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Approximate calculation of the matrix elements of Coulomb and exchange operators for the "core" electrons of the atoms Ga through Kr

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A method which allows to approximate the Coulomb and exchange integrals employed in valence-electron-only SCF calculations with a few parameters, as described in previous papers, is extended to the atoms from Ga to Kr. All the necessary parameters for these atoms are given. Extension to other atoms is in progress.

Key words: Pseudopotential — Valence-electron-only SCF

1. Introduction

In two recent papers [1, 2], where more detailed discussion and bibliography can be found, we have proposed an approximate method for calculating the matrix elements of the Coulomb and exchange operators generated by the atomic core electrons. This method, along with the introduction of a Phillips-Kleinman pseudopotential [3], allows one to treat in a quite simple and cheap way also systems containing a large number of inner electrons: nearly all the computational effort is in fact devoted to finding the valence orbitals $\{\sigma_v\}$. In this scheme, they must be eigenfunctions of the operator

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

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, where $P_i = |\Phi_i\rangle\langle\Phi_i|$ and Φ_i are core orbitals, is properly called the Phillips–Kleinman pseudopotential and prevents the valence electron orbitals from the variational collapsing into the core region. The matrix related to the G_c operator which, in an all-electron SCF calculation ought to be build using a large number of bielectronic integrals accounting for core-valence interaction, in our scheme becomes a simple matrix of monoelectronic integrals and can be evaluated, as well as h and pseudopotential matrices, quite rapidly.

2. The effective potential

For approximating the $\langle\sigma_v|G_c|\sigma_v\rangle$ matrix elements, we take into account separately the exchange and Coulomb terms. The approximating formula for the Coulomb operator generated by the core electrons of an atom centered on $\bar{R}_c$ has the same structure of the expression for the Coulomb operators calculated by SCF orbitals expanded on a gaussian basis set and is:

$$J_c(|\bar{r}-\bar{R}_c|) = \sum_{s}^{M_r} c_s \frac{\operatorname{erf}(a_s|\bar{r}-\bar{R}_c|)}{|\bar{r}-\bar{R}_c|} + \sum_{s}^{M_x} d_s \exp[-b_s(r-R_c)^2]. \tag{2}$$

The exchange integrals between the core of an atom and two generic functions Φ_1 and Φ_2 are computed by the formula

$$\langle\Phi_1|K_c|\Phi_2\rangle = \sum_{i,j}^{N} \sum_{l}^{M} H^l_{ij} \sum_{m=-l}^{l} f_{lm}(r^l_i) g_{lm}(r^l_j) \tag{3}$$

where

$$\Phi_1(r-R_1) = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} f_{lm}(r) r^l Y_{lm}(\Omega)$$

$$\Phi_2(r-R_2) = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} g_{lm}(r) r^l Y_{lm}(\Omega).$$

l and m are the azimuthal and magnetic quantum numbers and $f_{lm}(r)$ is the average value of the function f on a spherical surface of radius r, i.e.:

$$f_{lm}(\Omega_p) = \sum_{p=1}^{n_p} C_{lmp} f(r, \Omega_p)$$

and

$$C_{lmp} = \frac{S_{lm}(\Omega_p)}{\sum_{p=1}^{n_p} S_{lm}(\Omega_p)^2},$$

where $S_{lm}(\Omega_p)$ is the value at Ω_p of the spherical harmonic in real form S_{lm}. The nonlocal character of the exchange operator is kept. In order to get the right contribution $f_{lm}(r^l_i)$ at least up to l quantum number, it is sufficient to compute the f function for n_p points on a sphere with radius r^l_i and to sum them after multiplication by the appropriate coefficients. In [2] C_{lmp} for $n_p = 14$ is

Table 1. Parameters to fit Coulomb potentials $2J_c$ by (2) for atoms from Ga to Kr[a]

Atom	a_1	a_2	a_3	b_1	d_1	b_2	d_2
Ga	27.0379	5.9037	1.6215	27.2128	−1.6752	1.3840	−0.9600
Ge	27.6148	6.1197	1.7239	26.0096	−1.7520	1.8384	−0.9920
As	28.8061	6.3357	1.8253	27.8704	−1.6288	2.7712	−1.0592
Se	29.6902	6.5518	1.9259	28.3888	−1.6128	3.7584	−1.1296
Br	30.5744	6.7679	2.0262	28.9904	−1.6000	4.8832	−1.2048
Kr	31.4585	6.9842	2.1262	29.7264	−1.5920	6.0704	−1.2800

[a] $c_1=2.0$, $c_2=8.0$ and $c_3=18.0$ for all atoms

shown, while in [4] more details on this method of approximation for the exchange integrals can be found.

3. Results

Throughout our calculations we have adopted the Huzinaga’s 14*s*, 11*p*, 5*d* basis sets as reference for SCF orbitals [5]. We freeze the *K*, *L* and *M* shells, while 4*s* and 4*p* are the valence orbitals. In order to get a good approximation to the G_c matrix elements it is sufficient to employ a number of erf terms equal to the principal quantum number, while for the exponential contribution it is sufficient to put $M_x=M_r-1$. In Table 1, the necessary parameters to fit $2J_c(r)$ are reported and in Fig. 1 we match the profiles of $2J_c(r)$ potential given by SCF reference orbitals and approximated by means of Eq. (2), for the Ga atom. As far as the exchange integrals are concerned, a good approximation is achieved by employing one point for each of the inner core shells, two points for the outer core shell; in Table 2 we report the points and the weights needed to approximate exchange integrals by Eq. (3). Finally, in Table 3 we compare the values of some representative integrals $\langle\sigma_v|J_c|\sigma_v\rangle$ and $\langle\sigma_v|k_c|\sigma_v\rangle$ calculated by means of formulae (2) and

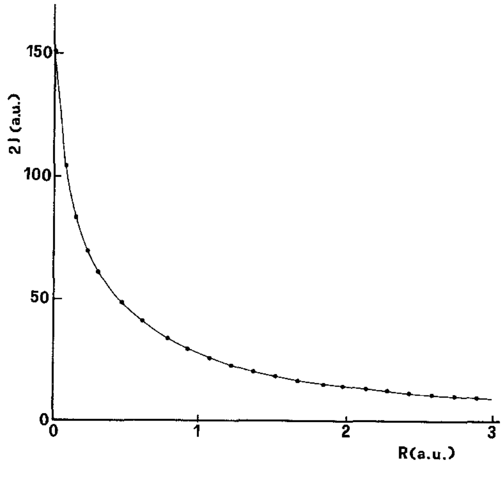

Fig. 1. Plots of $2J_c(r)$ for the Ga atom: (a) —— calculated by complete SCF core orbitals (b) ····· calculated by approximating formula (2)

Table 2. Parameters to fit exchange integrals by (3) for atoms Ga-Kr

	Ga	Ge	As	Se	Br	Kr
K shell						
r_1	0.852896*D*−01	0.824802*D*−01	0.798468*D*−01	0·773753*D*−01	0.750522*D*−01	0.728637*D*−01
H^0_{11}	0.581946*D*−02	0.544238*D*−02	0.510041*D*−02	0.478956*D*−02	0.450626*D*−02	0.424730*D*−02
r_1	0.114031*D*+00	0·109633*D*+00	0.105385*D*+00	0.101625*D*+00	0.987322*D*−01	0.953564*D*−01
H^1_{11}	0.166067*D*−04	0.142780*D*−04	0.122581*D*−04	0.106549*D*−04	0.953822*D*−05	0.833712*D*−05
r_1	0·159166*D*+00	0.154281*D*+00	0.149697*D*+00	0.145326*D*+00	0.142334*D*+00	0.139277*D*+00
H^2_{11}	0.793008*D*−07	0.657749*D*−07	0.548866*D*−07	0.459456*D*−07	0.405531*D*−07	0.356006*D*−07
L shell						
r_1	0.217443*D*+00	0.209777*D*+00	0.202607*D*+00	0.195902*D*+00	0.189621*D*+00	0.183725*D*+00
H^0_{11}	0.694746*D*−01	0.646622*D*−01	0.603177*D*−01	0.563917*D*−01	0.528334*D*−01	0.495991*D*−01
r_1	0.327686*D*+00	0.314499*D*+00	0.302270*D*+00	0.290954*D*+00	0.280470*D*+00	0.270585*D*+00
H^1_{11}	0.554861*D*−02	0.470790*D*−02	0.401729*D*−02	0.344864*D*−02	0.297780*D*−02	0.257967*D*−02
r_1	0.391738*D*+00	0.378491*D*+00	0.365691*D*+00	0.353325*D*+00	0.341377*D*+00	0.329833*D*+00
H^2_{11}	0.637975*D*−03	0.523480*D*−03	0.429704*D*−03	0.353027*D*−03	0.291988*D*−03	0.240783*D*−03
M shell						
r_1	0.369910*D*+00	0.348459*D*+00	0.331235*D*+00	0.316537*D*+00	0.303575*D*+00	0.291730*D*+00
r_2	0.844153*D*+00	0.795201*D*+00	0.755895*D*+00	0.722352*D*+00	0.692772*D*+00	0.665743*D*+00
H^0_{11}	0.268212*D*+00	0.238007*D*+00	0.215060*D*+00	0.196397*D*+00	0.180641*D*+00	0.166821*D*+00
H^0_{12}	0.101427*D*+00	0.900045*D*−01	0.813266*D*−01	0.742691*D*−01	0.683111*D*−01	0.630846*D*−01
H^0_{22}	0.117531*D*+00	0.104295*D*+00	0.942396*D*−01	0.860616*D*−01	0.791575*D*−01	0.731012*D*−01
r_1	0.355500*D*+00	0.332813*D*+00	0.314574*D*+00	0.298904*D*+00	0.285194*D*+00	0.273497*D*+00
r_2	0.756739*D*+00	0.708447*D*+00	0.669622*D*+00	0.636265*D*+00	0.607082*D*+00	0.582184*D*+00
H^1_{11}	0.255424*D*−01	0.196203*D*−01	0.156602*D*−01	0.127653*D*−01	0.105795*D*−01	0.894785*D*−02
H^1_{12}	0.105432*D*−01	0.809875*D*−02	0.646410*D*−02	0.526917*D*−02	0.436696*D*−02	0.369344*D*−02
H^1_{22}	0.119993*D*−01	0.921719*D*−02	0.735680*D*−02	0.599685*D*−02	0.497004*D*−02	0.420351*D*−02
r_1	0.537511*D*+00	0.507846*D*+00	0.480028*D*+00	0.450181*D*+00	0.428402*D*+00	0.410352*D*+00
r_2	0.108366*D*+01	0.102385*D*+01	0.967766*D*+00	0.907593*D*+00	0.863685*D*+00	0.827294*D*+00
H^2_{11}	0.355184*D*−01	0.250348*D*−01	0.177095*D*−01	0.119477*D*−01	0.876009*D*−02	0.670289*D*−02
H^2_{12}	0.156450*D*−01	0.110272*D*−01	0.780061*D*−02	0.526269*D*−02	0.385861*D*−02	0.295246*D*−02
H^2_{22}	0.176177*D*−01	0.124177*D*−01	0.878421*D*−02	0.592627*D*−02	0.434515*D*−02	0.332474*D*−02

(3) or by using exact SCF orbitals. It is remarkable that the differences for all these core-valence integrals are very small (errors <1%), despite the fact that they have been calculated for a monocentric case. For integrals involving valence orbitals on a center and core on a different center, errors on the $J_c(r)$ shape, for small r values, are obviously much less important.

Table 3. Exact SCF and approximated by (2) or (4) formulae values of some Coulomb and exchange integrals[a]

		$\langle\sigma\|J_c\|\sigma\rangle$		$\langle\sigma\|K_c\|\sigma\rangle$	
Atom	σ	Exact	Approx.	Exact	Approx.
Ga	4*s*	6.7271	6.7193	0.0894	0.0894
Ga	4*p*	5.0990	5.0995	0.0400	0.0400
As	4*s*	8.2293	8.2296	0.1217	0.1217
As	4*p*	6.7779	6.7774	0.0706	0.0706
Br	4*s*	9.5900	9.5941	0.1521	0.1521
Br	4*p*	8.1073	8.1093	0.0966	0.0966

[a] SCF orbitals and basis sets from [5]

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