Theoret. Chim. Acta (Berl.) 62, 461–475 (1983)

THEORETICA CHIMICA ACTA

Applicability of a Pseudopotential CI Method to the Investigation of Ground and Excited States of Molecular Systems: NaCO, Li_2H, Al_2 and AlH

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The potential energy curves for the ground and first excited states of some molecules involved in very different problems of theoretical chemistry have been determined employing the pseudopotential (PP) SCF procedure followed by multireference double-excitation configuration interaction treatment (MRD CI).

The influence of the choice of the basis set is widely discussed. The PP results are overall in excellent agreement with the results obtained from the analogous all electron (AE) calculations when sufficiently flexible basis sets are adopted. Some small discrepancies encountered are due to the use of minimal basis sets.

Key words: Pseudopotential method – Configuration interaction – Excited states.

1. Introduction

Determination of electronic structure of chemical systems by solving Schrödinger equation is a difficult problem since the number of integrals to be computed grows very rapidly with the number of electrons and atomic orbitals present in the system. Only for small molecules it is possible to take into account all the electrons, i.e., core and valence electrons.

In all other cases it is necessary to apply methods which consider explicitly only the valence electrons and which simulate the effect of the inner electrons by

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0040-5744/83/0062/0461/$03.00

means of the potential generated by the nuclei and the core electrons. Such methods, as for example empirical and semiempirical methods in quantum chemistry or band calculations in solid state physics, have been successfully tested in the last twenty years, in particular in the field of solid state physics. However, their use is limited because of theoretical approximations: some matrix elements are neglected or parametrized in order to reproduce experimental values or other all electron calculations. On the contrary, the use of the pseudopotential theory allows to achieve a compromise between the computationally expensive all electron methods and the theoretically not well defined semiempirical treatments.

The fundamental idea is to replace cores, that are supposed to be chemically invariant when transferred from the atom to the molecule, with an analytical potential fitted at atomic level, facilitating in such a manner a detailed treatment of the chemically significant valence region of the molecules. The potential is determined in order to generate nodeless pseudovalence orbitals forced to overlap as much as possible with the all electron atomic solution outside the core region; these are the so called "*ab initio* pseudopotential" methods because the determination of the parameters is based on a pure *ab initio* all electron calculation. If the potential is determined in order to reproduce experimental data as for instance, experimental energies of one-valence-electron ions, we refer to the method as an "empirical pseudopotential" [1–4].

Many different PP models have been reported in the last years. Among them the "*ab initio*" pseudopotential proposed by Durand and Barthelat [5] seems to be very efficient because of its capability to reproduce the results of the corresponding all electron calculations and because of its relative computational simplicity. However, few examples of pseudopotential calculations estimating the valence-shell correlation energy are available and in general they are applied to the description of the molecular ground states [6–11].

The aim of this work is to show that the combination of the pseudopotential version of the IBMOL program (PSIBMOL) with the multireference double excitation configuration interaction procedure (MRD CI) [12] represents a very flexible method even in the study of the excited states of a molecule.

The PP MRD CI procedure has been already successfully used in the study of clusters of alkali (Li, Na, K) [13] and alkaline-earth (Be, Mg, Ca) [14] metal atoms and in this work an extension of the application of the method to different molecular systems will be shown.

In the following sections the results of our PP MRD CI calculations are compared with reference AE MRD CI calculations performed using basis sets of comparable quality. We have considered energy curves involved in the quenching process of the Na atom in its ^2P excited state by a CO molecule, the interaction of atomic hydrogen with a Li_2 cluster, the potential energy curves of Al_2 dimer and the electronic properties of AlH. However, in this work the emphasis has not been put on the chemical and physical aspects of the considered problems. A special attention has been paid to the basis sets extension effects.

The computational details are given in Sect. 2 and some general conclusions are drawn in the last part.

2. Computational Method

In the framework of the present pseudopotential method the atomic Hamiltonian takes the form [5]:

$$H_{PP} = \sum_{i=1}^{N_v} \left\{ -\frac{\nabla^2}{2} + W_{PP}(i) \right\} + \sum_{i<j}^{N_v} \frac{1}{r_{ij}} \tag{1}$$

where the $W_{PP}(i)$ operator is defined as a product of a radial operator and an angular projection operator:

$$W_{PP}(i) = -\frac{Z}{r_i} + \sum_l W_l(r_i)\hat{P}_l.$$

Here $Z = N_v$ is the net charge of the ion formed by the core electrons and the nucleus of the atom. $\hat{P}_l$ is an angular projector operator onto the lth subspace of the spherical harmonics and $W_l(r)$ is a radial function given by the general expression

$$W_l(r) = \sum_K c_l^k r^{n_l^k} \exp(-\alpha_l^k r^2).$$

The parameters c_l^k, n_l^k and α_l^k have been determined in such a way that the valence Hartree–Fock energy levels and the form of the valence orbitals (outside the core region) of the corresponding AE calculations are reproduced [15]. In the original work the AE reference solutions were obtained using a double-zeta basis set of Slater orbitals (STO) and the PP atomic orbitals were expanded in the same basis set [15]. Since the use of STO basis sets is practicable in molecular calculations only with high computational effort, the most economical way to carry out molecular calculations is to adopt a basis set of Gaussian type orbitals (GTO).

The orbital exponents and the contraction coefficients of the GTO's used in this work have been previously optimized at atomic level [16] and tested both in SCF [17] and CI [13] molecular calculations.

The CI spaces in the MRD CI procedure [12] consist from configurations arising by single and double excitations with respect to one or more leading reference configurations M. From all these generated configurations are explicitly included in the final diagonalization only those which give an energy lowering of the required root R of the secular equation larger than a given selection threshold T.

The last step of the procedure consists in the extrapolation of the total energy to the whole CI space ($T \rightarrow 0$). The following discussion refers always to the results of the CI extrapolated energies. In the case of AE calculations only correlation among valence electrons has been considered.

3. Results and Discussion

3.1 NaCO

The investigation of nonadiabatic processes is of fundamental importance in photochemistry. In recent years many experimental [18, 19] and theoretical studies [20–22] have been reported in the literature. Among them, the quenching of excited alkali metal atoms by diatomic molecules such as N_2, NO and CO represents a relatively simple model for the analysis of the electronic, vibrational and rotational energy transfer [22].

As a representative example of this type of chemical problems we have considered the interaction of a single Na* atom with a CO molecule: the potential energy curves for the ground and low-lying excited states of the Na*–CO system have been determined in the framework of the PP MRD CI and of the AE MRD CI approaches.

In all CI calculations a selection threshold $T = 5$ μhartree was employed and the size of the corresponding CI spaces to be diagonalized range from 1500 to 4000 configurations.

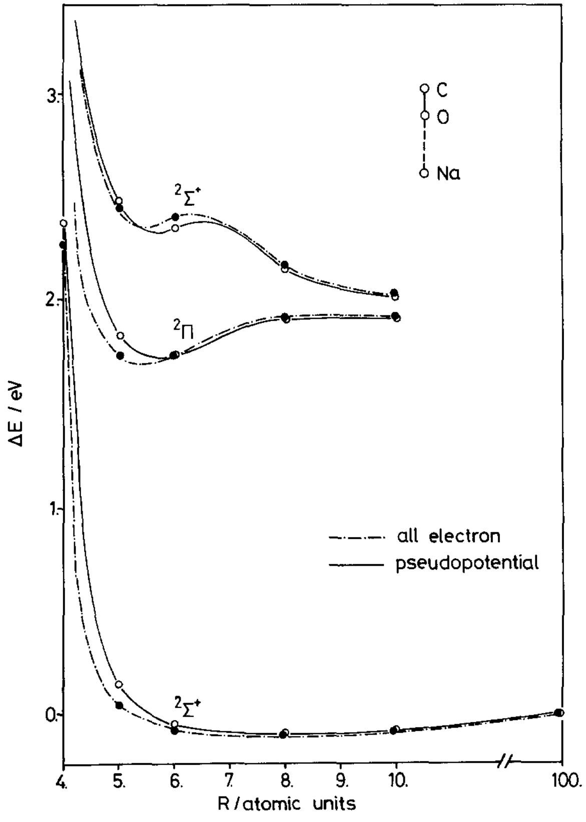

Fig. 1. CI potential energy curves for the ground and first excited states of NaCO in colinear approach on the O-end. The C-O distance is fixed to the value of the free molecule (2.15 a.u.)

For the first set of calculations a GTO basis set of double-zeta type was chosen. For the PP calculation the [4*s*4*p*] basis set *B* of Ref. [16] was contracted to [2*s*2*p*] for carbon and oxygen. This contraction scheme was adopted also for the 3*s* orbital of the sodium atom. Two 3*p* polarization functions have been added, giving rise finally to a [4*s*2*p*/2*s*2*p*] PP basis set. The results obtained from PP method employing this basis set will be compared with the results of the AE treatment using Siegbahn's basis set [23] extended by the same polarization functions [24]. With these basis sets the computed electronic excitation energy $Na(3^2S) \rightarrow Na(3^2P)$ are 1.94 and 1.99 eV in the AE and PP calculations, respectively; these two quantities are to be compared with the experimental value of 2.1 eV.

The potential energy curves for the interactions $Na(3^2S) + CO(^1\Sigma^+) \rightarrow NaCO(^2\Sigma^+)$ and $Na(3^2P) + CO(^1\Sigma^+) \rightarrow NaCO(^2\Pi)$ have been obtained changing the distance *R* of the Na atom from the center of the mass of the CO for two different colinear approaches: Na on the O-side and on the C-side of the CO molecule (see Figs. 1 and 2). The agreement between the AE and the PP curves is very

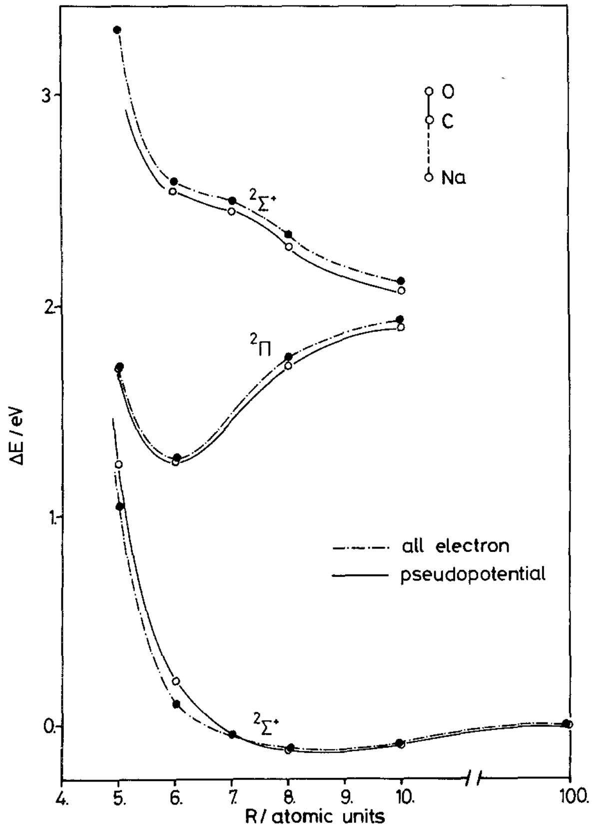

Fig. 2. CI potential energy curves for the ground and first excited states of NaCO in colinear approach on the C-end. The C-O distance is fixed to the value of the free molecule (2.15 a.u.)

good; a deep potential well is observed for the $^2\Pi$ excited state for both the Na–OC and Na–CO approaches. In particular for this latter case the energetically lowest point of the curve (at a distance $R = 6$ a.u.) lies 0.73 eV below the asymptotic dissociation limit for this state.

The existence of a crossing of the first $^2\Pi$ excited state with the $^2\Sigma^+$ ground state of the molecule is crucial for the discussion of the quenching process. Very recently has been demonstrated that this crossing occurs when the relaxation of the CO molecule is allowed [22]. Therefore, we have considered the stretching of the CO distance from 2.1 to 2.8 a.u. for the fixed Na–CO separation $R = 6$ a.u. The PP results have been compared with the AE MRD CI curves recently reported (see Fig. 9 of Ref. [22]).

These AE results have been obtained with an AE basis set larger than that previously described including one *s* and one *p* diffuse function more on carbon and oxygen atoms and two diffuse *s* and one diffuse *p* function on Na atom (see Ref. [22]).

In order to compare the position of crossing point between $^2\Pi$ and $^2\Sigma^+$ states the same diffuse functions have been included in the PP basis set (C and O [$5s5p/3s3p$], Na [$6s3p/4s3p$]). The PP and AE curves are given in Fig. 3. The expected crossing of the $^2\Pi$ and $^2\Sigma^+$ states is perfectly reproduced by the PP calculations. This means that discrepancies between AE and PP are not to be expected also if the atomic pseudopotential operator is used in connection with

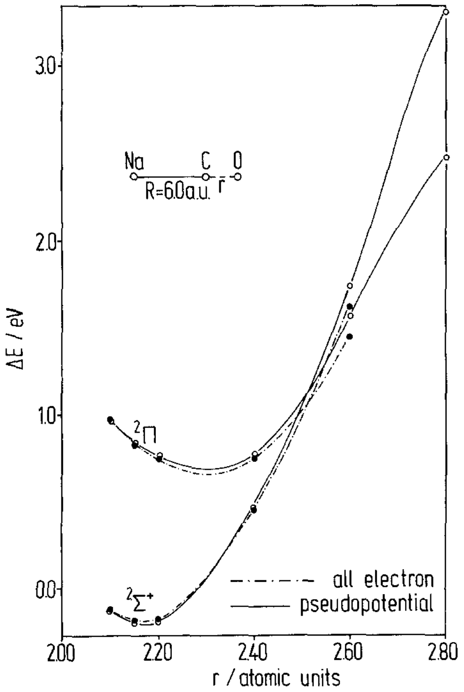

Fig. 3. CI potential energy curves for the occurring crossing of the $^2\Sigma^+$ and $^2\Pi$ states of Na-CO when the C-O distance is stretched. The Na-C distance has been fixed to the value of 6 a.u.

valence basis sets augmented by polarization functions taken from different AE calculations.

3.2 Li_2H

The analysis of the interaction of the hydrogen atom with a small lithium cluster has been the subject of a great number of theoretical investigations [25], mainly because of considering these systems as simple models of very dispersed catalysts or of the chemisorption sites on metal surface itself. In the following we present the results of our investigation concerning the adsorption of the hydrogen atom on the "bridge" position of the Li_2 molecule. The Li–Li distance has been hold fixed at the value of 6.614 a.u., which is the Li–Li separation experimentally observed in the (100) face of the *bcc* lithium metal.

In both AE and PP CI treatments all configurations obtained by single and double excitations with respect to the leading reference configuration are explicitly considered ($T=0$). The two lowest potential energy curves for the Li_2–H interaction are shown in Fig. 4 for the $^2B_2$ and $^2A_1$ electronic states. The AE curves have been computed with a [$8s2p/6s2p$] basis set [26]. For the PP calculations an uncontracted basis set, [$4s2p$] was adopted (basis set *B* of Ref. [16]). Both these basis sets are of better quality than triple-zeta. The *p* polarization functions at Li atom and the [$4s1p/2s1p$] [27] basis set for the hydrogen atom are the same in the AE and PP treatments.

The AE potential energy curves are perfectly reproduced quantitatively by the PP ones; the two $^2B_2$ and $^2A_1$ electronic states crosses each other for the same distances of the hydrogen atom from the middle point of the Li_2 molecule (1.55 a.u. and 1.53 a.u. in the AE and PP treatments, respectively). The

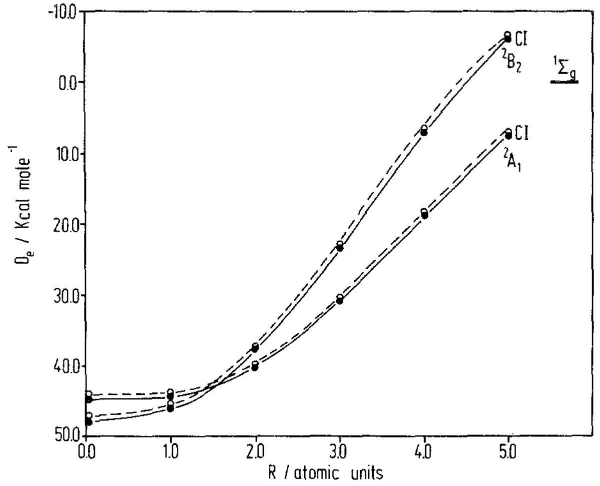

Fig. 4. CI curves for the $^2A_1$ and $^2B_2$ states of the adsorption of hydrogen atom on Li_2 (100) cluster. The basis sets adopted for the lithium atoms are: AE [$8s2p/6s2p$] (——), PP [$4s2p$] (– – –)

chemisorption energies are 48.1 kcal/mole (AE) and 47.3 kcal/mole (PP) for the $^2B_2$ ground state, and 45.2 kcal/mole (AE) and 44.2 kcal/mole (PP) for the first $^2A_1$ excited state.

In a second series of calculations, the reference AE potential energy curves, obtained with a [6*s*1*p*/2*s*1*p*] GTO basis set of single-zeta quality, have been taken from Ref. [25]. This small basis set has been originally chosen in Ref. [25] in order to extend the calculations to larger systems. In PP we describe the valence region of the lithium atoms by means of the same set of 4*s* GTO previously mentioned, contracted into two *s* functions. The same *p* function of the AE calculation has been added in order to take into account the polarization effects which are not negligible. The resulting potential energy CI curves are shown in Fig. 5, from which a good agreement between the results of the AE and PP treatments can be seen. This suggests that also double-zeta quality PP basis set yields reliable results with acceptable computational costs.

On the contrary, a substantially different situation arises if the smaller PP basis set *A* of Ref. [16], [3*s*1*p*/1*s*1*p*], contracted to a really minimal single-zeta type basis set is employed. The two PP CI curves are shifted towards higher energies with respect to the AE ones in the minimum region. The computed binding energies for the $^2B_2$ ground state are 31.6 kcal/mole (PP) against the value of 42.1 kcal/mole obtained with the minimal AE basis set. For large distances between the hydrogen atom and the Li_2 molecule these differences nearly disappear (see Fig. 5).

The reasons for these discrepancies are to be looked for in the deficiency of the PP basis set; in fact, in this case only one Gaussian function is used to describe the 2*s* atomic orbital of lithium. From the analysis of the $3a_1$ highest occupied

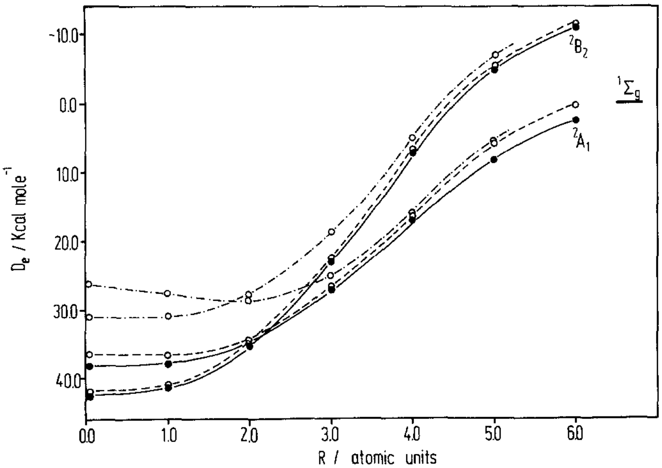

Fig. 5. CI curves for the $^2A_1$ and $^2B_2$ states of the adsorption of hydrogen atom on Li_2 (100) cluster. The basis sets adopted for the lithium atoms are: AE [6*s*1*p*/2*s*1*p*] (——), PP [4*s*2*p*/2*s*1*p*] (- - -), PP [3*s*1*p*/1*s*1*p*] (- · -)

molecular orbital (HOMO) of the Li_2-H system, obtained from the AE treatment, follows that the participation of the core orbitals of the lithium atoms is not negligible. This is true in particular in the region of the minimum. This means that at least two *s* functions are necessary for the description of the valence MO's of the Li_2-H molecule, and this conclusion is well confirmed by the more reliable results obtained with the double-zeta $[4s1p/2s1p]$ PP basis set.

Finally, we report some estimated correlation energies of the $^2A_1$ excited state in the region of the minimum. For basis sets of comparable quality we have obtained: AE $[6s1p/2s1p]$, −0.0274 a.u., PP $[4s1p/2s1p]$ −0.0279 a.u.; AE $[8s2p/6s2p]$ −0.0283 a.u., PP $[4s2p]$ −0.0284 a.u. Therefore, the error between AE and PP treatments in the evaluation of the correlation energy is always smaller than 2%.

3.3 Al_2

The understanding of the nature of the bond in Al_2 can be a useful tool in the study of larger Al clusters and of their interaction with small molecules. The only previously reported studies on the Al_2 molecule have been done for comparative purpose [28–29] or in the repulsive region of the potential energy curve [30]. For the investigation of the Al dimer we have adopted four PP and two AE basis sets. The PP basis sets have been derived from the $[4s4p]$ GTO basis set of Ref. [16] by means of two different contraction schemes and are the $[4s4p/2s1p]$, $[4s4p/2s2p]$ and the uncontracted $[4s4p]$. The fourth basis set

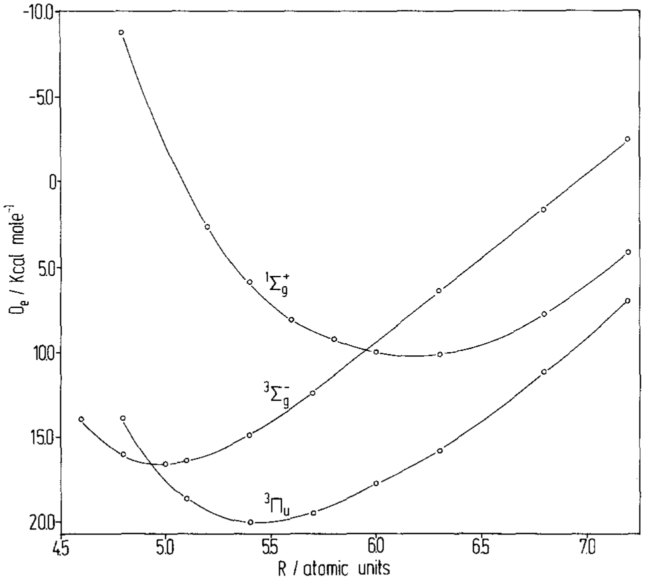

Fig. 6. PP MRD CI curves for the three low lying states $^3\Pi_u$, $^3\Sigma_g^-$ and $^1\Sigma_g^+$ of the Al_2 molecule obtained with a $[4s4p/2s2p]$ PP basis set. The inclusion of *d*-polarization functions gives shorter equilibrium distances and larger binding energies (see Table 1)

has been obtained adding one *d*-polarization function to the [4*s*4*p*/2*s*2*p*] basis set. The Gaussian exponent has been optimized at molecular level for the diatomic Al_2 ($\alpha = 0.220667$). The two AE basis sets, [9*s*5*p*/3*s*2*p*] and [13*s*10*p*/5*s*4*p*], are of single- and double-zeta type, respectively. The exponents and the contraction coefficients have been taken from Ref. [31].

The results for the two lowest triplet states of the Al_2 molecule are summarized in Table 1. The equilibrium separations and the binding energy obtained with the [13*s*10*p*/5*s*4*p*] AE basis set coincide with the PP ones obtained with the uncontracted [4*s*4*p*] basis set. Moreover, the contraction of the three inner *s* and *p* functions, giving rise to the double-zeta type basis set [4*s*4*p*/2*s*2*p*], practically does not alter the results which are very similar to the AE ones.

With this latter basis set we have performed a complete analysis of the potential energy curves of the three low-lying states of Al_2, namely $^3\Pi_u$, $^3\Sigma_g^-$, and $^1\Sigma_g^+$ (see Fig. 6). For a distance close to the experimental equilibrium separation (4.7 a.u.) the $^3\Sigma_g^-$ exhibits a minimum corresponding to a dissociation energy of about 16 kcal/mole. At 4.9 a.u. a crossing of the two $^3\Sigma_g^-$ and $^3\Pi_u$ states has been found. The $^3\Pi_u$ state has the minimum around the distance of 5.4 a.u. with a binding energy of 20 kcal/mole. The singlet state lies at higher energies and exhibits a shallow minimum (about 10 kcal/mole) at larger nuclear separation.

As already pointed out in the previous section, the further contraction of the *p* functions giving rise to the nearly single-zeta type basis set [4*s*4*p*/2*s*1*p*] change the results substantially producing too large interatomic distances and relatively small dissociation energies. It is worth of mentioning that the AE treatment with the minimal basis set [9*s*5*p*/3*s*2*p*] yields even less realistic results. This effect is to be attributed to a basis set superposition error.

However, all these theoretical treatments predict the $^3\Pi_u$ ($3p\sigma_g 3p\pi_u$) state of Al_2 to be more stable than the $^3\Sigma_g^-(3p\pi_u^2)$, in contrast with the experimental data [32]. This result is in the same line with the other previously reported theoretical investigations [28, 30] which also predict the $^3\Pi_u$ to be the ground state of the Al_2 molecule.

In order to obtain more realistic results we have performed a set of PP calculations adding one *d*-polarization function to the [4*s*4*p*/2*s*2*p*] basis set. The results are reported in Table 1. The $^3\Pi_u$ is still the ground state, but the energy difference between the $^3\Pi_u$ and the $^3\Sigma_g^-$ states is only 1.8 kcal/mole. Moreover, the minimum of the $^3\Sigma_g^-$ potential energy curve is now very close to the experimental value (4.70 a.u. instead of 4.66 a.u.). The computed dissociation energy for the $^3\Sigma_g^-$ state, 24.2 kcal/mole, is still too small with respect to the experimental value of 34.6 kcal/mole.

The correction introduced in the results by the inclusion of one *d* function in the PP calculation is in the right direction, confirming that the discrepancies encountered are due to the poorness of the basis set and not to the PP method itself.

Table 1. Results for the Al_2 molecule[a]

	$^3\Pi_u$				$^3\Sigma_g^-$			
	SCF		CI		SCF		CI	
	R_{min}	E_T/D_e	R_{min}	E_T/D_e	R_{min}	E_T/D_e	R_{min}	E_T/D_e
PP[4*s*4*p*/2*s*1*p*]	5.50	−3.7778/8.3	5.51	−3.8293/19.3	5.20	−3.7663/1.2	5.17	−3.8244/16.3
PP[4*s*4*p*/2*s*2*p*]	5.46	−3.7821/11.0	5.48	−3.8490/20.2	5.07	−3.7681/2.2	5.01	−3.8435/16.8
PP[4*s*4*p*]	5.44	−3.7826/11.3	5.45	−3.8595/21.3	5.04	−3.7690/2.8	4.97	−3.8542/18.0
AE[13*s*10*p*/5*s*4*p*][b]	5.41	−483.7230/12.3	5.42	−483.7926/22.1	5.05	−483.7079/2.9	4.99	−483.7863/18.2
PP[4*s*4*p*1*d*/2*s*2*p*1*d*]	5.28	−3.7923/17.4	5.23	−3.8984/26.0	4.80	−3.7805/10.4	4.70	−3.8955/24.2

[a] All values are in a.u. except the dissociation energies which are in kcal/mole. The experimental ground state is the $^3\Sigma_g^-$ with the $R_e = 4.66$ a.u. and $D_e = 34.6$ kcal/mole [32].

[b] Only valence electrons are correlated.

The use of basis sets including polarization functions of higher angular momentum and of large scale CI treatments is probably necessary in order to obtain a better agreement with the experimental results.

3.4 AlH

An important requirement of the PP method is the capability to reproduce not only energetical data, but also other properties which are directly influenced by

Table 2. Electronic properties of the AlH molecule

	PP MRD CI [4*s*4*p*/2*s*2*p*]		PP MRD CI [4*s*4*p*1*d*/2*s*2*p*1*d*]		AE MRD CI[a] [13*s*10*p*/5*s*4*p*]	
Equilibrium distance (a.u.)	3.22		3.17		3.16	3.11[b]
Dissociation energy (kcal/mole)	60.3		64.2		61.3	69.4[b]
Natural orbitals						
σ^+ 1	1.9685	1	1.9615	1	1.9681	
2	1.9080	2	1.8785	2	1.9081	
3	0.0300	3	0.0289	3	0.0292	
4	0.0065	4	0.0064	4	0.0074	
5	0.0017	5	0.0051	5	0.0040	
6	0.0009	6	0.0018	6	0.0011	
7	0.0003	7	0.0004	7	0.0004	
		8	0.0003			
		9	0.0001			
		10	0.0000			
π 1	0.0407	1	0.0515	1	0.0396	
2	0.0011	2	0.0057	2	0.0011	
3	0.0002	3	0.0007	3	0.0002	
		4	0.0003			
Population analysis						
Al 3*s*	1.8161		1.7671		1.8601	
$3p_\pi$	0.0818		0.0960		0.1097	
$3p_\sigma$	0.7560		0.8777		0.7767	
3*d*	—		0.0900		—	
H 1*s*	1.3380		1.1614		1.3183	
$2p_\pi$	0.0022		0.0028		0.0022	
$2p_\sigma$	0.0059		0.0051		0.0060	
Dipole moment						
$\mu_e(D)$	−0.247		0.061		−0.064	−0.098[c]
$\mu'_e(D/\text{Å})$	−4.46		−3.82		−4.20	−3.76[c]
Quadrupole moment						
Q_{xx}, Q_{yy}	−7.925		−7.958		−9.290	
Q_{zz}	−14.485		−13.387		−15.703	

[a] Only valence electrons are correlated.
[b] Experimental values from Ref. [33].
[c] CEPA values from Ref. [34].

the quality of the correlated wavefunction. This point has been investigated in the case of the slightly polar AlH molecule. The calculations have been carried out with the previously described [4*s*4*p*/2*s*2*p*] (PP), [4*s*4*p*1*d*/2*s*2*p*1*d*] (PP) and [13*s*10*p*/5*s*4*p*] (AE) basis sets for Al and [4*s*1*p*/2*s*1*p*] basis set for the hydrogen atom [27].

First, we compare the PP and AE results obtained without including *d* function in the basis set. All the single and double excitations generated from the starting leading configuration give rise to a CI space of the same dimension (108 configurations) in PP and AE. The corresponding computed correlation energies are −0.0510 (PP) and −0.0512 (AE) a.u. The CI treatments are therefore strictly comparable and the results of Table 2 show that the PP approach is able to reproduce with a satisfactory accuracy the electronic properties determined from the AE wavefunction.

However, as in the case of Al_2, some discrepancies are observed between theoretical and experimental results (Table 2). Again, the inclusion of one *d*-function in the PP basis set improve the results giving a shorter equilibrium distance and a larger binding energy with respect to the result obtained with the [4*s*4*p*/2*s*2*p*] PP basis set.

In Table 2 are also reported the values of the dipole moments and of the derivatives of the dipole moment functions. These values are compared with the results of the CEPA calculations of Meyer and Rosmus [34] performed with a large basis set. The high value of the dipole moment computed with the PP basis set without *d*-functions reflects the error in the determination of the equilibrium distance. The inclusion of the *d*-function reduce this effect, but the dipole moment remains very sensitive to the internuclear separation as shown by the too large values of the derivative of the dipole moment functions (Table 2).

Let us emphasize that the exclusion of core–core and core–valence correlation can play a non negligible role on electronic properties such as dipole and quadrupole moments.

4. Conclusion

The results of the PP MRD CI method applied to a number of various systems which have been presented in the previous sections are encouraging because of the excellent agreement with the results obtained with the AE methods. Similarly it has been recently shown that the PP approach is adequate for the study of the electronic properties of clusters of alkali [13] and alkaline-earth [14] metal atoms. For this class of compounds, in the cases for which reliable AE results are available, a satisfactory agreement with the PP results has been always observed.

The errors in the evaluation of equilibrium bond distances, dissociation energies and vertical ionization potentials are in general very small [13, 14].

On the other hand, it has been shown that the PP MRD CI approach is able to describe in a satisfactory manner quantities which are very sensitive to the choice of the basis set and to the inclusion of the electronic correlation. A convincing example is the reproduction of the singlet–triplet splitting of some alkali metal clusters as obtained by accurate AE calculations [13]. Also when applied to the very different class of alkaline-earth metal aggregates, whose atoms are characterized by a closed shell electronic configuration, the conclusions obtained with the PP treatments parallel those of the AE studies [14].

The estimate of the correlation effects with the PP MRD CI procedure can be considered very successful; in fact it is not possible to exclude *a priori* that a pseudopotential operator determined from atomic SCF calculations will not generate undesired results when transferred into molecular configuration interaction calculations.

In particular the influence of correlation effects on bond lengths and dissociation energies of ground and excited states of the molecules are very similar in AE and PP. This opens possibility to employ the latter method for the investigation of photochemical or catalytical processes involving heavier atoms or larger systems. A correct description is to expect in all cases if an adequate choice of the basis set is made. The importance to build up the GTO basis sets as variational solutions of the atomic PP problem has been widely demonstrated [16, 17], but the contraction scheme to adopt deserves some special care [35]. We have shown, for instance, the failure of a PP minimal basis set to reproduce quantitatively the results of the corresponding AE CI calculations due to the small but important contribution of the core atomic functions. However, already the PP basis set of double-zeta quality represents a reasonable alternative to the larger uncontracted basis sets and yields the same results as accurate AE treatments.

To summarize, the PP MRD CI approach seems to be rather versatile, giving reliable results in very different fields. It represents a well-grounded theoretical treatment since the pseudo-hamiltonian operator is built up in such a manner that the variationally determined pseudo-orbitals coincide as much as possible with the true Hartree–Fock atomic orbitals in the valence region.

The method seems to be applicable for the study of the electronic structure of molecular systems containing various atoms of the periodic table, as shown by some recent applications on compounds involving the Pd atom [36].

Acknowledgments. The author is indebted to Dr. M. Persico and Dr. V. Bonačić-Koutecký for making available unpublished results on NaCO. The continuous support and the interesting suggestions of Prof. J. Koutecký and Dr. V. Bonačić-Koutecký are also gratefully acknowledged. The work was supported by DFG-Sonderforschungsbereich 6 "Structure and Dynamics of Interfaces".

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Received August 10/November 2, 1982