

1D states of the beryllium atom: Quantum mechanical nonrelativistic calculations employing explicitly correlated Gaussian functions

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Very accurate finite-nuclear-mass variational nonrelativistic calculations are performed for the lowest five 1D states ($1s^2 2p^2$, $1s^2 2s^1 3d^1$, $1s^2 2s^1 4d^1$, $1s^2 2s^1 5d^1$, and $1s^2 2s^1 6d^1$) of the beryllium atom (^9Be). The wave functions of the states are expanded in terms of all-electron explicitly correlated Gaussian functions. The exponential parameters of the Gaussians are optimized using the variational method with the aid of the analytical energy gradient determined with respect to those parameters. The calculations exemplify the level of accuracy that is now possible with Gaussians in describing bound states of a four-electron system where some of the electrons are excited into higher angular states.

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I. INTRODUCTION

We recently investigated the Rydberg series of 2D states of the lithium atom in very accurate quantum-mechanical calculations carried out with explicitly correlated Gaussian functions [1,2]. A total of nine states were computed. For the upper states the results obtained in the calculation enabled refinement of the experimentally determined energies of those states. Rydberg D states have also been measured with high accuracy for the beryllium atom, and the corresponding data are gathered in the NIST atomic spectra database [3]. The database lists eleven 1D and ten 3D states of this system. In the lithium calculations we noticed that the difference between the energies of the 2D states calculated at the nonrelativistic level of theory with the finite-nuclear-mass approach and the experimental energies become almost constant at higher quantum numbers, indicating that the relativistic and quantum electrodynamic (QED) corrections for the states corresponding to those numbers are virtually identical. The calculations also showed that the difference converges to the energy difference between the ground-state energies of Li and Li^+ as it should. This is because by exciting the valence electron to increasingly higher 2D states we essentially remove it from the atom and form the $\text{Li}^+ + e^-$ system. One aim of the present calculations is to test if a similar convergence occurs for a four-electron atom where the relativistic and QED corrections are considerably larger in magnitude.

The variational approach we developed that employs the explicitly correlated Gaussians for describing excited higher angular momentum states of small atoms is currently the only method capable of delivering energies of these types of states for atomic systems with more than three electrons with an absolute accuracy of 10^{-7} – 10^{-8} hartree. An important feature of the method that enables achieving the high accuracy is the use of the analytic gradient of the energy in the variational optimizations of the exponential parameters of the Gaussians. In this work we test what level of energy convergence can be achieved with the method for the five lowest 1D Rydberg states of the beryllium atom. Can the sub- 0.01-cm^{-1} accuracy

achieved for the D states of the ^7Li atom [1] be also achieved for ^9Be ? The states considered in this work correspond to the following electronic configurations: $1s^2 2p^2$, $1s^2 2s^1 3d^1$, $1s^2 2s^1 4d^1$, $1s^2 2s^1 5d^1$, and $1s^2 2s^1 6d^1$. These states are calculated with high accuracy.

The gradient-aided optimization and related algorithms were described in our previous works [2,4,5]. These algorithms were derived using a nonrelativistic Hamiltonian that explicitly depends on the mass of the nucleus. This Hamiltonian, called the internal Hamiltonian \hat{H}_{int} is obtained by rigorously separating the kinetic energy of the center-of-mass motion from the laboratory-frame Hamiltonian. It has the following form in atomic units:

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

where n is the number of electrons, \mathbf{r}_i is the distance between the i th electron and the nucleus, m_0 is the nucleus mass ($16424.2037m_e$ for ^9Be , 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 ($m_i = m_e$, $i = 1, \dots, n$). Prime indicates the matrix or vector transpose.

Because \hat{H}_{int} is explicitly dependent on the mass of the nucleus, it allows the direct calculation of energy levels of a particular isotope without resorting to accounting for the finite mass of the nucleus using the perturbation approach. It also allows infinite-nuclear-mass (INM) calculations by setting the mass of the nucleus in Eq. (1) to infinity. Since the results of such calculations can be directly compared with conventional calculations performed with an infinite nuclear mass, we have included the INM results in this work.

II. BASIS SET AND ITS OPTIMIZATION

While the wave functions of higher 1D states of Be are described as corresponding to the $1s^2 2s^1 nd^1$ configurations,

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the lowest state corresponds to the $1s^2 2p^2$ configurations. This indicates that in all 1D states the two types of configurations mix to some extent. This mixing reflecting the different ways the angular momenta of single electrons are added to form a 1D state has to be properly represented by the basis set used in the calculations. Because there are five degenerate states for each 1D energy level (the states correspond to five different values of the M_L quantum number), one needs to perform calculations for only one of them. In this work we have calculated the $M_L = 0$ states. An appropriate explicitly correlated Gaussian basis set for such states consists of the following functions [2]:

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

where electron labels i_k and j_k are either equal or not equal 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. Gaussians (2) have to be square integrable which implies that the A_k matrix has to be positive definite. To make it happen we use 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. The advantage of using A_k as $L_k L_k'$ in the variational minimization of the energy is that this minimization can be carried out with respect to the L_k parameters without any constraints regarding their values.

In the approach employed in the present calculations we use the spin-free formalism 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. [6]. For 1D states of beryllium, the Young operator can be chosen as $\hat{Y} = (1 - \hat{P}_{13})(1 - \hat{P}_{24})(1 + \hat{P}_{12})(1 + \hat{P}_{34})$, where \hat{P}_{ij} denotes the permutation of the spatial coordinates of the i th and j th electrons. Since 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 $\hat{Y}^\dagger \hat{Y}$).

The variational optimization of the basis set for each of the five states considered in this work has been performed separately. For each set of basis functions, the L_k parameters

and the i_k and j_k indices were optimized. As mentioned, the analytical gradient was employed in the minimization of the energy with respect to the L_k parameters. A more detailed description of the procedure can be found in our previous works [1,2,5]. The basis sets for the considered states were only optimized for ^9Be . In the case of the infinite nuclear mass ($^\infty\text{Be}$), we only reoptimized the linear expansion coefficients in the basis functions, because the change in the wave function due to setting m_0 to infinity is relatively small.

III. RESULTS

The most time-consuming step of the calculations was the generation of the Gaussian basis sets for the considered states. The basis set for each state was grown from a small number of randomly chosen number of functions to the size of 4200 functions. The growing process involved adding subsets of 100 functions to the basis and optimizing them one by one with the gradient-aided optimization procedure. At this stage, the i_k and j_k indices involved in the preexponential factor of each Gaussian were also optimized. After the addition of each subset was completed, the whole basis set was optimized by cycling over all functions and optimizing them again one by one. The optimization of basis functions may yield linearly dependencies between basis 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 optimization procedure. In the approach we use, the linear dependencies are eliminated by checking whether each function after its parameters are reoptimized overlaps too much with any other function in the basis set. If this happens the parameters of the function are reset to their values before the reoptimization. We noticed that linear dependencies appear more often for smaller basis sets, but tend to become less frequent as the size of the basis set increases.

In Table I we show the convergence of the energies of the five considered states with the number of functions in the basis set. With the results obtained with 4200 Gaussians we also show estimates by how much the particular energy differs from the estimated exact value. As one notices, the convergence is not quite uniform. It indicates that it is somewhat more difficult to converge the lowest $1s^2 2p^2$ state than the next $1s^2 2s^1 3d^1$ state. For higher states, as expected, the convergence becomes slower as the level of excitation

TABLE I. Convergence of the total variational nonrelativistic finite-nuclear-mass energies (in hartrees) of the $1s^2 2p^2$, $1s^2 2s^1 3d^1$, $1s^2 2s^1 4d^1$, $1s^2 2s^1 5d^1$, and $1s^2 2s^1 6d^1$ 1D states of ^9Be with the number of basis functions. For the largest basis set of 4200 functions, we also show $^\infty\text{Be}$ energies. The values in parentheses indicate the estimated difference between our variational upper bounds and the exact energies.

	Basis	$1s^2 2p^2$	$1s^2 2s^1 3d^1$	$1s^2 2s^1 4d^1$	$1s^2 2s^1 5d^1$	$1s^2 2s^1 6d^1$
^9Be	2100	-14.40734958	-14.37292338	-14.35308024	-14.34295507	-14.33726185
	2400	-14.40735018	-14.37292393	-14.35308080	-14.34295582	-14.33726318
	2700	-14.40735055	-14.37292425	-14.35308114	-14.34295629	-14.33726404
	3000	-14.40735072	-14.37292439	-14.35308137	-14.34295650	-14.33726452
	3300	-14.40735086	-14.37292451	-14.35308148	-14.34295670	-14.33726489
	3600	-14.40735097	-14.37292461	-14.35308157	-14.34295685	-14.33726516
	3900	-14.40735105	-14.37292468	-14.35308165	-14.34295696	-14.33726536
	4200	-14.40735112(40)	-14.37292473(30)	-14.35308171(50)	-14.34295705(60)	-14.33726551(70)
$^\infty\text{Be}$	4200	-14.40823703(40)	-14.37382438(30)	-14.35398265(50)	-14.34385775(60)	-14.33816595(70)

TABLE II. Convergence of the energies (in cm^{-1}) of the $1s^2 2p^2$, $1s^2 2s^1 3d^1$, $1s^2 2s^1 4d^1$, $1s^2 2s^1 5d^1$, and $1s^2 2s^1 6d^1$ 1D states of Be atom determined with respect to the ground 1S ($1s^2 2s^2$) state.^a The calculated energies are compared with the experimental energies. For $^\infty\text{Be}$ only the energies obtained with the largest basis set are shown.

	Basis	$1s^2 2p^2$	$1s^2 2s^1 3d^1$	$1s^2 2s^1 4d^1$	$1s^2 2s^1 5d^1$	$1s^2 2s^1 6d^1$	$1s^2 2s^1 \infty d^1$ ^b
^9Be	2100	56862.79	64418.46	68773.53	70995.75	72245.27	
	2400	56862.66	64418.34	68773.41	70995.58	72244.97	
	2700	56862.58	64418.27	68773.33	70995.48	72244.79	
	3000	56862.54	64418.24	68773.28	70995.43	72244.68	
	3300	56862.51	64418.22	68773.26	70995.39	72244.60	
	3600	56862.48	64418.20	68773.24	70995.36	72244.54	
	3900	56862.46	64418.18	68773.22	70995.33	72244.50	
	4200	56862.45(5)	64418.17(5)	68773.21(5)	70995.31(10)	72244.46(15)	75185.87
$^\infty\text{Be}$	4200	56668.01(5)	64220.72(5)	68575.47(5)	70797.63(10)	72046.84(15)	75190.54
	Experiment [3]	56882.43	64428.31	68780.86	71002.34	72251.27	75192.64
	Difference ^c	-19.98	-10.14	-7.65	-7.03	-6.81	-6.77

^aThe ground-state energy $E(^9\text{Be}) = -14.666435504$ hartree, and $E(^\infty\text{Be}) = -14.667356486$ hartree were taken from Ref. [7]

^bEnergy difference between the ground $1s^2 2s^2$ state of Be and the ground $1s^2 2s^1$ state of Be^+ . $E(^9\text{Be}^+) = -14.3238634944$ hartree and $E(^\infty\text{Be}^+) = -14.3247631764$ hartree [8].

^cDifference between the calculated ^9Be value and the experimental transition energy.

increase (i.e., as n in $1s^2 2s^1 nd^1$ increases). However, overall, even for the highest considered state ($1s^2 2s^1 6d^1$), the estimated error with respect to the exact energy is only 0.000 000 70 hartree. In Table I we also show the INM results calculated in the basis sets of 4200 Gaussians.

In Table II we show the convergence of the relative energies of the five states ^9Be calculated with respect to the ground-state ($1s^2 2s^2$) energy. The relative energies are also shown for $^\infty\text{Be}$. The calculated values are compared with the experimental transition energies [3] and the differences between the experimental and the calculated transition frequencies are shown. As mentioned, these differences are due to the relativistic, QED, and other higher-order effects not accounted for in the calculations.

In Table II we also include the ^9Be electron ionization energy obtained experimentally and in the calculations. This entry is marked as $1s^2 2s^1 \infty d^1$ because removing an electron from the Be atom is equivalent to exciting it to the Rydberg ∞d state. As mentioned, one may expect that as the excitation level increases, the experimental–calculated difference of the transition energies should show convergence to the difference between the experimental and calculated ionization energies, if the calculated energies are obtained at the nonrelativistic level. Upon examination of the values

shown in the table, it is clear that the expected trend indeed occurs. The experimental–calculated difference smoothly converges from below to the value of -6.77 cm^{-1} , which is the difference between the calculated nonrelativistic ionization potential of ^9Be and the experimental value of this potential.

IV. SUMMARY

In this work we have presented high-accuracy calculations of the five lowest 1D states of the ^9Be atom. Up to 4200 all-electron explicitly correlated Gaussian functions were used for each state and their exponential parameters were extensively optimized using a procedure which utilizes the gradient of the energy determined with respect to these parameters. It was shown that, as expected, the difference between the experimental and relative energies determined with respect to the ground 1S $1s^2 2s^2$ state and the corresponding energy calculated at the nonrelativistic level of the theory converges with the increasing level of the electronic excitation to the difference between the experimental and calculated ionization potentials of ^9Be . Since the difference can be primarily attributed to the relativistic and QED effects not yet accounted for in the calculations, it shows that the contribution of these effects becomes almost constant for higher Rydberg states.

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