

Benchmark energy calculations on Be-like atoms

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Upper bounds to the nonrelativistic ground-state energies of beryllium isoelectronic ions with $3 \leq Z \leq 10$ were computed from 1600-term exponentially correlated Gaussian functions. The energies obtained substantially improve over previous variational results known from literature. The mass polarization corrections to the energy are also presented.

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I. INTRODUCTION

An important role in the development of new methods of accounting for correlation effects in many-electron systems is played by comprehensive investigations aiming at the evaluations of their reliability. Due to the absence of mathematical tools helpful in this respect, the only truly meaningful assessments of these methods must rely on comparisons with highly accurate or exact (for model systems) theoretical results. For real systems, results of spectroscopic accuracy are presently available only for very small ones including two, three, or four electrons.

For atoms, of special interest are highly accurate results for several entries of the isoelectronic series, which offer the possibility of understanding better the dependence of various factors determining the electronic structure of the nuclear charge. In this work we are concerned with Be-like atoms, which are the largest real systems studied so far at the highest accuracy level. These systems are the simplest for studies of the two following important features: First, intrashell and intershell correlations, and second, ground-state quasidegeneracy (near-degeneracy, dynamical correlation) effects, which are defined by the $1s^2 2s^2 ({}^1S)$ and $1s^2 2p^2 ({}^1S)$ configurations. The Be-like atoms are also very attractive for testing multireference state (MR) formulations of the many-body perturbation theory and the coupled-cluster (CC) method, which are known to be plagued with so-called *intruder state problems* [1]. This significance is due to the fact that for the individual entries of the series we have to deal with various types of intruder states. For example, for the Be atom there are infinitely many intruder states of a specific type, whereas for the C^{+2} ion there are no such states. As a result, for Be, essential problems are encountered by solving the equations of the valence-universal version of the MR-CC method [2,3].

The attractive features of Be-like systems just mentioned are the reason why they currently represent the most reliable test grounds for various *ab initio* methods as well as sources of information in the estimations of basis-set limits and for scaling of semiempirical approximate methods. They are also

often used for modeling quasidegeneracy effects in larger atoms. Very recently Be-like systems have even been applied in reliability studies of the Monte Carlo method for states disclosing quasidegeneracy effects [4,5].

Presently, an important field of applications of accurate energies for Be-like systems are investigations aiming at improving the reliability of density-functional theory (DFT) methods. These results are useful in several ways: they provide hints helpful in calibrating new functionals and provide reliability tests for the existing DFT models (cf. [6–8]). It is known (cf. [7]) that DFT methods seem to perform poorly when quasidegeneracy effects have to be accounted for. Therefore, work on the problem of an improved simulation of these effects, which is of key importance for dependable applications of DFT methods, has been pursued for 20 years (for a short review, see, e.g., [9,10]). Here are some recent examples of such investigations: (1) Recently Valderrama *et al.* [11] have examined the significance of nondynamical correlation effects in the context of the local scaling transformation of the DFT. (2) Miehlich *et al.* [12] have tested a density functional for dynamical effects that can be used in connection with complete active space (CAS) self-consistent field wave functions. (3) Colonna and Savin have studied the relation of the Kohn-Sham system to the physical system by means of various adiabatic connection procedures (for references, see [13]).

Four-electron atoms are also useful in the studies of the influence of core-valence separation on the structure of electron densities. Recently Kohout and Savin [14] have for the Be atom constructed the electron localization function of Becke and Edgecombe [15] directly from the density obtained in highly accurate calculations.

Davidson and co-workers [6,7] have obtained very accurate correlation energies for the ground states of atomic systems by combining experimental data and improved *ab initio* calculations. On the other hand, the knowledge of very accurate variational correlation energies for the Be-isoelectronic series could be useful for verifying the assumption made by these authors during the evaluation process, e.g., for the Z dependence of the relativistic corrections to the energy.

The aim of this paper is the presentation of the results of the most accurate variational energy calculations on the

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TABLE I. Comparison of the upper bounds E_{ub} to the nonrelativistic energies and the correlation energies ΔE_{corr} of the Be-like ions calculated from 1600-term ECG wave functions (all signs reversed).

Ion	$E_{\text{ub}}/\text{hartree}$	$\Delta E_{\text{corr}}/\text{mhartree}$	Reference
Li^-	7.500 7727	72.541	This work
	7.500 186	71.954	Sims <i>et al.</i> [22]
	7.500 5298	72.298	Chung and Fullbright [23]
	7.500 5775	72.346	Froese Fischer [24]
Be	14.667 3555	94.333	This work
	14.667 3550	94.332	Komasa <i>et al.</i> [19]
	14.666 9598	93.937	Rizzo <i>et al.</i> [25]
	14.667 0434	94.020	Chung <i>et al.</i> [26]
	14.667 276	94.253	Jitrik and Bunge [27]
	14.667 3547	94.332	Büsse <i>et al.</i> [28]
B^+	24.348 8832	111.308	This work
	24.348 5161	110.941	Chung <i>et al.</i> [26]
C^{+2}	36.534 8497	126.355	This work
	36.534 4359	125.941	Chung <i>et al.</i> [26]
N^{+3}	51.222 7083	140.391	This work
	51.222 2720	139.955	Chung <i>et al.</i> [26]
O^{+4}	68.411 5353	153.824	This work
	68.411 0741	153.363	Chung <i>et al.</i> [26]
F^{+5}	88.100 9188	166.866	This work
	88.100 4408	166.388	Chung <i>et al.</i> [26]
Ne^{+6}	110.290 6495	179.637	This work
	110.290 2780	179.265	Rizzo <i>et al.</i> [25]
	110.290 1586	179.146	Chung <i>et al.</i> [26]

ground state of the beryllium-isoelectronic series with the nuclear charge $3 \leq Z \leq 10$. Special attention is paid to the comparison of the present results with their variational and nonvariational *ab initio* counterparts as well as with the estimates obtained from experimental energies by means of the systematic procedure by Davidson and co-workers [6,7] and by a purely semiempirical approach. Our results have also been used for calculating very accurate values of the finite nuclear mass correction to the energy for the Be-like systems considered.

II. METHOD OF COMPUTATION

In this work we are interested in variational solutions to the stationary Schrödinger equation with the nonrelativistic clamped nucleus Hamiltonian (in atomic units)

$$\hat{H} = -\frac{1}{2} \sum_{i=1}^n \nabla_i^2 + \sum_{i=1}^{n-1} \sum_{j=i+1}^n \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} - Z \sum_{i=1}^n \frac{1}{|\mathbf{r}_i|}. \quad (1)$$

The ansatz for the atomic n -electron trial wave function of $3n$ position (\mathbf{r}) and n spin ($\boldsymbol{\sigma}$) variables reads

$$\Psi(\mathbf{r}, \boldsymbol{\sigma}) = \hat{\mathcal{A}} \left(\Xi_{n,S,M_S}(\boldsymbol{\sigma}) \sum_{k=1}^K c_k \psi_k(\mathbf{r}) \right), \quad (2)$$

where $\hat{\mathcal{A}}$ is permutation symmetry operator and Ξ_{n,S,M_S} is an n -electron spin function with the spin quantum numbers S and M_S . The singlet spin function used in this work was

$$\Xi_{4,0,0} = \alpha\beta\alpha\beta - \beta\alpha\alpha\beta - \alpha\beta\beta\alpha + \beta\alpha\beta\alpha. \quad (3)$$

Though other spin functions can be selected to describe the same spin state, it is sufficient to use only one such function without loss of completeness [16]. The n -electron spatial basis functions are assumed in the form of exponentially correlated Gaussians (ECG),

$$\psi_k(\mathbf{r}) = \exp[-\mathbf{r} \mathbf{A}_k \mathbf{r}^T]. \quad (4)$$

The $n \times n$ matrices \mathbf{A}_k collect the nonlinear variational parameters. Equation (4) represents a simplified form of Singer basis [17] adapted to S -state atoms. The linear, c_k , and the nonlinear parameters, $A_{k,ij}$, were determined variationally in a laborious optimization process. Detailed description of the optimization method can be found in [18–21].

III. RESULTS AND DISCUSSION

The upper bounds E_{ub} to the nonrelativistic energies of eight Be-like ions are listed in Table I. They were computed from 1600-term ECG expansions optimized separately for each Z . The correlation energy $\Delta E_{\text{corr}} = E_{\text{ub}} - E_{\text{HF}}$ was computed as a difference of our upper bound energies and the numerical Hartree-Fock energies given by Davidson *et al.*

[6] (except the value for C^{+2} , which amounts to $-36.408\,495$ hartree). The present results are compared with their most exact counterparts calculated in the last decade. We consider in the table also the results for Li^- obtained earlier by Sims *et al.* [22], who have employed a 147-term singly linked Hylleraas configuration-interaction (CI) wave function [28], which explicitly includes the interelectronic distances. This result represented for more than 15 years the best upper bound for the ion considered. The variational result of these authors has been considerably improved by Chung and Fullbright [23] in CI calculations based on 729 configuration state functions (CSFs) carefully chosen to include the bulk of valence-shell correlation effects. The result obtained was used as a starting point for an extrapolation procedure including both core correlations and angular-basis incompleteness. The same system, together with the Be atom, has been studied by Froese Fischer [24] who performed very extensive multiconfiguration Hartree-Fock (HF) calculations followed by a systematic extrapolation of the energy. The results given in Table I have been calculated by using 3381 CSFs selected from a set of 652 683 CSFs. The energies for Be and Ne^{+10} by Rizzo *et al.* [25] were obtained in CI calculations based on partially optimized 6225 CSFs. As one can see in the table, so far only Chung *et al.* [26] have performed systematic variational calculations (based for all systems on 913 CSFs) including both Be and the positive ions considered in this work. Next, to obtain improved estimates of the total nonrelativistic energies, these results were corrected for basis-set incompleteness effects by a method of partial saturation of the angular components. For Be we consider also the very accurate results by Jitrik and Bunge [27] (CI based on a set of CSFs including orbitals up to $l=13$) and by Büsse *et al.* [28], who have employed their double-linked Hylleraas CI wave function.

Perusing Table I one can see that for all Be-like systems considered, the energies obtained in this work represent the lowest upper bounds to the exact values. For the Be atom the reported result represents a correction of the recent result by Komasa *et al.* [19] and Büsse *et al.* [28] by only $0.5\ \mu$ hartree and $0.8\ \mu$ hartree, respectively. For Li^- the improvement of the upper bound is more pronounced and amounts to $195\ \mu$ hartree with respect to the best previous one. For the positive ions systematic comparison is only possible with the bounds found by Chung *et al.* [26]. From this comparison one can see that when proceeding to higher Z values our bounds disclose an almost monotonic improvement ranging from $367\ \mu$ hartree to $491\ \mu$ hartree. For $Z=10$ our bound differs from the result of Rizzo *et al.* only by $119\ \mu$ hartree.

Let us now proceed to the comparison of our variational results with various accurate estimates of the nonrelativistic energies for the Be-like systems collected in Table II. To make the table more concise, we present only the correlation energies. Moreover, to facilitate the comparison we give in the lower part of the table the differences of the present results with the remaining entries listed in the upper part. In addition to extrapolated *ab initio* energies obtained by the authors mentioned when discussing the upper bounds, Table II includes the results by Gdanitz [29], who has used an MR-CI version of the $R12$ approach proposed by Kutzelnigg

(cf. Ref. [30]). Approaches of this type are believed to establish basis-set limits for atomic and molecular systems. However, since the $R12$ approaches are based on some approximations, referred to as “the standard approximations,” they do not have the upper bound property. Table II shows of course the very accurate estimates of the correlation by Davidson and co-workers [6,7] mentioned above and also the purely semiempirical results obtained when using the method by Clementi and Corongiu [31], who correct the Hartree-Fock method by selecting an effective Hamiltonian with small perturbations proportional to a function of the electronic density for the Coulomb, nuclear-electron, and kinetic HF matrix elements.

Comparison of the present results with those of the $R12$ -MRCI method shows that the latter are of larger magnitudes, the differences range from 0.012 mhartree to 0.062 mhartree. They are larger for B^+ and C^{+2} and decrease in a nonmonotonic way when proceeding to higher Z . The minimum difference is found for the Be atom. At present it is difficult to indicate the sources of these differences. It seems to us that they may be caused both by the fact that our upper bounds are still above the exact energy by a few microhartrees as well as by the overestimation of correlation energy by the $R12$ -MRCI method. An indication that the latter cause may in fact take place might be the observation that the magnitudes of all but one extrapolated correlation energies shown in Table II are smaller than the present results by several microhartrees. The only exception is the estimate by Jitrik and Bunge which is larger by just $1\ \mu$ hartree.

Proceeding to the comparison of the present correlation energies and those by Davidson and co-workers [6,7], one can see that the latter are of larger magnitudes. These energies take the minimum values for Be and increase in a monotonic way when proceeding to larger Z . Notice that for $Z > 7$ the magnitudes of the correlation energies are significantly larger than the $R12$ -MRCI ones. This increase might be explained by the lack of truly dependable experimental results for higher than the second ionization potentials employed in the evaluation process, which according to Chakravorty and Davidson [33] limits the accuracy of nonrelativistic energies to about 1 mhartree for higher Z values. These results might also be slightly affected by the fact that the relativistic corrections were computed only for the CAS wave function in the $2s, 2p$ space. From Table II one can see that the error estimate by Chakravorty and Davidson might be too pessimistic for the Be series, where for the sixfold ionized Ne the difference with the present values amounts only to 0.24 mhartree. Let us recall that for the $R12$ -MRCI method this difference is minimum just for the largest Z values.

The present results may be compared with the energies obtained when using the valence-universal version of the MR-CC theory mentioned above. Very extensive calculation for the ground states of the Be and C^{+2} systems employing a cluster operator including one- and two-electron excitations [34] yield correlation energies amounting to -94.087 mhartree and -129.350 mhartree, respectively. Whereas the inaccuracy of the first result can be to a large extent attributed to the basis-set incompleteness error, for the

TABLE II. Comparison of the present results with nonvariational correlation energies for Be-like systems (in mhartree, all signs reversed). The lower part consists of differences of the present results with the remaining entries of the upper part.

Ion	Calculated			Experiment	
	This work	R12-MRCI ^a	Extrapolated		HF-CC ^b
Li ⁻	72.541		72.519 ^c 72.526 ^d		
Be	94.333	94.345	94.292 ^d 94.325 ^f 94.334 ^h	94.34 ^e 94.330 ^g	92.3
B ⁺	111.308	111.370	111.295 ^f	111.34 ^e	88.4
C ⁺²	126.355	126.405	126.327 ^f	126.44 ^e	94.3
N ⁺³	140.391	140.413	140.372 ^f	140.53 ^e	
O ⁺⁴	153.824	153.856	153.807 ^f	154.00 ^e	
F ⁺⁵	166.866	166.883	166.849 ^f	167.08 ^e	
Ne ⁺⁶	179.637	179.652	179.617 ^f	179.88 ^e	
Li ⁻			-0.022 ^c -0.015 ^d		
Be		0.012	-0.041 ^d -0.008 ^f 0.001 ^h	0.01 ^e -0.003 ^g	-2.0
B ⁺		0.062	-0.013 ^f	0.03 ^e	-22.9
C ⁺²		0.050	-0.028 ^f	0.08 ^e	-32.1
N ⁺³		0.022	-0.019 ^f	0.14 ^e	
O ⁺⁴		0.032	-0.017 ^f	0.18 ^e	
F ⁺⁵		0.017	-0.017 ^f	0.21 ^e	
Ne ⁺⁶		0.015	-0.020 ^f	0.24 ^e	

^aGdanitz [29].

^bSemiempirical HF-CC model, Clementi and Corongiu [31].

^cChung and Fullbright [23].

^dFroese Fisher [24].

^eChakravorty *et al.* [7].

^fChung *et al.* [26].

^gLindroth *et al.* [32].

^hJitrik and Bunge [27].

second one proceeding to the more complete basis sets would contribute to the increase of the error. The only way to improve the accuracy is the inclusion of three-electron excitations in the cluster operator.

Finally, one can also see from the results of Clementi and Corongiu displayed in the last column of Table II that the accurate estimation of the atomic correlation energies for positive ions by presently available semiempirical methods seems to be a rather difficult task. When proceeding from the neutral Be atom to the B⁺ and C⁺² ions the error of the semiempirical energy increases from 2.2% to 25.4%.

The effect of the finite nuclear mass on the energy can be computed as a sum of the normal (NMS) and specific (SMS) mass shifts. The NMS covers a major part of the total mass correction. It is computed by means of the energy rescaling $\Delta E_{\text{NMS}} = -(m_r/M)E$ (in $\mu\text{hartree}$), where $m_r = m_e M / (m_e + M)$ is the reduced mass of the electron. The most common procedure to take NMS into account is switching from hartree units of energy [$1 \text{ hartree} = e^2 / (4\pi\epsilon_0 a_0)$] to the units based on atomic mass, i.e., with the Bohr radius a_0 replaced

by $a_r = (m_e/m_r)a_0$. For this reason the NMS is not displayed separately.

The SMS depends on the expectation value of the $\nabla_i \nabla_j$ operator $\Delta E_{\text{SMS}} = -(m_r/M)(m_r/m_e)\langle \nabla_i \nabla_j \rangle$ (in hartrees). We calculated these expectation values using the 1600-term ECG wave functions. The convergence of $\langle \nabla_i \nabla_j \rangle$ with the size of the wave-function expansion, studied previously for beryllium [19], makes us believe that the uncertainty in ΔE_{SMS} appears only at the fifth significant digit. The expectation values and the final ΔE_{SMS} values for the most abundant isotopes are listed in Table III. Appropriate nuclear masses were obtained from atomic masses compiled by Audi and Wapstra [35].

IV. SUMMARY

In this paper we report very accurate variational results for several members of the Be-isoelectronic series obtained by using the 1600-term ECG expansion. Our results lead to a significant improvement of the variational upper bounds for all ionic entries of the series. As indicated in the Introduc-

TABLE III. Specific mass shift, ΔE_{SMS} , computed from 1600-term ECG wave functions for the most abundant isotopes.

Ion	$-\langle \nabla_i \nabla_j \rangle / \text{hartree}$	Nuclear mass/ m_e	$\Delta E_{\text{SMS}} / \mu \text{hartree}$
${}^7\text{Li}^-$	0.308 344	12 786.393	24.111
${}^9\text{Be}$	0.460 229	16 424.203	28.018
${}^{11}\text{B}^+$	0.595 140	20 063.736	29.660
${}^{12}\text{C}^{+2}$	0.713 671	21 868.662	32.631
${}^{14}\text{N}^{+3}$	0.816 044	25 519.042	31.975
${}^{16}\text{O}^{+4}$	0.902 377	29 148.946	30.955
${}^{19}\text{F}^{+5}$	0.972 739	34 622.970	28.094
${}^{20}\text{Ne}^{+6}$	1.027 164	36 433.989	28.191

tion, these results should be useful for cross-checking and further refining of various methods accounting for electron correlation and quasidegeneracy effects, especially in the framework of the DFT methodology. Indirectly, our results may also be helpful for verifying the theoretical models employed to filter out relativistic and quasidegeneracy effects on correlation energies. Comparison of the present results with those recently obtained by other researchers made it possible to get an idea about the accuracy of several sets of

presently available correlation energies for Be-like systems, especially for the ionic ones for which benchmark results have been unavailable so far.

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