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Singlet–triplet energy splitting between ^1D and ^3D ($1s^2\,2s\,nd$), $n = 3$, 4, 5, and 6, Rydberg states of the beryllium atom (^{9}Be) calculated with all-electron explicitly correlated Gaussian functions

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ABSTRACT

Accurate variational nonrelativistic quantum-mechanical calculations are performed for the five lowest ^1D and four lowest ^3D states of the ^{9}Be isotope of the beryllium atom. All-electron explicitly correlated Gaussian (ECG) functions are used in the calculations and their nonlinear parameters are optimized with the aid of the analytical energy gradient determined with respect to these parameters. The effect of the finite nuclear mass is directly included in the Hamiltonian used in the calculations. The singlet–triplet energy gaps between the corresponding ^1D and ^3D states, are reported.

1. Introduction

We have recently investigated the lowest five Rydberg ^1D states of the ^{9}Be isotope of the beryllium atom [1] with very accurate variational quantum mechanical calculations carried out with explicitly correlated Gaussian (ECG) functions [1]. 4200 ECGs were used for each state. It was shown that the difference between the energies relative to the ground ($1s^2\,2s^2$) ^1S state obtained in the calculations and the experimental energies [2] converge to the energy difference between the ground state of the ^{9}Be$^+$ ion and the ground state of the neutral ^{9}Be atom of about 6.77 cm^{-1}. As the calculations were performed at the nonrelativistic level of theory, the difference between the calculated values and the experimental results were due to the relativistic and quantum electrodynamics (QED) effects which were not included in the calculations. The Hamiltonian used in the calculations reported in Ref. [1] was obtained by rigorously separating out the kinetic energy of the motion of the center of mass from the laboratory-frame Hamiltonian. Thus it was explicitly dependent of the mass of the nucleus. Therefore the adiabatic and nonadiabatic effects were directly included in the calculations. It can be expected that the effects are dominated by the adiabatic contribution with the nonadiabatic effect being only a very small correction to the total energy. Thus the total energy correction due to the finite nuclear mass can be likely very accurately determined within the conventional framework using the first-order perturbation theory and the infinite-nuclear-mass (BO) wave function.

In the present work the approach used in the calculations of the ^1D singlet states of ^{9}Be [1] is applied to calculate the energies of the lowest four triplet ^3D states of this atom. The lowest five ^1D beryllium states correspond to the following electronic configurations: ($1s^2\,2p^2$) and ($1s^2\,2s\,nd$), $n = 3$, 4, 5, and 6, while the lowest four ^3D states correspond to the configurations ($1s^2\,2s\,nd$), $n = 3$, 4, 5, and 6 [2]. Among the lowest triplet states there are no states dominated by configurations with two p electrons like the ($1s^2\,2p^2$) configuration. All lowest triplets are dominated by configurations with three s electrons and one d electron. The calculated energies allow for estimating the triple-singlet energy gaps for the corresponding states.

This work is a part of the on-going effort in our laboratory to develop, implement, and apply quantum mechanical methods for very accurately predicting spectra of small atoms. The methods employ explicitly-correlated all-electron Gaussian functions. Beryllium is the smallest system which is hard to describe accurately using any other type of basis functions (i.e. non-Gaussian), due to complications arising in the calculation of the Hamiltonian matrix elements. Beryllium is also a system whose spectra have been measured with very high accuracy; thus it provides a very good model for the validation of the calculation methods. One of the properties which can be used as a stringent test of the accuracy of atomic calculations is the determination of the singlet–triplet

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energy gaps between atomic excited states corresponding to the same electronic configurations. These gaps are determined in the experiment with very high precision. In this work we show that such high precision is now possible in the theoretical calculations involving ECGs. The very accurate calculations, such as those presented in this work, are also useful as benchmarks for testing calculations performed with other methods and, as such, they can contribute to further development of theoretical methods for calculating atomic spectra of increasingly larger and complex atomic systems.

The nonlinear parameters of the ECGs used in our calculations are extensively variationally optimized using a procedure which employs the analytic energy gradient determined with respect to these parameters. The basis set for each state is generated independently in a process which involves adding ECGs in groups and optimizing their nonlinear parameters. A basis set including 8100 ECGs is generated for each of the considered ^3D states. As this is an almost two times the number of functions used in the previous calculations of the ^1D states, additional calculations are performed to increase the basis sets for the ^1D states from 4200 functions to 8100 functions. This allows for the calculations of the singlet–triplet energy gaps to be carried out with the same number of ECGs for both ^1D and ^3D states.

The energies of the Rydberg D states of beryllium were measured with high accuracy and the results are available from the NIST atomic spectra database [2]. The database lists eleven ^1D and ten ^3D states of this system. The transition energies with respect to the ground $^1S\,(1s^2\,2s^2)$ state expressed in wavenumbers are given with the accuracy of two significant figures after the decimal point. We aim to achieve a similar precision in the calculations performed in this work. However, as mentioned, due to neglecting the relativistic and QED effects, the relativistic energies obtained in the present calculations are expected to be off from the experiment by a few wavenumbers. A good estimation of this difference can be obtained by calculating the difference between the nonrelativistic energies of the ground states of ^{9}Be and ^{9}Be$^+$ [3,4] and the corresponding difference obtained from the experiment [2]. As mentioned, the value obtained this way is 6.77 cm^{-1}. This is the value of the difference between the experimental and the calculated nonrelativistic energies of the $(1s^2\,2s\,nd)$ (for both ^1D singlet and ^3D triplet) states should be converging to as the excitation level (i.e. the n value) increases.

The variational approach employing the explicitly correlated Gaussian is currently the only method capable of delivering energies of higher-angular-momentum states for atomic systems with more than three electrons with absolute accuracy of 10^{-7} to 10^{-8} hartree. To achieve this level of accuracy one needs to use large ECG basis sets with the number of functions counted in thousands and one needs to perform a thorough optimization of the ECGs. In the ECG approaches we have developed, the analytic gradient of the energy determined in terms of the Gaussian nonlinear parameters has been used to variationally optimize these parameters. In the present work the aim is to calculate the nonrelativistic energies of the five lowest ^1D states and the four lowest ^3D states at an about 0.01 cm^{-1} accuracy level. This would be similar to the accuracy achieved for the D states of the ^{7}Li atom in our previous calculations [5]. This is the first time the D states of beryllium are calculated with such high accuracy.

The gradient-aided optimization and the related algorithms were described in our previous works [6–8]. These algorithms have been derived using a non-relativistic Hamiltonian that explicitly depends on the mass of the nucleus. This Hamiltonian, called the internal Hamiltonian, $\hat{H}_{\rm int}$, is obtained by rigorously separating the kinetic energy of the center-of-mass motion from the laboratory-frame Hamiltonian. The internal Hamiltonian has the following form in atomic units:

$$\hat{H}_{\rm int} = -\frac{1}{2}\left(\sum_{i=1}^{n}\frac{1}{\mu_i}\nabla^2_{\mathbf{r}_i} + \sum_{\substack{i,j=1\\ i\neq j}}^{n}\frac{1}{m_0}\nabla'_{\mathbf{r}_i}\nabla_{\mathbf{r}_j}\right) + \sum_{i=1}^{n}\frac{q_0 q_i}{r_i} + \sum_{i>j=1}^{n}\frac{q_i q_j}{r_{ij}}, \tag{1}$$

where n is the number of electrons, $\mathbf{r}_i$ is the distance between the ith electron and the nucleus, m_0 is the nucleus mass ($16424.2037 m_e$ for ^{9}Be, where $m_e = 1$ is the electron mass), q_0 is its charge, q_i are electron charges, and $\mu_i = m_0 m_i/(m_0 + m_i)$ are electron reduced masses ($m_i = m_e$, $i = 1, \ldots, n$). Prime indicates the matrix/vector transpose. The explicit dependence of $\hat{H}_{\rm int}$ on the mass of the nucleus allows for direct calculation of energy levels of a particular isotope. This isotope in the present calculation is ^{9}Be. It also allows for performing infinite-nuclear-mass calculations by setting the mass of the nucleus in Eq. (1) to infinity. Such calculations are also done in this work, as they can be directly compared with the conventional Born-Oppenheimer calculations.

2. Basis set and its optimization

The ^1D Rydberg states of Be include a state dominated by $(1s^2\,2p^2)$ configuration, which is the lowest state of this symmetry, and states dominated by $(1s^2\,2s\,nd)$ configurations, which have higher energies. However, in all ^1D states, as well as in ^3D states, the two types of configurations mix to some degree. This mixing reflects the different ways the angular momenta of single electrons are added to form the ^1D and ^3D states. The configuration mixing has to be properly represented by the basis set used in the calculation. As there are five possible M_L values for $L = 2$ and the nonrelativistic energy is degenerate for all five, only states with a particular M_L need to be calculated. In the present work these are the $M_L = 0$ states. Thus, the following all-electron ECGs are used [6]:

$$\phi_k = \left(x_{i_k}x_{j_k} + y_{j_k}y_{i_k} - 2z_{i_k}z_{j_k}\right)\exp\left[-\mathbf{r}'(A_k\otimes I_3)\mathbf{r}\right], \tag{2}$$

where electron labels i_k and j_k are either equal (the $(1s^2\,2s\,nd)$ configurations) or not equal (the $(1s^2 2p^2)$ configurations) to each other and can range from 1 to n. A_k in Eq. (2) is an $n\times n$ symmetric matrix, $\otimes$ is the Kronecker product, I_3 is a 3×3 identity matrix, and $\mathbf{r}$ is a $3n$ vector of the electron coordinates. ECGs (2) have to be square integrable which implies that the A_k matrix has to be positive definite. This can be accomplished by expressing the A_k matrix in the following Cholesky factored form of A_k: $A_k = L_k L_k'$, where L_k is a lower triangular matrix with matrix elements ranging from ∞ to $-\infty$. A_k in such a form is automatically positive definite and the Gaussian is square integrable. In the variational optimization in this work the matrix elements of L_k (not A_k) are the ones that are optimized. As their optimization can be performed without any constraints regarding their values, they are convenient parameters to use.

The so-called spin-free formalism [9,10] is used in this work to implement the correct permutational symmetry of the wave function. In this formalism, an appropriate symmetry projector is applied to the spatial parts of the wave function to impose the desired symmetry properties. The symmetry projector can be constructed using the standard procedure involving Young operators as described, for example, in Ref. [11]. For ^1D and ^3D states of beryllium, the Young operators can be chosen as: $\hat{Y}=(1-\hat{P}_{13})(1-\hat{P}_{24})(1+\hat{P}_{12})(1+\hat{P}_{34})$ and $\hat{Y}=(1+\hat{P}_{12})(1-\hat{P}_{14}-\hat{P}_{34})(1-\hat{P}_{13})$, respectively, where $\hat{P}_{ij}$ denotes the permutation of the spatial coordinates of the ith and jth electrons. As the internal Hamiltonian (1) commutes with all electron permutations, in the calculation of the overlap and Hamiltonian matrix elements, $\hat{Y}$ may be applied to the *ket* basis functions only (as $\hat{Y}^\dagger\hat{Y}$).

Table 1
The convergence of the total variational nonrelativistic finite-nuclear-mass energies (in hartrees) of the $(1s^2\,2s^2)$, $(1s^2\,2s\,nd)$, $n=3, 4, 5, 6$, ^1D states and the $(1s^2\,2s\,nd)$, $n=3, 4, 5, 6$, ^3D states of ^{9}Be with the number of the Gaussian basis functions. ^1D and ^3D $^\infty$Be energies, obtained with 8100 ECGs, are also shown.

	Basis	$1s^2\,2p^2$	$1s^2\,2s\,3d$	$1s^2\,2s\,4d$	$1s^2\,2s\,5d$	$1s^2\,2s\,6d$
^1D ^{9}Be	5400	−14.40735126817	−14.37292484606	−14.35308185745	−14.34295724585	−14.33726584864
	5700	−14.40735128819	−14.37292486218	−14.35308187927	−14.34295727535	−14.33726589351
	6000	−14.40735130269	−14.37292487873	−14.35308189329	−14.34295730524	−14.33726592990
	6300	−14.40735131419	−14.37292489022	−14.35308190235	−14.34295732543	−14.33726596692
	6600	−14.40735132360	−14.37292489927	−14.35308191065	−14.34295734030	−14.33726599355
	6900	−14.40735133127	−14.37292490632	−14.35308191845	−14.34295735300	−14.33726601478
	7200	−14.40735133732	−14.37292491226	−14.35308192498	−14.34295736312	−14.33726603148
	7500	−14.40735134240	−14.37292491611	−14.35308193059	−14.34295737182	−14.33726604509
	7800	−14.40735134646	−14.37292492176	−14.35308193576	−14.34295737953	−14.33726605668
	8100	−14.40735134996	−14.37292492512	−14.35308193996	−14.34295738616	−14.33726606667
$^\infty$Be	8100	−14.40823725876	−14.37382457934	−14.35398288149	−14.34385808410	−14.33816650933
^3D ^{9}Be	5400		−14.38373107153	−14.35690196726	−14.34477209179	−14.33827538070
	5700		−14.38373109063	−14.35690199376	−14.34477214670	−14.33827545744
	6000		−14.38373110458	−14.35690202051	−14.34477218481	−14.33827551811
	6300		−14.38373111539	−14.35690204015	−14.34477221320	−14.33827556492
	6600		−14.38373112396	−14.35690205452	−14.34477223556	−14.33827560397
	6900		−14.38373113125	−14.35690206591	−14.34477225429	−14.33827563641
	7200		−14.38373113705	−14.35690207531	−14.34477226805	−14.33827565848
	7500		−14.38373114210	−14.35690208295	−14.34477228068	−14.33827568079
	7800		−14.38373114662	−14.35690208955	−14.34477229138	−14.33827570468
	8100		−14.38373115044	−14.35690209496	−14.34477229961	−14.33827572560
$^\infty$Be	8100		−14.38463459713	−14.35780391205	−14.34567332942	−14.33917633118u

The ECG basis set for each considered state is obtained in a separate calculation. The basis set is built starting from a small set of ECGs constructed by using a standard orbital basis set (in this case all A_k are diagonal matrices). A procedure to grow the basis set we found effective is to add one ECG at a time to the basis and optimizing its nonlinear parameters (i.e. the matrix elements of its L_k matrix) with the gradient-aided procedure. After addition of each new hundred ECGs all basis functions are reoptimized again using the one-function-at-a-time approach. After cycling over all basis functions 2–5 times in this reoptimization the calculation moves on to adding next hundred functions. The initial forms of the newly added functions are generated by randomly perturbing the parameters of the functions already included in the basis set and choosing the function which after the perturbation contributes the most to the total energy. After a function is generated it is checked for linear dependency with all other functions in the basis set. Linear dependencies between basis functions are undesirable because they may cause inaccuracies in the computed energies or even a complete failure of the calculation. If a linear dependency is found, the function is rejected and a new function is generated. Also, after optimization (reoptimization) each function is checked for linear dependency and, if any is detected, the function is reset to it original form before the optimization. In this way the linear-dependency problem is controlled. A more detailed description of the procedure can be found in our previous works [5,6,8]. The basis sets are only optimized for the states of the ^{9}Be isotope. For Be with an infinite nuclear mass ($^\infty$Be) only the linear expansion coefficients of the wave functions in terms of the ECGs are reoptimized. This is done by solving the secular equation while the basis functions are taken from the calculations of the corresponding states of ^{9}Be. Such an approach is justified by the observation made in our previous calculations that the change of the wave function due to setting m_0 to infinity is small and very little can be gained by reoptimizing the nonlinear parameters.

3. Results

The generation of the ECG basis sets for the considered states is by far the most time consuming step of the calculations. As mentioned before the basis set for each state is grown to the size of 8100 ECGs. This assures that the relative energies between states are determined with the accuracy of about 0.01–0.04 cm^{-1} or better. In Table 1 the convergence of the total energies of the five ^1D states and four ^3D states considered in the calculations is shown for the basis set increasing from 5400 to 8100 ECGs. As one notices the convergence is not quite uniform. As expected, it is better for the lower states than for the higher ones. In Table 1 we also show the infinite-nuclear-mass results calculated in the basis sets of 8100 ECGs for both ^1D and ^3D states. These latter values can be compared with the energies obtained in conventional BO calculations. Also the differences between the ^{9}Be and $^\infty$Be energies give a very accurate estimation of the nuclear-mass effect in the total energies of the D states.

An interesting feature, which shows in the results, is the absence of the $1s^22p^2$ state among the ^3D states and it presence among the ^1D states. The experiment [2] confirms this prediction. It likely results from the singlet $(1s^2\,2p^2)$ (or more general $(1s^2\,np\,mp)$) configurations having lower energies than the corresponding triplet configurations. This difference in energies is also the reason why more ECGs with different i_k and j_k (see Eq. (2)) appear in the basis sets of the ^1D states than of the ^3D states. For example, in the 7 500 ECG basis set of the $^1D\,(1s^2\,2s\,6d)$ state there are 1741 ECGs with different i_k and j_k, while in the 7 500 ECG basis set of the $^3D\,(1s^2\,2s\,6d)$ state there are only 595 such ECGs. This also shows that the ^1D states of Be have a more significant $(1s^2\,np\,mp)$ character than the ^3D states.

The convergence of the relative energies for the considered states with respect to the $^1S\,(1s^2\,2s^2)$ state is shown in Table 2. These relative energies are compared with the experimental energies [2]. As one can see, the difference between the experimental energies and the calculated ones converges to the difference between ^{9}Be and ^{9}Be$^+$ for both ^1D and ^3D states. This is an expected behavior because this difference is due to not accounting for the relativistic and QED effects in the present calculations. The magnitudes of these effects become progressively closer for higher lying $1s^22snd$ states because the excited nd electron contributes increasingly less to the effects as its excitation level increases. Eventually the relativistic contribution to the total energy of the $(1s^2\,2s\,nd)$ states becomes very similar to this contribution for the ground state of ^{9}Be$^+$ (equal to 6.77 cm^{-1}). For example, for the $(1s^2\,2s\,6d)$ ^1D and ^3D states the values are 6.93 and 6.75 cm^{-1}, respectively. This explains the convergence pattern of Δ(exp. – calc.) shown in Table 2.

Table 2
The convergence of the nonrelativistic energies of the $(1s^2 2s^2, 1s^2 2snd)$, $n = 3, 4, 5, 6\ ^1D$ states and the $(1s^2 2snd)$, $n = 3, 4, 5, 6\ ^3D$ states of ^{9}Be with the number of the Gaussian basis functions. The energies are determined with respect to the ground $(1s^2 2s^2)\ ^1S$ state [3]. The energy corresponding to the $(1s^2 2s \infty d)$ state is equal to the ground state energy of the $^9Be^+$ ion [4]. Δ(exp. – calc.) is the difference between the experimental and the calculated (with 8100 ECGs) relative energies. All values are given in cm^{-1}. The values in parentheses are estimated uncertainties due to the finite size of the basis.

	Basis	$1s^2\,2s^2$	$1s^2\,2s\,3d$	$1s^2\,2s\,4d$	$1s^2\,2s\,5d$	$1s^2\,2s\,6d$	$1s^2\,2s\,\infty\,d$
$^1D\ ^9$Be	5400	56 862.4172	64 418.1435	68 773.1761	70 995.2715	72 244.3888	
	5700	56 862.4128	64 418.1400	68 773.1714	70 995.2651	72 244.3790	
	6000	56 862.4097	64 418.1364	68 773.1683	70 995.2585	72 244.3710	
	6300	56 862.4071	64 418.1338	68 773.1663	70 995.2541	72 244.3629	
	6600	56 862.4051	64 418.1319	68 773.1645	70 995.2508	72 244.3570	
	6900	56 862.4034	64 418.1303	68 773.1628	70 995.2480	72 244.3524	
	7200	56 862.4021	64 418.1290	68 773.1613	70 995.2458	72 244.3487	
	7500	56 862.4009	64 418.1282	68 773.1601	70 995.2439	72 244.3457	
	7800	56 862.4000	64 418.1269	68 773.1590	70 995.2422	72 244.3432	
	8100	56 862.3993 (100)	64 418.1262 (200)	68 773.1580 (200)	70 995.2407 (200)	72 244.3410 (300)	
	8000						75 185.8656
	Experiment	56 882.43	64 428.31	68 780.86	71 002.34	72 252.27	75 192.64
	Δ(exp. – calc.)	20.03	10.18	7.70	7.10	6.93	6.77
$^3D\ ^9$Be	5400		62 046.4512	67 934.7590	70 596.9589	72 022.8222	
	5700		62 046.4470	67 934.7531	70 596.9468	72 022.8053	
	6 000		62 046.4439	67 934.7473	70 596.9385	72 022.7920	
	6300		62 046.4416	67 934.7430	70 596.9323	72 022.7817	
	6600		62 046.4397	67 934.7398	70 596.9273	72 022.7732	
	6900		62 046.4381	67 934.7373	70 596.9232	72 022.7660	
	7200		62 046.4368	67 934.7352	70 596.9202	72 022.7612	
	7500		62 046.4357	67 934.7336	70 596.9175	72 022.7563	
	7800		62 046.4347	67 934.7321	70 596.9151	72 022.7511	
	8100		62 046.4339 (200)	67 934.7309 (200)	70 596.9133 (300)	72 022.7465 (400)	
	8000						75 185.8656
	Experiment		62 053.72	67 941.66	70 603.76	72 029.50	75 192.64
	Δ(exp. – calc.)		7.29	6.93	6.85	6.75	6.77

The ground state energy of ^{9}Be, $E(^9\text{Be}) = -14.666435504$ hartree, is taken from Ref. [3].
The ground state energy of $^9Be^+$, $E(^9\text{Be}^+) = -14.3238634944$ hartree, is taken from Ref. [4].

Table 3
Calculated and experimental, singlet–triplet (s–t), ^1D-^3D, energy differences (in cm^{-1}) between states of ^{9}Be corresponding to the electronic configurations the $(1s^2\,2s\,nd)$, $n = 3, 4, 5$, and 6. The total energies for both singlet and triplet states used in the s–t energy-difference calculation are obtained with 8100 ECGs. The values in parenthesis are estimated uncertainties.

	$1s^2\,2s\,3d$	$1s^2\,2s\,4d$	$1s^2\,2s\,5d$	$1s^2\,2s\,6d$
Calculated	2371.69 (1)	838.43 (1)	398.33 (2)	221.59 (2)
Experimental	2374.59	839.20	398.58	221.77
Exp. – calc.	2.90	0.77	0.25	0.18

Finally, the total energies of the lowest $(1s^2\,2s\,nd)\ ^1D$ and ^3D states of ^{9}Be allow for the calculation of the singlet–triplet energy gaps and for comparing these gaps with the experiment. In these calculations the lowest $(1s^2\,2p^2)\ ^1D$ state is not included, as it does not have a counterpart in the spectrum of the ^3D states. The results of the singlet–triplet gap calculations are presented in Table 3. As one can see, also in this case the experimental and calculated values get closer as the level of excitation increases. Again, the absence of the relativistic and QED effects in the calculated energies is responsible for the exp. – calc. difference. However, as the core electronic configurations $(1s^2\,2s)$ in the ^1D and ^3D states become increasingly more similar when the Rydberg *nd* electron becomes excited to higher levels and contributes less to the relativistic effects, the difference between the experimental and calculated energy gaps decreases. For the $(1s^2\,2s\,6d)$ it is only equal to 0.18 cm^{-1}.

4. Summary

This work presents the first high-accuracy calculations of the four lowest ^3D states of the ^{9}Be atom. Up to 8100 all-electron explicitly correlated Gaussian functions are used for each state and their exponential parameters are extensively optimized using a procedure which utilizes the energy gradient determined with respect to these parameters. It is shown that, as expected, the difference between the experimental and calculated relative energies determined with respect to the ground $^1S\ (1s^2\,2s^2)$ state converges with the increasing level of the electronic excitation to the difference between the experimental and calculated ionization potentials of ^{9}Be. It is also shown that the singlet–triplet gap between the experimental and calculated energies of the corresponding ^1D and ^3D states becomes smaller with the increasing level of excitation. In order to see full convergence of the experimental and calculated energies at all excitation levels the relativistic and QED effects need to accounted for in the calculations. The capabilities to do such calculations are hard to describe accurately currently being explored.

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