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Original investigations

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

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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 a previous paper, is extended to the atoms from K to Zn. 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

It is a well established fact that the valence electrons are the ones mainly responsible for chemical behavior of the molecular species, while the core electrons (i.e. the inner closed shells of each atom) remain localized on their atom. Starting from this consideration, in order to simplify the computational effort, effective potentials have been introduced to replace the effect of the core electrons on the valence electrons. This 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, applied with different kinds of effective potentials [6–15], has proved to be capable of giving nearly the same accuracy in predicting molecular properties of the 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:

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

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 in (1), where $P_i=|\varphi_i\rangle\langle\varphi_i|$, is properly called the Phillips–Kleinman pseudopotential and prevents the valence electron orbitals from collapsing in the core region. The most ponderous matrix to calculate in this framework is that related to G_c operator which contain a very large number of two electron terms which account for the core-valence interaction. For this reason in past years many approximate potentials $U_c(r)$ such as 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 proposed by several authors. In a recent paper, hereafter referred to as [19], we have proposed an expression which, using only a few parameters, approximates the Coulomb and exchange terms of G_c and maintains the nonlocal character of the exchange operators. The necessary parameters for the atoms of the first and second row were reported there; now we present the results for the third row's atoms K through Zn, along with the potential energy curves of some states of the radical CaCl calculated by means of our approximation.

2. The effective potential

The expression we have proposed in [19] to approximate the matrix elements $\langle\varphi|G_c|\varphi\rangle$ takes the exchange and Coulomb terms into account separately. The latter, calculated with SCF orbitals expanded on a gaussian basis set, turns out to be a combination of erf and gaussian terms; for this reason we have adopted, to approximate the Coulomb operator of the core electrons of the K and L shells of an atom centered on $\vec{R}_c$, an expression like:

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

In order to account for the electrons up to $3s$ and $3p$ orbitals of the core of the atoms K through Zn it is sufficient to extend the expansion to $M_r=3$ and $M_x=2$.

The exchange integrals between the core of an atom and two generic functions f and g were computed by means of the formula

$$\langle f|K_c|g\rangle=\sum_{i,j}^{N}[H_{ij}^{0}f^{0}(r_i)g^{0}(r_j)+H_{ij}^{1}f^{1}(t_i)g^{1}(t_j)] \tag{3}$$

where the first term in the summation represents the contribution of the spherical part, while the second term comes out from the p part. Proceeding on the third row it is necessary to introduce also the d-type functions, so we can generalize (3) by

$$\langle f|K_c|g\rangle=\sum_{i,j}^{N}\sum_{l}^{M}H_{ij}^{l}\sum_{m=-l}^{l}f_{lm}(r_i^l)g_{lm}(r_j^l) \tag{4}$$

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

Atom	a_1	a_2	a_3	b_1	d_1	b_2	d_2
K	16.4369	4.5272	1.1747	15.6923	−12.9936	0.9233	−3.2910
Ca	17.3185	4.8274	1.3197	17.9115	−13.8834	1.1496	−3.7152
Sc	18.2002	5.1281	1.4324	20.2799	−14.7787	1.3386	−4.0396
Ti	19.0833	5.4281	1.5393	22.7926	−15.6753	1.5314	−4.3462
V	19.9666	5.7277	1.6436	25.4516	−16.5739	1.7325	−4.6449
Cr	20.8505	6.0268	1.7461	28.2553	−17.4743	1.9425	−4.9381
Mn	21.7338	6.3255	1.8467	31.1976	−18.3750	2.1602	−5.2252
Fe	22.6473	6.6327	1.9347	34.4457	−19.2881	2.3580	−5.4751
Co	23.0844	6.7028	1.9766	36.2513	−19.4686	2.5503	−5.5568
Ni	24.1490	7.1725	2.1257	40.1994	−20.9511	2.7970	−6.0197
Cu	26.1225	7.8634	2.3185	46.2664	−23.1011	3.0928	−6.6557
Zn	26.1538	7.8154	2.3491	48.0722	−22.8931	3.4198	−6.6586

[a] $c_1 = 2$ and $c_2 = c_3 = 8$ for all atoms.

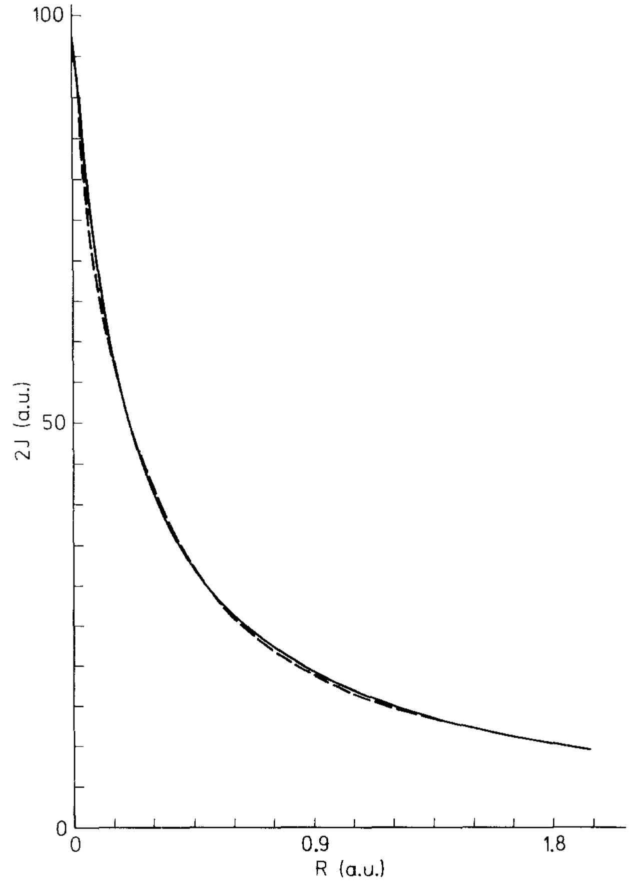

Fig. 1. Plots of $2J_c(r)$ for Mn atom: (a) —— calculated by complete SCF core orbitals (b) --- calculated by approximating formula (8)

Table 2. Parameters to fit exchange integrals by (4) for atoms K–Cr

	K	Ca	Sc	Ti	V	Cr
K shell						
r_1	0.143570	0.135773	0.128827	0.122553	0.116870	0.111724
H^0_{11}	0.207219	0.185322	0.166844	0.150990	0.137311	0.125484
r_1	0.170772	0.161497	0.153235	0.145772	0.139013	0.132891
H^1_{11}	0.011617	0.010476	0.009500	0.008653	0.007913	0.007266
r_1	—	—	0.167792	0.159620	0.152218	0.145515
H^2_{11}	—	—	0.001785	0.001630	0.001491	0.001366
L shell						
r_1	0.366216	0.344031	0.324777	0.307645	0.292269	0.278373
H^0_{11}	1.834368	1.618855	1.442725	1.294527	1.168367	1.059902
r_1	0.532032	0.499803	0.471831	0.446941	0.424604	0.404415
H^1_{11}	2.778927	2.122904	1.687847	1.382044	1.155565	0.983185
r_1	—	—	0.509854	0.482958	0.458821	0.437005
H^2_{11}	—	—	0.199828	0.177818	0.159496	0.144231
M shell (*s* and *p* only)						
r_1	0.685118	0.625683	0.586526	0.552814	0.523126	0.496695
r_2	1.623257	1.482436	1.389662	1.309788	1.239447	1.176825
H^0_{11}	6.474712	5.400048	4.755307	4.215487	3.774865	3.403057
H^0_{12}	3.000080	2.502131	2.198755	1.953260	1.749097	1.576818
H^0_{22}	2.732742	2.279165	2.002823	1.779204	1.593234	1.436307
r_1	0.860911	0.786225	0.737022	0.694659	0.657353	0.624141
r_2	1.898104	1.733439	1.624957	1.531559	1.449307	1.376082
H^1_{11}	4.103957	3.391608	2.918383	2.550184	2.252830	2.007760
H^1_{12}	0.941397	0.777993	0.669441	0.584981	0.516771	0.460555
H^1_{22}	0.382928	0.316461	0.272306	0.237950	0.210205	0.187338
r_1	—	—	0.834171	0.786225	0.744002	0.707412
r_2	—	—	1.625085	1.531679	1.449421	1.376191
H^2_{11}	—	—	1.128699	0.949307	0.820199	0.720251
H^2_{12}	—	—	0.100819	0.084796	0.073263	0.064335
H^2_{22}	—	—	0.040223	0.033830	0.029229	0.025667

where N is the number of points used to approximate the exchange integral and M is the maximum angular momentum quantum number of the atom; moreover we define:

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

and

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

where $S_{lm}(\omega_p)$ is the value at ω_p of the spherical harmonic in real form S_{lm}. Practically we only need to compute the function f for n_p points on a sphere with radius r, and to sum them after multiplication for the appropriate coefficients,

Table 3. Parameters to fit exchange integrals by (4) for atoms Mn–Zn

	Mn	Fe	Co	Ni	Cu	Zn
K shell						
r_1	0.107006	0.102635	0.098608	0.094956	0.091482	0.088304
H^0_{11}	0.115110	0.105898	0.097752	0.090646	0.084134	0.078389
r_1	0.127279	0.122081	0.117291	0.112947	0.108815	0.105034
H^1_{11}	0.006695	0.006186	0.005735	0.005334	0.004969	0.004643
r_1	0.139371	0.133678	0.128433	0.123677	0.119152	0.115012
H^2_{11}	0.001259	0.001165	0.001079	0.001001	0.000933	0.000870
L shell						
r_1	0.265780	0.254243	0.243703	0.234008	0.225644	0.216784
H^0_{11}	0.966178	0.884118	0.812331	0.748984	0.696403	0.642788
r_1	0.386121	0.369360	0.354048	0.339963	0.327812	0.314941
H^1_{11}	0.848150	0.739150	0.650172	0.577070	0.502801	0.464721
r_1	0.417237	0.399125	0.382579	0.367359	0.354229	0.340320
H^2_{11}	0.131061	0.119789	0.109953	0.101300	0.093495	0.086869
M shell (s and p only)						
r_1	0.472974	0.451276	0.431636	0.413667	0.397255	0.382070
r_2	1.120622	1.069212	1.022680	0.980105	0.941220	0.905242
H^0_{11}	3.085775	2.809138	2.569955	2.360431	2.176846	2.013608
H^0_{12}	1.429804	1.301624	1.190798	1.093714	1.008649	0.933012
H^0_{22}	1.302394	1.185636	1.084685	0.996253	0.918768	0.849871
r_1	0.594333	0.567067	0.542389	0.519809	0.499185	0.480104
r_2	1.310364	1.250249	1.195839	1.146055	1.100585	1.058516
H^1_{11}	1.803180	1.626886	1.477122	1.347851	1.235778	1.137387
H^1_{12}	0.413627	0.373187	0.338833	0.309180	0.283472	0.260902
H^1_{22}	0.168249	0.151800	0.137826	0.125764	0.115307	0.106126
r_1	0.672675	0.641815	0.613883	0.588327	0.564985	0.543389
r_2	1.310467	1.250347	1.195933	1.146145	1.100672	1.058599
H^2_{11}	0.639446	0.575780	0.521120	0.474136	0.433493	0.397839
H^2_{12}	0.057118	0.051431	0.046548	0.042352	0.038721	0.035536
H^2_{22}	0.022788	0.020519	0.018571	0.016897	0.015448	0.014178

Table 4. Coefficients C_{lmp} up to d-type functions for 14 points defined in the text

$$a=\sqrt{\pi}/7 \quad b=\sqrt{3\pi}/7 \quad c=\sqrt{5\pi}/15 \quad d=\sqrt{15\pi}/20 \quad e=\sqrt{15\pi}/15$$

	Points													
Type	1	2	3	4	5	6	7	8	9	10	11	12	13	14
s	a	a	a	a	a	a	a	a	a	a	a	a	a	a
p_z	a	a	a	a	$-a$	$-a$	$-a$	$-a$	0	0	0	0	b	$-b$
p_x	a	$-a$	$-a$	a	a	$-a$	$-a$	a	b	$-b$	0	0	0	0
p_y	a	a	$-a$	$-a$	a	a	$-a$	$-a$	0	0	b	$-b$	0	0
d_{z^2}	0	0	0	0	0	0	0	0	$-c$	$-c$	$-c$	$-c$	$2c$	$2c$
d_{xz}	d	$-d$	$-d$	d	$-d$	d	d	$-d$	0	0	0	0	0	0
d_{yz}	d	d	$-d$	$-d$	$-d$	$-d$	d	d	0	0	0	0	0	0
$d_{x^2-y^2}$	0	0	0	0	0	0	0	0	e	e	$-e$	$-e$	0	0
d_{xy}	d	$-d$	d	$-d$	d	$-d$	d	$-d$	0	0	0	0	0	0

Table 5. Exact SCF and approximated by (2) or (4) formulae values of some Coulomb and exchange integrals[a]

		$\langle\varphi\|2J_c\|\varphi\rangle$		$\langle\varphi\|K_c\|\varphi\rangle$	
Atom	φ	Exact	Approx.	Exact	Approx.
V	$4s$	5.9725	5.9715	0.0345	0.0345
V	$3d$	16.2830	16.2577	0.4079	0.4079
Mn	$4s$	6.4229	6.4217	0.0351	0.0351
Mn	$3d$	18.8383	18.8122	0.4812	0.4812
Ni	$4s$	7.1196	7.1156	0.0368	0.0368
Ni	$3d$	22.1782	22.0945	0.5721	0.5721

[a] SCF orbitals and basis sets from Ref. [18].

Table 6. CaCl potential energy values[a] of the $X\,^2\Sigma^+$, $A\,^2\Pi$ and $B\,^2\Sigma^+$ states obtained by all-electron (A.E.) and valence-electron-only (V.E.) SCFs

	$X\,^2\Sigma^+$		$A\,^2\Pi$		$B\,^2\Sigma^+$	
R	A.E. [20]	V.E.[b]	A.E. [20]	V.E.[b]	A.E. [20]	V.E.[b]
∞	0	0	0	0	0.0941	0.0945
15	−0.0001	0	—	—	0.0264	0.0257
12	−0.0001	−0.0001	—	—	0.0093	0.0059
10	−0.0124	−0.0075	—	0.0004	0.0099	0.0062
8	−0.0457	−0.0592	0.0024	0.0032	0.0239	0.0308
6	−0.1012	−0.1165	0.0139	0.0172	0.0525	0.0635
5	−0.1229	−0.1222	—	0.0519	0.0794	0.0984
4.5	−0.1135	−0.0889	0.0675	0.1042	—	0.1426
4	−0.0598	0.0114	—	—	0.1364	0.2411

[a] All energies (a.u.) are referred to molecular dissociation limit.

[b] Basis: Ca ($3s, 3p$) from Ref. [9], Cl ($3s, 3p$) from Ref. [8].

to get the right contribution $f_{lm}(r_i^l)$ at least up to l quantum number. As an example we have used the following 14 points: $\bar{r}_1 \div \bar{r}_8$ are the vertices of the cube inscribed in the sphere or radius r, $\bar{r}_9 \div \bar{r}_{14}$ are the meeting points of the same sphere, on the positive and negative sides respectively, with the x, y and z axis (in the order). For convenience in Table 4 we report the coefficients C_{lmp}, which give the right contribution up to d-type functions, for these 14 points. More details on this method of approximation for the exchange integrals can be found in Ref. [21].

3. Results

As concerns the atoms K through Zn the expression (2) extended to $M_r = 3$ and $M_x = 2$ is a very good approximation to the Coulomb operator of the core electrons. The necessary parameters to fit $2J_c(r)$ are shown in Table 1, while in

Fig. 1 the $2J_c(r)$ potential given by SCF orbitals expanded on an extended gaussian basis set [18] is matched with the approximate potentials calculated for the Mn atom by means of Eq. (2). The results are equally good for the other atoms.

In Tables 2 and 3 we report the points and the weights needed to approximate the exchange integrals by Eq. (4). In Table 5 the values of some integrals $\langle\varphi_v|2J_c|\varphi_v\rangle$ and $\langle\varphi_v|K_c|\varphi_v\rangle$ calculated by the approximating formulae (2) and (4) or of exact SCFs are compared.

Recently some SCF calculations with large basis sets have been performed on the radicals CaF, CaCl and MgCl [20]. As a test of our approximation we have repeated the calculus for the potential energy curves of three states of CaCl adopting the valence optimized basis from Khan et al. [8] for Cl and Topiol et al. [9] for Ca atom. The results are reported in Table 6 and plotted in Fig. 2. If we keep in mind that the all-electron curves need a basis set of 75 functions, while our valence-electron curves come out from only 18 functions basis set, the good representation obtained is noticeable. The slight lengthening of interatomic distances (0.2–0.3 a.u.) can be ascribed to basis effects and does not affects so much the quality of results.

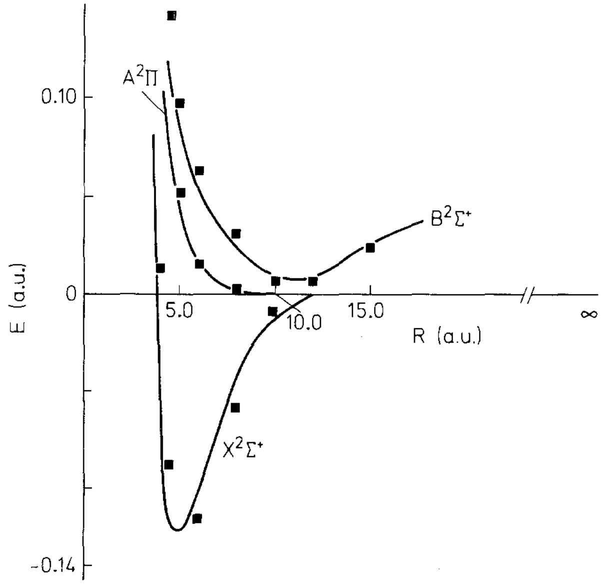

Fig. 2. CaCl $X\,^2\Sigma^+$, $A\,^2\Pi$ and $B\,^2\Sigma^+$ states: Comparison of the valence-electron-only (■) and all-electron SCF potential energy curves (——)

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