

ANALYTIC APPROACH TO THE HERMAN AND SKILLMAN THEORY OF ATOMS

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An analytic approach to the Herman and Skillman modification of the Hartree-Fock-Slater theory of atoms is derived and tested. As follows from the calculations for C, Cu⁺, Ca and Xe the analytic approach seems to be unexpectedly superior to the original Herman and Skillman method.

1. Introduction

In many quantum-chemical calculations good atomic orbitals are required. For most purposes, however, it suffices to solve the appropriate Hartree-Fock-Slater equations (Slater 1960):

$$\left\{ -\Delta - \frac{2Z}{r} + \int \varrho(\mathbf{r}') \frac{2}{|\mathbf{r}-\mathbf{r}'|} dV' - 6 \left[\frac{3}{8\pi} \varrho(\mathbf{r}) \right]^{1/3} \right\} u_i(\mathbf{r}) = E_i u_i(\mathbf{r}), \quad (1)$$

$$\varrho(\mathbf{r}) = \sum_j \nu_j u_j(\mathbf{r})^* u_j(\mathbf{r}) \quad (2)$$

where ν_j is the population of the atomic orbital u_j . Averaging the Hartree-Fock-Slater operator out over all possible orientations of the coordinate system we can put

$$u_i(\mathbf{r}) = \frac{1}{r} P_{nl}(r) Y_{lm}(\vartheta, \varphi), \quad (3)$$

where $Y_{lm}(\vartheta, \varphi)$ is the familiar angular part of the hydrogenic atomic orbital. The radial part, according to Herman and Skillman, follows then from the following eigenvalue equation:

$$\hat{F}^{\text{HS}} P_{nl}(r) = E_{nl} P_{nl}(r) \quad (4)$$

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where

$$\hat{F}^{\text{HS}} = -\frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} + V(r), \quad (5)$$

$$V(r) = -\frac{2Z}{r} + \frac{2}{r} \int_0^r \sigma(t) dt + 2 \int_r^\infty \frac{\sigma(t)}{t} dt - 6 \left[\frac{3\sigma(r)}{32\pi^2 r^2} \right]^{1/3} \quad (6)$$

for $r \leq r_0$,

$$V(r) = -\frac{(2Z - N + 1)}{r} \quad (7)$$

for $r \geq r_0$,

$$\sigma(r) = \sum_n \sum_l \omega_{nl} P_{nl}(r)^2, \quad (8)$$

ω_{nl} is the population of the subshell nl , N is the total number of electrons, Z is the nuclear charge and r_0 is the radius which follows from the comparison of equation (6) and (7).

A programme in FORTRAN was published by Herman and Skillman (HS, for brevity), which produces atomic orbitals in a numerical form. However, the numerical form is rather cumbersome in many applications. For this reason we have decided to elaborate an analytical version of the method. The appropriate programme was written in Algol-60.

Unexpectedly, however, both treatments seem not to be entirely equivalent, the analytic approach yielding somewhat better results.

2. The analytic version of the Herman and Skillman method

Let us expand the radial parts of atomic orbitals into Slater-type functions:

$$P_{nl}(r) = \sum_{i=1}^K C_{ni}^l Q_{ii}(r) \quad (9)$$

where

$$Q_{ii}(r) = N_{ii} r^{n_i} \exp(-\mu_{ii} r) \\ \stackrel{\text{def}}{=} [n_{ii}, \mu_{ii}]. \quad (10)$$

The choice of n_{ii} 's and μ_{ii} 's will be discussed later. N_{ii} is the normalization factor of $Q_{ii}(r)$.

Applying the standard Ritz method we obtain from Eq. (4)–(10) the typical equations

$$\mathbf{H}^l \mathbf{C}^l = \mathbf{S}^l \mathbf{C}^l \mathbf{E}^l \quad (11)$$

$$(\mathbf{C}^l)^T \mathbf{S}^l \mathbf{C}^l = \mathbf{1}^l$$

in which l is the orbital quantum number, $(\mathbf{S}^l)_{ij}$ is the overlap integral $\int Q_i Q_j dr$, $(\mathbf{H}^l)_{ij} = \int Q_i \hat{F}^{\text{HS}} Q_j dr$.

Omitting all the lengthy formulae we would like to add that in the programme all integrals have been evaluated analytically (Alder, Fernbach and Rotenberg 1963) except the following one:

$$\int_0^{r_0} Q_{ii} V(r) Q_{ji} dr. \quad (12)$$

The remaining integral was calculated numerically basing on the Simpson scheme and the Herman and Skillman network.

Parameters $\{n_{ii}\}$ and $\{\mu_{ii}\}$ can be estimated in several ways. One can use, for example, the appropriate values known from the related Roothaan-type calculations. This was the way we proceeded, in principle, in the case of the carbon atom (Clementi 1965). Alternatively it is possible to estimate the exponents from the Slater rules. Adding some virtual Slater orbitals we can make the choice of these parameters not crucial. In this way we proceeded in the case Ca and Cu^+ . The best choice, however, would follow from the minimization of the total energy,

$$E_{\text{tot}} = \frac{1}{2} \left\{ \sum_n \sum_l \omega_{nl} E_{nl} + \bar{T} + \bar{V}_N \right\} \quad (13)$$

where \bar{T} is the average kinetic energy of the electrons and \bar{V}_N is the average interaction energy between the electrons and the nucleus.

The programme can be supplied on request. In its present form it does not optimize the exponents. It yields, however, the total energy in accordance with Eq. (13).

3. Discussion

The convergence of the analytic expansion was tested for four atomic systems: C, Cu, Cu^+ and Xe.

In the case of the carbon atom we have used an extended basis of Clementi (1965):

(1) ns(C): [1, 5.23090], [1, 7.96897], [2, 1.16782],

[2, 1.82031], [2, 0.5],

np(C): [2, 1.25572], [2, 2.72625], [2, 0.5];

In the case of the next two atomic systems Slater-type orbitals have been used, extended by two to three virtual orbitals:

(2) ns(Ca): [1, 19.7], [2, 7.975], [3, 2.910], [4, 0.725],

[5, 0.085], [6, 0.015],

np(Ca): [2, 7.975], [3, 2.910], [4, 0.5], [5, 0.1];

(3) ns(Cu^+): [1, 28.7], [1, 20.675], [2, 12.425], [2, 9.17],

[3, 5.916], [3, 4.083],

np(Cu^+): [2, 12.425], [2, 10.0], [3, 5.916], [3, 5.0],

nd(Cu^+): [3, 2.616], [3, 1.5], [3, 1.0].

The calculated diagonal Lagrangian multipliers (orbital energies) are compared with the Hartree-Fock results in Table I. $\sigma(\text{HF})$ means there the standard deviation of the multipliers from the HF results. It is striking and certainly unexpected that the presented analytic method yields results which are closer to the Hartree-Fock values, in average, than those

Diagonal Lagrangian multipliers for C, Cu⁺ and Ca atoms

Atom	Subshell	Multipliers in atomic units		
		Hartree-Fock*	Herman-Skillmann	analytic HS-methód
C	1s	22.677	21.378	21.386
	2s	1.426	1.290	1.285
	2p	0.814	0.660	0.656
	$\sigma(\text{HF})$	—	0.759	0.748
Cu ⁺	1s	658.40	650.40	657.222
	2s	82.30	78.872	85.598
	3s	10.651	9.354	12.863
	2p	71.83	69.740	76.403
	3p	7.279	6.429	9.882
	3d	1.613	1.459	1.532
	$\sigma(\text{HF})$	—	4.074	3.158
Ca	1s	298.40	293.52	293.897
	2s	30.70	31.627	30.945
	3s	3.537	3.875	4.212
	4s	0.357	0.399	0.327
	2p	25.590	26.180	26.637
	3p	2.156	2.482	2.999
	$\sigma(\text{HF})$	—	2.247	2.175

* HF-results for C according to Jucys (1939), for Cu⁺ according to Hartree, Hartree (1936), for Ca according to Hartree, Hartree (1938).

of the original method. In the case of the Cu⁺ ion, for example, the average difference is around 1 a. u.

One might certainly expect that extending the basis one should approach the results of Herman and Skillman. For this reason we have made a more detailed analysis for xenon. It is a large atomic system in the case of which the differences should be well pronounced.

The calculations have been carried out for three different sets. The first one was identical with that derived by Synek and Stungis (1965):

- (4) ns(Xe): [1, 52.9191], [2, 19.9014], [3, 11.8671],
 [4, 6.53980], [5, 2.85210],
 np(Xe): [2, 24.9174], [3, 11.8887], [4, 6.24010],
 [5, 2.48130],
 nd(Xe): [3, 13.3150], [4, 5.47170].

TABLE II

Diagonal Lagrangian multipliers for xenon orbitals

Subshell	HF-Roothaan method*	Herman-Skillmann method	analytic HS-method		
			set 4	set 5	set 6
1s	2448.592	2434.4	2438.15	2438.91	2438.43
2s	373.944	372.05	370.377	371.097	370.646
3s	77.836	76.945	76.243	76.849	76.497
4s	14.756	14.184	13.996	14.422	14.223
5s	1.610	1.600	1.393	1.548	1.524
$\sigma(\text{HFR})$	—	7.178	5.588	5.073	5.390
$\sigma(\text{HS})$	—	—	2.088	2.309	2.146
2p	354.928	351.05	353.447	354.179	353.718
3p	69.696	67.91	68.877	69.491	69.132
4p	11.554	10.923	11.151	11.571	11.377
5p	0.720	0.837	0.675	0.806	0.793
$\sigma(\text{HFR})$	—	2.493	1.005	0.451	0.779
$\sigma(\text{HS})$	—	—	1.501	2.058	1.721
3d	50.782	50.955	51.292	51.936	51.550
4d	4.950	5.257	5.240	5.658	5.463
$\sigma(\text{HFR})$	—	0.352	0.587	1.353	0.923
$\sigma(\text{HS})$	—	—	0.337	1.060	0.912

* according to Synek and Stungis (1965).

TABLE III

Comparison of some results obtained for the xenon atom

Property	Herman-Skillmann method	analytic HS-method		
		set 4	set 5	set 6
E_{tot}	—	-14418.79	-14419.56	-14419.00
V/T	—	-1.99857	-1.99966	-1.99879
$\sigma(\text{HFR})$	4.74	3.57	3.25	3.45
$\sigma(\text{HS})$	—	1.56	1.87	1.68
I^*	0.837	0.675	0.806	0.793

* $I_{\text{obs}} = 0.891$, $I_{\text{HFR}} = 0.720$.

To the next two sets few additional functions have been added:

- (5) ns(Xe): [6, 1.2], [7, 0.5],
 np(Xe): [6, 1.2], [7, 0.5],
 nd(Xe): [5, 2.3],
 (6) ns(Xe): like in (5),
 np(Xe): like in (5),
 nd(Xe): [5, 1.2], [6, 0.5].

The principle results of the analysis can be found in Tables II–III. As follows from Table III the extended set (5) is the best. It leads to a lowest total energy and to the best fulfillment of the virial theorem. The other extended set, (6), is slightly worse although still much better than the unextended one, (4). It is interesting to note that the better the analytic expansion (in the sense of the total energy) the closer the multipliers lie to the Hartree-Fock-Roothaan values and simultaneously the farther from the original Herman and Skillman ones (Table III).

In accordance with Table II the d levels only are reproduced now worse. However, Synek and Stungis have perhaps used too small a basis for this particular case. Indeed, just in the case of the set (4) our d levels are closest to those obtained by other authors.

It is difficult to show the origin of this behaviour. This way or the other, however, the presented analytic approach seems to yield not only a more practical form of the orbitals. It also yields results which lie closer, in general, to the Hartree-Fock ones.

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