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

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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 Rb to Cd are reported. Extension to other atoms is in progress.

Key words: Pseudopotential — Valence-electron-only SCF

We have recently proposed [1-4] an approximate method for calculating the matrix elements of the Coulomb and exchange operators generated by the core electrons. By means of this method and using a Phillips-Kleinman [5] pseudopotential, one can perform molecular SCF calculations on the valence electrons only, with a substantial reduction of computational effort.

This is only to report that the necessary parameters for our method have been evaluated also for atoms Rb through Cd; in [1-3] the same parameters for lighter atoms Li though Kr can be found.

The Coulomb operator generated by the core electrons of an atom centered on $\bar{R}_c$ is approximated by the formula

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

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

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

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. The right contributions $f_{lm}(r_i^l)$ at least up to l quantum number are obtained by computing the f function for n_p points on a sphere having r_i^l radius, and adding them after multiplication by the appropriate C_{lmp} coefficients.

Throughout the present calculations we have adopted the Huzinaga's [6] 17*s*, 11*p*, 6*d* (Rb, Sr) and 17*s*, 11*p*, 8*d* (Y—Cd) basis sets as reference for SCF atomic orbitals. We freeze *K*, *L*, *M* and partially *N* shells: 5*s* and 4*d* are the valence orbitals.

We report c_s, a_s, d_s and b_s parameters for Coulomb operator approximation in Tables 1 and 2, while r_i^l points and H_{ij}^l weights necessary for the exchange

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

	Rb	Sr	Y	Zr	Nb	Mo
a_1	32.3429	33.2272	34.1116	34.9962	35.8809	36.7656
a_2	7.2008	7.4174	7.6343	7.8512	8.0682	8.2853
a_3	2.2249	2.3240	2.4230	2.5215	2.6198	2.7177
a_4	0.6946	0.7614	0.8170	0.8686	0.9114	0.9588
b_1	125.0176	121.8144	117.8240	113.3136	108.7456	104.3888
d_1	−4.3368	−4.2008	−4.0520	−3.8968	−3.7448	−3.6008
b_2	6.2992	7.3888	8.5264	9.6800	10.8624	12.0496
d_2	−1.1960	−1.2520	−1.3064	−1.3608	−1.4168	−1.4712
b_3	0.9216	1.0224	1.1040	1.1824	1.2432	1.3232
d_3	−0.4960	−0.5552	−0.6000	−0.6400	−0.6672	−0.7024

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

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

	Tc	Ru	Rh	Pd	Ag	Cd
a_1	37.6503	38.5351	39.4200	40.3049	41.1899	42.0749
a_2	8.5025	8.7199	8.9372	9.1547	9.3722	9.5898
a_3	2.8153	2.9124	3.0093	3.1059	3.2022	3.2992
a_4	1.0128	1.0595	1.1054	1.1505	1.1951	1.2392
b_1	100.5856	97.3776	94.7760	92.6512	91.0848	89.8608
d_1	−3.4712	−3.3560	−3.2552	−3.1656	−3.0888	−3.0200
b_2	13.2640	14.5024	15.7696	17.1008	18.4352	19.9008
d_2	−1.5272	−1.5832	−1.6392	−1.6984	−1.7560	−1.8136
b_3	1.4240	1.5120	1.6032	1.6944	1.7904	1.8944
d_3	−0.7456	−0.7824	−0.8176	−0.8528	−0.8880	−0.9232

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

Table 3. Parameters to fit exchange integrals by (2) for atoms Rb-Mo

	Rb	Sr	Y	Zr	Nb	Mo
K Shell						
r_1	0.707341D−01	0.687666D−01	0.669080D−01	0.651495D−01	0.634789D−01	0.618918D−01
H^0_{11}	0.400265D−02	0.378307D−02	0.358134D−02	0.339556D−02	0.322366D−02	0.306447D−02
r_1	0.103492D+00	0.100650D+00	0.979569D−01	0.954042D−01	0.929837D−01	0.906806D−01
H^1_{11}	0.121008D−04	0.109002D−04	0.984410D−05	0.891202D−05	0.808896D−05	0.735725D−05
r_1	0.135911D+00	0.132291D+00	0.128980D+00	0.126078D+00	0.123290D+00	0.120624D+00
H^2_{11}	0.307401D−07	0.261439D−07	0.224594D−07	0.195890D−07	0.171295D−07	0.150235D−07
L Shell						
r_1	0.177838D+00	0.172468D+00	0.167493D+00	0.162806D+00	0.158371D+00	0.154160D+00
H^0_{11}	0.464712D−01	0.437073D−01	0.412220D−01	0.389471D−01	0.368540D−01	0.349204D−01
r_1	0.261293D+00	0.252614D+00	0.244521D+00	0.236946D+00	0.229815D+00	0.223117D+00
H^1_{11}	0.224317D−02	0.195966D−02	0.172034D−02	0.151688D−02	0.134235D−02	0.119256D−02
r_1	0.327654D+00	0.320831D+00	0.314286D+00	0.308002D+00	0.301966D+00	0.296161D+00
H^2_{11}	0.228860D−03	0.202304D−03	0.210062D−03	0.191951D−03	0.175327D−03	0.161066D−03
M Shell						
r_1	0.522878D+00	0.503427D+00	0.485986D+00	0.469908D+00	0.454946D+00	0.440718D+00
H^0_{11}	0.539152D+00	0.499786D+00	0.465755D+00	0.435448D+00	0.408159D+00	0.383030D+00
r_1	0.457269D+00	0.442579D+00	0.428407D+00	0.414863D+00	0.402086D+00.	0.389882D+00
H^1_{11}	0.379557D−01	0.333081D−01	0.292425D−01	0.257163D−01	0.226916D−01	0.200595D−01
r_1	0.111665D+01	0.104552D+01	0.982952D+00	0.925087D+00	0.875477D+00	0.830091D+00
H^2_{11}	0.425126D+02	0.272347D+02	0.247913D+00	0.172268D+00	0.123759D+00	0.899207D−01
N Shell (*s* and *p* only)						
r_1	0.776247D+00	0.739328D+00	0.709133D+00	0.682143D+00	0.660032D+00	0.637183D+00
r_2	0.168002D+01	0.160012D+01	0.153477D+01	0.147635D+01	0.142850D+01	0.137905D+01
H^0_{11}	0.818962D+00	0.742914D+00	0.683469D+00	0.632433D+00	0.592097D+00	0.551813D+00
H^0_{12}	0.373945D+00	0.339220D+00	0.312078D+00	0.288774D+00	0.270356D+00	0.251962D+00
H^0_{22}	0.378398D+00	0.343260D+00	0.315794D+00	0.292213D+00	0.273576D+00	0.254963D+00
r_1	0.115117D+01	0.106854D+01	0.100557D+01	0.953420D+00	0.911659D+00	0.871758D+00
r_2	0.235569D+01	0.218661D+01	0.205774D+01	0.195103D+01	0.186557D+01	0.178392D+01
H^1_{11}	0.196551D+01	0.145912D+01	0.114439D+01	0.924823D+00	0.773129D+00	0.646407D+00
H^1_{12}	0.953382D+00	0.707757D+00	0.555092D+00	0.448591D+00	0.375011D+00	0.313544D+00
H^1_{22}	0.960495D+00	0.713037D+00	0.559234D+00	0.451938D+00	0.377809D+00	0.315883D+00
r_1	0.137161D+01	0.129758D+01	0.123114D+01	0.117116D+01	0.111676D+01	0.106719D+01
r_2	0.254612D+01	0.240869D+01	0.228535D+01	0.217402D+01	0.207303D+01	0.198101D+01
H^2_{11}	0.748436D+01	0.588164D+01	0.166932D+01	0.117060D+01	0.872721D+00	0.642555D+00
H^2_{12}	0.252206D+01	0.198198D+01	0.562524D+00	0.394465D+00	0.294088D+00	0.216527D+00
H^2_{22}	0.403188D+01	0.316849D+01	0.899276D+00	0.630610D+00	0.470142D+00	0.346150D+00

Table 4. Parameters to fit exchange integrals by (2) for atoms Tc–Cd

	Tc	Ru	Rh	Pd	Ag	Cd
K Shell						
r_1	0.603812D−01	0.589433D−01	0.575715D−01	0.562621D−01	0.550108D−01	0.538138D−01
H^0_{11}	0.291671D−02	0.277945D−02	0.265158D−02	0.253234D−02	0.242095D−02	0.231674D−02
r_1	0.884889D−01	0.864006D−01	0.844106D−01	0.825083D−01	0.806898D−01	0.789515D−01
H^1_{11}	0.670793D−05	0.612954D−05	0.561297D−05	0.514894D−05	0.473158D−05	0.435601D−05
r_1	0.118038D+00	0.115601D+00	0.113218D+00	0.110902D+00	0.108674D+00	0.106546D+00
H^2_{11}	0.131921D−07	0.116401D−07	0.102726D−07	0.907430D−08	0.803395D−08	0.713509D−08
L Shell						
r_1	0.150167D+00	0.146377D+00	0.142776D+00	0.139348D+00	0.136070D+00	0.132953D+00
H^0_{11}	0.331349D−01	0.314836D−01	0.299535D−01	0.285324D−01	0.272058D−01	0.259738D−01
r_1	0.216793D+00	0.210825D+00	0.205164D+00	0.199800D+00	0.194708D+00	0.189869D+00
H^1_{11}	0.106300D−02	0.950698D−03	0.852627D−03	0.766891D−03	0.691655D−03	0.625415D−03
r_1	0.290559D+00	0.285181D+00	0.279998D+00	0.275000D+00	0.270177D+00	0.265521D+00
H^2_{11}	0.148606D−03	0.137372D−03	0.127288D−03	0.118050D−03	0.110066D−03	0.103006D−03
M Shell						
r_1	0.427263D+00	0.414663D+00	0.402901D+00	0.391764D+00	0.381258D+00	0.371254D+00
H^0_{11}	0.359999D+00	0.339079D+00	0.320115D+00	0.302664D+00	0.286647D+00	0.271803D+00
r_1	0.378223D+00	0.367270D+00	0.356913D+00	0.347091D+00	0.337791D+00	0.329033D+00
H^1_{11}	0.177656D−01	0.157954D−01	0.140877D−01	0.125998D−01	0.113027D−01	0.101753D−01
r_1	0.788898D+00	0.754007D+00	0.722152D+00	0.692969D+00	0.665420D+00	0.638438D+00
H^2_{11}	0.662570D−01	0.505079D−01	0.389833D−01	0.304360D−01	0.238606D−01	0.186131D−01
N Shell (*s* and *p* only)						
r_1	0.613789D+00	0.594521D+00	0.576186D+00	0.559083D+00	0.542997D+00	0.527786D+00
r_2	0.132842D+01	0.128671D+01	0.124703D+01	0.121002D+01	0.117520D+01	0.114228D+01
H^0_{11}	0.512038D+00	0.480394D+00	0.451220D+00	0.424831D+00	0.400736D+00	0.378599D+00
H^0_{12}	0.233800D+00	0.219352D+00	0.206031D+00	0.193981D+00	0.182979D+00	0.172871D+00
H^0_{22}	0.236585D+00	0.221964D+00	0.208484D+00	0.196291D+00	0.185158D+00	0.174930D+00
r_1	0.832962D+00	0.799986D+00	0.770107D+00	0.742682D+00	0.717517D+00	0.694270D+00
r_2	0.170453D+01	0.163705D+01	0.157591D+01	0.151979D+01	0.146829D+01	0.142072D+01
H^1_{11}	0.538794D+00	0.458407D+00	0.393663D+00	0.340513D+00	0.296654D+00	0.260038D+00
H^1_{12}	0.261345D+00	0.222353D+00	0.190949D+00	0.165168D+00	0.143894D+00	0.126133D+00
H^1_{22}	0.263295D+00	0.224012D+00	0.192374D+00	0.166400D+00	0.144967D+00	0.127074D+00
r_1	0.102202D+01	0.980341D+00	0.941932D+00	0.906418D+00	0.873486D+00	0.842863D+00
r_2	0.189716D+01	0.181980D+01	0.174850D+01	0.168258D+01	0.162145D+01	0.156460D+01
H^2_{11}	0.468855D+00	0.360284D+00	0.279648D+00	0.219515D+00	0.174147D+00	0.139355D+00
H^2_{12}	0.157994D+00	0.121408D+00	0.942352D−01	0.739715D−01	0.586836D−01	0.469595D−01
H^2_{22}	0.252576D+00	0.194088D+00	0.150649D+00	0.118254D+00	0.938143D−01	0.750716D−01

integrals approximation are in Tables 3 and 4. The quality of the approximation has been tested and is the same as previously reported for other atoms.

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