

# Approximate calculation of the matrix elements of Coulomb and exchange operators for the “core” electrons of the atoms Li through Ar

Raffaele Montagnani and Oriano Salvetti

Istituto di Chimica Quantistica ed Energetica Molecolare del C.N.R., Via Risorgimento 35,  
I-56100 Pisa, Italy

A method is described which allows to approximate with a few parameters the Coulomb and exchange integrals employed in valence-electron-only SCF calculations. The necessary parameters for atoms from Li to Ar are given. Very good transferability from atomic to molecular systems and near coincidence with all-electron calculations are found for LiH, HF and HCl molecules. Extension to other atoms is in progress.

**Key words:** Pseudopotential—Valence-electron-only SCF.

## 1. Introduction

In calculating molecular wavefunctions it is often necessary, in order to avoid prohibitive calculations, to take into account separately valence and core parts. The latter can be regarded, with a good approximation, as invariant against the variation of geometrical parameters and can be replaced by suitable effective potentials which ought to possess a good degree of transferability. This kind of approach, which dates back to the beginning of Quantum Chemistry [1–3], has been refined by the introduction of the pseudopotential of Phillips–Kleinman [4] and its generalizations [5], and later on by several authors [6–18] to the point at which it can give nearly the same accuracy, in predicting molecular properties of valence electrons, as all-electron calculations.

The equations which the valence orbitals must fulfil in this scheme lead to an operator, of which they must be eigenfunctions, which can be written in the

Phillips–Kleinman form:

$$F = h + G_c + G_v + \sum_i^{\text{Core}} (\varepsilon_v - \varepsilon_i) P_i \quad (1)$$

where  $h$  is the one-electron Hamiltonian,  $G_c$  and  $G_v$  include the Coulomb and exchange operators generated respectively by the core and valence electrons. The last term in (1), where  $P_i = |\varphi_i\rangle\langle\varphi_i|$ , is properly called the Phillips–Kleinman pseudopotential and is related to the condition of orthogonality between valence and core orbitals. In fact the valence pseudoorbitals  $\varphi_v$  are allowed to overlap the core and the terms  $P_i$  prevent their collapsing into the core. It should be noticed that these terms would disappear in a natural way if the variation of the valence orbitals were orthogonal to the core orbitals. In this case also the operators which appear in  $G_v$  could be rigorously constructed starting only from the basis functions used.

From the work of Huzinaga et al. [16, 17] it appears that the valence orbitals arising from an operator as

$$F = h + G_c + G_v + \sum_i^{\text{Core}} B_i P_i \quad (2)$$

where  $B_i$  are optimized parameters, come out to be very similar to those which could be obtained by a complete self consistent calculation.

Starting from an approximate operator of this kind, it remains only to calculate the matrix elements of  $G_c$ ; this operator would contain, if evaluated in detail also in a frozen core approximation, a large number of two-electron terms for the valence-core interaction. For this reason, approximate potentials  $U_c(r)$ , such that the integrals  $\langle\varphi_v|U_c|\varphi_v\rangle$  are as close as possible to the exact values  $\langle\varphi_v|G_c|\varphi_v\rangle$ , have been introduced by several authors [8–16]. It is however clear that such a condition cannot be fulfilled for all functions  $\varphi_v$ , since the exchange operator is not simply multiplicative. Dixon et al. [14, 15] carried out an accurate investigation on the calculation of the matrix elements generated by Coulomb and exchange core operators. They get the matrix elements relative to Coulomb potentials from atomic charge densities approximated by a sum over  $1s$  Gaussian functions. For what concerns the exchange operators, their kernels have been approximated, with the aim of keeping the non-local character, by a combination of projection operators. While many authors adopt local [12, 13, 16] or semi-local [9, 10] operators to represent the effects of core on the valence electrons, we agree with the philosophy of Dixon's non-local method but propose some different kind of approximations for Coulomb and exchange operators.

Recently a method has been proposed for obtaining an approximate representation of the exchange operator [19]. This method is simple and reliable and it therefore seems appropriate to use it, along with a new kind of approximation for the Coulomb potential, to get both the Coulomb and exchange parts of the operator  $G_c$ . The following sections contain a description (2) of the approximation employed for the representation of the Coulomb operators along with the

parameters necessary for the atoms from Lithium to Argon; (3) an analogous description for the exchange operators and (4) some results obtained with these approximations in atomic and molecular calculations.

## 2. The Coulomb operator approximation

Gaussian type basis functions are among the most commonly used in Quantum Chemistry calculations, and among these the modified form of Golebiewsky and Mrozek [20] offers several practical advantages. In the present work we use this kind of function, but similar considerations could apply to other forms of Gaussian basis sets.

Let us consider an atom having  $K$  and  $L$  core shells and the orbitals expanded on a basis  $\{\chi\}$  of modified Gaussians, with  $n_s$   $s$ -type functions and  $n_p$   $p$ -type; then the core Coulomb operator is

$$\begin{aligned}
 J_c(r_1) &= J_{1s}(r_1) + J_{2s}(r_1) + J_{2p}(r_1) \\
 &= \int \frac{1s^*(r)1s(r)}{|\mathbf{r}_1 - \mathbf{r}|} d\mathbf{r} + \int \frac{2s^*(r)2s(r)}{|\mathbf{r}_1 - \mathbf{r}|} d\mathbf{r} + \int \frac{2p_x^*(r)2p_x(r)}{|\mathbf{r}_1 - \mathbf{r}|} d\mathbf{r} \\
 &\quad + \int \frac{2p_y^*(r)2p_y(r)}{|\mathbf{r}_1 - \mathbf{r}|} d\mathbf{r} + \int \frac{2p_z^*(r)2p_z(r)}{|\mathbf{r}_1 - \mathbf{r}|} d\mathbf{r} \\
 &= \sum_{i,j}^{n_s} (C_{i,2s}C_{j,1s} + C_{i,2s}C_{j,2s}) \int \frac{\chi_i^*(r)\chi_j(r)}{|\mathbf{r}_1 - \mathbf{r}|} d\mathbf{r} \\
 &\quad + \sum_{k,l}^{n_p} C_{k,2p}C_{l,2p} \left[ \int \frac{\chi_k^{x*}(r)\chi_l^x(r)}{|\mathbf{r}_1 - \mathbf{r}|} d\mathbf{r} + \int \frac{\chi_k^{y*}(r)\chi_l^y(r)}{|\mathbf{r}_1 - \mathbf{r}|} d\mathbf{r} \right. \\
 &\quad \left. + \int \frac{\chi_k^{z*}(r)\chi_l^z(r)}{|\mathbf{r}_1 - \mathbf{r}|} d\mathbf{r} \right]. \tag{3}
 \end{aligned}$$

Remembering from [20] that

$$\chi_i = g(u_i, v_i, w_i, a_i, \mathbf{R}_i) = \frac{\partial^{u_i+v_i+w_i}}{\partial X_i^{u_i} \partial Y_i^{v_i} \partial Z_i^{w_i}} S(a_i, \mathbf{R}_i) \tag{4}$$

where

$$S(a_i, \mathbf{R}_i) = g(0, 0, 0, a_i, \mathbf{R}_i) = \left(\frac{2a_i}{\pi}\right)^{3/4} \exp[-a_i(\mathbf{r} - \mathbf{R}_i)^2]$$

and making use of the relationship

$$\frac{1}{|\mathbf{r}_1 - \mathbf{r}|} = \frac{1}{2\pi^2} \int \exp[i\mathbf{k} \cdot (\mathbf{r}_1 - \mathbf{r})] \int \exp(-tk^2) d\mathbf{k} dt \tag{5}$$

we easily obtain the integrals

$$J_{1s}(r_1) + J_{2s}(r_1) = \sum_{i,j}^{n_s} (C_{i,1s}C_{j,1s} + C_{i,2s}C_{j,2s}) S_{ij} \frac{\text{erf}(r_1\sqrt{a_i + a_j})}{r_1} \tag{6}$$

$$J_{2p}(r_1) = \sum_{k,l}^{n_p} (C_{k,2p} C_{l,2p}) S_{kl} \left\{ \frac{3 \operatorname{erf}(r_1 \sqrt{a_k + a_l})}{r_1} - 2 \sqrt{\frac{a_k a_l}{\pi}} \exp[-(a_k + a_l) r_1^2] \right\}. \quad (7)$$

Guided by these results we have approximated the total Coulomb operator for the core electrons of the  $K$  and  $L$  shells of an atom centered on  $\mathbf{R}_c$  by a sum of terms of the type

$$2J_c(|\mathbf{r} - \mathbf{R}_c|) = \sum_s^{M_r} c_s \frac{\operatorname{erf}(a_s |\mathbf{r} - \mathbf{R}_c|)}{|\mathbf{r} - \mathbf{R}_c|} + \sum_s^{M_x} d_s \exp[-b_s (\mathbf{r} - \mathbf{R}_c)^2] \quad (8)$$

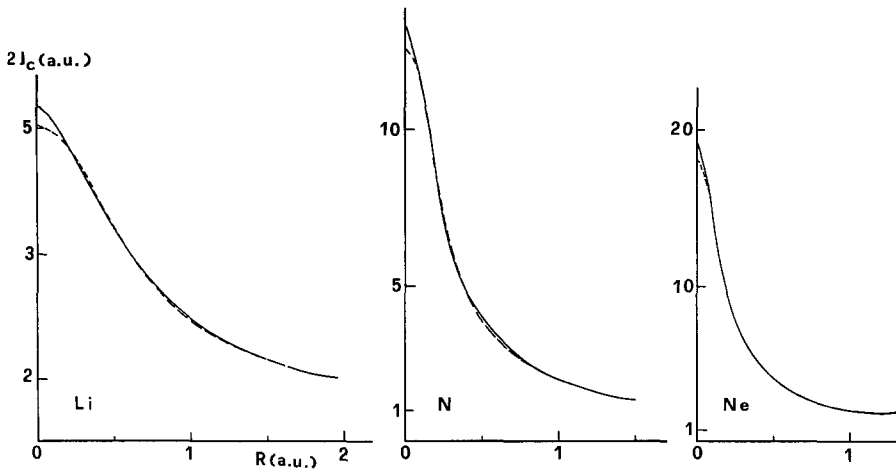
in which, and for each atom,  $2(M_r + M_x)$  parameters have been optimized.

We have found that choosing  $M_r = 1$ ,  $M_x = 1$  for  $K$  shells (atoms Li through Ne) and  $M_r = 2$ ,  $M_x = 1$  for  $K$  and  $L$  shells together (atoms Na through Ar) gives a very good approximation to  $J_c$ . In Table 1 are reported the values of the optimized parameters for the atoms of the second and third row of the periodic table. In Figs. 1 and 2 the plots of  $2J_c(r)$  given by our approximation (8) are compared with those calculated using accurate SCF core orbitals, for Li, N, Ne, Mg, Si and Cl atoms. In all these cases (and in the others not reported here) the representation is remarkably accurate.

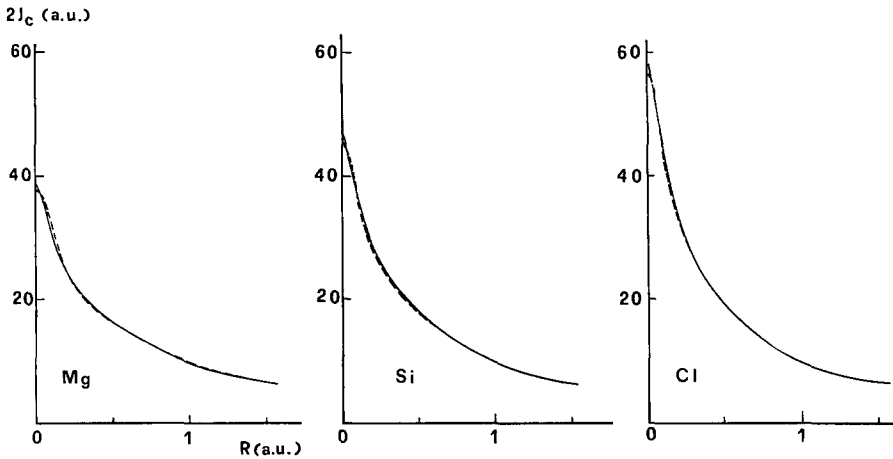
Our choice of the expression (8) to approximate  $J_c$  does not imply, as regards the erf terms, the need of new formulae for the subsequent integrations, because they lead again to the expressions given by Golebiewsky [20] for electronic repulsion integrals. Concerning the second term of (8), the calculation of the integrals over valence orbitals is also very simple. Thus, remembering (4), we let  $s(a, \mathbf{R}_A)$  and  $s(b, \mathbf{R}_B)$  be two  $s$ -type basis functions and write  $s(c, \mathbf{R}_c)$  for

**Table 1.** Parameters to fit Coulomb potentials  $2J_c$  by (8) for atoms from Li to Ar

Atom	$c_1$	$a_1$	$c_2$	$a_2$	$d_1$	$b_1$
Li	2	2.379	—	—	-0.292	1.304
Be	2	3.263	—	—	-0.397	2.535
B	2	4.142	—	—	-0.508	4.170
C	2	5.020	—	—	-0.625	6.300
N	2	5.896	—	—	-0.750	8.953
O	2	6.773	—	—	-0.880	12.088
F	2	7.648	—	—	-1.020	15.924
Ne	2	8.524	—	—	-1.170	20.472
Na	2	9.400	8	2.105	-6.075	3.280
Mg	2	10.278	8	2.413	-7.000	4.406
Al	2	11.157	8	2.722	-7.933	5.701
Si	2	12.036	8	3.019	-8.826	7.082
P	2	12.915	8	3.337	-9.790	8.742
S	2	13.795	8	3.361	-10.676	10.401
Cl	2	14.675	8	3.922	-11.555	12.188
Ar	2	15.556	8	4.227	-12.480	14.222



**Fig. 1.** Plots of  $2J_c(r)$  for Li, N and Ne atoms: (a) — calculated by complete SCF core orbitals (b) --- calculated by approximating formula (8)



**Fig. 2.** Plots of  $2J_c(r)$  for Mg, Si and Cl atoms: (a) — calculated by complete SCF core orbitals (b) --- calculated by approximating formula (8)

one of the Gaussian terms of (8), then:

$$\begin{aligned}
 & I(0, 0, 0, a; 0, 0, 0, b; c; \mathbf{R}_A; \mathbf{R}_B; \mathbf{R}_c) \\
 &= N_A N_B \int \exp[-a(\mathbf{r} - \mathbf{R}_A)^2 - c(\mathbf{r} - \mathbf{R}_c)^2 - b(\mathbf{r} - \mathbf{R}_B)^2] d\mathbf{r} \\
 &= \left[ \frac{4ab}{(a+b+c)^2} \right]^{3/4} \\
 &\quad \times \exp \left\{ -[ab(\mathbf{R}_A - \mathbf{R}_B)^2 + ac(\mathbf{R}_A - \mathbf{R}_c)^2 + bc(\mathbf{R}_B - \mathbf{R}_c)^2] / (a+b+c) \right\} \quad (9)
 \end{aligned}$$

while the matrix element for any pair of functions becomes

$$\begin{aligned}
 & I(u_A, v_A, w_A, a; u_B, v_B, w_B, b; c; \mathbf{R}_A; \mathbf{R}_B; \mathbf{R}_c) \\
 &= N_A N_B \frac{\partial^{u_A+v_A+w_A+u_B+v_B+w_B}}{\partial X_A^{u_A} \partial Y_A^{v_A} \partial Z_A^{w_A} \partial X_B^{u_B} \partial Y_B^{v_B} \partial Z_B^{w_B}} \\
 & \times I(0, 0, 0, a; 0, 0, 0, b; c; \mathbf{R}_A; \mathbf{R}_B; \mathbf{R}_c) \tag{10}
 \end{aligned}$$

where  $N_A = [a^{u_A+v_A+w_A}(2u_A+1)!!(2v_A+1)!!(2w_A+1)!!]^{-1/2}$ . The expression (9) comes out to be very similar to that for an overlap integral and can be programmed in an analogous manner.

### 3. The exchange operator approximation

The exchange integral between the core of an atom and two generic functions  $f$  and  $g$  is computed by the formula

$$\langle f | K_c | g \rangle = \sum_{i,j}^N [H_{ij}^0 f^0(r_i) g^0(r_j) + H_{ij}^1 f^1(t_i) g^1(t_j)] \tag{11}$$

where the first term in the summation represents the contribution of the spherical part, while the second term comes out from the  $p$  part. If both  $f$  and  $g$  are centered on  $\mathbf{R}_c$ , like the  $K_c$  operator, the two terms are reduced to only one: the first if both the functions are  $s$ -type, the second if they are  $p_x, p_y$  or  $p_z$ -type. We define  $f^0$  and  $f^1$  as follows;

$$f^0(r_i) = \frac{\sqrt{\pi}}{3} \sum_{l=1}^6 f(p_{il}) \tag{12}$$

$p_{il}$  being the six points where a sphere, centered on  $\mathbf{R}_c$  and with radius  $r_i$  meets the three coordinate axis coming out from  $\mathbf{R}_c$ , and

$$f^1(r_i) = \sqrt{\frac{\pi}{3}} \sum_{l=1}^6 (-1)^l f(p_{il}) \tag{13}$$

for which the supplementary condition holds that  $p_{i,1}$  and  $p_{i,2}$  are on the  $x$ -axis

**Table 2.** Parameters to fit exchange integrals by (11) for atoms Li through Ne ( $H_{ij} = H_{ji}$ )

	Li	Be	B	C	N	O	F	Ne
$r_1$	0.473696	0.343544	0.270020	0.222567	0.189352	0.164752	0.145827	0.130811
$R_2$	1.485335	1.077228	0.846684	0.697886	0.593739	0.516601	0.457258	0.410174
$H_{11}^0$	3.174117	1.669513	1.031376	0.700719	0.507184	0.383959	0.300814	0.242054
$H_{12}^0$	1.255917	0.660584	0.408089	0.277257	0.200680	0.151923	0.119024	0.095774
$H_{22}^0$	1.012273	0.532433	0.328921	0.223470	0.161749	0.122450	0.095934	0.077194
$t_1$	0.569190	0.413193	0.323640	0.266782	0.226927	0.197242	0.174514	0.156490
$t_2$	1.784770	1.295621	1.014815	0.836528	0.711558	0.618479	0.547211	0.490695
$H_{11}^1$	0.332389	0.175161	0.107462	0.073020	0.052833	0.039915	0.031246	0.025125
$H_{12}^1$	0.094024	0.049548	0.030398	0.020655	0.014945	0.011291	0.008839	0.007107
$H_{22}^1$	0.124301	0.065504	0.040187	0.027307	0.019757	0.014927	0.011685	0.009396

**Table 3.** Parameters to fit exchange integrals by (11) for atoms Na through Ar ( $H_{ij} = H_{ji}$ )

	Na	Mg	Al	Si	P	S	Cl	Ar
<i>K</i> shell								
$r_1$	0.261067	0.237044	0.217080	0.200208	0.188641	0.173255	0.162319	0.152683
$H_{11}^0$	0.685179	0.564881	0.473740	0.402961	0.357743	0.301766	0.264875	0.234358
$t_1$	0.211496	0.194245	0.178040	0.164155	0.154029	0.141898	0.133002	0.125032
$H_{11}^1$	0.029979	0.025288	0.021244	0.018060	0.015901	0.013495	0.011856	0.010477
<i>L</i> shell								
$r_1$	0.620605	0.562882	0.513740	0.471311	0.441042	0.403593	0.376351	0.352503
$r_2$	1.631869	1.480088	1.350870	1.239303	1.159702	1.061239	0.989607	0.926899
$H_{11}^0$	5.967799	4.909290	4.089501	3.441902	3.013997	2.523886	2.194667	1.925344
$H_{12}^0$	2.522695	2.075245	1.728705	1.454953	1.274071	1.066892	0.927725	0.813877
$H_{22}^0$	2.269572	1.867018	1.555250	1.308966	1.146233	0.959842	0.834639	0.732214
$t_1$	0.691664	0.608182	0.530033	0.477851	0.434584	0.392235	0.362037	0.334850
$t_2$	1.818717	1.599203	1.393710	1.256500	1.142731	1.031373	0.951969	0.880483
$H_{11}^1$	3.366246	2.602693	1.976791	1.606721	1.328935	1.082549	0.922276	0.788965
$H_{12}^1$	1.449811	1.120956	0.851386	0.692000	0.572360	0.466244	0.397216	0.339800
$H_{22}^1$	1.268503	0.980774	0.744915	0.605461	0.500783	0.407937	0.347541	0.297306

respectively on the negative and positive side; the same for  $p_{i,3}$  and  $p_{i,4}$  (on  $y$ -axis) and for  $p_{i,5}$  and  $p_{i,6}$ . More details on this approach can be found in Ref. [19].

For the atoms of the first row, the core of which comes down to the *K* shell, we have found that  $N=2$  gives a good approximation, while when the core is made up by *K* and *L* shells we can represent them separately and need  $N=1$  for *K* plus  $N=2$  for *L* shell. In Table 2 the values of  $r_i$ ,  $t_i$ ,  $H_{ij}^0$  and  $H_{ij}^1$  for the atoms of the first row are shown; in Table 3 the analogous values for the atoms of the second row can be found.

**Table 4.** Exact SCF and approximated by (8) or (11) formulae values of some Coulomb and exchange integrals

Atom	$\varphi$	$\langle \varphi   2J_c   \varphi \rangle$		$\langle \varphi   K_c   \varphi \rangle$	
		Exact	Approx.	Exact	Approx.
Na	3s	2.8933	2.8946	0.0199	0.0199
Na	4s	2.2216	2.2229	0.0189	0.0187
Na	3p	5.2533	5.2520	0.1062	0.1062
Na	4p	7.4996	7.5067	0.2041	0.1190
Si	3s	5.5267	5.5299	0.0670	0.0670
Si	4s	4.3413	4.3443	0.0566	0.0551
Si	3p	4.0818	4.0813	0.0274	0.0274
Si	4p	5.1075	5.1063	0.0695	0.0638
Ar	3s	8.5923	8.5988	0.1279	0.1279
Ar	4s	6.6575	6.6629	0.0979	0.0952
Ar	3p	7.6228	7.6225	0.0850	0.0849
Ar	4p	6.3717	6.3714	0.0787	0.0735

#### 4. Results

The approximations proposed for Coulomb and exchange integrals have been tested in SCF pseudopotential calculations on atoms from Li to Ar and on some molecules, using the reduced basis sets of Huzinaga [16] or those of Kahn et al. [10] valence optimized.

In all atomic cases total and orbital energies are in very good agreement with those obtained from all-electron SCF calculations using a much bigger number of basis functions. The same agreement is also found between the values of the integrals  $\langle \varphi_v | 2J_c | \varphi_v \rangle$  and  $\langle \varphi_v | K_c | \varphi_v \rangle$  calculated by the approximating formulae (8) and (11) and those of exact SCFs. Some of these typical integrals are shown

**Table 5.** LiH  $X^1\Sigma^+$  potential energy values<sup>a</sup>

R	All-electron <sup>b</sup>		Valence-electron <sup>c</sup>	
	E(R)	E(R) – E( $\infty$ )	E(R) – E( $\infty$ )	E(R)
$\infty$	-7.93192	0	0	-0.69419
10	-7.93210	-0.00018	-0.00013	-0.69432
7	-7.93792	-0.00600	-0.00593	-0.70012
5	-7.96511	-0.03319	-0.03342	-0.72761
4	-7.98848	-0.05656	-0.05658	-0.75077
3.1	-8.00241	-0.07049	-0.07039	-0.76458
3	-8.00220	-0.07028	-0.07030	-0.76449
2.9	-8.00131	-0.06939	-0.06962	-0.76381
2.5	-7.98785	-0.05593	-0.05881	-0.75300
$D_e$	1.918 eV	Exp.: 2.429 eV [22]		1.916 eV
$R_e$	3.081	Exp.: 3.015 [22]		3.065

<sup>a</sup> In Tables 5 through 7 all units in a.u. when not otherwise specified.

<sup>b</sup> Basis: Li (11s) from Ref. [16]+(5p) from Ref. [9]; H(4s/3s) from Ref. [23]+1p ( $\alpha = 0.8$ ).

<sup>c</sup> Basis: Li (4s, 5p) from Ref. [9]; H as (b).

**Table 6.** HF  $X^1\Sigma^+$  potential energy values

R	All-electron <sup>a</sup>		Valence-electron <sup>b</sup>	
	E(R)	E(R) – E( $\infty$ )	E(R) – E( $\infty$ )	E(R)
$\infty$	-99.90054	0	0	-24.31895
3.5	-99.92662	-0.02608	-0.02268	-24.34163
3	-99.95548	-0.05494	-0.05117	-24.37012
2.5	-100.00213	-0.10159	-0.09701	-24.41596
1.9	-100.06093	-0.16039	-0.15865	-24.47760
1.8	-100.06428	-0.16374	-0.16330	-24.48225
1.7	-100.06246	-0.16192	-0.16313	-24.48208
1.3	-99.94086	-0.04032	-0.04721	-24.36616
$D_e$	4.456 eV	Exp.: 6.12 eV [22]		4.457 eV
$R_e$	1.786	Exp.: 1.73 [22]		1.754

<sup>a</sup> Basis: F(11s, 5p) from Ref. [16]; H as (b) Table 5.

<sup>b</sup> Basis: F (4s, 4p) from Ref. [10]; H as (a).



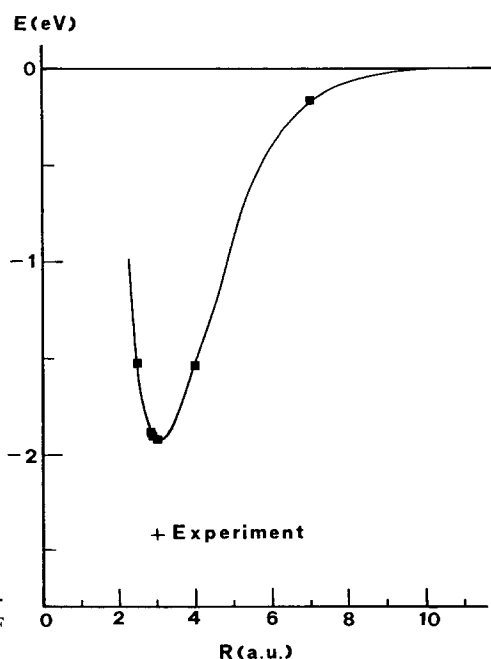
**Table 7.** HCl X  $1\Sigma^+$  potential energy values

R	All-electron <sup>a</sup>		Valence-electron <sup>b</sup>	
	E(R)	E(R) - R( $\infty$ )	E(R) - E( $\infty$ )	E(R)
$\infty$	-459.96428	0	0	-14.25536
5	-459.97412	-0.00984	-0.01185	-14.26721
4	-460.00355	-0.03927	-0.04496	-14.30032
3	-460.06776	-0.10348	-0.10459	-14.35995
2.5	-460.09248	-0.12820	-0.12658	-14.38194
2.49	-460.09255	-0.12827	-0.12659	-14.38195
2.44	—	—	-0.12618	-14.38154
2.41	-460.09203	-0.12775	-0.12552	-14.38088
2	-460.03864	-0.07436	-0.06410	-14.31946
$D_e$	3.491 eV	Exp.: 4.62 eV [22]		3.444 eV
$R_e$	2.472	Exp.: 2.41 [22]		2.492

<sup>a</sup> Basis: Cl (12s, 8p) from Ref. [21]; H as (b) Table 5.

<sup>b</sup> Basis: Cl (3s, 3p) from Ref. [10]; H as (a).

in Table 4. Another important characteristic required in this kind of approximation is its transferability from atoms to molecular systems; this has been examined by calculating the potential curves of the LiH, HF and HCl molecules. In order to avoid collapse into the core we have introduced the out-of-core projection operator in (1) in a very similar way to the method outlined by Huzinaga [16]. The values obtained for the total energies and bond lengths are compared with those derived from all-electron calculations in Tables 5, 6 and 7 respectively;



**Fig. 3.** LiH X  $1\Sigma^+$ : Comparison of the valence-electron-only (■) and all-electron MCSCF potential energy curves (—●—)

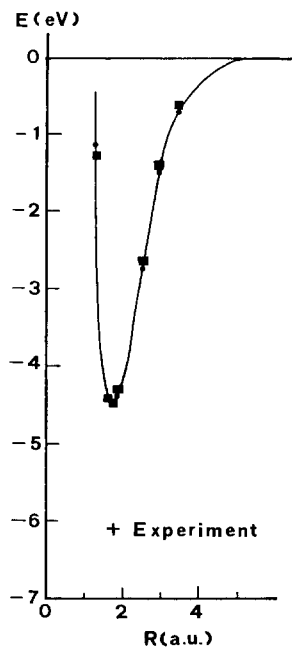


Fig. 4. HF  $X^1\Sigma^+$ : Comparison of the valence-electron-only (■) and all-electron MCSCF potential energy curves (—●—)

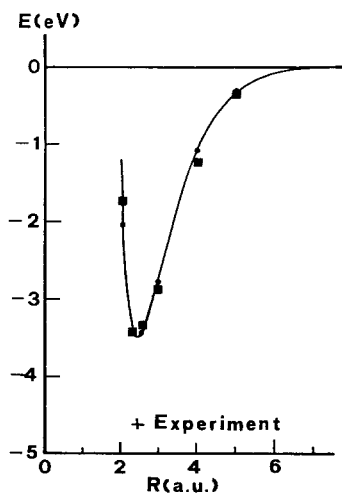


Fig. 5. HCl  $X^1\Sigma^+$ : Comparison of the valence-electron-only (■) and all-electron MCSCF potential energy curves (—●—)

the relative plots are shown in Figs. 3, 4 and 5. The nearly perfect coincidence attained is evident, especially if one takes into account that a slight worsening in the representation is inevitable when the basis set is reduced so drastically.

## 5. Conclusions

The matrix elements between valence functions and Coulomb and exchange operators can be obtained by the approximating formulae (8) and (11), with a

very good degree of precision and a minimum computational effort. When using pseudopotentials in molecular calculations the main difficulties arise from a poor evaluation of the core-valence interaction, and more attention will have to be paid to this aspect of the problem. As far as the approximation of the Coulomb and exchange matrix elements are concerned, the results obtained encourage us to extend the method to the next rows of the periodic table and to use it for some more complicated molecular systems.

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