

Analysis of Correlation Effects in HeI, LiI and BeI Iso-electronic Sequences by Z-expansion Methods

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Correlation effects for the energy and the expectation values of the electron-nuclear attraction and the inter-electronic repulsion in atomic states are discussed in terms of Z expansions for these quantities. Numerical examples are given for the HeI, LiI and BeI iso-electronic sequences.

It is shown that a series expansion of the type $\langle V_{en} \rangle = 2\varepsilon_0 Z^2 + \varepsilon_1 Z$ (a.u.) gives very accurate results for the expectation value of the electron-nuclear attraction.

Der Korrelationsanteil an der Energie und an den Erwartungswerten der Elektron-Kernanziehung sowie der Elektronenabstoßung für atomare Zustände wird mit Hilfe der Z -Entwicklung dieser Größen diskutiert. Für die isoelektronischen Reihen HeI, LiI und BeI werden numerische Beispiele angegeben. Es wird gezeigt, daß eine Reihenentwicklung vom Typ $\langle V_{en} \rangle = 2\varepsilon_0 Z^2 + \varepsilon_1 Z$ (a.E.) sehr genaue Ergebnisse für den Erwartungswert der Elektron-Kernanziehung liefert.

1. Introduction

Recently, an interpretation of the correlation energy in atoms in terms of the expectation values of the various terms in the Hamiltonian has been suggested by Gruninger, Öhrn and Löwdin [1], hereafter referred to for the sake of brevity, as G.O.L. These authors quote as examples some numerical results for the ground states of the HeI and LiI iso-electronic sequences.

In the present paper, we indicate a method of an analysis of the correlation energy in atoms and ions of iso-electronic sequences based on Z -expansions for the energy and expectation values for the electron-nuclear attraction and electron-electron repulsion energies. Such an analysis was suggested by Löwdin [2] several years ago, but seems to have received little attention. We have presented elsewhere [3], an analysis of some anomalies surrounding the interpretation of Hund's Rule based on similar series expansions.

We shall here briefly review the necessary formalism. Consider the non-relativistic Hamiltonian $H = T + V_{en} + V_{ee}$, where T is the kinetic energy operator, and V_{en} and V_{ee} the electron-nuclear attraction and electron-electron repulsion operators, respectively. Applying the Hellmann-Feynman theorem, we have,

$$\frac{\partial E}{\partial Z} = \left\langle \frac{\partial H}{\partial Z} \right\rangle = \frac{\partial}{\partial Z} \langle V_{en} \rangle = Z^{-1} \langle V_{en} \rangle. \quad (1)$$

The Virial theorem states, $2E = \langle V_{en} \rangle + \langle V_{ee} \rangle$; hence, from (1) we obtain

$$\langle V_{ee} \rangle = 2E - Z \frac{\partial E}{\partial Z} \quad (2)$$

E as a function of Z is given by the well-known Hylleraas expansion [2, 4]

$$E = \varepsilon_0 Z^2 + \varepsilon_1 Z + \varepsilon_2 + \frac{\varepsilon_3}{Z} + \frac{\varepsilon_4}{Z^2} + \dots \quad (3)$$

which, when substituted into (1) and (2) leads to

$$\langle V_{en} \rangle = 2\varepsilon_0 Z^2 + \varepsilon_1 Z - \frac{\varepsilon_3}{Z} - \frac{2\varepsilon_4}{Z^2} - \dots \quad (4)$$

and

$$\langle V_{ee} \rangle = \varepsilon_1 Z + 2\varepsilon_2 + \frac{3\varepsilon_3}{Z} + \frac{4\varepsilon_4}{Z^2} + \dots \quad (5)$$

The coefficients ε_n are the n^{th} order perturbation energy corrections obtained by taking V_{ee} as the perturbation [2, 4]. Hence in zeroth order, the wavefunction is a Slater determinant constructed from hydrogenic orbitals.

Eqs. (1), (2), and (3), and hence (4) and (5) are satisfied by exact wavefunctions. That the Hellmann-Feynman theorem and the Virial theorem are satisfied by solutions to the full Hartree-Fock equations has been shown by Coulson [5] and Löwdin [2] respectively. The validity of Eq. (3) for exact Hartree-Fock energies has been demonstrated by Linderberg and Shull [6]. Consequently, (3), (4), and (5) are valid in both exact and Hartree-Fock cases. In what follows, primed symbols will refer to Hartree-Fock, and unprimed symbols to exact cases, respectively. It has been shown [6] that $\varepsilon_0 = \varepsilon'_0$, and moreover, that when no zeroth order degeneracy exists between states with the same spectroscopic designation, $\varepsilon_1 = \varepsilon'_1$. Such is the case for the ground states of the HeI and LiI sequences, but for the BeI sequence, where the $2s^2$ and $2p^2\ ^1S$ states are degenerate in zeroth order, $\varepsilon_1 \neq \varepsilon'_1$, and ε_1 is calculated from degenerate perturbation theory. The coefficients ε_1 and ε'_1 have been calculated for first row atoms and ions [6].

Defining the correlation energy E_c , by $E_c = E_{\text{exact}} - E_{\text{HF}}$, we obtain

$$E_c = (\varepsilon_1 - \varepsilon'_1) Z + (\varepsilon_2 - \varepsilon'_2) + \frac{(\varepsilon_3 - \varepsilon'_3)}{Z} + \frac{(\varepsilon_4 - \varepsilon'_4)}{Z^2} + \dots \quad (6)$$

where the zeroth order term has vanished. Similarly the effect of correlation on electron-nuclear attraction, and electron-electron repulsion is given by

$$\langle V_{en} \rangle_c = (\varepsilon_1 - \varepsilon'_1) Z - \frac{(\varepsilon_3 - \varepsilon'_3)}{Z} - \frac{2(\varepsilon_4 - \varepsilon'_4)}{Z^2} - \dots \quad (7)$$

and

$$\langle V_{ee} \rangle_c = (\varepsilon_1 - \varepsilon'_1) Z + 2(\varepsilon_2 - \varepsilon'_2) + \frac{3(\varepsilon_3 - \varepsilon'_3)}{Z} + \frac{4(\varepsilon_4 - \varepsilon'_4)}{Z^2} + \dots \quad (8)$$

The first order terms in (6), (7), and (8) will vanish for the HeI and LiI sequences, but not for the BeI sequence, and so we shall discuss the two separately.

2. Helium I and Lithium I Sequences

Hartree-Fock, configuration interaction and exact non-relativistic energies of atoms and ions of the HeI and LiI sequences for Z up to 8, are reported in several places in the literature [1, 7–9].

We have carried out least-square fits of the available data, to Eq. (3) correct up to the term in ε_4 , where we have made use of the exact theoretical values for ε_0 and $\varepsilon_1(\varepsilon'_1)$ given by Linderberg and Shull [6], and have fitted the remaining parameters. We found that the expression fitted the reported values of the energy extremely accurately. In all cases, the relative error was found to be of the order of $10^{-4}\%$. The perturbation energy coefficients to fourth order, for the various types of wavefunction are displayed in Tables 1 and 2.

Table 1. Summary of perturbation energy coefficients ε_n for the HeI sequence (in a.u.)

n	HF	CI		Exact	
	Weiss [8]	G.O.L. [1]	Weiss [8]	H.M. [14]	S.K. [13]
0	-1.0	-1.0	-1.0	-1.0	-1.0
1	0.625	0.625	0.625	0.625	0.625
2	-0.11116	-0.15551	-0.15674	-0.15766	-0.15766
3	0.00011	0.00690	0.00842	0.00854	0.00869
4	-0.00239	-0.00218	-0.00266	-0.00034	-0.00089

Table 2. Summary of perturbation energy coefficients ε_n , for the LiI sequence (in a.u.)

n	HF	CI		Exact	
	G.O.L. [1]	G.O.L. [1]	Weiss [8]	S.S.M. [9]	Weiss [8]
0	-1.125	-1.125	-1.125	-1.125	-1.125
1	1.0228	1.0228	1.0228	1.0228	1.0228
2	-0.35577	-0.40280	-0.40679	-0.41054	-0.41175
3	-0.02379	-0.01854	-0.00432	0.00918	0.01987
4	-0.11138	-0.08515	-0.11027	-0.12588	-0.14737

It is not completely obvious that (4) and (5) should apply to configuration interaction wavefunctions, which although very good, are still nevertheless not exact. If the wavefunctions are suitably scaled, however, the Virial theorem is certainly satisfied [2].

Moreover, calculations of $\langle V_{en} \rangle$ and $\langle V_{ee} \rangle$ according to (4) and (5) based on the perturbation coefficients corresponding to CI (G.O.L.) in Tables 1 and 2 reproduce rather pleasingly the results calculated directly from the wavefunctions. We also notice that, in accordance with (5), the calculated values for $\langle V_{ee} \rangle$ of those authors is approximately linear in Z , with slope near to ε_1 .

In Table 3, $\varepsilon_n - \varepsilon'_n$ have been displayed for $n = 2, 3, 4$, describing the correlation effects up to fourth order, for the helium and lithium sequences. In Table 4, we summarize for the lithium sequence, the values of E_c , $\langle V_{ee} \rangle_c$ and $\langle V_{en} \rangle_c$ as given

by (6)–(8) and the coefficients from Table 3, together with the corresponding values reported by G.O.L. [1]. One notices that E_c is reproduced by the series expansion with almost perfect accuracy, but that the agreement for $\langle V_{ee} \rangle_c$ is less good especially for $Z = 3, 4$. On the other hand, the discrepancy is only about 4%. For $\langle V_{en} \rangle_c$, however, the agreement between the results of our series expansion (7), and the results of the above authors direct calculation is peculiarly unsatisfactory.

Table 3. Summary of expansion coefficients $e_n - e'_n$ for the correlation energy, for various wavefunctions in the HeI and LiI sequences (in a.u.)

Wavefunction			n		
			2	3	4
Helium					
CI	G.O.L. [1]		-0.04435	0.00679	0.00021
		Weiss [8]	-0.04558	0.00831	0.00027
Exact	H.M. [14]		-0.04650	0.00843	0.00205
		S.K. [13]	-0.04650	0.00858	0.00150
Lithium					
CI	G.O.L. [1]		-0.04703	0.00525	0.02623
		Weiss [8]	-0.05102	0.01947	0.00111
Exact	S.S.M. [9]		-0.05477	0.03297	-0.01450
		Weiss [8]	-0.05598	0.04366	-0.03599

Table 4. Comparison of E_c , $\langle V_{ee} \rangle_c$ and $\langle V_{en} \rangle_c$ for the LiI sequence (in a.u.)

Z	G.O.L. [1]			Z Exp.		
	E_c	$\langle V_{ee} \rangle_c$	$\langle V_{en} \rangle_c$	E_c	$\langle V_{ee} \rangle_c$	$\langle V_{en} \rangle_c$
3	-0.0424	-0.0804	-0.0044	-0.0424	-0.0772	-0.0076
4	-0.0440	-0.0852	-0.0028	-0.0441	-0.0836	-0.0046
5	-0.0448	-0.878	-0.0018	-0.0449	-0.0867	-0.0032
6	-0.0456	-0.0902	-0.0011	-0.0454	-0.0885	-0.0018
7	-0.0460	-0.0465	-0.0016	-0.0458	-0.0897	-0.0014
8	-0.0457	-0.0901	-0.0014	-0.0459	-0.0905	-0.0014

One is dealing here with small numbers and might expect a somewhat larger relative error. It appears, however, that $\langle V_{en} \rangle_c + \langle V_{ee} \rangle_c = 2E_c$ for all values of Z reported by G.O.L.; that is, the Virial theorem is satisfied for the correlation energy. The splitting of the correlation effect for the total potential energy into a repulsive and attractive part requires the Hellmann-Feynman theorem to be valid for the Hartree-Fock and configuration-interaction energies, and hence for their differences. So, we have

$$\langle V_{en} \rangle_c = Z \frac{\partial E_c}{\partial Z}. \quad (9)$$

This expression, however, does not seem to be obeyed by the reported values of $\langle V_{en} \rangle_c$ and E_c of G.O.L. Noticing the trend of these authors' values of E_c ,

$\partial E_c/\partial Z$ clearly changes sign between $Z = 6$ and $Z = 8$, and hence one should expect this to be reflected by a change in sign of the corresponding $\langle V_{en} \rangle_c$. Since this is not the case, one may conclude that these wavefunctions, whilst satisfying the Virial theorem do not satisfy the Hellmann-Feynman theorem completely exactly. The deviation from the Hellmann-Feynman theorem is of course a minor one, but we should like to point out that this theorem furnishes a sensitive test of the internal consistency of the accuracy of wavefunctions in an isoelectronic sequence.

By virtue of the development of our formalism, the Virial theorem and Hellmann-Feynman theorem are automatically satisfied. However, we do not wish to convey the impression that we consider our values of $\langle V_{en} \rangle_c$ as very accurate. Our values and those of G.O.L. are small and the same order of magnitude, and this is probably the best one can say. We note in this context that higher order terms may have a relatively greater effect on $\langle V_{en} \rangle_c$ than on either of the quantities E_c and $\langle V_{ee} \rangle_c$ (see (6), (7) and (8) for $\varepsilon_1 - \varepsilon'_1 = 0$). In the limit of infinite Z we see that $\langle V_{ee} \rangle_c = 2E_c = 2(\varepsilon_2 - \varepsilon'_2)$. G.O.L. have made a similar observation from their numerical results [1]. Reference to (6), (7), and (8) with $\varepsilon_1 - \varepsilon'_1 = 0$, and Table 3, shows that E_c and $\langle V_{ee} \rangle_c$ are dominated by the second order terms, whereas $\langle V_{en} \rangle_c$ depends only on higher order terms whose contributions diminish for increasing Z .

It is customary [1] to define a quantity $\Delta E_c = E_{\text{exact}} - E_{\text{Cl}}$, where E_{exact} is the non-relativistic exact eigenvalue usually obtained from experimental data and corrected for relativistic effects. A Z -expansion for ΔE_c can be obtained by subtracting the appropriate component expressions. For E_{exact} as reported by Matsen [9], and the E_{Cl} reported by G.O.L. [1] (see Table 3) we find for the lithium sequence

$$\Delta E_c = -0.0077 + \frac{0.0277}{Z} - \frac{0.0407}{Z^2} + \dots \quad (10)$$

This expression gives very accurately the ΔE_c reported by G.O.L. We note that this formula contains only corrections in second and higher order. It is interesting that the third and fourth order coefficients are larger than the second order term. With reference to Table 3, it is apparent that whilst the second order coefficients obtained from configuration interaction approximate fairly closely the exact coefficients, the third and fourth order coefficients are to a noticeably lesser degree consistent with each other. We remark also that the exact second order coefficients calculated from energy values published by different authors are not precisely the same. This variance can probably be largely attributed to the difference in ways of correcting for relativistic effects.

We have confined ourselves above to a discussion of the lithium sequence, although the data tabulated for the helium sequence may be similarly analysed. We only remark that application of (9) to the E_c and $\langle V_{en} \rangle_c$ of G.O.L. leads to no obvious discrepancy so that the Hellmann-Feynman theorem for the correlation energy is more exactly obeyed by the wavefunctions of G.O.L. for the helium sequence than for the lithium sequence.

3. Beryllium I Sequence

For the Beryllium I sequence, $\varepsilon_1 \neq \varepsilon'_1$ as we have noted before. Hartree-Fock, configuration interaction and exact energies are available in the literature [7–9], for $Z = 3$ to 8. We have made a least-squares fit for these energies using the theoretical values of ε_0 , ε_1 and ε'_1 [6]. The results are summarized in Table 5. In this case, (6), (7), and (8) show a much stronger Z -dependence than occurs in the LiI sequence. In particular, $\langle V_{en} \rangle_c$, which is almost negligible for the HeI and LiI

Table 5. Summary of perturbation energy coefficients ε_n for BeI sequence (in a.u.)

n	Wavefunction		
	HF (R.S.W.) [7]	CI (Weiss) [8]	Exact (Weiss) [8]
0	-1.125	-1.125	-1.125
1	1.57100	1.55927	1.55927
2	-0.80972	-0.85678	-0.88973
3	-0.06712	-0.12142	0.09419
4	-0.48768	-0.17439	-0.61549

sequences, and which vanishes for high Z values, is clearly non-vanishing for the BeI sequence, and becomes linear in Z for high Z values. For HeI and LiI sequences, the ratio of $\langle V_{ee} \rangle_c$ to E_c is 2 : 1 for high Z , but in the case of the BeI sequence, this ratio approaches 1 : 1 for high Z . As $(\varepsilon_1 - \varepsilon'_1)$ is smaller than $(\varepsilon_2 - \varepsilon'_2)$, one has to go to fairly high Z values in order to approach the limit 1 (unity). For the helium and lithium sequences however, the limiting value of 2 is already approximately obeyed for the neutral atoms. Finally, we notice that ε_2 according to the CI wavefunction is closer to the ε_2 for the exact energies in the HeI and LiI sequences than in the case of the BeI sequence.

4. Two-Term Expansion for $\langle V_{en} \rangle$

We see in (4) in the Z expansion for $\langle V_{en} \rangle$, a constant term ε_2 is not present. One may expect contributions from terms in $1/Z$ and higher, to be very small compared to terms in Z^2 and Z . Hence, the simple two-term expansion,

$$\langle V_{en} \rangle = 2\varepsilon_0 Z^2 + \varepsilon_1 Z \quad (11)$$

should be a relatively accurate approximation for $\langle V_{en} \rangle$ and approach the exact values in the limit for high Z . Moreover, ε_0 and ε_1 have been tabulated for many cases and are otherwise reasonably easy to calculate on the basis of hydrogenic orbitals [10, 11].

For the HeI sequence, one gets

$$\langle V_{en} \rangle = -2Z^2 + 0.625Z \quad (12)$$

and for the LiI sequence,

$$\langle V_{en} \rangle = -2.25Z^2 + 1.0228Z. \quad (13)$$

Table 6 lists our calculations for the HeI and LiI sequences, with those calculated by G.O.L. from their CI wavefunctions. The above two-term expansions reproduce the calculated values with 99.97% accuracy for the lower Z values, and rather better for the higher Z values. For the ground state of the Boron atom,

$$\langle V_{en} \rangle_{\text{HF}} = -2.75Z^2 + 2.3345Z,$$

whereas in the CI approximation we obtain for the same,

$$\langle V_{en} \rangle_{\text{CI}} = -2.75Z^2 + 2.3275Z.$$

This leads to $\langle V_{en} \rangle_{\text{HF}} = -57.0778$ a.u. and $\langle V_{en} \rangle_{\text{CI}} = -57.1124$ a.u. Direct calculations give $\langle V_{en} \rangle_{\text{HF}} = -56.8972$ a.u. and $\langle V_{en} \rangle_{\text{CI}} = -56.9462$ a.u. [12]. The accuracy with which we reproduce this value is less good than for the HeI and LiI sequences, but is still about 99.7% accurate. Hence, the two-term expansion provides a simple and relatively accurate way of calculating $\langle V_{en} \rangle$.

Table 6. Electron-nuclear attraction energies calculated from two-term expansion for HeI and LiI sequences (in a.u.)

Z	Helium		Lithium	
	Eq. (12)	CI (G.O.L.) [1]	Eq. (13)	CI (G.O.L.) [1]
2	- 6.7500	- 6.7523		
3	- 16.1250	- 16.1268	- 17.1816	- 17.1508
4	- 29.5000	- 29.5015	- 31.9088	- 31.8920
5	- 46.8750	- 48.8762	- 51.1360	- 51.1244
6	- 68.2500	- 68.2510	- 74.8632	- 74.8540
7	- 93.6250	- 93.5295	-103.0904	-103.0837
8	-123.0000	-123.0008	-135.8176	-135.8119

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