orbitals. To some extent this approximation compensates for the errors introduced by the two previous assumptions, 2 and 3 [10]. Furthermore, small overlap between pseudovalence and core orbitals justifies this approximation very well.

In case assumptions 1-5 are incorporated into Eqs. (2) and (4) calculations on systems with heavy atoms are greatly simplified:

1. In the SCF procedure less orbitals need to be explicitly evaluated since the core orbitals have been incorporated into the one-electron part of the Hartree-Fock operator.
2. The number of basis functions may be reduced drastically because the oscillations of the valence orbitals in the vicinity of the nucleus which normally cause slow convergence can be smoothed out to a large degree [8].

The computation of the matrix elements of the pseudopotential operator V_R presents no difficulties and is easily implemented into any conventional Hartree-Fock program. Here we used a version of the program MOLPRO, written by W. Meyer and P. Pulay, which was modified to run on an IBM 360/44 computer [11].

3. Application of the Pseudopotential Formalism to Some Cation-Molecule Complexes

The interaction of ions with polar molecules has long attracted the interest of many authors[1]. For computational reasons the main emphasis in the field of "*ab initio*" calculations was restricted to the interaction of first-row ions like Li^+ and Be^{2+} and small ligands like H_2O.

We thought pseudopotential theory might provide a practicable tool in order to overcome this restriction. Consequently we tested the above procedure for a number of ion-molecule complexes and compared the results with full HFR calculations. Results of Hartree-Fock calculations on similar systems may be found in the literature [15-17].

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[1] For a collection of recent data see e.g. Schuster, P., Jakubetz, W., and Marius, W. "Molecular Models for the Solvation of Ions and Polar Molecules" in: Topics in Current Chemistry **60**, 1-107 (1976).

Table 3. Results of pseudopotential and Hartree-Fock calculations on H_2O–X^+ complexes

		Equilibrium distance R_{OX^+} in [a.u.]	Dissociation energy ΔE in [a.u.]
H_2O–Li^+	[a]	3.57	−0.0631
	[b] $\alpha = 0.182$,	3.56	−0.0633
	[c]	3.46	−0.0675
H_2O–Na^+	[a]	4.48	−0.0428
	[b] $\alpha = 1.421$,	4.47	−0.0431
	[c]	4.13	−0.0498
H_2O–K^+	[a]	5.50	−0.0288
	[b] $\alpha = 5.88$,	5.48	−0.0292

[a] Pseudopotential calculation.

[b] Including alkali-core polarization. Values α for the cation polarizabilities were taken from Ref. [18].

[c] Hartree-Fock calculation including all electrons.

The results for equilibrium geometries and dissociation energies obtained with the pseudopotential method are summarized in Tables 3 and 4 and compare well with the results of full HFR calculations also presented in these tables.

Figs. 1 and 2 give an impression of the shape of the energy curves for an approach of the cation along the C_2 axes of the ligands together with the electrostatic potential generated by the ligands' charge distribution and some Hartree Fock results.

4. Polarization of the Alkali Core Electrons

Since the core orbitals are excluded from the variational process, no polarization of core electrons can be described by this formalism. The error introduced thereby into binding energies and equilibrium geometries can be estimated by the classical electrostatic formula, if the core electrons are represented by a polarizable charge with spherical symmetry located at the centre of the ion and in the electric field created by the ligand.

Table 4. Results of pseudopotential and Hartree-Fock calculations on H_2CO complexes

		Equilibrium distance R_{OX^+} in [a.u.]	Dissociation energy ΔE in [a.u.]
H_2CO–Li^+	[a]	3.47	−0.0685
	[b] $\alpha = 0.182$,	3.46	−0.0686
	[c]	3.38	−0.0731
H_2CO–Na^+	[a]	4.35	−0.0472
	[b] $\alpha = 1.42$,	4.34	−0.0474
H_2CO–K^+	[a]	5.35	−0.0322
	[b] $\alpha = 5.88$,	5.33	−0.0326

[a] Pseudopotential calculation.

[b] Including polarization correction. Values α for the cation polarizabilities were taken from Ref. [18].

[c] Hartree-Fock calculation including all electrons.

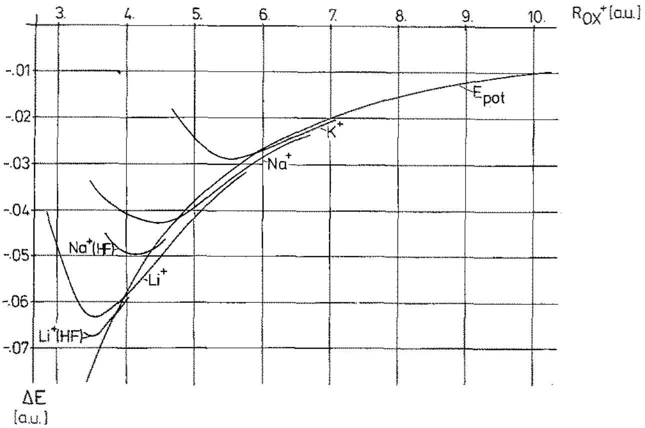

Fig. 1. Alkali-ion water interaction energies (Li^+, Na^+ and K^+ denote curves obtained by pseudopotential calculations. Li^+(HF) and Na^+(HF) represent the corresponding HFR curves calculated with the same basis sets (Table 1); E_{pot} is the classical electrostatic potential of the H_2O molecule derived from the HFR charge distribution; a dipole moment of $\mu = 1.027$ a.u. was obtained for H_2O with this basis set)

We calculated the electric field strength from the charge distribution of the free ligand according to classical electrostatics. Experimental values of polarizabilities [18] were used in the calculation of polarization energy according to formula (7):

$$E_{\mathrm{pol}} = -\tfrac{1}{2}\alpha|E|^2 \tag{7}$$

Modified values for equilibrium geometries and dissociation energies are summarized in Tables 3 and 4. As expected the binding energies increase and the bond lengths decrease somewhat due to electronic core relaxation; on the whole, however, the corrections are very small.

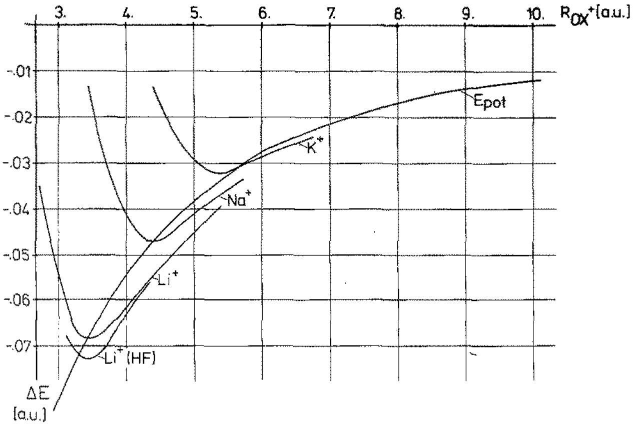

Fig. 2. Alkali-ion formaldehyde interaction energies (Li^+, Na^+ and K^+ denote curves obtained by pseudopotential calculations. Li^+(HF) represents the corresponding HFR curve calculated with the same basis set (Table 1); E_{pot} is the classical electrostatic potential of the H_2CO molecule derived from the HFR charge distribution; a dipole moment of $\mu = 1.275$ a.u. was obtained for H_2CO with this basis set)

5. Discussion

Bond energies and equilibrium geometries obtained from pseudopotential calculations show systematic deviations from the corresponding HFR results. The pseudopotential approximation destabilizes the cation molecules complex along the energy curve shown in Figs. 1 and 2 thus leading to over-estimated equilibrium distances and reduced dissociation energies. As polarization of the cation cores does not reduce this error to a large extent we are inclined to assume that out of all approximations made the assumption of an effective point charge potential in Eq. (6) is responsible at least in part for the deviations observed. As we mentioned already Eq. (6) introduces an underestimation of an attractive contribution to the energy of interaction and therefore leads to a net destabilization of the complex. Finally, it has to be admitted that the other simplifications made might also cause non-negligible contributions to the errors in the energy curves. If not too high accuracy is required, however, the present approximation provides an appropriate tool for investigations giving qualitatively correct answers and a good overall picture for certain classes of large electronic systems for which Hartree-Fock calculations would be extremely time-consuming.

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