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Ground state correlation energy of the Be-sequence for $Z=4$–20 in MCDF approximation

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The ground state ($J=0$) electronic correlation energy of the 4-electron Be-sequence is calculated in the Multi-Configuration Dirac-Fock approximation for $Z=4$–20. The 4 electrons were distributed over the configurations arising from the $1s$, $2s$, $2p$, $3s$, $3p$ and $3d$ orbitals. Theoretical values obtained here are in good agreement with experimental correlation energies.

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Introduction

The four-electron Be-like atom/ions are few-electron systems on which a great amount of theoretical work has been performed during the last few decades. Main emphasis was the calculation of the total electronic as well as the correlation energy which is defined as the difference between the Hartree(Dirac)-Fock energy with relativistic corrections in the Hartree-Fock case and the experimental total binding energy. Of course for the Be-atom the relativistic corrections are very small. Therefore the non-relativistic approaches have yielded very accurate results. However for increasing Z the non-relativistic approaches need to be extended to include relativistic corrections.

Calculations for the ground state have been made by many authors in various approximations [1–6]. All of these calculations are non-relativistic with the inclusion of relativistic effects by perturbation. A survey of these calculations is given in [7]. The first accurate result of the ground state correlation energy was obtained by Kelly [1] who applied the many body theory of Brueckner [8] and Goldstone [9]. Byron and Joachain [2] used the Hartree-Fock theory. They decoupled the four-electron problem into a series of helium-like equations describing pair correlation between electrons. After applying variational perturbation method to each of these equations to fifth order in the energy they obtained the correlation energy for Be and B+. Froese-Fischer and Saxena [3] made a separated pair correlation study of the ground state of Be by using a numerical Multi-Configuration Hartree-Fock procedure. Combining the resulting functions in a configuration interaction calculation they were able to account for a very large amount of the correlation energy.

The most accurate determination of the total energy of Be ground state was carried out by Bunge [4], who performed a configuration interaction calculation involving 650 terms. More recently Li Baiwen et al. [5] have applied variational correlation techniques to obtain the correlation energy of the Be-sequence for $Z=3$–10. Ivanova and Safranova [6] investigated the Z dependence of the correlation energy of atomic systems with 2 to 10 electrons by means of perturbation calculations of atomic energy levels

Table 1. Experimental, MCDF and DF total energies and the resulting correlation energies of the 4-electron Be-sequence for the $J=0$ ground state up to $Z=20$. All values in eV. Experimental data quoted in [11] are from [13] and [14]

Z	Total energies					Correlation energies	
	Experiment			Theory		Experimental	Theoretical
	Ref. 11	Kelly [15]	Moore [17]	MCDF	DF	$E_{\mathrm{exp}}[11] - E_{\mathrm{DF}}$	$E_{\mathrm{MCDF}} - E_{\mathrm{DF}}$
4	− 399.14	− 399.15	− 399.03	− 398.76	− 396.61	−2.53	−2.15
5	− 662.65	− 662.69	− 662.49	− 662.27	− 659.69	−2.96	−2.57
6	− 994.44	− 994.47	− 994.17	− 994.01	− 991.08	−3.36	−2.93
7	− 1394.42	− 1394.49	−1394.07	− 1393.99	− 1390.72	−3.70	−3.27
8	− 1862.72	− 1862.78	−1862.19	− 1862.25	− 1858.65	−4.07	−3.60
9	− 2399.30	− 2399.40		− 2398.84	− 2394.91	−4.39	−3.93
10	− 3004.32	− 3004.42		− 3003.84	− 2999.59	−4.73	−4.25
11	− 3677.78	− 3677.91		− 3677.34	− 3672.78	−5.00	−4.57
12	− 4419.89	− 4420.31		− 4419.46	− 4414.58	−5.31	−4.88
13	− 5230.70	− 5231.65		− 5230.30	− 5225.11	−5.59	−5.19
14	− 6110.34	− 6110.54		− 6110.00	− 6104.51	−5.83	−5.49
15	− 7058.96	− 7059.21		− 7058.71	− 7052.92	−6.05	−5.79
16	− 8076.71	− 8176.94		− 8076.57	− 8070.49	−6.21	−6.08
17	− 9163.74	− 9164.00		− 9163.77	− 9157.41	−6.34	−6.37
18	−10319.6(10)	−10319.93		−10320.49	−10313.85	−5.7(10)	−6.66
19	−11546.3(22)	−11546.5		−11546.92	−11540.01	−6.3(22)	−6.92
20	−12843.5(22)	−12843.0		−12843.29	−12836.11	−7.4(22)	−7.19

in powers of $(1/Z)$. For the ground state of the 4-electron systems they obtained an expression of the form

$$E_{\mathrm{corr}}/\mathrm{eV} = -0.3192 * Z - 1.9592.$$

In their definition the correlation energy is the difference between their theoretical total binding energy and their expression for the Hartree-Fock energy, both gained non-relativistically by Z-expansion techniques. Their calculated energies are overestimated by about 20% for the Be atom when compared with the empirical values of Clementi [10]. For increasing Z the agreement between these calculated values and empirical values of Clementi improves significantly, so that for $Z=30$ the two values agree to within 0.2%. This is a somewhat surprising result since Clementi's empirical values were derived from the experimental ionisation potentials available in 1963, which were certainly bound with experimental uncertainties at least of the same order as the correlation energy for high Z. In a very recent study we obtained 'experimental' values for the correlation energies from the present experimental data and Dirac-Fock calculations for various many-electron ions [11], which show that Clementi's values were overestimated, particularly for higher Z. We report here a fully relativistic ab initio calculation for the ground state energy of the four electron system for $Z=4$–20 in the Multiconfiguration Dirac-Fock approximation (MCDF).

Method

The MCDF method is described in various publications [12] and will therefore not be discussed here. It represents the relativistic analogue of the non-relativistic Multiconfiguration Hartree-Fock approximation [7]. The wave functions are expanded in terms of configuration state functions which themselves are constructed from linear combinations of Slater-determinants such that they are eigenfunctions to J^2. The Slater-determinants are constructed from one electron wave functions, which are kept orthogonal via off-diagonal Lagrange multipliers.

The problem in the actual calculations lies in the choice of the configurations and the convergence of the runs. For the $J=0$ ground state of the Be-like atom/ions we distributed the four electrons over 61 configuration state functions, all that can be constructed from the $1s$, $2s$, $2p$, $3s$, $3p$ and $3d$ one-electron orbitals. In the self-consistent procedure the convergence is being achieved by varying succesively the radial part of the one electron orbitals and the expansion coefficients of the 61 configurations.

Results and discussion

The results of the MCDF calculations are presented in Table 1, where we list the total energies and the resulting correlation energies. For completeness we have included the experimental as well as the Dirac-Fock total energies. One set of experimental values is taken from [11] which critically summarizes the ionization potentials given in the Grotrian tables [13] for $Z \leqq 18$ and in the work of Sugar and Corliss [14] for $Z > 18$. The other set consists of values quoted in the latest edition of Kelly [15] that are identical to the values given in Cowan's book [16]. As already noted for $Z=4$ there exists a slight discrepancy between the values of Clementi obtained nearly thirty years ago and the recent values [11]. In principal the same empirical procedure is adopted in [10] and [11] for obtaining the correlation energy, i.e.

$$E_{\text{corr}} = E_{\text{exact}} - E_{\text{HF}} + \text{relativistic corrections}$$

where the last two terms in the relativistic calculations are replaced by $-E_{\text{DF}}$. The value E_{exact} is constructed from the sum of the ionisation potentials for all ionic states from the one to the four electron ions from [13] and [14]. The values E_{corr} of Clementi build a rather smoothly increasing function of Z right up to $Z=30$ whereas the E_{corr} values of [11] show large fluctuations beyond $Z=18$. These arise from errors in the experimental ionisation energies. It appears that Clementi must have used some kind of regularisation procedure to smooth out these fluctuations.

In Table 1 the first three columns present the experimental total energies. The first column gives the values of [11], the original data being from [13] and [14]. Column two and three quote data from Kelly [15] and Moore [17], respectively. Multiconfiguration-Dirac-Fock (61 configuration calculations) and Dirac-Fock (Single configuration calculation: $1s^2\,2s^2$) total energies follow in column four and five. Relying on the figures from [11] the difference between the first and the fifth columns are the correlation energies by definition which we therefore call (experimental) correlation energies which are given in column six. The seventh column presents the 'theoretical' correlation energies of these calculations which are the differences between the Multiconfiguration Dirac-Fock and Dirac-Fock total energies. The difference between the last two columns is at most 0.5 eV which shows that the MCDF calculations with the configurations discussed here already represent 80% and for the higher Z values 90% of the (experimental) correlation energy. In fact an approximately constant part of roughly 0.4 eV which is the difference between our 'theoretical' correlation energy and the (experimental) correlation energy is still missing. Unfortunately the experimental data often do not include error bars even not in the original data used. Especially data for higher members of the isoelectronic sequence are therefore to be considered carefully and they call for an improved remeasurement in order to serve as a test for the theoretical data.

Table 2. Survey of ab initio calculations and (experimental) correlation energy (in eV) of $J=0$ ground state of the Be-sequence. A detailed survey for Be may be found in [7]

Z	Experiment		Theory		
	Ref. 10	Ref. 11	Other results		Present
4	-2.569	-2.53	-2.566^4 -2.503^3 -3.236^6	-2.503^2 -2.569^5	-2.150
5	-3.056	-2.96	-3.025^5 -2.982^2	-3.555^6	-2.574
6	-3.450	-3.36	-3.450^5	-3.874^6	-2.929
7	-3.842	-3.70	-3.842^5	-4.194^6	-3.269
8	-4.220	-4.07	-4.218^5	-4.513^6	-3.600
9	-4.582	-4.39	-4.582^5	-4.832^6	-3.927
10	-4.936	-4.73	-4.934^5	-5.151^6	-4.248
11	-5.282	-5.00	-5.470^6		-4.567
12	-5.622	-5.31	-5.790^6		-4.879
13	-5.959	-5.59	-6.109^6		-5.189
14	-6.294	-5.83	-6.428^6		-5.494
15	-6.626	-6.05	-6.747^6		-5.793
16	-6.955	-6.21	-7.006^6		-6.084
17	-7.284	-6.34	-7.386^6		-6.370
18	-7.611	$-5.7(10)$	-7.707^6		-6.650
19	-7.937	$-6.3(22)$	-8.024^6		-6.923
20	-8.264	$-7.4(22)$	-8.343^6		-7.188

As already mentioned the correlation energy for the neutral Be atom ($Z=4$) is believed to be very accurately known from the calculation of Bunge [4]. The values from the various calculations together with the experimental values of the Be-sequence are listed in Table 2.

For the experimental correlation energies we note that there is a slight discrepancy between the value of Clementi [10] and that of [11]. One possible explanation is the approximative nature of relativistic corrections used by Clementi. On the other hand one has to be aware that the three tables usually used for experimental ionization energies differ by more than 0.1 eV. Moore's tables [17] give 399.033 eV, the Grotrian tables [13] 399.139 eV, and Kelly [15] finally 399.150 eV. Clementi used the first value and the second was used in [11].

The theoretical values for the Be atom differ only by very small amounts except for the value by Ivanova et al. [6]. Knowing the experimental uncertainties it is somewhat surprising that the best calculated value [4] is nearly on top of Clementi's old value. In view of these discrepancies it is absolutely important that the experimental results are either repeated or newly analysed.

Table 3. Convergence of MCDF procedure for $J=0$ ground state of Be-like atoms. All values in eV

Basis	No. of conf.	$Z=4$	$Z=5$	$Z=12$	$Z=19$
$1s^2 2s^2 + 1s^2 2p^2$	2	-1.193	-1.599	-3.949	-5.941
all $1s^2$ nl^2 and $2s^2$ nl^2, $n=3$	15	-2.098	-2.496	-4.822	-6.871
all conf. from $1s, 2s, 2p, 3s, 3p, 3d$	61	-2.150	-2.575	-4.880	-6.923
$E_{\text{corr}}(\text{exp})^{11}$		-2.53	-2.96	-5.31	$-6.3\,(22)$

In Table 3 we present the convergence of the MCDF procedure for increasing numbers of one-electron orbitals for the elements $Z=4$, 5, 12 and 19. The major contributions come from the $1s$, $2s$ and $2p$ orbitals, where the $1s^2\,2p^2$ configuration, lying in the same complex as $1s^2\,2s^2$ is responsible for the part of the correlation energy that is linear in Z (Intrashell correlation). All the contributions from $3s$, $3p$ and $3d$ are essentially constant for all Z values.

A linear fit to the theoretical correlation energies, presented by these calculations with 61 configurations (Fig. 1) gives the expression $E_{\text{corr}}/\text{eV} = -(0.3075 \pm 0.0030) * Z - (1.1358 \pm 0.0394)$. This should be compared to the expression by Ivanova et al. [6] with their result $E_{\text{corr}}/\text{eV} = -0.3192 * Z - 1.9592$. As [6] is a nonrelativistic study we repeated our calculations in a nonrelativistic mode. A linear fit to these data results in $E_{\text{corr}}/\text{eV} = -(0.3268 \pm 0.0006) * Z - (0.9721 \pm 0.0085)$. In fact the relativistic data show deviations for higher Z that are due to relativistic effects, which do not turn up in the nonrelativistic results. The linear component in the expression of the theoretical correlation energy can be exclusively contributed to the mixing with the configuration $1s^2\,2p^2$. A linear fit to these contributions (triangles in Fig. 1) yields $E_{\text{corr}}/\text{eV} = -(0.3067 \pm 0.0043) * Z - (0.2000 \pm 0.0576)$. Finally we provide as well data for the experimental correlation energy (data from ref. 11): $E_{\text{corr}}/\text{eV} = -(0.3092 \pm 0.0092) * Z - (1.505 \pm 0.099)$. While Ivanova et al. [6] overestimates the constant part of the correlation energy we miss out further contributions that are constant over Z and should be calculated, if convergence allows, by mixing of other outer shell contributions $4f$, $5g$ etc.

Summary

In summary we can conclude that the MCDF method is able to reproduce about 90% of the correlation energy with only a relatively small number of configurations and is therefore able to provide a good order of magnitude of the correlation energy. This statement is especially important for heavier systems where the direct influence of the relativistic terms increases strongly with increasing Z. We may note that this is the only method which is also able to include the correlation contribution from the magnetic interaction, which has been shown to be of great importance for systems with Z greater than 30 [18].

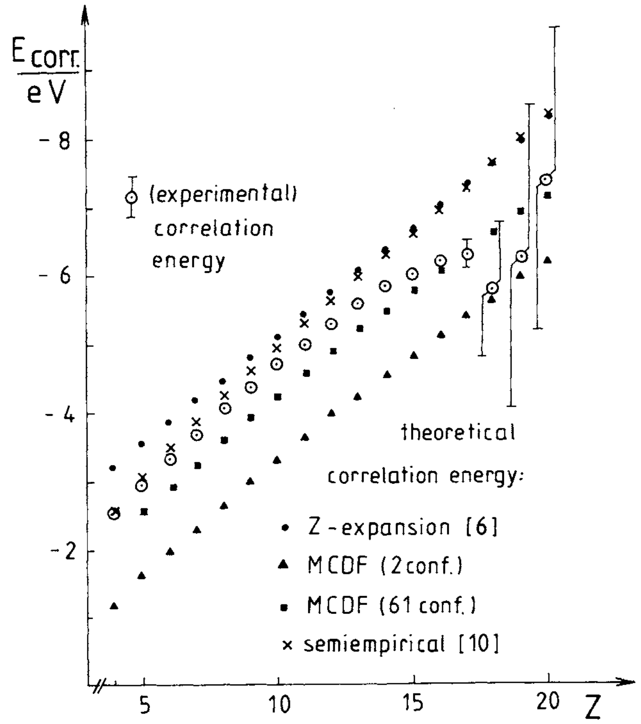

Fig. 1. Correlation energies along the isoelectronic sequence of Be-like four-electron ions. The error bars for the experimental correlation energy for elements below chlorine are below a tenth of an eV

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