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Perturbation Treatment of Hartree-Fock Equations*

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For atomic configurations ($1s^2$), ($1s^22s$), and ($1s^22s^2$) perturbation theory has been used to obtain ($1/Z$) expansions for the Hartree-Fock energies.

INTRODUCTION

MODIFIED Schrödinger perturbation theory as developed by Löwdin[1] is used in this paper to evaluate solutions to the Hartree-Fock problem for 2-, 3-, and 4-electron ions in their ground state. The iterative techniques used in earlier methods for solving the nonlinear integro-differential equations[2] are thus replaced by a scheme where the difference between two approximations to the exact solution is calculated directly. Furthermore, it is possible to separate out the dependence of the solutions on the nuclear charge by a procedure used first by Hylleraas[3] in his work on 2-electron ions. A scaling procedure deviced by Fröman and Hall[4] gives another tool to improve the results obtained.

THE HARTREE-FOCK EQUATIONS

In this paragraph the equations in the Hartree-Fock approximation are established for the ground states $(1s^2)^1S$, $(1s^22s)^2S$, and $(1s^22s^2)^1S$ of 2-, 3-, and 4-electron ions.

The following units and notations are used: Reduced and modified Hartree atomic units,[5,2] where a modified unit charge $eZ^{\frac{1}{2}}$ is introduced, giving a unit of energy $1H_{RM}=Z^2H_R$. Radial part of $1s$ orbital $=u(r)$; radial part of $2s$ orbital $=v(r)$;

$$(a|b)=\int_0^\infty a(r)b(r)r^2dr,$$

$$|ab)=r^{-1}\int_0^r a(s)b(s)s^2ds+\int_r^\infty a(s)b(s)sds,$$

$$(ab|cd)=\int_0^\infty a(r)b(r)|cd)r^2dr,$$

$$h_0=-\frac{1}{2}\left(\frac{d}{dr}\right)^2-\frac{1}{r}\frac{d}{dr}-\frac{1}{r}.$$

The radial Hartree-Fock equations then read:

(i) for two-electron ions,

$$h_0u+Z^{-1}u|uu)=\epsilon(1s)\cdot u;\tag{1}$$

(ii) for three-electron ions where it is necessary to introduce a so-called nondiagonal Lagrangian multiplier,

$$h_0u+Z^{-1}u|uu)+Z^{-1}u|vv)-\tfrac{1}{2}Z^{-1}v|uv)=\epsilon(1s)\cdot u+\tfrac{1}{2}\epsilon(1s,2s)\cdot v,\tag{2}$$

$$h_0v+2Z^{-1}v|uu)-Z^{-1}u|uv)=\epsilon(2s)\cdot v+\epsilon(1s,2s)\cdot u;\tag{3}$$

(iii) for four-electron ions,

$$h_0u+Z^{-1}u|uu)+2Z^{-1}u|vv)-Z^{-1}v|uv)=\epsilon(1s)\cdot u,\tag{4}$$

$$h_0v+Z^{-1}v|vv)+2Z^{-1}v|uu)-Z^{-1}u|uv)=\epsilon(2s)\cdot v;\tag{5}$$

and the conditions in all three cases

$$(u|u)=1,\tag{6}$$

$$(u|v)=0,\tag{7}$$

$$(v|v)=1.\tag{8}$$

These equations depend on the parameter Z^{-1} and we are going to solve for the ϵ's, u, and v as functions of that parameter. We use power series representations for these functions and proceed as suggested by Löwdin.[1] We define

$$u=u_0+Z^{-1}u_1+Z^{-2}u_2+\cdots,\tag{9}$$

$$v=v_0+Z^{-1}v_1+Z^{-2}v_2+\cdots,\tag{10}$$

$$\epsilon(1s)=\epsilon_0(1s)+Z^{-1}\epsilon_1(1s)+Z^{-2}\epsilon_2(1s)+\cdots,\tag{11}$$

$$\epsilon(1s,2s)=\epsilon_0(1s,2s)+Z^{-1}\epsilon_1(1s,2s)+Z^{-2}\epsilon_2(1s,2s)+\cdots,\tag{12}$$

$$\epsilon(2s)=\epsilon_0(2s)+Z^{-1}\epsilon_1(2s)+Z^{-2}\epsilon_2(2s)+\cdots.\tag{13}$$

The series will be evaluated to the first order in the wave functions, to third order in the energy for the two-electron case, otherwise to the second order in the energy.

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[1] P. O. Löwdin, Technical Note, June, 1959, Quantum Chemistry Group, Uppsala University, Uppsala, Sweden (unpublished).

[2] For the numerical procedure see D. R. Hartree, *The Calculation of Atomic Structure* (John Wiley & Sons, New York, 1957) and for the analytical variation method see G. G. Hall, Proc. Roy. Soc. (London) **A205**, 541 (1951); C. C. J. Roothaan, Revs. Modern Phys. **23**, 69 (1951).

[3] E. A. Hylleraas, Z. Physik **65**, 209 (1930).

[4] A. Fröman and G. G. Hall, Technical Note No. 42, March 15, 1960, Uppsala Quantum Chemistry Group (unpublished).

[5] H. Shull and G. G. Hall, Nature **184**, 1599 (1959).

ZERO ORDER FUNCTIONS: ZERO AND FIRST ORDER ENERGIES

To zeroth order the functions and energies are obtained from the solution of Eqs. (1)–(5) when $Z^{-1}=0$. This immediately gives the well-known hydrogen wave functions and energy eigenvalues:

$$u_0=2e^{-r}, \qquad \epsilon_0(1s)=-\tfrac{1}{2},$$
$$v_0=\sqrt{2}(1-\tfrac{1}{2}r)e^{-\frac{1}{2}r}, \quad \epsilon_0(2s)=-\tfrac{1}{8}$$

in all cases and with

$$\epsilon_0(1s,2s)=0$$

in (ii). These wave functions also give the first order energies:

(i) $\epsilon_1(1s)=(u_0u_0|u_0u_0)=\frac{5}{8}$,

(ii) $\epsilon_1(1s)=(u_0u_0|u_0u_0)+(u_0u_0|v_0v_0)-\frac{1}{2}(u_0v_0|u_0v_0)$
$=\frac{5}{8}+145/729$,

$\epsilon_1(2s)=2(u_0u_0|v_0v_0)-(u_0v_0|u_0v_0)=290/729$,

$\epsilon_1(1s,2s)=-(u_0v_0|v_0v_0)=-512\sqrt{2}/84375$,

(iii) $\epsilon_1(1s)=(u_0u_0|u_0u_0)+2(u_0u_0|v_0v_0)-(u_0v_0|u_0v_0)$
$=\frac{5}{8}+290/729$,

$\epsilon_1(2s)=(v_0v_0|v_0v_0)+2(u_0u_0|v_0v_0)-(u_0v_0|u_0v_0)$
$=77/512+290/729$.

FIRST ORDER FUNCTIONS: SECOND ORDER ENERGIES

For solution of the first order functions, we find that we can form the functions u_1 and v_1 as linear combinations of the solutions u_u, u_v, v_u, v_v of the following equations:

$$(h_0+\tfrac{1}{2})u_u=(u_0u_0|u_0u_0)u_0-u_0|u_0u_0), \tag{14}$$

$$(h_0+\tfrac{1}{2})u_v=[2(u_0u_0|v_0v_0)-(u_0v_0|u_0v_0)]u_0 -2u_0|v_0v_0)+v_0|u_0v_0), \tag{15}$$

$$(h_0+\tfrac{1}{8})v_u=[2(u_0u_0|v_0v_0)-(u_0v_0|u_0v_0)]v_0 -2v_0|u_0u_0)+u_0|u_0v_0), \tag{16}$$

$$(h_0+\tfrac{1}{8})v_v=(v_0v_0|v_0v_0)v_0-v_0|v_0v_0), \tag{17}$$

adding in case (ii)

$$(h_0+\tfrac{1}{2})u'=-\tfrac{1}{2}(u_0v_0|v_0v_0)v_0, \tag{18}$$

$$(h_0+\tfrac{1}{8})v'=-(u_0v_0|v_0v_0)u_0. \tag{19}$$

We have then

(i) $u_1=u_u$,

(ii) $u_1=u_u+\frac{1}{2}u_v+u'$,
$v_1=v_u+v'$,

(iii) $u_1=u_u+u_v$,
$v_1=v_u+v_v$,

if orthogonality is required between u_0 and each of the functions u_u, u_v, u' as well as between v_0 and each of v_u, v_v, v'. The equations (14)–(17) are solved here by means of expansions in first order Laguerre functions[6] $\{L_k{}^1(2\alpha r)e^{-\alpha r}\}$. Direct integration is also possible, as well as the Laplace transform method.[7] The following functions are obtained:

$$u_u=e^{-r}\textstyle\sum_n a_nL_n{}^1(2r),$$
$$a_1=5/16, \quad a_2=5/32,$$
$$n!a_n=(n-7)(n-1)^{-1}2^{-n-2}, \quad n>2$$
$$u_v=e^{-r}\textstyle\sum_n b_nL_n{}^1(2r),$$
$$b_1=46/2187, \quad b_2=23/2187,$$
$$n!b_n=(112n^3-1840n^2+9272n-14552)(n-1)^{-1}3^{-n-6}, \quad n>2$$
$$v_u=\sqrt{2}e^{-\frac{1}{2}r}\textstyle\sum_n c_nL_n{}^1(r),$$
$$c_1=-16/243, \quad c_2=206/2187, \quad c_3=-896/19683,$$
$$n!c_n=(n^2+71n-1040)(n-2)^{-1}\times 2^{n-3}\times 3^{-n-5}, \quad n>3$$
$$v_v=\sqrt{2}e^{-\frac{1}{2}r}\textstyle\sum_n d_nL_n{}^1(r),$$
$$d_1=-1/512, \quad d_2=77/4096, \quad d_3=13/1536,$$
$$n!d_n=(n^4-30n^3+283n^2-910n+504)(n-2)^{-1}2^{-n-9}, \quad n>3.$$

The equations (18) and (19) have the solutions:

$$u'=-(4/3)(u_0v_0|v_0v_0)v_0, \quad v'=(8/3)(u_0v_0|v_0v_0)u_0.$$

Second order contributions to the energy are derived from (1)–(5):

(i) $\epsilon_2(1s)=3(u_0u_0|u_0u_1)$,

(ii) $\epsilon_2(1s)=3(u_0u_0|u_0u_1)+(u_0u_1|v_0v_0)-\frac{1}{2}(u_0v_0|u_1v_0)$
$+2(u_0u_0|v_0v_1)-(u_0v_0|u_0v_1)$
$+\frac{1}{2}(u_0v_0|v_0v_0)(u_0|v_1)$,

$\epsilon_2(2s)=2(u_0u_0|v_0v_1)-(u_0v_0|u_0v_1)+4(u_0u_1|v_0v_0)$
$-2(u_0v_0|u_1v_0)+(u_0v_0|v_0v_0)(u_1|v_0)$,

(iii) $\epsilon_2(1s)=3(u_0u_0|u_0u_1)+2(u_0u_1|v_0v_0)-(u_0v_0|u_1v_0)$
$+4(u_0u_0|v_0v_1)-2(u_0v_0|u_0v_1)$,

$\epsilon_2(2s)=3(v_0v_0|v_0v_1)+2(u_0u_0|v_0v_1)-(u_0v_0|u_0v_1)$
$+4(u_0u_1|v_0v_0)-2(u_0v_0|u_1v_0)$.

There are six basic quantities entering in these expressions. They are given in exact and decimal form in Table I. With the proper functions inserted in the above formulas we get the values of the second order energy parameters tabulated in Table II.

THIRD ORDER ENERGIES

The knowledge of first order functions enables us to calculate the energy contributions of the third order. There is, however, a considerable amount of work

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[6] For the definition used here, see L. I. Schiff, *Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1955), 2nd ed., p. 85.

[7] C. Schwartz, Ann. Phys. 6, 156 (1959); A. Dalgarno, Proc. Phys. Soc. (London) 75, 439 (1960).

TABLE I. Contributions to second order energy terms.[a]

Parameter	Exact value	Decimal
$(u_0u_0\|u_0u_u)$	$-\frac{13}{864}+\frac{9}{64}\ln\left(\frac{3}{4}\right)$	−0.05550159
$\left.\begin{array}{r}(u_0u_0\|u_0u_v)\\ 2(u_0u_u\|v_0v_0)-(u_0v_0\|u_uv_0)\end{array}\right\}$	$\frac{23\,110\,282}{218\,700\,000}+\frac{146}{243}\ln\left(\frac{5}{6}\right)$	−0.00387184
$2(u_0u_v\|v_0v_0)-(u_0v_0\|u_vv_0)$	$\frac{986\,249\,849}{3\,265\,173\,504}+\frac{1\,364\,224}{531\,441}\ln\left(\frac{8}{9}\right)$	−0.00030108
$(v_0v_0\|v_0v_v)$	$\frac{114\,947}{8\,957\,952}+\frac{2601}{32\,768}\ln\left(\frac{3}{4}\right)$	−0.01000328
$\left.\begin{array}{r}(v_0v_0\|v_0v_u)\\ 2(u_0u_0\|v_0v_u)-(u_0v_0\|u_0v_v)\end{array}\right\}$	$-\frac{988\,649}{71\,663\,616}+\frac{2533}{31\,104}\ln\left(\frac{2}{3}\right)$	−0.04681534
$2(u_0u_0\|v_0v_u)-(u_0v_0\|u_0v_u)$	$-\frac{928\,911\,128}{4\,982\,259\,375}+\frac{44\,402}{531\,441}\ln\left(\frac{5}{9}\right)$	−0.23555344

[a] All energies in H_{RM}'s.

which is difficult to check and which must be judged according to the amount of resulting information. Nevertheless, for the two-electron case the calculations are carried through here, and we get the following result:

$$\begin{aligned}\epsilon_3(1s)&=8(u_0u_u|u_0u_u)+4(u_0u_0|u_uu_u)\\&\qquad-4(u_0u_0|u_0u_0)(u_u|u_u)\\&=(9216)^{-1}[775+39\,912\ln 2-25\,332\ln 3\\&\qquad+11\,664I(-1/3)-13\,608I(-1/4)].\end{aligned}$$

Here the notation

$$I(x)=\int_0^x (dt/t)\ln(1+t)=-\sum(-x)^n n^{-2}$$

is used.

THE TOTAL ENERGY

A formula first used by Fröman[8] is applied in order to get the total energy in the Hartree-Fock approximation. If

$$E_{\mathrm{HF}}=E_0+Z^{-1}E_1+Z^{-2}E_2+Z^{-3}E_3+\cdots,$$

then the following relation is valid for the configuration $(1s^22s^p)$

$$2\epsilon(1s)+p\epsilon(2s)=\left(1-Z\frac{\partial}{\partial Z}\right)E_{\mathrm{HF}},$$

which gives

$$2\epsilon_n(1s)+p\epsilon_n(2s)=(n+1)E_n.$$

The values of the parameters E_n are tabulated in Table II.

SCALED EXPANSIONS

It has been shown here that it is possible to determine coefficients in an expansion of the Hartree-Fock energy for an atomic system in descending powers of the nuclear charge. Fröman and Hall[4] have also shown that a change of variable in such an expansion can give a more rapidly convergent expansion. This procedure corresponds to a partition of the Hamiltonian such that part of the nuclear attraction term is included in the perturbing potential. We consider here directly a change of variables and assume that the following expansion exists (H_R units):

$$E_{\mathrm{HF}}=E_0Z^2+E_1Z+E_2+\sum\nolimits_n a_n(Z-s)^{-n},$$

$$a_n=\sum\nolimits_i\binom{n-1}{i}(-s)^iE_{n+2-i}.$$

A four-term formula is chosen to represent the Hartree-

TABLE II. Coefficients in $(1/Z)$ expansions of orbital and total energies.[a]

Configuration	Energies	Z^0	Z^{-1}	Z^{-2}	Z^{-3}
$1s^2\,{}^1S$	$\epsilon(1s)$	−0.50000000	0.62500000	−0.16650476	−0.00211049
	E_{HF}	−1.00000000	0.62500000	−0.11100317	−0.00105525
$1s^22s\,{}^2S$	$\epsilon(1s)$	−0.50000000	0.82390261	−0.40982806	not calc.
	$\epsilon(2s)$	−0.12500000	0.39780521	−0.24399097	not calc.
	E_{HF}	−1.12500000	1.02280521	−0.35454903	not calc.
$1s^22s^2\,{}^1S$	$\epsilon(1s)$	−0.50000000	1.02280521	−0.74703075	not calc.
	$\epsilon(2s)$	−0.12500000	0.54819584	−0.46117048	not calc.
	E_{HF}	−1.25000000	1.57100105	−0.80546750	not calc.

[a] All energies in units of H_{RM}.

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[8] A. Fröman, Phys. Rev. **112**, 870 (1958).

TABLE III. Third order correction term as determined by least square deviation condition.[a]

State	E_3	s
$1s^2$	(-0.00105525)	0.440
$1s^22s$	-0.04109	1.079
$1s^22s^2$	-0.1336	1.400

[a] All energies in units of H_{RM}.

TABLE IV. Second and third order perturbation calculations compared to results from the variation method.[a]

State	Z	E_{HF}[b]	$E_0Z^2+E_1Z+E_2$	$R(1/Z)$[c]	$E_0Z^2+E_1Z$ $+E_2+E_3/$ $(Z-s)$
$1s^2$	2	− 2.861680	− 2.861003	−0.000677	− 2.861680
	3	− 7.236415	− 7.236003	−0.000412	− 7.236415
	4	− 13.61130	− 13.61100	−0.00030	− 13.61130
	5	− 21.98623	− 21.98600	−0.00023	− 21.98623
	6	− 32.36119	− 32.36100	−0.00019	− 32.36119
	7	− 44.73616	− 44.73600	−0.00016	− 44.73616
	8	− 59.11115	− 59.11100	−0.00015	− 59.11114
	9	− 75.48613	− 75.48600	−0.00013	− 75.48613
	10	− 93.86112	− 93.86100	−0.00012	− 93.86111
$1s^22s$	3	− 7.432727	− 7.411133	−0.021594	− 7.432523
	4	− 14.27740	− 14.26333	−0.01407	− 14.27740
	5	− 23.37599	− 23.36552	−0.01047	− 23.37600
	6	− 34.72606	− 34.71772	−0.00834	− 34.72607
	7	− 48.32685	− 48.31991	−0.00694	− 48.32685
	8	− 64.17804	− 64.17211	−0.00593	− 64.17804
	9	− 82.27949	− 82.27430	−0.00519	− 82.27949
	10	−102.6311	−102.6265	−0.0046	−102.6311
$1s^22s^2$	3	− 7.428232	− 7.342464	−0.085768	− 7.425964
	4	− 14.57302	− 14.52146	−0.05156	− 14.57285
	5	− 24.23758	− 24.20046	−0.03712	− 24.23757
	6	− 36.40850	− 36.37946	−0.02904	− 36.40850
	7	− 51.08231	− 51.05846	−0.02385	− 51.08232
	8	− 68.25771	− 68.23746	−0.02025	− 68.25770
	9	− 87.93404	− 87.91646	−0.01758	− 87.93404
	10	−110.1110	−110.0955	−0.0155	−110.1110

[a] All energies in units of H_R.
[b] See reference 9.
[c] $R(1/Z)=E_{\mathrm{HF}}-E_0Z^2-E_1Z-E_2$.

Fock energy. With

$$R(1/Z)=E_{\mathrm{HF}}-E_0Z^2-E_1Z-E_2,$$

the fourth term is determined by

$$\sum_Z|R(1/Z)-E_3(Z-s)^{-1}|^2=\min.$$

For the state $1s^2$ the value of E_3 is known and the equation determines the "best" s. The states $1s^22s$ and $1s^22s^2$ give equation systems from which the "best" combination E_3 and s are derived. The equations are solved with use of values for E_{HF} determined by Roothaan *et al.*[9] by means of the variation procedure.[2] The ranges of Z considered in the equations were $2\leq Z\leq 10$ for the $1s^2$, $4\leq Z\leq 10$ for the state $1s^22s$, and $5\leq Z\leq 10$ for the state $1s^22s^2$. The parameters thus derived are given in Table III.

RESULTS

The perturbation calculations presented above give reasonably rapidly convergent expansions for the Hartree-Fock energies of 2-, 3-, and 4-electron ions in their ground state. Especially the scaled expansions are well adapted for a functional representation of the energies. Table IV displays the comparison between the variationally determined values at reference 9 and the truncated series given in Table II and III. The four-term formulas fail to reproduce the Hartree-Fock energies of the systems Li, Li$^-$, and Be. A further extended approach to the rest-terms of the series is necessary to fit these systems into the scheme of the perturbation treatment used here.

Perturbation calculations for atomic systems have been suggested as an alternative to the Hartree-Fock approximation.[10] The two approaches can be brought together through a variation principle for the second order energy correction in perturbation theory.[3] Work is in progress on this scheme.

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[9] C. C. J. Roothaan, L. M. Sachs, and A. W. Weiss, Revs. Modern Phys. **32**, 186 (1960).

[10] D. Layzer, Ann. Phys. **8**, 271 (1959); J. Linderberg and H. Shull, J. Mol. Spectroscopy **5**, 1 (1960).