Theor Chim Acta (1989) 76: 1–5

Theoretica Chimica Acta

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

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(Received June 30, 1988; revised and accepted January 6, 1989)

Summary. Following a previously described method which approximates the Coulomb and exchange integrals in valence–electron–only SCF calculations, the necessary parameters for the atoms from In to Xe are reported.

Key words: Pseudopotential — Valence–electron–only SCF

We have carried out the optimization of the parameters needed for the approximation of the matrix elements of Coulomb and exchange operators generated by the core electrons of atoms In, Sn, Sb, Te, I and Xe. This paper is the last of the series which has covered, in successive steps, atoms Li through Cd [1–5].

A widely adopted way to reduce the computational effort is to restrict the molecular calculation to the valence electrons of the system. Core electrons are not involved, but their effects—the core–valence interaction—must be taken into account. These effects, which in a usual all-electron calculation are brought by numerous dielectronic integrals, can be quite adequately approximated by the monoelectronic integrals we have proposed.

We shortly recall that the Coulomb operator generated by the core electrons of an atom centered on $\boldsymbol{R}_c$ may be approximated by the formula

$$J_c(|\boldsymbol{r} - \boldsymbol{R}_c|) = \sum_s^{M_r} c_s \frac{\operatorname{erf}(a_s|\boldsymbol{r} - \boldsymbol{R}_c|)}{|\boldsymbol{r} - \boldsymbol{R}_c|} + \sum_s^{M_x} d_s \exp[-b_s|\boldsymbol{r} - \boldsymbol{R}_c|^2] \tag{1}$$

where M_r is the number of core shells and $M_x = M_r - 1$.

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

$$\langle \Phi_1 | K_c | \Phi_2 \rangle = \sum_{i,j}^{N} \sum_{l}^{M} H_{ij}^{l} \sum_{m=-l}^{l} f_{lm}(r_i^l) g_{lm}(r_j^l), \quad (2)$$

where

$$\Phi_1(|\boldsymbol{r} - \boldsymbol{R}_1|) = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} f_{lm}(r) r^l Y_{lm}(\Omega)$$

$$\Phi_2(|\boldsymbol{r} - \boldsymbol{R}_2|) = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} g_{lm}(r) r^l Y_{lm}(\Omega),$$

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 its real form, S_{lm}. The nonlocal character of the exchange operator is kept. The right contributions $f_{lm}(r_i^l)$ at least up to quantum number l are obtained by computing the f function for n_p points on a sphere having radius r_i^l, multiplying by the appropriate C_{lmp} coefficients, and then adding them. The monoelectronic integral matrix so obtained can be added to the kinetic and nuclear attraction matrices and a Phillips–Kleinman pseudopotential matrix [6], which prevents a variational collapse into the core orbitals, and used in a SCF (valence electron) calculation.

Throughout the present calculations we have adopted Huzinaga's 18(16)s, 14(12)p, 8d basis sets as reference for SCF atomic orbitals [7]. We freeze the K, L, M and N shells; 5s and 5p are the valence orbitals. We report c_s, a_s, d_s and b_s parameters for the Coulomb operator approximation in Table 1; points, r_i^l, and weights, H_{ij}^l, necessary for the exchange integral approximation are in Table 2.

Table 1. Parameters used to fit Coulomb potentials $2J_c$ by Eq. (1), for atoms from In to Xe[a]

	In	Sn	Sb	Te	I	Xe
a_1	42.9599	43.8448	44.7298	45.6148	46.4999	47.3848
a_2	9.8073	10.0251	10.2429	10.4608	10.6788	10.8969
a_3	3.3956	3.4920	3.5883	3.6847	3.7811	3.8774
a_4	1.1380	1.1998	1.2606	1.3206	1.3798	1.4388
b_1	89.1488	88.6208	88.3744	88.3376	88.5008	88.8704
d_1	−2.9616	−2.9088	−2.8624	−2.8208	−2.7840	−2.7520
b_2	21.3680	22.8768	24.4400	26.0240	27.7088	29.4288
d_2	−1.8752	−1.9360	−1.9984	−2.0592	−2.1248	−2.1904
b_3	1.2896	1.4896	1.6752	1.8576	2.0320	2.2096
d_3	−1.3568	−1.4464	−1.5344	−1.6240	−1.7104	−1.8000

[a] $c_1 = 2$, $c_2 = 8$, $c_3 = c_4 = 18$ for all atoms

Table 2. Parameters used to fit the exchange integrals by Eq. (2) for atoms from In to Xe

	In	Sn	Sb	Te	I	Xe
K shell						
r_1	0.526626*D* − 01	0.515599*D* − 01	0.505021*D* − 01	0.494864*D* − 01	0.485107*D* − 01	0.475726*D* − 01
H^0_{11}	0.221868*D* − 02	0.212674*D* − 02	0.204037*D* − 02	0.195912*D* − 02	0.188263*D* − 02	0.181053*D* − 02
r_1	0.772456*D* − 01	0.756495*D* − 01	0.741196*D* − 01	0.726488*D* − 01	0.712352*D* − 01	0.698770*D* − 01
H^1_{11}	0.403538*D* − 05	0.373060*D* − 05	0.345474*D* − 05	0.320424*D* − 05	0.297578*D* − 05	0.276837*D* − 05
r_1	0.104381*D* + 00	0.102427*D* + 00	0.100510*D* + 00	0.986446*D* − 01	0.968952*D* − 01	0.951428*D* − 01
H^2_{11}	0.630811*D* − 08	0.563190*D* − 08	0.502833*D* − 08	0.449386*D* − 08	0.403640*D* − 08	0.361773*D* − 08
L shell						
r_1	0.129971*D* + 00	0.127073*D* + 00	0.124325*D* + 00	0.121713*D* + 00	0.119180*D* + 00	0.116756*D* + 00
H^0_{11}	0.248214*D* − 01	0.237270*D* − 01	0.227119*D* − 01	0.217675*D* − 01	0.208709*D* − 01	0.200306*D* − 01
r_1	0.183661*D* + 00	0.179146*D* + 00	0.174839*D* + 00	0.170744*D* + 00	0.166832*D* + 00	0.163077*D* + 00
H^1_{11}	0.547546*D* − 03	0.495655*D* − 03	0.449677*D* − 03	0.409010*D* − 03	0.372795*D* − 03	0.340347*D* − 03
r_1	0.261035*D* + 00	0.256674*D* + 00	0.252467*D* + 00	0.248397*D* + 00	0.244455*D* + 00	0.240627*D* + 00
H^2_{11}	0.966124*D* − 04	0.909669*D* − 04	0.859136*D* − 04	0.813620*D* − 04	0.771313*D* − 04	0.731109*D* − 04
M shell						
r_1	0.361440*D* + 00	0.352143*D* + 00	0.343314*D* + 00	0.334901*D* + 00	0.326837*D* + 00	0.319068*D* + 00
H^0_{11}	0.257622*D* + 00	0.244539*D* + 00	0.232430*D* + 00	0.221178*D* + 00	0.210655*D* + 00	0.200760*D* + 00
r_1	0.318223*D* + 00	0.309986*D* + 00	0.302127*D* + 00	0.294604*D* + 00	0.287471*D* + 00	0.280614*D* + 00
H^1_{11}	0.890261*D* − 02	0.801596*D* − 02	0.723349*D* − 02	0.653950*D* − 02	0.592880*D* − 02	0.538302*D* − 02
r_1	0.611903*D* + 00	0.588377*D* + 00	0.566179*D* + 00	0.546986*D* + 00	0.529548*D* + 00	0.500739*D* + 00
H^2_{11}	0.144278*D* − 01	0.114036*D* − 01	0.905380*D* − 02	0.736150*D* − 02	0.606089*D* − 02	0.433287*D* − 02

Table 2. *(continued)*

	In	Sn	Sb	Te	I	Xe
N shell						
r_1	0.566413*D* + 00	0.539578*D* + 00	0.518014*D* + 00	0.499212*D* + 00	0.482686*D* + 00	0.467625*D* + 00
r_2	0.120336*D* + 01	0.114635*D* + 01	0.110054*D* + 01	0.106059*D* + 01	0.102548*D* + 01	0.993484*D* + 00
H^0_{11}	0.574962*D* + 00	0.521773*D* + 00	0.480902*D* + 00	0.446624*D* + 00	0.417544*D* + 00	0.391893*D* + 00
H^0_{12}	0.234387*D* + 00	0.212704*D* + 00	0.196043*D* + 00	0.182069*D* + 00	0.170215*D* + 00	0.159758*D* + 00
H^0_{22}	0.270630*D* + 00	0.245594*D* + 00	0.226357*D* + 00	0.210222*D* + 00	0.196535*D* + 00	0.184461*D* + 00
r_1	0.553850*D* + 00	0.527099*D* + 00	0.505406*D* + 00	0.486070*D* + 00	0.469002*D* + 00	0.453922*D* + 00
r_2	0.111531*D* + 01	0.106144*D* + 01	0.101776*D* + 01	0.978819*D* + 00	0.944450*D* + 00	0.914081*D* + 00
H^1_{11}	0.151451*D* + 00	0.124243*D* + 00	0.105018*D* + 00	0.898457*D* − 01	0.778758*D* − 01	0.683322*D* − 01
H^1_{12}	0.661909*D* − 01	0.542999*D* − 01	0.458976*D* − 01	0.392667*D* − 01	0.340353*D* − 01	0.298643*D* − 01
H^1_{22}	0.752085*D* − 01	0.616975*D* − 01	0.521506*D* − 01	0.446163*D* − 01	0.386722*D* − 01	0.339330*D* − 01
r_1	0.916135*D* + 00	0.872551*D* + 00	0.833434*D* + 00	0.797673*D* + 00	0.764856*D* + 00	0.738603*D* + 00
r_2	0.176573*D* + 01	0.168173*D* + 01	0.160633*D* + 01	0.153741*D* + 01	0.147416*D* + 01	0.142356*D* + 01
H^2_{11}	0.738167*D* + 00	0.546432*D* + 00	0.411513*D* + 00	0.314016*D* + 00	0.242666*D* + 00	0.195570*D* + 00
H^2_{12}	0.339555*D* + 00	0.251357*D* + 00	0.189295*D* + 00	0.144447*D* + 00	0.111626*D* + 00	0.899616*D* − 01
H^2_{22}	0.382992*D* + 00	0.283512*D* + 00	0.213510*D* + 00	0.162925*D* + 00	0.125905*D* + 00	0.101470*D* + 00

Table 3. Values of some exact and approximate $\langle \Phi|(2J-K)_c|\Phi\rangle$ integrals

Molecule	core	Φ function			Integral		Error	%
		Atom	type	g	Exact	Approx.		
HIn[a]	In	H	s	1.	13.181690	13.187937	0.006248	0.047
HIn	In	H	s	0.3	13.149572	13.175141	0.025569	0.194
HI[b]	I	H	s	1.	15.117575	15.131328	0.013753	0.091
HI	I	H	s	0.3	15.057442	15.091883	0.034441	0.229
TeH_2[c]	Te	H	s	1.	13.525858	13.529376	0.003518	0.026
TeH_2	Te	H	s	0.3	13.502629	13.517710	0.015081	0.112
SbI_3[d]	Sb	I	s	0.6	9.116720	9.117938	0.001218	0.013
SbI_3	Sb	I	s	0.1	9.092672	9.097697	0.005026	0.055
SbI_3	Sb	I	p	0.3	9.713456	9.714765	0.001309	0.013
SbI_3	Sb	I	p	0.09	10.697852	10.744498	0.046646	0.436
SbI_3	I	Sb	s	0.5	9.110846	9.117925	0.007078	0.078
SbI_3	I	Sb	s	0.08	9.056620	9.067403	0.010783	0.119
SbI_3	I	Sb	p	0.5	9.469277	9.476178	0.006901	0.073
SbI_3	I	Sb	p	0.07	10.753629	10.810537	0.056908	0.529

[a] $r_e = 3.488$ a.u.
[b] $r_e = 3.04$ a.u.
[c] $r_e = 3.4$ a.u.
[d] $r_e = 5.045$ a.u.

The quality of this approximation has been tested and is found to be good. In Table 3 we compare the values of several $\langle \Phi|(2J-k)_c|\Phi\rangle$ integral calculated exactly, and by means of our approximations (1) and (2), for the molecules HIn, HI, TeH_2 and SbI_3. The Φ are gaussian basis functions (exponent $= g$); the operator $(2J-K)_c$ is built with the Huzinaga's atomic core orbitals. The error introduced by our approximations is always much less than 1.0%.

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