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A Theoretical Method to Determine Atomic Pseudopotentials for Electronic Structure Calculations of Molecules and Solids

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The characteristic features of model potentials, effective potentials and pseudopotentials are carefully investigated. Then we justify our choice to work only with hermitian pseudopotential operators, and we develop a general non-empirical method to determine atomic pseudopotentials. In view of their numerical use for molecular calculations, these pseudopotentials are cast into semi-local forms, and their parameters are obtained by a least-squares process; tables of parameter values are given for the two first rows of the periodic system.

Key words: Atomic pseudopotentials, theoretical determination of ~

1. Introduction

To determine the electronic structure of matter using the Schrödinger equation is a rather difficult problem. All the electrons, i.e. core and valence electrons, are taken into account only for calculations on light atomic molecules. In all the other cases, we appeal to methods which study the valence electrons into the potential of atomic ions formed by the nuclei and the core electrons: empirical or semi-empirical methods of quantum chemistry, band calculations in solid state physics. All these methods are relevant, implicitly or not, to the general theory of pseudopotentials and model potentials; these concepts have been systematically developed since a few fifteen years, particulary in the field of solid state physics [1, 2]. Their use in molecular physics and quantum chemistry is more recent, and there is now a renewed interest for the theoretical insight they introduce in atomic and molecular physics [3, 4].

A careful investigation of all the existing computational methods for the study of the valence electronic structure of matter shows their present inadequacy: on the one hand, empirical and semi-empirical methods of quantum chemistry (Hückel method, extended Hückel method, ...) do not possess a welldefined theoretical status; the matrix elements they involve are determined by means of *adhoc* processes whose only proof is the partial success of these methods; moreover, they are not entirely variational: for instance, we cannot minimize the total valence energy of an alkane molecule with respect to the exponents ζ of the $2p$ orbitals of the carbon atoms. On the other hand, the pseudopotential methods applied to band calculations for solids are characterized by the use of non-hermitian operators and the systematic use of plane wave basis sets which are often little compatible with the form of atomic orbitals remaining quasi-localized in solids, such as the *d* orbitals of transition metals or the *f* orbitals of rare earths. Moreover, many approximations are made in the estimate of the Coulomb or exchange electrostatic energy terms. Consequently, most of the methods of band calculations possess a status similar to the one of semi-empirical methods of quantum chemistry, and they are insufficient to reproduce with a good accuracy most of the basic experimental data: interatomic distances, vibrational force constants, etc.

The experience is yet partial with regard to the use of pseudopotential techniques to determine valence molecular orbitals. But it already appears a great abundance of models and methods which give most frequently a great importance to energy terms to the prejudice of the form of the valence ground state wave functions; in addition, these methods are often parameterized by using experimental data, in most cases atomic spectroscopy data.

We have here two goals: firstly, to develop a general theory of hermitian pseudopotentials which will be able to get together the pseudopotential models already proposed; secondly, to provide entirely *ab initio* atomic pseudopotentials which can be used easily in molecular and solid state calculations. Preliminary tests [5] carried out with not very elaborated pseudopotential models allow us to be sure of the efficiency of these methods in valence molecular calculations. In a previous publication [6], pseudopotentials we suggest here, have been used successfully to compute the valence molecular orbital energies of the ground state of the silane molecule; good results concerning other observables and other molecules have also been obtained [7].

In Section 2 we define precisely the concepts of hamiltonian and potential model, effective hamiltonian and effective potential, pseudo-hamiltonian and pseudopotential. It seems to us that the concept of pseudo-hamiltonian is more fruitful, and we study it in Section 3. Pseudopotential operators are fixed as soon as the form of atomic pseudo-orbitals has been chosen; Section 4 is devoted to an original method to determine these atomic pseudo-orbitals. Pseudopotential techniques introduced in Section 3 bring in a monoelectronic operator W_R which plays a fundamental part in our method. But this operator is not easy to handle in molecular calculations (it involves particulary the calculation of exchange and Coulomb energy terms between core and valence functions); therefore, we cast the operator W_R into simpler forms. This useful determination of the operator W_R by means of a least-squares process, forms the subject of Section 5; simple analytical expressions are given for the first two rows of the periodic system. At last, in Section 6, our pseudopotential method is compared to other various pseudopotential models; the analysis is about the two main points: the hermitian character of pseudopotential operators, and the features which closely link pseudo-orbital shapes and pseudopotential forms.

2. Total Hamiltonian, Pseudo-Hamiltonian and Effective Hamiltonian for an Atom

The atomic total hamiltonian may be written in atomic units:

$$\mathscr{H} = \sum_{i=1}^{N} h(i) + \sum_{i<j}^{N} \frac{1}{r_{ij}} \tag{1}$$

where

$$h(i) = -\frac{1}{2}\Delta_i - \frac{Z}{r_i}. \tag{2}$$

N is the number of electrons, and Z is the nuclear charge. We divide afterwards these N electrons into N_c core electrons, i.e. those of the inner shells of the atoms, and N_v valence electrons:

$$N = N_c + N_v. \tag{3}$$

To solve the Eq. (1) within the framework of a one-electron method, e.g. Hartree-Fock method, leads to a monoelectronic hamiltonian operator according to:

$$\mathscr{H} \xrightarrow{\text{one-electron model}} H = T + V. \tag{4}$$

T is the kinetic energy operator, and V the potential energy operator. The eigensolutions of the operator H are given by:

$$H\varphi_i = \varepsilon_i \varphi_i. \tag{5}$$

Let us suppose that φ_c, φ_v, and φ_e are, respectively, the core orbitals, the valence orbitals and the excited state orbitals, and ε_c, ε_v, ε_e the corresponding eigenvalues.

We then write:

$$H = \sum_i \varepsilon_i |\varphi_i\rangle\langle\varphi_i| \tag{6}$$

or

$$H = \sum_c \varepsilon_c |\varphi_c\rangle\langle\varphi_c| + \sum_v \varepsilon_v |\varphi_v\rangle\langle\varphi_v| + \sum_e \varepsilon_e |\varphi_e\rangle\langle\varphi_e|.$$

Projection operators on the core states, the valence states and the excited states are defined by:

$$P = \sum_c |\varphi_c\rangle\langle\varphi_c|\,; \qquad Q = \sum_v |\varphi_v\rangle\langle\varphi_v|\,; \qquad R = \sum_e |\varphi_e\rangle\langle\varphi_e|. \tag{7}$$

We recall successively the definitions of pseudo-hamiltonians and model hamiltonians, then we introduce the most wide class of effective hamiltonians. The hamiltonians belonging to these three classes possess valence eigensolutions which come very near to the monoelectronic H operator solutions.

We can symbolically write:

$$\{H_{ps}\} \subset \{H_M\} \subset \{H_{\text{eff}}\}. \tag{8}$$

The pseudo-hamiltonian set is included in the model hamiltonian set which is itself included in the effective hamiltonian set.

A *pseudo-hamiltonian* is defined by:

$$H_{ps} = H + V_R = T + V + V_R = T + V_{ps}. \tag{9}$$

V_{ps} represents the total potential in which the valence electron is set. V_R is an hermitian[1] monoelectronic operator; it is repulsive near the nucleus, and such as the lowest eigenvalues of H_{ps} are coincident with the eigenvalues of H in the valence region:

$$H_{ps}\phi_v = \varepsilon_v \phi_v. \tag{10}$$

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[1] There are also non-hermitian pseudopotentials (cf. the discussion of Section 6). As for us, the used operators V_R will always be hermitian.

Thus H_{ps} may be written:

$$H_{ps} = \sum_v \varepsilon_v |\phi_v\rangle\langle\phi_v| + \sum_k E_k |\phi_k\rangle\langle\phi_k| \, . \tag{11}$$

ϕ_v denotes a valence pseudo-orbital, and ϕ_k an excited pseudo-function with the corresponding eigenvalue E_k.

Pseudo-orbitals ϕ_v are linear combinations of core orbitals φ_c and valence orbitals φ_v with the same symmetry:

$$\phi_v = a_v \varphi_v + \sum_c a_c \varphi_c \, . \tag{12}$$

The coefficients a_c are small in front of the coefficient a_v which is close to unity.

Similarly, a *model hamiltonian* is defined by:

$$H_M = T + V_M \tag{13}$$

where V_M is a model potential. The spectral representation of H_M may always be cast into the form (11), but now the pseudo-orbitals have the following form:

$$\phi_v = a_v \varphi_v + \sum_c a_c \varphi_c + \sum_e a_e \varphi_e \, , \tag{14}$$

where the coefficients a_c and a_e remain small with respect to the coefficient a_v which is close to unity.

An interesting special case occurs when the relation (12) is nearly satisfied for a model hamiltonian; then we have a *model pseudo-hamiltonian.* Practically, the concepts of model pseudo-hamiltonian and pseudo-hamiltonian are sufficiently similar so that it is not necessary to distinguish between them. So in this article, we shall only use the term of pseudo-hamiltonian with the notation H_{ps}.

The concept of *effective hamiltonian* appears when the lowest eigensolutions (E_v, ϕ_v) of this hamiltonian are only in the neighbourhood of the valence eigensolutions $(\varepsilon_v, \varphi_v)$ of H:

$$H_{\text{eff}} = T + V_{\text{eff}} \tag{15}$$

where V_{eff} is an effective potential. The hamiltonian H_{eff} may be cast into the form:

$$H_{\text{eff}} = \sum_v E_v |\phi_v\rangle\langle\phi_v| + \sum_k E_k |\phi_k\rangle\langle\phi_k| \tag{16}$$

As for H_{ps}, each valence pseudo-orbital ϕ_v is a linear combination of core and valence orbitals [relation (12)]. The valence pseudo-orbital energies E_v are different, but near to the valence orbital energies ε_v. As previously, we obtain a *model effective hamiltonian* when the valence pseudo-orbitals ϕ_v only roughly satisfy the relation (12). So practically, we do not distinguish between the concepts of model effective hamiltonian and effective hamiltonian; later on we shall only use the word of effective hamiltonian with the notation H_{eff}.

The schematic Fig. 1 shows the eigensolutions of these various hamiltonians H, H_{ps} (or H_M), and H_{eff}.

Öhrn and McWeeny [8] have already suggested an effective hamiltonian for a valence electron outside a closed shell described by a highly accurate wave function. To generalize this work for several valence electrons would lead to unnecessary and intricate atomic potentials; the simplest way is to stay at the level of pseudopotential: to keep the atomic orbital energies is a good starting point for subsequent molecular calculations, as it is expected that the molecular

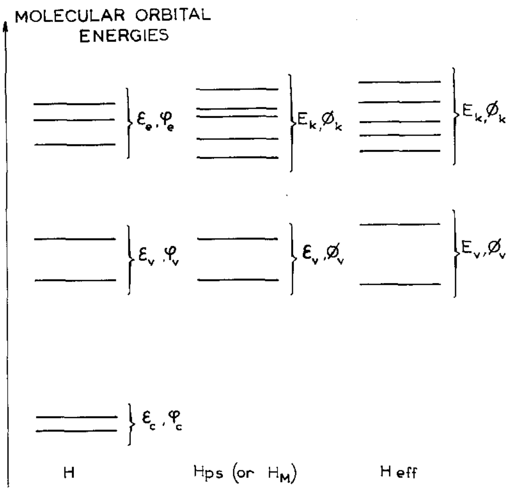

Fig. 1. Schematic representation of the eigensolutions of the previously defined hamiltonians

level splitting is primarily due to the overlapping of the outermost part of the atomic orbitals. For this reason, we have chosen to work only with pseudo-hamiltonians H_{ps} and the corresponding total valence pseudo-hamiltonians $\mathscr{H}_{ps}$.

3. Total Valence Pseudo-Hamiltonian

The monoelectronic hamiltonian operator H (relation (4)) is obtained from the expression (1) of the atomic total hamiltonian $\mathscr{H}$. In the same way, the mono-electronic pseudo-hamiltonian H_{ps} is obtained from the following total pseudo-hamiltonian:

$$\mathscr{H}_{ps}=\sum_{i=1}^{N_v}\left[-\frac{\Delta_i}{2}+W_{ps}(i)\right]+\sum_{i<j}^{N_v}\frac{1}{r_{ij}}.$$

W_{ps} is a monoelectronic operator which is then given by:

$$W_{ps}=V_{ps}-V_{\phi_v} \tag{18}$$

or

$$W_{ps}=-\frac{Z}{r}+V_{\varphi_c}+V_{\varphi_v}-V_{\phi_v}+V_R.$$

V_{φ_c}, V_{φ_v} and V_{ϕ_v} denote the sum of Coulomb and exchange operators relating to, respectively, the core orbitals, the valence orbitals and the valence pseudoorbitals. $\left(\text{So we have the following equality: } V=-\frac{Z}{r}+V_{\varphi_c}+V_{\varphi_v}.\right)$ W_{ps} represents the interaction potential between a valence electron and the ion made of the core electrons and the nucleus of the atom. Let us suppose that $z=N_v$ is the net charge of this ion. The operator W_{ps} tends to the Coulombic energy $-\frac{z}{r}$ far from the nucleus.

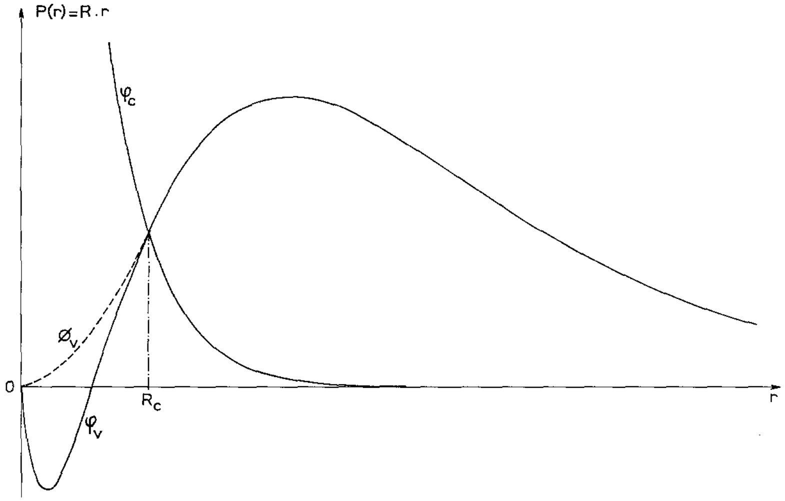

Fig. 2. Radial parts of the orbital φ_v and the corresponding pseudo-orbital ϕ_v

So we introduce the operator W_R such as:

$$W_{ps} = -\frac{z}{r} + W_R \tag{19}$$

From the Eq. (18), it follows that:

$$W_R = V_{\varphi_c} - \frac{N_c}{r} + V_{\varphi_v} - V_{\phi_v} + V_R\,. \tag{20}$$

This operator W_R is a fundamental one for applying our method; it is repulsive near the nucleus, attractive in the region common to the core and valence orbitals, and it cancels out in the valence region where the pseudo-orbitals ϕ_v become identical with the orbitals ϕ_v. The operator W_R, which is dependent on pseudo-orbitals ϕ_v, also depends on the used one-electron model through the term $(V_{\varphi_v} - V_{\phi_v})$. But this term is associated with a null charge distribution, and therefore this dependence on the one-electron model is weak: it cancels out in the valence region.

We must notice that the use of the operator W_R [relation (20)] allows us to write the monoelectronic pseudo-hamiltonian through the following form:

$$H_{ps} = -\frac{1}{2}\Delta - \frac{z}{r} + V_{\phi_v} + W_R\,. \tag{21}$$

4. Determination of the Valence Pseudo-Orbitals

In opposition to most of the pseudopotential techniques used in solid state physics, where one looks for pseudopotentials V_{ps} as "weak" as possible in order to have valence pseudo-orbitals looking like plane waves, we propose to construct systematically hermitian operators V_R and pseudo-hamiltonian operators in such a way that their variational solutions ϕ_v coincide at best with the true orbitals φ_v in the valence region, and cancel out in the atomic core region. Figure 2 gives the

Table 1. Atomic double-zeta valence pseudo-orbitals ϕ_{2s} from Li ($Z=3$) up to Ne ($Z=10$). The exponents ζ_i are those of the Clementi's double-zeta functions [16]. All the quantities are in atomic units

Atom	Orbital	R_c	n_i	ζ_i	C_i	f	Charge
Li	2*s*	1.49	2	0.45000	0.53630	0.0007	0.96
			2	0.85000	0.52373		
Be	2*s*	1.03	2	0.50000	−0.11068	0.0009	0.97
			2	0.90000	1.08733		
B	2*s*	0.97	2	0.88143	0.20413	0.0006	0.91
			2	1.40704	0.81678		
C	2*s*	0.64	2	1.16782	0.31803	0.0015	0.96
			2	1.82031	0.70751		
N	2*s*	0.54	2	1.39327	0.35354	0.0017	0.96
			2	2.22157	0.67617		
0	2*s*	0.47	2	1.62705	0.36939	0.0018	0.95
			2	2.62158	0.66226		
F	2*s*	0.42	2	1.94665	0.45141	0.0017	0.95
			2	3.09603	0.58081		
Ne	2*s*	0.37	2	2.18390	0.45940	0.0019	0.95
			2	3.49207	0.57367		

aspect of the radial parts of the orbital φ_v and the pseudo-orbital ϕ_v according to the previous criterion.

In a first approach, one may take as pseudo-orbitals ϕ_v Slater type orbitals non-orthogonal to the core orbitals, whose exponents are given either by the Slater rules [9] or by calculations [10, 11]. But only one Slater orbital is not sufficient to reproduce accurately the outer part of a valence orbital even if its parameters are fixed in order to obtain this result [12]. It would also be possible to use nodeless valence orbitals calculated by means of a statistical pseudopotential [13]. Nevertheless, it seems to us that it would be better to operate from all-electron Hartree-Fock calculations: the valence pseudo-orbitals are then admixtures of core and valence orbitals having the same symmetry [14, 15]. But it is yet difficult, whatever the used criterion of relocalization of the valence orbitals may be, to remove oscillations in the core region and at the same time, to get in coincidence the orbitals and the pseudo-orbitals in the valence region. As for us, we prefer to get out from the core-valence admixture restriction and to determine valence pseudo-orbital ϕ_v in such a way that its radial part coincides at best with the one of the orbital φ_v at a distance r from the nucleus greater than a cut-off radius R_c. For a given orbital, the value of R_c is obtained by intersecting the radial part $P(r)$ of the valence orbital with the one of the outermost core orbital of the same symmetry (cf. Fig. 2). Although our definition of R_c appears to be an arbitrary one, we have noticed that the pseudo-orbital shape is not strongly dependent on the value of R_c.

The pseudo-orbitals are determined by minimizing the function:

$$f = \langle \phi_v - \varphi_v | \phi_v - \varphi_v \rangle_{R_c} \qquad (22)$$

Table 2. Atomic double-zeta valence pseudo-orbitals ϕ_{3s} and ϕ_{3p} from Na ($Z=11$) up to Ar ($Z=18$). The exponents ζ_i are those of the Clementi's double-zeta functions [16]. All the quantities are in atomic units

Atom	Orbital	R_c	n_i	ζ_i	C_i	f	Charge
Na	3*s*	1.64	3	0.75485	0.81338	0.0003	0.98
			3	1.25944	0.22273		
Mg	3*s*	1.42	3	0.90759	0.66833	0.0008	0.96
			3	1.50587	0.38116		
Al	3*s*	1.23	3	1.15946	0.68101	0,0012	0.95
			3	1.86836	0.36223		
	3*p*	1.38	3	0.89522	0.77588	0.0003	0.97
			3	1.60850	0.27796		
Si	3*s*	1.08	3	1.39955	0.72686	0.0016	0.94
			3	2.23938	0.31192		
	3*p*	1.18	3	1.09340	0.71473	0.0005	0.96
			3	1.86255	0.33626		
P	3*s*	0.97	3	1.63895	0.82897	0.0021	0.94
			3	2.92052	0.21461		
	3*p*	1.04	3	1.23975	0.63025	0.0007	0.95
			3	2.08127	0.42363		
S	3*s*	0.89	3	1.81513	0.79009	0.0027	0.93
			3	3.15955	0.25600		
	3*p*	0.93	3	2.33358	0.49126	0.0010	0.95
			3	1.32171	0.57534		
Cl	3*s*	0.82	3	2.00905	0.77133	0.0026	0.93
			3	3.34163	0.26959		
	3*p*	0.84	3	1.60921	0.70708	0.0010	0.94
			3	2.85870	0.35302		
Ar	3*s*	0.76	3	2.18470	0.77255	0.0034	0.93
			3	3.74910	0.27347		
	3*p*	0.77	3	1.81174	0.76148	0.0014	0.94
			3	3.42549	0.30471		

with the constraint:

$$\langle\phi_v|\phi_v\rangle = 1\,. \tag{23}$$

In the expression (22), the index R_c shows that the integration concerning the radial parts is restricted to the interval $[R_c, \infty]$. We search for pseudo-orbitals being linear combinations of Slater orbitals χ_i:

$$\phi_v = \sum_{i=1}^{n} C_i\chi_i\,. \tag{24}$$

To minimize (22), by taking the relations (23) and (24) into account, leads to the system of linear equations:

$$\sum_{j=1}^{n} [\langle\chi_i|\chi_j\rangle_{R_c} - \lambda\langle\chi_i|\chi_j\rangle] C_j = \langle\chi_i|\varphi_v\rangle_{R_c} \tag{25}$$

where λ is a Lagrangian multiplier; it is close to zero because the orbitals φ_v and ϕ_v are very near for $r > R_c$. The coefficients C_i are obtained by solving the system (25); this resolution is iterative. We have determined the valence pseudo-orbitals from the atomic double-zeta orbitals of Clementi et al. [16] for lithium ($Z=3$) up to krypton atom ($Z=36$).

Each pseudo-orbital is expanded into the two outermost Slater orbitals of the double-zeta basis. The pseudo-orbital parameters are given in Tables 1 and 2 for the atoms of the two first rows of the periodical system. The minimum of the function f and the electronic charge fractional part $\langle\varphi_v|\varphi_v\rangle_{R_c}$ associated with the orbital φ_v, which lies outside the sphere of radius R_c, appears also in these tables. The R_c values have been obtained by interpolation from numerical Hartree-Fock solutions [17].

We take notice that the agreement between valence orbitals and pseudo-orbitals is good for all the studied atoms because the greatest value of the function f is 0.003; this value is often smaller than 0.001. With the chosen R_c values, we have always outside the sphere of radius R_c a fractional charge associated with the orbital ranging about 0.95 electron. This charge is sufficiently close to unity in order to consider the value R_c as an approximate measure of the atomic core radius.

5. Practical Determination of the Operators V_R and W_R

With a view to simplify calculation techniques, it is interesting to cast V_R and W_R into a simpler semi-local form which depends only on a small number of parameters:

$$V_R=\sum_l V_{R,l}(r)P_l\,, \tag{26}$$

$$W_R=\sum_l W_{R,l}(r)P_l\,, \tag{27}$$

with:

$$P_l=\sum_{m=-l}^{+l}|Y_{lm}\rangle\langle Y_{lm}|\,.$$

P_l denotes the projection operator over the l^{th} subspace of spherical harmonics.

The numerical determination of the operators V_R and W_R takes place only after we have chosen a simple analytical form for the functions $V_{R,l}(r)$ and $W_{R,l}(r)$. We propose the following forms:

$$\sum_n \frac{A_{n,l}}{r^n} \quad n \text{ integer such as} \quad n<2l+3\,, \tag{28}$$

$$\sum_i C_{i,l}\frac{\exp[-\alpha_{i,l}r(\text{or } r^2)]}{r^{n_i}}\,. \tag{29}$$

The parameters $A_{n,l}$; $C_{i,l}$; $\alpha_{i,l}$; n_i are obtained in an entirely theoretical way by a least-squares method.

These forms and other ones have already been used by several authors for the functions $W_{R,l}$ (see the discussion in Section 5.5).

5.1. Numerical Determination of the Operators V_R

The operators V_R have an obvious physical meaning: they allow us to pass from the solutions of the true monoelectronic hamiltonian H to the ones of the pseudo-hamiltonian H_{ps} owing to the relation (9).

The parameters on which the operators V_R depend, may be determined without ambiguity for a given set of pseudo-orbitals ϕ_v and valence orbital energies ε_v. The Eq. (10) must be satisfied and the pseudo-hamiltonian H_{ps} may be written:

$$H_{ps}=\sum_v \varepsilon_v|\phi_v\rangle\langle\phi_v|+\sum_k E_k|\phi_k\rangle\langle\phi_k|\,. \tag{30}$$

If we choose the form (28) for the functions $V_{R,l}(r)$ and if the corresponding parameters have the arbitrary values $A'_{n,l}$, then the value of the pseudo-hamiltonian is:

$$H'_{ps}=H+\sum_l\sum_n \frac{A'_{n,l}}{r^n}P_l\,. \tag{31}$$

H'_{ps} is cast into diagonal form in the basis set constructed with the core orbitals φ_c and the valence orbitals φ_v which are solutions of the hamiltonian H. Let ε'_v be the energies associated with the valence pseudo-functions ϕ'_v and E'_k the energies associated with the pseudo-states ϕ'_k, which are obtained by diagonalizing H'_{ps}. We then write:

$$H'_{ps}=\sum_v \varepsilon'_v|\phi'_v\rangle\langle\phi'_v|+\sum_k E'_k|\phi'_k\rangle\langle\phi'_k|\,. \tag{32}$$

The two operators H_{ps} and H'_{ps} will have their valence part all the more near as the norm of the operator $\mathcal{O}$ defined by:

$$\mathcal{O}=\sum_v\left[\varepsilon'_v|\phi'_v\rangle\langle\phi'_v|-\varepsilon_v|\phi_v\rangle\langle\phi_v|\right] \tag{33}$$

will be close to zero.

The parameter values $A_{n,l}$ which are such as the valence eigensolutions of the pseudo-hamiltonian H'_{ps} may be ε_v and ϕ_v, are also the ones for which the norm of the operator $\mathcal{O}$ is minimum. This minimization is made by means of the Powell algorithm [18].

As an example, we give the result concerning the carbon in the ^3P state in a simple case:

$$V_{R,0}=-\frac{0.354}{r}+\frac{0.953}{r^2}$$

in atomic units; the value of the norm $\|\mathcal{O}\|$ is then 0.02. This result has been obtained from the atomic Clementi's double-zeta orbitals [16], the valence pseudo-orbital ϕ_{2s} being represented by a Slater orbital the exponent of which has been optimized by Clementi and Raimondi [10].

5.2. Semi-Local Representation of the Operators W_R

The straightforward determination of the operators W_R into the semi-local form (27) may be carried out according to a process similar to the previous one. If we choose to cast the functions $W_{R,l}(r)$ into the form (28), and if the corresponding parameters have the arbitrary values $B'_{n,l}$, the pseudo-hamiltonian may be written:

$$H'_{ps}=T-\frac{z}{r}+V_{\phi_v}+\sum_l\sum_n \frac{B'_{n,l}}{r^n}P_l\,. \tag{34}$$

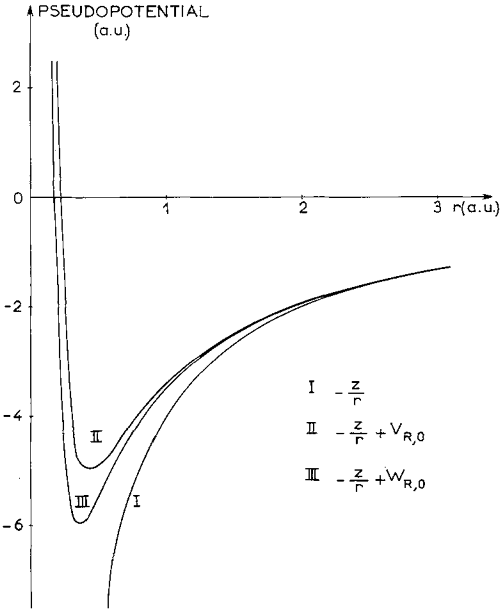

Fig. 3. Pseudopotential curves for the ^3P state of the carbon atom

After casting H'_{ps} into diagonal form for a given basis set, we obtain:

$$H'_{ps}=\sum_v \varepsilon'_v|\phi'_v\rangle\langle\phi'_v|+\sum_k E'_k|\phi'_k\rangle\langle\phi'_k|\,. \tag{35}$$

The parameter values $B_{n,l}$ which are such as the pseudo-hamiltonian H'_{ps} possesses the same valence part as the operator H_{ps}, are also the ones which lead to a minimum value for the norm of the operator previously defined by (33).

This determination of the operators W_R is less easy than the one of the operators V_R; as a matter of fact, it is here necessary to choose a one-electron model and to calculate the bielectronic integrals V_{ϕ_v}. The results concerning the carbon atom in the ^3P state are in atomic units:

$$W_{R,0}=-\frac{0.248}{r}+\frac{0.758}{r^2} \quad \text{with} \quad \|\mathcal{O}\|=0.02\,,$$

$$W_{R,1}=-\frac{0.064}{r^2} \quad \text{with} \quad \|\mathcal{O}\|=0.05\,.$$

These results have been obtained from the same atomic data than those used to determine V_R. All the calculations presented here have been carried out in the framework of the Hartree-Fock-Roothaan one-electron model.

5.3. *Discussion of the Previous Results*

The semi-local forms of the operators V_R and W_R have the advantage to allow a graphical representation of the potential acting on a valence electron of symmetry l. The Fig. 3 gives the aspect of the curves (I) $-\frac{z}{r}$, (II) $-\frac{z}{r}+V_{R,0}$ and (III) $-\frac{z}{r}+W_{R,0}$

Table 3. Silicon atom in the ^3P state. Comparison between the parameter values $B_{n,l}$ of the operator W_R according to the valence pseudo-orbital form

Nature of the valence pseudo-orbitals ϕ_v	$l=0$			$l=1$		
	$B_{1,0}$	$B_{2,0}$	$\|\mathcal{O}\|$	$B_{1,1}$	$B_{2,1}$	$\|\mathcal{O}\|$
One Slater orbital according to Clementi and Raimondi	-1.04901	2.36160	0.04203	-0.27853	0.95883	0.03330
Our double-zeta valence pseudo-orbitals	-0.97730	2.37354	0.01089	-0.48028	1.38379	0.00425

Table 4. Parameters $B_{1,l}$ and $B_{2,l}$ for the semi-local representation of the operator $W_R\left(W_{R,l}=\frac{B_{1,l}}{r}+\frac{B_{2,l}}{r^2}\right)$ from lithium to neon (a.u.)

Atom		l	$B_{1,l}$	$B_{2,l}$	$\|\mathcal{O}\|$
Li	^2S	0	-0.20214	0.89606	0.00121
Be	^1S	0	-0.33055	1.00088	0.00573
B	^2P	0	-0.47157	1.09411	0.00421
		1	—	-0.06249	0.00650
C	^3P	0	-0.63753	1.17715	0.00449
		1	—	-0.04932	0.00762
N	^4S	0	-0.77759	1.21265	0.00538
		1	—	-0.04322	0.00836
0	^3P	0	-0.92354	1.24276	0.00413
		1	—	-0.03853	0.00888
F	^2P	0	-1.08150	1.27283	0.00369
		1	—	-0.03432	0.01024
Ne	^1S	0	-1.23346	1.29335	0.00319
		1	—	-0.03083	0.01003

for the carbon atom in the ^3P state; the used functions $V_{R,0}$ and $W_{R,0}$ depend on two parameters and are those previously defined.

We must notice that there is no term $V_{R,1}(r)$ in the expression of the operator V_R defined for the carbon atom, because this atom does not possess core electrons of symmetry p. Therefore in the curves of the Fig. 3 only the terms of symmetry s occur.

Both graphs corresponding to $V_{R,0}$ and $W_{R,0}$ present the same aspect: they correspond to a potential which is very repulsive in the core region, attractive in the region common to the core and valence orbitals in such a way that the valence pseudo-orbital energy remains equal to the energy ε_{2s} of the true valence orbital φ_{2s}. Nevertheless, we point out that the curve (III) is always underneath the curve (II): therefore $W_{R,0}$ is less repulsive than $V_{R,0}$ in the core region. This fact is

Table 5. Parameters $B_{1,l}$ and $B_{2,l}$ for the semi-local representation of the operator $W_R\left(W_{R,l}=\frac{B_{1,l}}{r}+\frac{B_{2,l}}{r^2}\right)$ from sodium to argon (a.u.)

Atom		l	$B_{1,l}$	$B_{2,l}$	$\|\mathcal{O}\|$
Na	^2S	0	−0.29566	1.23332	0.00569
Mg	^1S	0	−0.48345	1.64792	0.00820
Al	^2P	0	−0.72773	2.05147	0.01032
		1	−0.33891	1.16927	0.00268
Si	^3P	0	−0.97730	2.37354	0.01089
		1	−0.48028	1.38370	0.00425
P	^4S	0	−1.23199	2.63794	0.00348
		1	−0.60688	1.52763	0.00625
S	^3P	0	−1.41816	2.77039	0.00525
		1	−0.70102	1.60256	0.00853
Cl	^2P	0	−1.64802	2.93599	0.01103
		1	−0.89178	1.78393	0.00621
Ar	^1S	0	−1.83310	3.03094	0.00789
		1	−1.02073	1.86633	0.00415

in agreement with what we may deduce from the relation (20); W_R differs only from V_R by the two following terms: $\left(V_{\varphi_c}-\frac{N_c}{r}\right)$ and $(V_{\varphi_v}-V_{\phi_v})$; the first one is negative in the core region and the second one has only a very small contribution to W_R.

5.4. *Tables of Semi-Local Operators W_R from Lithium to Argon Atom*

The method is the same as in Section 5.2, but the basis set is a more extended one for each atom: it is constructed with the functions χ_{lp} which have been used to define Clementi's double-zeta atomic orbitals.

In addition to the used one-electron model, the operator W_R is essentially determined by the set of energies ε_v and the form of the pseudo-orbitals ϕ_v. Table 3 gives the values of the parameters $B_{n,l}$ of the operator W_R for the silicon atom in the ^3P state, when the valence pseudo-orbitals ϕ_v are successively described by one Slater orbital the exponent of which has been optimized by Clementi and Raimondi [10], then by the double-zeta orbitals that we have previously defined; in both cases, the energies ε_v are the valence orbital energies obtained by Clementi [16] with a double-zeta basis set.

The use of our double-zeta valence pseudo-orbitals gives the lowest values of the norm of the operator $\mathcal{O}$. Then it clearly appears that these double-zeta pseudo-orbitals allow a better adjustment, in a least-squares meaning, to the W_R operator chosen in its semi-local representation (28). Therefore we have chosen the double-zeta pseudo-orbitals defined in the previous section to build up a table of semi-local operators W_R from lithium ($Z=3$) to argon atom ($Z=18$). The results are listed in Tables 4 and 5; they are pictured in the Figs. 4 and 5 that show the potential acting on an s symmetry valence electron.

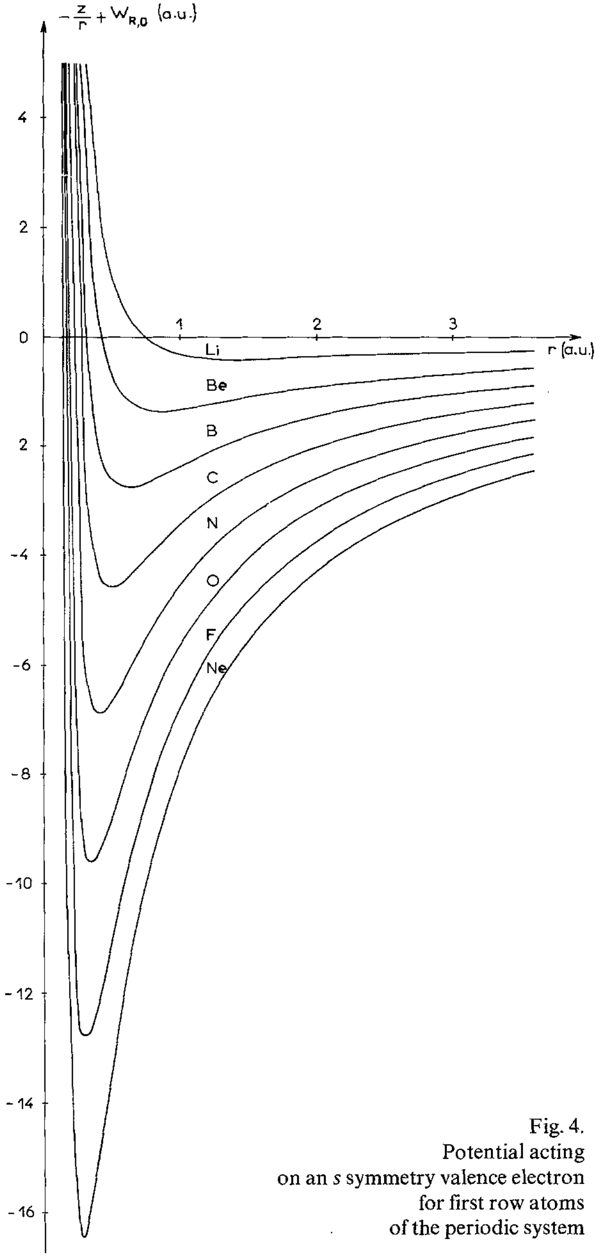

Fig. 4.
Potential acting
on an s symmetry valence electron
for first row atoms
of the periodic system

5.5. Discussion on the Analytical Expressions for the Functions $V_{R,l}(r)$ and $W_{R,l}(r)$

We have chosen very simple analytical expressions to reproduce the dependence on r of the operators V_R and W_R in their semi-local representation. We are going to compare our expressions with those already suggested by various authors. We will only investigate the potentials V_R and W_R that are very repulsive near the

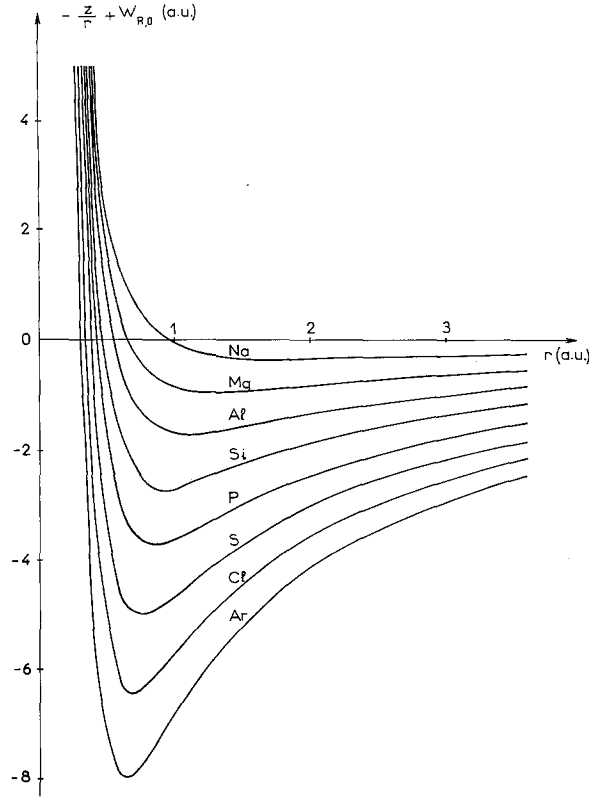

Fig. 5. Potential acting on an *s* symmetry valence electron for second row atoms of the periodic system

core in agreement with valence pseudo-orbitals which cancel out in the core region (for a discussion on "flat bottom" and repulsive pseudo-potentials, see section 6). A simple pseudo-potential with only one parameter has been proposed by Simons [19]:

$$W_{R,l}=\frac{a_l}{r^2}. \tag{36}$$

However, the most commonly used pseudopotential is the Hellmann's one [20] in its local form [21, 22]:

$$W_R=A\frac{\exp(-\alpha r)}{r} \tag{37}$$

or in its semi-local representation [23–26]:

$$W_{R,l}=A_l\frac{\exp[-\alpha_l r\,(or\ r^2)]}{r}. \tag{38}$$

The advantage of the dependence on r in $e^{-\alpha_l r^2}$ clearly appears when the molecular calculations are performed with a basis of gaussian functions [27].

The potentials (36), (37), and (38) are too rough to give accurately an account of the variations of the quantities $W_{R,l}$ in function of r. Ladanyi [28] has then proposed a potential that consists of two terms of Hellmann type:

$$W_R = A\frac{\exp(-\alpha r)}{r} + B\frac{\exp(-\beta r)}{r} \tag{39}$$

where the coefficients A and B are generally of opposite sign [22, 29, 30]. Sums of exponential functions are also easily used in atomic calculations [31]. Most of the expressions of $W_{R,l}$ which have been used [27, 32, 33], are particular cases of relations (28) and (29) given at the beginning of this section.

As a reminder, we quote more complicated analytical dependences [34, 35] or dependences which introduce an angular point [36, 37]: all these pseudopotentials would be probably uneasy to handle in molecular calculations.

On the numerical point of view, we do not have to prefer any particular form for $W_{R,l}$. It is sufficient to use a basis set of radial functions complete enough to reproduce the $W_{R,l}$ as a function of r. But in the future, the non-local forms [38, 39] could be preferred: for the molecular calculations include only overlaps between atomic orbitals that are very easily calculated.

6. Discussion

The operators V_R and W_R are hermitian operators. Since some authors [15, 40, 41] have suggested the introduction of non-hermitian operators, it is necessary to justify the reason why we use only hermitian operators in a general theory of pseudopotentials. Austin et al. [40] define V_R by:

$$\begin{aligned} &V_R = PA \\ &V_R = PAP + PAQ + PAR \end{aligned} \tag{40}$$

where A is any operator. Owing to (40), the relation (12) is always satisfied: it means that the pseudo-orbital ϕ_v is exactly a linear combination of the Hartree Fock core φ_c and valence φ_v orbitals. With an appropriate choice for A, it is always possible to obtain a good valence pseudo-orbital ϕ_v with but few oscillations in the atomic core. The advantage of a non-hermitian formulation of pseudopotential theory is that the valence spectrum is automatically preserved whatever the A operator may be. But this pseudopotential V_R has the great disadvantage of making all the formalism non-hermitian, in particular the total pseudo-hamiltonian. So we think that the use of non-hermitian operator, as proposed by Weeks et al. [41] is not a good solution. Therefore, in this work, we have mixed the core and valence orbitals according to an operator V_R which is defined in the subspace $(P+Q)$ by:

$$V_R = (P+Q)A(P+Q) \tag{41}$$

where A is an hermitian operator, which is chosen in order to maintain the valence spectrum by going from H to H_{ps}. Practically, to determine V_R, one has first to fix the shape of the valence pseudo-orbitals: then V_R is obtained by a least-squares

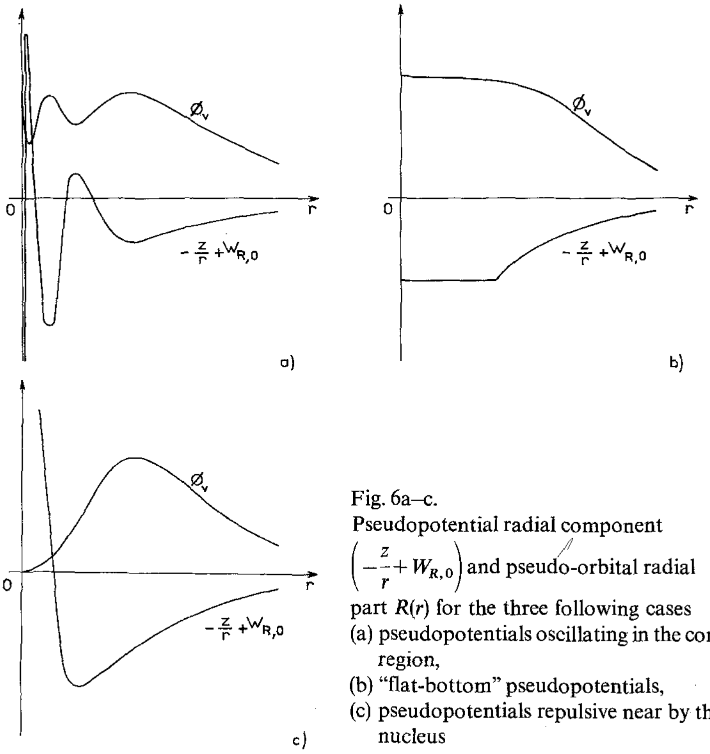

Fig. 6a–c.
Pseudopotential radial component $\left(-\frac{z}{r}+W_{R,0}\right)$ and pseudo-orbital radial part $R(r)$ for the three following cases
(a) pseudopotentials oscillating in the core region,
(b) "flat-bottom" pseudopotentials,
(c) pseudopotentials repulsive near by the nucleus

technique (see Section 5). In fact, the valence pseudo-orbitals that were chosen are rigorously nodeless in core region; they are only approximately linear combinations of valence orbitals φ_v and core orbitals φ_c. Consequently, the equality (41) is not exactly satisfied. But this last remark has no incidence on the grounds which have motivated our choice of hermitian operators.

Now we are going to analyse briefly the links between the shape of pseudo-orbitals and the aspect of pseudopotential W_R. The actually used pseudopotentials may be divided in three types: the pseudopotentials oscillating in the core region, the "flat-bottom" pseudopotentials and the very repulsive ones near the nucleus (Fig. 6).

The oscillating pseudopotentials [42–44] are associated with pseudo-orbitals in which the oscillations have not completely disappeared in the atomic core. This occurs when the valence pseudo-orbitals ϕ_v are strictly limited to a linear combination of core and valence orbitals. These pseudo-orbitals would be unsuitable for molecular calculations that need extended basis set to reproduce the oscillations of the wave function near the nucleus.

The flat-bottom pseudopotentials proceed from solid state physics and particularly from the model of Abarenkov and Heine [45]; they have been used by Kutzelnigg et al. [36]. These pseudopotentials modify considerably the shapes of valence atomic orbitals which have actually very slight variations as well inside the core as in the valence region. However they are very interesting if the solution is taken as a linear combination of plane waves $\exp(-i\mathbf{k}\cdot\mathbf{r})$ but they are inconsistent with pseudo-orbitals cancelling in the core region. Now, in some cases, *3d* orbitals of transition metals or *4f* orbitals of rare earth elements, the atomic orbitals are a little modified when an atom is engaged in a molecule or in a solid. So it would be unreasonable to try to reproduce these looking like Slater orbitals by pseudo-orbitals approximating to plane waves. When this is done, considerable difficulties are encountered: the parameters of pseudopotentials depend on the band energy levels and have resonances [46]. If these pseudopotentials seem badly adapted to the electronic ground state of a system, they can be used for excited states: the excited orbitals are much greater than the core atomic radius and the excited electrons "do not see" the details of the inner structure of the pseudopotential [36].

Bonifacic and Huzinaga's work [39] is the nearest one to ours[2]. They have determined theoretical pseudopotentials for the first row from lithium to neon, with the operator:

$$W_R = -\frac{Z}{r}[A_1 \exp(-\alpha_1 r^2) + A_2 \exp(-\alpha_2 r^2)] + B|\varphi_{1s}\rangle\langle\varphi_{1s}| \,. \tag{42}$$

If we compare this expression with (20), we remark that the first two negative terms describe approximately the Coulomb interaction energy with the core electrons whereas V_R is represented by the second term $|\varphi_{1s}\rangle\langle\varphi_{1s}|$. Such a representation of V_R by means of a projector on the core state φ_{1s} is not completely satisfying for it does not allow to mix the φ_{1s} and φ_{2s} orbitals. Therefore the pseudo-orbitals obtained by Bonifacic and Huzinaga show residual oscillations in the core (see Fig. 1 of Ref. [39]). Their pseudopotential would be more of the oscillating type.

7. Conclusion

We have chosen to work only with hermitian pseudopotentials; for we think that the hermitian pseudopotential set is large enough to afford the needs of quantum chemistry. We have presented a general theoretical method to determine atomic pseudopotentials. A part of the originality of this work lies in the initial choice of the valence pseudo-orbital ϕ_v. The potential operators are then determined by the simultaneous knowledge of these valence pseudo-orbitals and the valence atomic orbital energies ε_v obtained in a theoretical Hartree-Fock calculation for the ground state of the atom. Most of the pseudopotential methods introduce only a restricted information limited to the experimental energies ε_v. Our method introduces an equilibrated information between the ε_v's and the ϕ_v's.

Another interesting feature of this work lies in the choice of the numerical techniques. We have indeed cast the exact pseudopotentials into the simplest local representations which can be easily used in valence molecular calculations. We have systematically used least-squares techniques. These operators can consequently be obtained with all the required accuracy. We are now computing more

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[2] Before revising this manuscript, Melius et al. [47] have recently published new atomic repulsive pseudopotentials very similar to ours.

elaborate pseudopotentials with the analytical form (29); the corresponding parameter tables will be published in the near future.

The pseudopotential presented in this article have been checked in our laboratory on numerous valence molecular calculations. For molecules containing only light atoms of the first two rows of the periodic table, a valence Hartree-Fock calculation and an all-electron Hartree-Fock calculation lead to very similar results (molecular orbital energies, interatomic distances ...) [6]. The use of these atomic pseudopotentials for molecules containing heavier atoms of the third row of the periodic table gives an excellent agreement with experimental data, such as interatomic distances, bond angles, rotational barriers [7]. The results obtained will be published in a second article. This work is a first step towards the obtention of pseudopotential methods with well-defined theoretical status which will allow the approximate determination of the valence electronic structure of molecules and solids containing any atoms of the periodic table.

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