

Relativistic Correction for Analytic Hartree-Fock Wave Functions

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The relativistic energy associated with the closed-shell ground states of the atoms of the first three rows of the periodic table is computed by perturbation methods for recently obtained Hartree-Fock functions. The computations are extended to the isoelectronic series of the 2, 4, 10, 12, and 18 electron atoms with closed-shell configurations. The analysis of the data obtained reveals that, (1) different Hartree-Fock functions for a given atom give about the same relativistic energy provided the number of basis functions are about the same, (2) the contribution to the relativistic energy from electrons of a given subshell is approximately a constant, independent of the number of electrons in the outer shells, (3) the empirical estimate of the relativistic energy agrees with our theoretical computation within a few percent except for low Z where the disagreement is only slightly larger.

I. INTRODUCTION

SINCE the correlation problem for a many electron system is difficult to treat directly in terms of the Coulomb repulsion between electrons, other methods of estimating the correlation energy are important. One of these methods¹ of calculating correlation energies is, the use of the following relationship:

$$E_{\text{corr}} = E_{\text{exp}} - E_{\text{HF}} - E_{\text{rel}}, \quad (1)$$

where E_{HF} = Hartree-Fock energy of the system, E_{rel} = relativistic correction to the Hartree-Fock energy, and E_{exp} = experimental value of the energy. With Eq. (1) it is seen that good estimates of correlation energies depend upon accurate calculations of Hartree-Fock energy and the relativistic corrections.²

Hartree-Fock wave functions have been computed for a long time and the usual criteria for their "goodness" is that they produce the minimum energy. This paper shall discuss the effect of the form and number of the Hartree-Fock basis functions on the relativistic corrections to closed-shell atomic systems in their ground state. In addition, we shall compute E_{rel} for the 2, 4, 10, 12, and 18 electrons isoelectronic series.

The relativistic energy has been defined in the literature in a number of different ways and for the purpose of this paper the formulation and notation given by Bethe and Salpeter³ of the relativistic energy of a two electron system based on the Breit equation is extended to the N -electron system. The Breit equation describes the interaction of two relativistic electrons with each other and with an external electromagnetic field. The Hamiltonian of this system can be expanded in powers of $(Z\alpha)$ (Pauli's approximation, where Z is the nuclear charge and α is the fine structure constant) and consists of both one particle and two particle operators. We assume that the Hamiltonian for an N electron

system can be obtained by summing all one-particle operators over all N electrons and summing all two-particle operators over all pairs of electrons in the system. A great simplification occurs for closed-shell atomic systems. Up to and including the order of α^2 , the relativistic correction for such a system depends on three terms:

$$H_{\text{rel}} = H_1 + H_4 + H_5, \quad (2)$$

where

$$H_1 = \frac{-1}{8m^3c^2} \sum_{i=1} p_i^4, \quad (3a)$$

$$H_4 = \frac{e\hbar^2}{(2mc)^2} \sum_{i=1} (\nabla^2 V_i + \nabla V_i \cdot \nabla_i), \quad (3b)$$

and

$$H_5 = 4 \left(\frac{e\hbar}{2mc} \right)^2 \sum_{i \neq j} \mathbf{S}_i \cdot \mathbf{S}_j \left(\frac{-8\pi}{3} \right) \delta^3(\mathbf{r}_{ij}) \\ = \left(\frac{e\hbar}{mc} \right)^2 \sum_{i>j} \mathbf{S}_i \cdot \mathbf{S}_j \delta^3(\mathbf{r}_{ij}) \left(\frac{-8\pi}{3} \right). \quad (3c)$$

Here e is the absolute value of the electronic charge.

The Hartree-Fock orbital functions are taken in the form of⁴

$$\psi(x) = \sum_i U_i(x), \quad (4)$$

where $U_i(x)$'s are the single-particle wave functions of the type

$$U_i(x) = \sum_j C_{i,j} \frac{f_{nl}(r)}{r} Y_{lm}(\theta, \phi) \eta(\zeta) \quad (5)$$

and η is the spin wave function α or β . i runs from 1 to N = the number of electrons. Y_{lm} = normalized spherical harmonics. $f_{nl}(r)/r$ is the radial part of the exponential function in the form proposed by Slater.⁴ $C_{i,j}$ is the coefficient of the expansion of the Slater-type basis set, and is determined by the self-consistent field technique.

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¹ A. Fröman, Phys. Rev. **112**, 807 (1958); Rev. Mod. Phys. **32**, 317 (1960).

² E. Clementi, J. Chem. Phys. **38**, 2248 (1963); **39**, 175 (1963).

³ H. A. Bethe and E. E. Salpeter, *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1957), Vol. 35.

⁴ J. C. Slater, *Quantum Theory of Atomic Structures* (McGraw-Hill Book Company, Inc., New York, 1962), Vol. 2.

The energies E_1 , E_4 , E_5 can be written as follows¹:

$$E_1 = -\frac{1}{4m^3c^2} \sum_{nl} (2l+1) \int dr \left[f_{nl}{}''^2 - 2l(l+1) \frac{f_{nl}f_{nl}''}{r^2} + \frac{l^2(l+1)^2}{r^4} f_{nl}^2 \right], \quad (6)$$

$$E_4 = \frac{e^2\hbar^2}{4(mc)^2} \left[Z \sum_n \left(\frac{f_{n0}}{r} \right)^2 - \sum_{nl} (2l+1)(4l+1) \int \frac{f_{nl}^4}{r^2} - \sum_{nl>n'l'} 4(2l+1)(2l'+1) \int \frac{f_{nl}^2 f_{n'l'}^2}{r^2} dr \right], \quad (7)$$

and

$$E_5 = \left(\frac{e\hbar}{mc} \right)^2 \frac{1}{4} \sum_{nl} \sum_J \frac{2(2l+1)^2(2J+1)J!J!(2l-J)![(l+J/2)!]^2}{(2l+J+1)![(J/2)!]^4[(l-J/2)!]^2} \int \frac{f_{nl}^4}{r^2} dr \\ + \sum_{nl>n'l'} \sum_J \frac{4(2l+1)(2l'+1)(2J+1)(l'+J-l)!(l+J-l')!(l+l'-J)![(l+l'+J)/2!]^2}{(l+l'+J+1)![(l'+J-l)/2]![(l+J-l')/2]![(l+l'-J)/2!]^2} \int \frac{f_{nl}^2 f_{n'l'}^2}{r^2} dr. \quad (8)$$

The angular part Y_{lm} and the spin part are integrated out in Eqs. (6), (7), and (8). The f' and f'' designate the first and second derivatives of f , respectively. In the J summations of Eq. (8), the first sum is for $J=0, 2, 4, \dots, 2l$, the second sum is for those J 's in the series $J=|l-l'|, |l-l'+1|, \dots, |l+l'|$ for which $J+l+l'$ is even.

As indicated in Eq. (6), the term $\langle U(nl) | H_1 | U(n'l') \rangle$ is proportional to $\delta_{ll'}\delta_{nn'}$, while Eqs. (7) and (8) show that $\langle U(nl) | H_4 | U(n'l') \rangle$ and $\langle U(nl) | H_5 | U(n'l') \rangle$ are not equal to zero for $n \neq n'$ and $l \neq l'$. However, $\langle U(nl) | H_4 + H_5 | U(n'l') \rangle$ is proportional to $\delta_{ll'}\delta_{nn'}$, making it possible to analyze the total relativistic energy $E = E_1 + E_4 + E_5$ in terms of contributions from the different subshells of electrons (as designated by the quantum numbers n and l).

If we define

$$I_1(nl) = \int f_{nl}{}''^2 dr, \quad (9a)$$

$$I_2(nl) = \int \frac{1}{r^2} f_{nl}^4 dr, \quad (9b)$$

$$I_3(nl) = \int \frac{1}{r^2} f_{nl}'' f_{nl} dr, \quad (9c)$$

$$I_4(nl) = \int \frac{1}{r^4} f_{nl}^2 dr, \quad (9d)$$

and

$$I_5(nl) = Z \left[\frac{1}{r} f_{n0}^2 \right]_{r=0}, \quad (9e)$$

Eqs. (6) and (7), plus (8) take the form

$$E_1 = \frac{1}{4} \sum_{nl} (2l+1) [I_1(nl) - 2l(l+1)I_3(nl) \\ + l^2(l+1)^2 I_4(nl)], \quad (10a)$$

and

$$E_4 + E_5 = \frac{1}{4} \sum_n I_5(n0) + \frac{1}{4} \sum_{nl} (2l+1) I_2(nl) \quad (10b)$$

and, in general,

$$E_{rel} = E_1 + E_4 + E_5 = -\frac{1}{4} \sum_{n,l,i} d_{nli} I_i(nl), \\ i = 1, 2, 3, 4, 5. \quad (11)$$

The coefficients d_{nli} that are needed for the computation of the relativistic energies of closed shell states of 2, 4, 10, 12, and 18 electron systems are given in Table I.

TABLE I. The d_{nli} coefficients for closed-shell configurations up to Kr.

$nl=n'l'$	d_{nl1}	d_{nl2}	d_{nl3}	d_{nl4}	d_{nl5}
1s	0	1	0	1	1
2s	0	1	0	1	1
3s	0	1	0	1	1
4s	0	1	0	1	1
2p	12	3	12	1	0
3p	12	3	12	3	0
4p	12	3	12	3	0
3d	180	5	60	5	0

In order to estimate the accuracy of the correlation energy obtained from Eq. (1), one must know the errors in the energies on the right-hand side of the equation. The error in the relativistic energy can be estimated by computing the next higher-order correction, that is the Lamb shift of order $Z^2\alpha^3$ and $Z\alpha^3 \ln\alpha$. For a two-electron atom in its ground state, the lowest order Lamb shift is given by⁵

$$E_{L,2} + E_{L,2'} = \frac{4Z}{3} \alpha^3 \langle \delta(r_1) + \delta(r_2) \rangle_{00} \left[2 \ln(1/\alpha) - \ln \frac{k_0}{ry} + \frac{19}{30} \right] \\ - \frac{14}{3} \alpha^3 \langle \delta(r_{12}) \rangle_{00} \ln(1/\alpha) \text{ au}, \quad (12)$$

where k_0 is the average excitation energy.

⁵ P. K. Kabir and E. E. Salpeter, Phys. Rev. **108**, 1257 (1957).

TABLE II. Comparison of relativistic energies obtained from different analytical Hartree-Fock functions (in a.u.).

Atom	$E(1s)$	$E(2s)$	$E(2p)$	$E(3s)$	$E(3p)$	$E(\text{rel})$	Basis set		Total Hartree-Fock energy
							No. of s func- tions	No. of p func- tions	
He ^a	0.000004	0.	0.	0.	0.	0.000004	1	...	-2.8476563
He ^b	-0.000071	0.	0.	0.	0.	-0.000071	4	...	-2.8616785
He ^c	-0.000070	0.	0.	0.	0.	-0.000070	5	...	-2.8616800
Be ^a	-0.001269	-0.000209	0.	0.	0.	-0.001478	2	...	-14.556740
Be ^b	-0.002033	-0.000167	0.	0.	0.	-0.002200	5	...	-14.573014
Be ^d	-0.002033	-0.000165	0.	0.	0.	-0.002198	6	...	-14.573021
Ne ^a	-0.091114	-0.017796	-0.006330	0.	0.	-0.115239	2	1	-127.81219
Ne ^b	-0.106581	-0.013974	-0.010737	0.	0.	-0.131292	5	4	-128.54698
Ne ^d	-0.106628	-0.013845	-0.010737	0.	0.	-0.131210	6	4	-128.54701
Ne ^e	-0.106581	-0.013832	-0.010720	0.	0.	-0.131133	7	6	-128.54700
Mg ^a	-0.196680	-0.047166	-0.021659	-0.001603	0.	-0.267108	3	1	-198.85779
Mg ^b	-0.228309	-0.034600	-0.031100	-0.001369	0.	-0.295379	7	3	-199.61432
Mg ^d	-0.228050	-0.034385	-0.031241	-0.001363	0.	-0.295038	8	5	-199.61458
Mg ^d	-0.228050	-0.034385	-0.031252	-0.001363	0.	-0.295049	8	5	-199.61458
Mg ^f	-0.228179	-0.034491	-0.031174	-0.001370	0.	-0.295214	8	5	-199.61461
Ar ^a	-1.064433	-0.343563	-0.217982	-0.039579	-0.016647	-1.682205	3	2	-525.76526
Ar ^b	-1.225599	-0.235280	-0.257362	-0.025456	-0.022433	-1.766130	7	5	-526.81705
Ar ^d	-1.220565	-0.235286	-0.257391	-0.025308	-0.022395	-1.760944	8	8	-526.81731
Ar ^d	-1.220578	-0.235288	-0.257411	-0.025311	-0.022393	-1.760981	8	8	-526.81730
Ar ^f	-1.221091	-0.234993	-0.257323	-0.025295	-0.022410	-1.761113	7	8	-526.81733
Ar ^g	-1.217671	-0.235696	-0.256764	-0.025331	-0.022606	-1.758069	9	7	-526.81400

^a E. Clementi and D. L. Raimondi, J. Chem. Phys. **38**, 2686 (1963). These computations are done with the smallest possible basis set.

^b E. Clementi, J. Chem. Phys. **38**, 996 (1963); **38**, 1001 (1963).

^c E. Clementi, (unpublished functions).

^d E. Clementi, (unpublished functions). These functions are characterized by an exact value of the cusp [see C. C. J. Roothaan and P. S. Kelly, Phys. Rev. **131**, 1177 (1963)].

^e L. Sachs, Phys. Rev. **124**, 1283 (1961).

^f G. Malli, Department of Physics, University of Chicago (private communications).

^g R. E. Watson and A. J. Freeman, Phys. Rev. **123**, 521 (1961).

Estimates of the Lamb shift can be obtained by using⁵

$$\begin{aligned} k_0 &= 80.5 \text{ Ry for } Z=2, \\ &= 191.6 \text{ Ry for } Z=3, \\ &= 19.77Z^2 \text{ for } Z \geq 4, \end{aligned}$$

and

$$\langle \delta(r_1) + \delta(r_2) \rangle_{00} = \frac{2Z^3}{\pi} \left[1 - \frac{0.653}{Z} + \frac{0.138}{Z^2} \right], \quad (13a)$$

$$\langle \delta(r_{12}) \rangle_{00} = \frac{Z^3}{8\pi} \left[1 - \frac{1.877}{Z} + \frac{1.189}{Z^2} \right]. \quad (13b)$$

II. RESULTS

The relativistic energy corrections for different sets of Hartree-Fock functions for He, Be, Ne, Mg, and Ar atoms are presented in Table II. The wave functions differ in the number and type of basis functions as indicated in the table, but give about the same value of the total Hartree-Fock energy. The relativistic energy corrections are computed for each subshell of electrons $E(1s)$, $E(2s)$, etc., and then summed to give the total relativistic energy E_{rel} .

In Table III the contributions to the relativistic energy from the different subshells of electrons $E(nl)$ are given for the ground state of neutral argon and argon ions with closed electron shells. The wave functions used in this calculation are those of Clementi.^{6,7}

The total relativistic energy for the isoelectronic series of 2, 4, 10, 12, and 18 electrons is given in Table IV. Energies are computed for the relevant ions up to the atomic number of 36. The wave functions used in this calculation are those of Clementi.⁶⁻⁸

The lowest order Lamb shifts are computed, using Eqs. (12) and (13), for the two electron isoelectronic series and tabulated in Table V.

III. DISCUSSION

In Table II we have investigated the sensitivity of the relativistic energy in changes in "good" Hartree-Fock wave functions. It is found that although the relativistic energy depends on the number and type of basis functions, the energies computed are essentially the same

⁶ E. Clementi, J. Chem. Phys. **38**, 996 (1963).

⁷ E. Clementi, J. Chem. Phys. **38**, 1001 (1963).

⁸ E. Clementi, C. C. J. Roothaan, and M. Yoshimine, Phys. Rev. **127**, 1618 (1962).

TABLE III. The contribution to the relativistic energy corrections from the different subshells of electrons in argon and its ions.^a

Number of electrons	$E(1s)$	$E(2s)$	$E(2p)$	$E(3s)$	$E(3p)$	$E(\text{rel})$
2	-1.255705					-1.255705
4	-1.248403	-0.319488				-1.567891
10	-1.229899	-0.239205	-0.264833			-1.733937
12	-1.221075	-0.239976	-0.261252	-0.037670		-1.759973
18	-1.225599	-0.235280	-0.257362	-0.025456	-0.022433	-1.766130

^a The Hartree-Fock functions for these computations are given by E. Clementi, J. Chem. Phys. **38**, 996 (1963); **38**, 1001 (1963).

for Hartree-Fock functions with about the same number of basis functions.

Tables II and III indicate that $E(1s)$ is clearly the dominant term in the value of the relativistic energy, and that the n th subshell of electrons gives a larger

contribution to the relativistic energy than the $(n+1)$ th subshell.¹ Table II also indicates that the $1s$ contribution from argon atoms is about the same as the $1s$ contribution for the different argon ions. The small differences are due to the contraction of the electronic wave

TABLE IV. Relativistic energy for 2, 4, 10, 12, and 18 electron isoelectronic series (in au).

No. of electrons	$E(\text{rel})$				
	2	4	10	12	18
Z					
2	-0.000071				
3	-0.000539				
4	-0.002090	-0.002200			
5	-0.005654	-0.006165			
6	-0.012525	-0.014078			
7	-0.024307	-0.027975			
8	-0.042918	-0.050296			
9	-0.070591	-0.083885			
10	-0.109890	-0.132001	-0.131293		
11	-0.163676	-0.198315	-0.200652		
12	-0.235176	-0.286891	-0.295056	-0.295379	
13	-0.327911	-0.402248	-0.419983	-0.421399	
14	-0.445684	-0.549291	-0.581509	-0.584802	
15	-0.592741	-0.733382	-0.786226	-0.792616	
16	-0.773495	-0.960270	-1.041289	-1.052284	
17	-0.992841	-1.236271	-1.354438	-1.371852	
18	-1.255705	-1.567891	-1.733937	-1.759973	-1.766130
19	-1.567848	-1.962364	-2.188743	-2.225826	-2.234961
20	-1.934638	-2.427211	-2.728086	-2.779538	-2.794707
21	-2.362375	-2.970104	-3.361975	-3.431420	-3.456266
22	-2.857722	-3.599667	-4.100937	-4.192571	-4.231744
23	-3.427091	-4.324861	-4.956176	-5.075201	-5.133469
24	-4.077164	-5.154630	-5.938689	-6.091453	-6.174730
25	-4.816045	-6.098712	-7.061380	-7.254356	-7.368651
26	-5.650950	-7.166913	-8.336800	-8.577999	-8.729868
27	-6.590205	-8.370023	-9.778175	-10.076104	-10.273733
28	-7.642262	-9.718376	-11.398838	-11.764308	-12.014691
29	-8.815288	-11.223415	-13.213897	-13.656258	-13.969604
30	-10.117330	-12.897520	-15.238800	-15.768854	-16.155230
31	-11.559035	-14.751191	-17.487432	-18.116588	-18.587743
32	-13.149186	-16.796344	-19.977246	-20.714927	-21.285227
33	-14.898422	-19.048240	-22.723469	-23.579800	-24.267154
34	-16.817487	-21.517206	-25.744918	-26.725610	-27.551138
35	-18.915338	-24.215525	-29.057958	-30.164510	-31.155441
36	-21.202454	-27.160759	-32.681561	-33.906598	-35.101939

function at the nucleus with increasing atomic number. This then also verifies the assumption of Scherr *et al.*⁹ that the relativistic contribution of any subshell is roughly a constant independent of the number of electrons in the outer shell. Because of this quasiadditivity of the $E(nl)$ contributions to the relativistic energy it is not difficult to improve the computed values of the relativistic energy in the following manner: Instead of using the computed values of $E(1s)$ from the Hartree-Fock functions, we can use the $E(1s)$ obtained from the exact functions of Pekeris¹⁰ and then use the $E(nl)$ for $n \geq 1$ from our computations. Pekeris' relativistic energies are available up to $Z=10$ and have been extrapolated by Scherr⁹ to $Z=20$. These values have been tabulated in Table VI along with our computed values. The difference between our values for $E(1s)$ and those of Pekeris and Scherr are tabulated in the third column of the table and can then be used as a correction to all the terms in Table III. It should be noted that if this

TABLE V. Lowest-order Lamb shifts for 2 electron atoms (in a.u.).

Z	$E_{L,2}+E_{L,2'}$	Z	$E_{L,2}+E_{L,2'}$
2	0.000022	19	0.064270
3	0.000106	20	0.073933
4	0.000323	21	0.084081
5	0.000740	22	0.094600
6	0.001439	23	0.105350
7	0.002500	24	0.116174
8	0.004000	25	0.126887
9	0.006015	26	0.137283
10	0.008614	27	0.147130
11	0.011856	28	0.156165
12	0.015791	29	0.164110
13	0.020460	30	0.170665
14	0.025887	31	0.175480
15	0.032085	32	0.178194
16	0.039051	33	0.178422
17	0.046765	34	0.175742
18	0.055190	35	0.169699
		36	0.159823

⁹ C. W. Scherr, J. N. Silverman, and F. A. Matsen, Phys. Rev. **127**, 830 (1962).

¹⁰ C. L. Pekeris, Phys. Rev. **112**, 1649 (1958).

TABLE VI. Relativistic correction for a two-electron system.

Z	^a	^b	Δ
2	-0.000049	-0.000060	-0.000011
3	-0.000433	-0.000500	-0.000067
4	-0.001767	-0.001878	-0.000111
5	-0.004914	-0.005092	-0.000178
6	-0.011086	-0.011345	-0.000259
7	-0.021807	-0.022166	-0.000359
8	-0.038918	-0.039395	-0.000477
9	-0.064576	-0.065202	-0.000626
10	-0.101276	-0.102075	-0.000799
11	-0.151820	-0.152847	-0.001027
12	-0.219385	-0.220655	-0.001270
13	-0.307451	-0.308996	-0.001545
14	-0.419797	-0.421671	-0.001874
15	-0.560656	-0.562833	-0.002177
16	-0.734444	-0.736965	-0.002521
17	-0.946076	-0.948891	-0.002815
18	-1.200515	-1.203750	-0.003235
19	-1.503578	-1.507060	-0.003482
20	-1.860704	-1.864620	-0.003916

^a Our results including $E(\text{rel})+E_{L,2}+E_{L,2'}$.

^b Pekeris' relativistic energies up to $Z=10$ and their extrapolations by Scherr *et al.* for $Z>10$.

correction is used, the results for 4, 10, 12, and 18 electron systems will include Lamb-shift corrections for the 1s electrons, but not for the other electrons. This is justified because the Lamb-shift corrections are small compared with the main relativistic contribution, (compare Tables V and III), and the main contribution to the Lamb shift should come from the 1s electrons. Table VI indicates that the empirical estimates of Scherr *et al.* agree with our theoretical computations within a few percent except for low Z where the discrepancy is slightly larger.

When the relativistic corrections to the ground-state energy of closed-shell atomic systems are computed, Eq. (1) can be used to obtain the correlation energy as has been shown by Clementi.²

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