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Original Investigations

On the Use of Pseudopotentials in Molecular Calculations

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A series of tests was performed of the Kahn–Goddard–Melius–Topiol pseudopotentials in view of their utilization with small contracted basis sets in molecular computations. The effects of inner-shell separability and of basis set contraction are underlined. The utilizability of Topiol's valence least-squares fitted Gaussian basis sets is studied.

Key words: Pseudopotentials (Topiol–Melius')$\sim$, molecular calculations with$\sim$

1. Introduction

In view of increasing the possibilities of computations of *ab initio* quality on relatively large molecular systems of biochemical interest, we have undertaken, some time ago, an investigation of the utilizability of the pseudopotentials recently developed by Topiol *et al.* [1, 2] in the framework of the formalism of Kahn, Melius and Goddard [3–5]. We have already reported results concerning the computation of intermolecular interactions [6]. We concentrate here on intramolecular properties with a view to assess, in particular, the possibilities of using these pseudopotentials in conjunction with relatively small or highly contracted basis sets of Gaussian functions for the description of the valence electrons. The large biochemicals in which we are interested contain essentially light elements (mostly of the first row, with some second-row atoms like phosphorus and sulfur), but a large number of them, so that an SCF computation, even reduced to a valence electron problem is still large enough to preclude the utilization of extended basis sets. Moreover numerous studies (see for instance [7–15]) have shown that a number of properties of such molecules could be accounted for by full-electron computations at the SCF level using relatively small sets of Gaussian functions, namely (7*s*, 3*p*) for first-row atoms, 3*s* for hydrogen, (10*s*, 6*p*) for second-row atoms, contracted to a minimal basis. Reducing the problem to a valence-electron problem using these small basis sets, would extend the possibilities of computations to much larger systems.

Keeping this aim in mind, we started by testing Topiol's atomic systematics on molecules containing the atoms of interest to us, using appropriate extended basis sets and reducing them stepwise.

2. Computational Details

The details of the methodology are described in the original papers [1–5] and we recall only the features relevant to the present study.

The effective potentials developed by Melius [5] and Topiol [1] for replacing the core electrons in an *ab initio* SCF computation are determined in such a way as to generate, for the valence orbitals, energies as close as possible to those obtained in a full-electron computation, together with "coreless pseudo-orbitals" reproducing accurately the tail of the true valence orbital while going smoothly to zero in the core region.

In this determination the coreless valence orbitals are generated as linear combinations of the same Gaussian functions as those used in the corresponding full-electron computation excluding the functions which serve to represent the core electrons: for instance for first row atoms, the $11s$, $7p$ Gaussian basis set of Huzinaga and Sakai [16] was used with the contraction (5, 111111 / 3, 1111) for the full electron computation, and the valence coreless orbital was generated in terms of the last uncontracted $6s$ Gaussians.

A further distinct characteristic of Topiol's systematics is that after determining as described the appropriate effective potentials, he produces small sets of Gaussian functions containing less terms than the original one, the exponents being obtained by non-linear-least-squares fitting (LSQF) onto the coreless valence orbital. For instance, the six $2s$ functions of the first-row atoms can be replaced by appropriate sets of four functions to be used together with the effective potentials with very little loss in accuracy in the atomic case.

Two questions must be answered as a prerequisite to the study of the problem posed in the introduction:
a) how do Topiol's pseudopotentials perform in a molecular calculation, when used at their best, namely with the same basis sets as those utilized by Topiol for his atomic tests?
b) How does the replacement of this basis by the smaller least-square-fitted set of functions affect the accuracy of a *molecular* calculation?
Only after answering these two questions can one raise the next one:
c) How does the contraction affect the results?

In view of questions a) and b) we performed molecular computations for H_2O and CH_4, utilizing Huzinaga and Sakai's $11s/7p$ basis for O and C contracted, as in Topiol's atomic tests, into [5, 111111 / 3, 1111] and their $4s$ basis for hydrogen, contracted to [3, 1]. The full electron SCF computation is denoted as Ia. Two pseudo-potential computations Ib and Ic were performed on the same systems: in both of them the first five *s* functions of the basis were deleted and the appropriate pseudopotential was utilized to represent the 1*s* core; in computation Ib, the remaining six *s* functions were utilized uncontracted as in the full computation, together with the [3, 1111] *p* basis; in computation Ic the six preceding *s* functions were replaced by the four uncontracted least-squares-fitted functions defined above.

In computations denoted IIa, b, c we illustrate on the case of H_2O, the effect of different contractions of the same initial basis. Finally we compare a series of full-electron and pseudopotential computations with smaller contracted sets on H_2O, CH_4, C_2H_6, NH_3, H_2CO, NH_2CO, PH_3, $PO_4H_2^-$ and $PO_4(CH_3)_2^-$ considering various molecular properties: orbital energies, population analysis, rotational barriers and conformational energy differences as well as electron isodensity distributions and molecular electrostatic potentials.

For each of these compounds, we have adopted the experimental bond lengths and valence angles, and did not reoptimize them.

The geometry adopted in the case of $PO_4(CH_3)_2^-$ and $PO_4(H_2)^-$ results from an average of experimental values found in X-rays crystal structure analysis of phospholipids with standardized OPO valence angles of 109.5°, and is the same as in Ref. [27]. The geometry of NH_2CO is that of Ref. [28] while those of the other compounds can be found in Ref. [29].

We used in our computations the IBMOLH program [17], modified by one of us [18] in order to incorporate the calculation of the matrix elements of the pseudopotential as given by Melius [5].

3. Results

3.1. H_2O and CH_4 in Topiol's Atomic Systematics

Table 1 summarizes the results of the full (Ia) and pseudopotential computations (Ib and Ic) defined in Sect. 2. Given are the energies of the valence orbitals and the results of a Mulliken population analysis [19] on H_2O and CH_4.

It is seen that both types of pseudopotential calculations yield results on the values of the valence orbital energies that match the full SCF results within the same limits, the error remaining between 1 and $5 \cdot 10^{-3}$ atomic units with the larger discrepancy in the deepest molecular energy level where it does not exceed 0.5%. Comparison with the atomic tests of Refs. [1, 2] indicate that the loss of accuracy in going from the atomic to the molecular level is very small and furthermore that it is little affected by the use of the LSQF four terms basis instead of the six original Gaussians.

The conclusions concerning the Mulliken population analysis appear more nuanced: whereas the results of computation Ib compare very favorably with those of the full electron calculation (error less than $6 \cdot 10^{-3}$ e per hydrogen atom, and very similar overlap populations), the replacement of the 2*s* basis by the LSQF four term basis appreciably increases the difference: clearly the LSQF basis which is fitted on a more extended atomic 2*s* set cannot yield, in a molecular computation, molecular orbitals which fit as closely as in the atom the orbitals computed with the extended basis.

Table 1. Orbital energies and Mulliken populations in H_2O and CH_4 in full (Ia) and pseudopotential calculations, Ib and Ic[a]. ε: orbital energy (a.u.), $\Delta\varepsilon$: ε(pseudo) -ε(full) (10^{-3} a.u.) O, H, C, H: atomic net charges on the respective atoms; OH, HH, CH, HH: overlap populations

	Ia	Ib		Ic	
	ε	ε	$\Delta\varepsilon$	ε	$\Delta\varepsilon$
H_2O	−1.3678	−1.3658	2.0	−1.3636	4.2
	−0.7227	−0.7240	−1.3	−0.7238	−1.1
	−0.5743	−0.5754	−1.1	−0.5749	−0.6
	−0.5128	−0.5145	−1.7	−0.5138	−1.0
CH_4	−0.9454	−0.9407	4.7	−0.9410	+4.4
	−0.5456	−0.5469	−1.3	−0.5470	−1.4
	−0.5454	−0.5466	−1.2	−0.5468	−1.4
	−0.5453	−0.5467	−1.4	−0.5468	−1.5
O	−0.632	−0.638		−0.702	
H	+0.316	+0.319		+0.351	
OH	0.580	+0.573		+0.590	
HH	−0.020	−0.018		−0.043	
C	−0.776	−0.797		−0.572	
H	+0.194	+0.199		+0.143	
CH	0.732	0.729		0.777	
HH	−0.053	−0.053		−0.043	

[a] Ia: Huzinaga and Sakai's 11*s*, 7*p* basis contracted into [5, 111111 / 3, 1111].
Ib: valence orbitals represented by the same basis [111111, 3, 1111] as in Ia.
Ic: Topiol's uncontracted 4G functions for the 2*s* valence orbital; 2*p* set as in Ib.

3.2. The Influence of Contraction

The accuracy of the results in the pseudopotential calculation Ib compared to the full calculation Ia indicates that the separability of the 1*s* and 2*s* shells is appropriately satisfied at the 5/111111 contraction level. The influence of the contraction is evidenced further in the set of computations reported in Table 2 for H_2O. In this case a full-electron computation (IIa) was performed using the same (11*s*, 7*p*) basis set as before but contracted differently: [6, 1; 3, 1] for the *s* functions; [6, 1] for the *p* functions and [3, 1] for H.

Table 2. Orbital energies and Mulliken populations in H_2O in a full (IIa) and in two pseudopotential computations (IIb and IIc)[a]. ε: orbital energy (a.u.), $\Delta\varepsilon = \varepsilon(\text{pseudo}) - \varepsilon(\text{full})$ (10^{-3} a.u.) O,H net charges on O and H; OH, HH: overlap populations

	IIa	IIb		IIc	
	ε	ε	$\Delta\varepsilon$	ε	$\Delta\varepsilon$
	−1.3741	−1.0808	+293.3	−1.3647	+9.4
	−0.7231	−0.7747	−51.6	−0.7221	+1.0
	−0.5754	−0.5718	+3.6	−0.5741	+1.3
	−0.5145	−0.5643	−49.8	−0.5141	+0.4
O	−0.626	−0.466		−0.652	
H	+0.313	+0.233		+0.326	
OH	0.575	0.754		0.600	
HH	−0.062	−0.053		−0.080	

[a] IIa: Huzinaga and Sakai's (11*s*; 7*p*) set contracted into [6, 1] for 1*s* [3, 1] for 2*s*; [6, 1] for 2*p*. 4*s* for H contracted into [3, 1].
IIb: valence orbitals represented by the same set as in IIa.
IIc: Topiol's 4G set contracted into [3, 1] for the 2*s* valence orbital; 2*p* set as in IIb.

Two pseudopotential computations were made: one (IIb) with the same basis set for the 2*s* as in the full computation, and the other (IIc) with Topiol's LSQF basis set, also contracted to [3, 1], to represent the 2*s* orbital.

It is seen that the results obtained in computation IIb on the valence orbital energies are very poor (except for the second-highest molecular orbital which is pure *p*), whereas the agreement between the energies of the valence orbitals in IIa and IIc is very satisfactory. It appears that Topiol's LSQF basis set, originally fitted on an atomic wave function with the proper shape in the valence region retains no projection in the core region and conserves enough flexibility to adjust properly with this wave function even when contracted into [3, 1]. The comparison of the results of computations Ic and IIc is illustrative of this fact.

On the other hand, although the wave function generated by Huzinaga's basis set behaves properly at the uncontracted level, its separability into 1*s* and 2*s* orbitals is no longer possible at the contracted level, because the 2*s* Gaussian set then requires the 1*s* Gaussians to improve its representation.

One can see from Tables 1 and 2 that the valence orbital energies are not drastically affected from computation Ia to computation IIa (although the total molecular energy passes from −76.0145 a.u. to −75.5699 a.u.). However, if the 1*s* core orbitals are removed as in computation IIb, there results a drastic loss in the values of the energies of the valence molecular orbitals.

These comparisons give indications on the way to utilize Topiol's pseudopotentials when it is not possible to work at the same level of basis set accuracy as he used in his atomic computations. The comparison of the full SCF computations Ia and IIa indicate that although the separation of the 11*s* 7*p* basis into [5, 111111] is the most satisfactory, the [61, 31] contraction still leads to reasonable overall molecular results. But if then, starting from the latter case, one considers that the seven first functions correspond to the 1*s* orbital and deletes them to replace them by Topiol's pseudopotential, one must insure the generation of a correct "coreless" 2*s* orbital by using the appropriate LSQF basis.

This constraint is all the more stringent the smaller and more contracted the basis set, as will be seen now.

4. Computations with Small Basis Sets

As stated earlier, a large number of our former full SCF computations were made using Clementi's (7*s*, 3*p*/3*s*) basis [12] for first-row atoms, contracted into minimal, using five functions for the 1*s* shell and the remaining two for the 2*s* shell. It is clear from the preceding discussion that upon replacement of the 1*s* core by a pseudopotential, the remaining two *s* functions will not yield an appropriate representation. This is indeed what is observed in Table 3 where we compare a full SCF computation made with this basis on water (IIIa) with the corresponding pseudopotential computation IIIb made as in the full computation, only deleting the five first Gaussians from the basis: the orbital energies are all very poorly obtained and the populations are absurd.

	IIIa	IIIb	IIIc
ε	−1.3265	−0.9458	−1.3445
	−0.6903	−0.8108	−0.6852
	−0.5500	−0.5413	−0.5486
	−0.5022	−0.6439	−0.4978
q_O	−0.618	+0.164	−0.702
q_H	+0.309	−0.082	+0.351

Table 3. Orbital energies ε(a.u.) and Mulliken net charges q in H_2O in a full computation IIIa and two pseudopotential computations IIIb and IIIc[a]

[a] IIIa: Clementi's basis (7*s*, 3*p*/3*s*) contracted into minimal [5; 2; 3/3].
IIIb: valence orbitals represented by the same functions as in IIIa.
IIIc: Topiol's 4G set contracted into one for the 2*s* valence orbital; 2*p* set as in IIIb.

It is obvious that the representation of the 2*s* molecular orbital is greatly improved in the full computation by the 1*s* (5 Gaussians) core orbitals, and thus the two remaining Gaussians alone cannot match the shape of the true 2*s* orbital in the valence region (while still retaining nodes in the core region).

If one uses instead Topiol's LSQF set contracted into one function (IIIc) the results come back to a much more reasonable fit to those of the full computation.

In this connection it is instructive to recall the results obtained in Ref. [6], where a comparison of full and pseudo-potential calculations was made in the case of H_2O using different basis sets: the agreement between full and pseudo-potential valence orbital energies was the best where Gauss-fit type orbitals (STO 3G [20] or split basis [21]) were being handled at the full SCF level, that is, orbitals that can be readily split into 1*s*, 2*s*, etc., type orbitals. This is not the case for most of the available Gaussian basis sets (Huzinaga [16], Dunning [22], Siegbahn-Roos [23] etc...) where the *s* exponents are optimized on atoms regardless of their separability into 1*s*, 2*s*, etc., shells.

In view of the results obtained for H_2O in IIIc we deemed interesting to continue the systematic exploration of the validity of the pseudopotential computations consistently utilized in the same fashion. Thus in the full computation we used the exponents and contraction coefficients of the basis set adopted in our former computations [11], which include (7*s*; 3*p*) on first row atoms, (3*s*) on hydrogen and (10*s*; 6*p*; 1*d*) on 2nd row atoms, contracted into minimal as [5, 1; 1], [1], and [6, 2, 2; 4, 2; 1] respectively. In the pseudopotential computations we proceed as for water in computation IIIc for all the first-row elements. For second-row elements, the basis used to represent the 3*s* and 3*p* valence orbitals are Topiol's LSQF functions contracted to a minimal set.

It is clear from the previous discussion that the procedure adopted cannot yield results reproducing those of the full SCF computations with which we make a correspondence. Thus the aim is not to reproduce the results but rather to find, in the framework of Melius–Topiol's methodology a workable systematics with a level of accuracy *comparable* to that of the full computation.

We have performed computations on NH_3, CH_4, C_2H_6, H_2CO, NH_2CHO, PH_3, $PO_4H_2^-$ and $PO_4(CH_3)_2^-$.

4.1. Orbital Energies and Populations

Results obtained for the orbital energy values are very similar to those obtained for H_2O: an illustration of the results concerning the orbital energy values is given in Tables 4 and 5. It is seen that the differences are of 1 to $2 \cdot 10^{-2}$ a.u., but the trends upon different variations (C_2H_6 staggered to eclipsed, or PH_3 without and with *d* orbitals on phosphorus, etc.) are very closely followed. The populations, as observed before, show appreciable differences in total values, well illustrated by H_2O and PH_3 (Tables 3 and 5 respectively), the pseudopotential net charges being larger than in the full computations. Here again the trends observed upon chemical modifications are respected and the overall variation in the net populations are conserved as can be seen from Fig. 1 where we plotted all the net charges computed (pseudopotential *versus* full calculation).

The tendency to a linear trend is clear without being perfect. The largest difference occurs for the phosphorus atoms of $PO_4H_2^-$ and $PO_4(CH_3)_2^-$ (extreme upper two right points), which loose electronic charge in favor of their neighbors for which, however, the difference with the charges of the full computation is less apparent, due to the distribution of the effect on four atoms.

Table 4. Orbital energies ε in full (F) and pseudopotential (P) computations for NH_3, CH_4 and C_2H_6 staggered (s) and eclipsed (e)

	ε(a.u.)		
	F	P	$\lvert\Delta\varepsilon\rvert(10^{-3}$ a.u.)
NH_3	−1.1372	−1.1436	6.4
	−0.6287	−0.6197	9.0
	−0.6286	−0.6195	9.1
	−0.4376	−0.4299	7.7
CH_4	−0.9698	−0.9561	13.7
	−0.5791	−0.5623	16.8
	−0.5789	−0.5622	16.7
	−0.5789	−0.5622	16.7
C_2H_6 (s)	−1.0469	−1.0204	26.5
	−0.8596	−0.8533	6.3
	−0.6331	−0.6149	18.2
	−0.6331	−0.6149	18.2
	−0.5393	−0.5108	28.5
	−0.5192	−0.5039	15.3
	−0.5192	−0.5039	15.3
C_2H_6 (e)	−1.0465	−1.0198	27.7
	−0.8589	−0.8527	6.2
	−0.6339	−0.6158	18.1
	−0.6339	−0.6158	18.1
	−0.5387	−0.5102	28.5
	−0.5169	−0.5016	15.3
	−0.5169	−0.5016	15.3

Table 5. Orbital energies ε(a.u.) and net charges q in PH_3 in full (F) and pseudopotential (P) computations (a) without d orbitals on P. (b) with d orbitals on P

	(a)		(b)	
	F	P	F	P
ε	−0.8391	−0.8655	−0.8271	−0.8458
	−0.5422	−0.5427	−0.5452	−0.5453
	−0.5422	−0.5427	−0.5452	−0.5453
	−0.3435	−0.3533	−0.3435	−0.3513
q_P	−0.208	−0.284	−0.410	−0.434
q_H	+0.069	+0.095	+0.136	+0.145

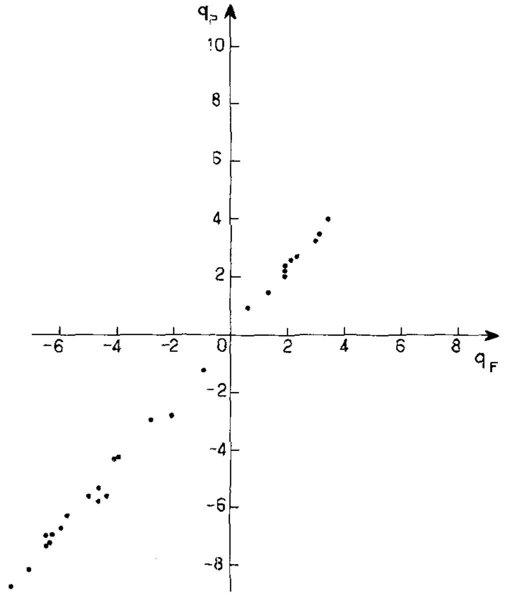

Fig. 1. Net atomic charges q_P (pseudopotential computation) versus q_F (full computation). Basis sets as in the text. Negative values: excess of electrons (10^{-1} e)

4.2. Barriers to Rotation and Conformational Energy Differences

The tests performed are summarized in Table 6. It is seen that the pseudopotential computed values are similar in magnitude to those obtained in the full calculation and that all the trends are reproduced (effect of *d* orbitals on DMP^-, effect of sodium binding). The largest difference occurs for formamide: it is likely that the effect of non-equivalence of the valence basis sets in the two computations (Topiol LSQF 2*s* function associated with the 2*p* of the full basis) has a different impact on the planar and perpendicular conformations. The value of the barrier remains in the range of a reasonable fit to the experimental values in various amides [24].

Table 6. Rotational barriers and conformational energy differences (kcal/mole) computed in full (*F*) and pseudopotential (*P*) calculations. Basis sets as explained in text

	F	*P*
C_2H_6	3.05	3.16
NH_2CHO	20.3	21.7
DMP^-	[a] 0.43	0.31
$gg \rightarrow gt$[d]	[b] 2.27	2.50
$Na^+ - DMP^-$[c]	4.3	4.6
$gg \rightarrow gt$[d]		

[a] without *d* orbitals on P.

[b] with *d* orbitals on P.

[c] Na^+ in bridge "position" (see Ref. [11]).

[d] *gg*, *gt*: *gauche-gauche* and *gauche-trans* conformers respectively (see Ref. [27]).

4.3. Isodensity and Isopotential Contours

Figures 2 and 3 compare, for the anion $PO_4H_2^-$, in the OPO plane of the *gauche-gauche* conformer, the isodensity contours (2a and 2b) and the electrostatic molecular potential [25] map (3a and 3b) in the full SCF and pseudopotential computations. To make the isodensity contours comparable, only the valence molecular orbitals of the full computations are included in the global density contours of Fig. 2a.

The density contours of Figs. 2a and 2b are very similar, except, as could be expected, for those very close to the heavy atoms. The most visible difference is seen close to the phosphorus atom where the deletion of the 1*s* and 2*s*, 2*p* orbitals and the replacement of the 3*s*, 3*p* Gaussians by Topiol's LSQF functions leads to a loss of electrons to the electronegative oxygen atoms, a feature equally observed in the global net charges (*vide supra*).

The molecular potentials of Figs. 3a and 3b are also very similar in the general image which they give of the anion. Both the shape of the potential curves, the

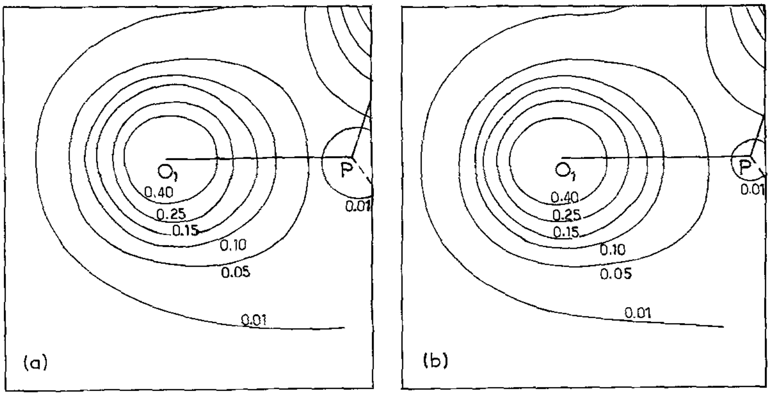

Fig. 2. Isodensity contours for PO$_4$H$_2^-$ in the O$_1$PO$_3$ plane of the anionic oxygens. a) full computation; valence electrons only; b) pseudopotential computation as explained in the text. There is a symmetry with respect to the bissectrix of the O$_1$PO$_3$ angle

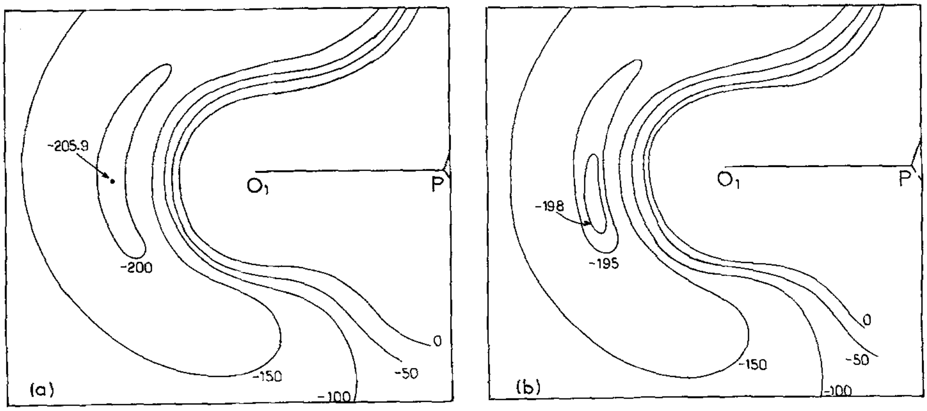

Fig. 3. Molecular electrostatic potential map for PO$_4$H$_2^-$ in the O$_1$PO$_3$ plane of the anionic oxygens. a) full computation; b) pseudopotential computation as explained in the text. There is a symmetry with respect to the bissectrix of the O$_1$PO$_3$ angle

position of the potential wells and the order of magnitude of the numerical values are the same. The differences observed (−199 instead of −206 kcal/mole) at the minimum reflect apparently the overall differences observed in the valence electron densities. Nevertheless it is clear that neither the replacement of the inner shells by the pseudopotential, nor the changes in the basis set for the valence electrons have an important effect on the conclusions which could be drawn for this molecule from the potential map.

5. Conclusion

The set of results presented here indicates that it is possible to use Topiol's pseudopotentials for molecular calculations. Good results are obtained when using as valence basis set in molecules the same uncontracted basis used by Topiol in the atomic tests. Replacement of the *2s* basis by Topiol's LSQF basis does not modify seriously the molecular orbital energies but affects some details of the atomic populations, obviously due to the smaller number of functions in the basis. When contraction is used care must be taken because the uncontracted basis chosen by Topiol is imperfectly separable into *1s*, *2s*, etc., orbitals. This apparently is alleviated by the flexibility at the uncontracted level, but at high contracted levels the utilization of the LSQF functions seems preferable insofar as it ensures separability from the core. The shortcomings of this procedure appear notable essentially in the Mulliken population analysis. However, the general qualitative image of the molecule as given by the valence electron density plots or the molecular electrostatic potentials do not change appreciably. Rotational barriers are correctly reproduced.

The computer time on an IBM 370/168 with the IBMOLH set of programs is reduced by approximately fifty per cent in the pseudopotential computation with respect to the full SCF processing. The procedure may be useful at least for delineating the gross features of a large molecular problem. This has been done recently for a theoretical study of the binding of sodium to the polar head of phosphatidylserine [26].

Although this should be clear from our commentaries, we would like to stress again that, as shown in Sect. 2, the ideal way to utilize the effective potentials is certainly to join them to the full appropriate basis sets for the valence electrons. When, however, this is precluded, they may be used with the LSQF basis, more or less contracted according to the possibilities.

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