Assessment of the accuracy the experimental energies of the $^1P^o$ $1s^22s6p$ and $1s^22s7p$ states of ^{9}Be based on variational calculations with explicitly correlated Gaussians

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Benchmark variational calculations are performed for the six lowest states of the $^1P^o$ $1s^22snp$ state series of the ^{9}Be atom. The wave functions of the states are expanded in terms of all-particle, explicitly correlated Gaussian basis functions and the effect of the finite nuclear mass is directly included in the calculations. The exponential parameters of the Gaussians are variationally optimized using the analytical energy gradient determined with respect to those parameters. Besides providing reference non-relativistic energies for the considered states, the calculations also allow to assess the accuracy of the experimental energies of the $^1P^o$ $1s^22s6p$ and $1s^22s7p$ states and suggest their refinement. [http://dx.doi.org/10.1063/1.4742764]

I. INTRODUCTION

The NIST Atomic Spectra Database[1] lists twelve $^1P^o$ states of the beryllium atom. These states correspond to the Rydberg electron configurations $1s^22snp$, where $n = 2, 3, \ldots, 13$. An examination of the energies of these states relative to the ground ^1S $1s^22s^2$ state reveals that higher states in this series have been measured much less precisely than the lower lying states. For example, while for the lowest five states the relative energies with respect to the ground ^2S $1s^22s^1$ state are reported with the precision of two significant digits after the decimal point (in wavenumbers), for the higher states they are reported with only one significant digit after the point and they are placed in parenthesis indicating that some additional issues may be involved in the reported values. In our previous work[2] we performed calculations of the four lowest members of the $^1P^o$ $1s^22snp$ series using all-electron explicitly correlated Gaussian (ECG) functions. Up to 5000 functions have been used for each state. In the present work we increased the number of basis functions and we have included in the calculations two additional states in the series, the $1s^22s6p$ and $1s^22s7p$ states. The calculations not only provided more accurate energies of the studied states, but also allow for assessing the accuracy of the experimental energies of the two highest states in the series and for suggesting their refinement. Thus the present work is an example of theoretical calculations assuming a predictive role vis-a-vis the experiment. This happens despite the experimental measurements of the spectra of small atomic systems being usually very accurate.

Improving the accuracy of quantum mechanical calculations of ground and excited states of small atoms has always provided motivation for the development of new, more accurate calculation techniques. As the experimental measurements of the atomic energy levels keep getting better, it is important to continue improving the calculations to match the progress on the experimental side. Much of the modern atomic and molecular spectroscopic data obtained in the measurements has a resolution that exceeds 0.01–0.001 cm^{-1} or even better. However, as the level of the electronic excitation increases, the accuracy of the experiment decreases due to the decreasing intensity of the spectral lines. Thus, for highly excited atomic states the theoretical calculations can provide valuable assistance to experiment. An example of that is presented in this work.

As the number of electrons in the studied atomic system increases the level of difficulty involved in performing very precise calculations on the system also increases. As these types of calculations involve basis functions which depend on the coordinates of all electrons of the system, as well as on the distances between them, one needs to deal with multidimensional integrals involved in calculating the Hamiltonian and overlap matrix elements. The calculation of these matrix elements requires large amount of the computational work which grows as $n^3 \times n!$, where n is the number of electrons in the atom.

Very accurate atomic calculations require that the coupled (correlated) motion of the electrons is very well described by the wave function used in the calculations. Among the methods which are capable to very effectively describe the electron correlation effects, the so called explicitly correlated approaches have been particularly successful. In those approaches the wave function is expanded in terms of basis functions that explicitly depend on the distances between the electrons, as well as on the nucleus–electron distances. When these types of basis functions are used in conjunction with the Rayleigh-Ritz variational method and their linear and nonlinear parameters are extensively optimized, the ground and excited states of atoms can be described with very high accuracy. However, such an optimization usually requires large computational effort. For two- and three-electron

atomic systems, such as the helium and lithium atoms, the explicitly correlated Hylleraas-type basis functions have provided the highest accuracy level in the calculations.[3–6] The wave functions constructed from Hylleraas-type functions can satisfy the Kato cusp conditions,[7] which is a desirable feature in very accurate calculations. Unfortunately, the applicability of Hylleraas-type basis functions is limited to atoms with no more than three electrons due to unresolved issues in calculating the Hamiltonian matrix elements (at least for the general form of the basis functions). Thus in the calculations of atoms with more than three electrons one needs to use alternative explicitly correlated basis functions, which are capable of effectively describing the electron correlation effects and at the same time sufficiently simple to allow analytic evaluation and fast computing of the Hamiltonian matrix elements. The only known type of functions which satisfy these criteria are all-electron ECG functions. They have been applied in the recent high-accuracy calculations of the Be atom and other four-electron atomic systems.[8–12] Very high accuracy was also recently achieved in the ECG calculations of low-lying S and P states of the boron atom.[13]

In this work we continue to study the spectrum of the beryllium atom and consider higher excited Rydberg $^1P^o$ states of this system. The wave functions of the states are expanded in terms of ECGs. The ECG basis set for each state is generated independently in a process involving incremental addition of small groups of functions to the basis and optimizing their nonlinear parameters. The key component of this optimization is the use of the analytical energy gradient determined with respect to the Gaussian nonlinear parameters.

II. METHOD

The standard non-relativistic atomic quantum-mechanical calculations are usually performed with infinite nuclear mass (INM). However in calculations where very high accuracy is desired, the energy needs to include the effect of the finite mass of nucleus. Thus the Hamiltonian used in the calculations needs to explicitly depend on the nuclear mass. Such a Hamiltonian, called here the internal Hamiltonian, is obtained from the laboratory-frame non-relativistic Hamiltonian by rigorously separating out the the center-of-mass motion. Such separation can be done by using a coordinate transformation from the laboratory Cartesian coordinated (LCC) system to a new coordinate system which comprises three coordinates of the center of mass in the LCC system and $3n$ internal Cartesian coordinates, where n is the number of the electrons. The internal coordinates describe the positions of the electrons with respect to the nucleus. By transforming the laboratory-frame Hamiltonian of the atom to the new coordinate system the separation of the operator representing the kinetic energy of the center-of-mass motion from the so-called internal Hamiltonian is achieved (for details see Ref. 14): The internal Hamiltonian has the following form:

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

where $\mathbf{r}_i$ is the distance between the ith electron and the nucleus, m_0 is the nucleus mass ($m_0(^9\mathrm{Be}) = 16\,424.2037 m_e$, where m_e 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. The Hamiltonian (2) describes the motion of n (pseudo)electrons, whose masses are the reduced masses, in the central field of the nuclear charge. We use the term pseudoelectrons because their masses are not the electron masses but the reduced masses. The motion of the pseudoelectrons is coupled through the Coulombic interactions between them, $\sum_{i>j=1}^{n}\frac{q_i q_j}{r_{ij}}$, where $r_{ij} = |\mathbf{r}_j - \mathbf{r}_i|$, as well as through the mass polarization term, $-\frac{1}{2}\sum_{\substack{i,j=1\\ i\neq j}}^{n}(1/m_0)\nabla_{\mathbf{r}_i}\cdot\nabla_{\mathbf{r}_j}$. By setting the mass of the nucleus to infinity in (2) the energy of the atom corresponding to the conventional calculations that assume the INM approximation can be determined.

In this work we consider the Rydberg series of the seven lowest $^1P^o$ states of the beryllium atom. In the orbital approximation these states involve three electrons being in s states and one in a p state resulting in the $1s^2 2snp$ configuration. To effectively describe such a configuration with ECGs the following functions need be included in the basis set:[15]

$$\phi_k = z_{i_k}\exp[-\mathbf{r}'(A_k \otimes I_3)\mathbf{r}], \tag{2}$$

where electron label i_k can vary from 1 to n. A_k in (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 that has the form:

$$\mathbf{r} = \begin{pmatrix}\mathbf{r}_1\\ \mathbf{r}_2\\ \vdots\\ \mathbf{r}_n\end{pmatrix} = \begin{pmatrix}x_1\\ y_1\\ z_1\\ \vdots\\ x_n\\ y_n\\ z_n\end{pmatrix}. \tag{3}$$

As the basis functions (2) are used in expanding wave functions of bound states, they have to be square integrable. This mandates that the A_k matrix is positive definite. This can be easily achieved by using the following Cholesky factored form of A_k:

$$A_k = L_k L_k', \tag{4}$$

where L_k is a lower triangular matrix. In practice, the elements of the L_k matrices and not the elements of the A_k matrices are the parameters which are optimized in our calculations. As A_k is positive definite regardless what the values of the elements of the L_k matrices are, the optimization of these elements can be performed without any restrictions (i.e., by using an unconstrained optimization). It should be noted that the $L_k L_k'$ representation of A_k matrix does not limit the flexibility of

basis functions, because any symmetric positive definite matrix can be represented in a Cholesky factored form.

The required antisymmetry of the wave function is implemented through appropriate symmetry projections applied to each basis function. As the so-called spin-free formalism is used in this work, the spatial symmetry projections need to be constructed. This is done using the Young projection operators, $\hat{Y}$, which are linear combinations of permutational operators, $\hat{P}_\gamma$. Since the Hamiltonian is invariant with respect to all permutations of the electrons, in calculating the overlap and Hamiltonian matrix elements the permutational operators are applied only to the *ket* (or the *bra*). More specifically, the *ket* basis functions in those matrix elements are operated on with the permutation operator $\hat{Y}^\dagger\hat{Y}$ (the dagger stands for conjugate), where the $\hat{Y}$ operator is derived using the appropriate Young tableaux for the state under consideration (for details of the formalism see, for example, Ref. 16). For the single states of beryllium the Young operator can be chosen as $\hat{Y} = (\hat{1} - \hat{P}_{24})(\hat{1} - \hat{P}_{35})(\hat{1} + \hat{P}_{23})(\hat{1} + \hat{P}_{45})$, where the nucleus is labeled as particle 1, and the electrons are labeled as particles 2, ... 6, $\hat{1}$ is the identity operator, and $\hat{P}_{ij}$ is the permutation operator of the spatial coordinates of the ith and jth electrons. As there is 24 possible different permutations of four electrons, each Hamiltonian and overlap matrix element is a sum of 24 different integrals.

III. RESULTS AND DISCUSSION

Each of the six states of the $^1P^o$ series of the beryllium atom considered in this work has been calculated independently. The generation and the optimization of the ECG basis set for each state has been performed for the ^{9}Be isotope and then the basis was used to also calculate the energy levels of $^\infty$Be, i.e., the beryllium atom with infinite nuclear mass. The $^\infty$Be states have been calculated because they can be compared with the results obtained in conventional calculations that involve the INM approximation. As the calculations are performed independently for each of the six states, an issue may arise whether the wave functions of the states are strictly orthogonal and whether the potential lack of the orthogonality affects the accuracy of the calculations. We dealt with this issue before[14] and determined that the approach introduces no inaccuracy in the calculations. Besides, the energies reported in this work are obtained from full diagonalization of the Hamiltonian, and thus, at least within the basis obtained for a particular state, the wave function of that state is orthogonal to the wave functions of other states obtained in the calculations.

The present calculations have been performed using the Rayleigh-Ritz variational scheme. In the variational energy minimization, the matrix elements of the L_k matrices of the basis functions have been optimized. Generating the basis set for a particular state was initiated with a small, randomly chosen set of functions and involved incremental addition of new functions and variationally optimizing them with an approach employing the analytic energy gradient. The new functions were added to the basis set one by one with L_k parameters chosen as a best guess out of several hundred candidates. The parameters of the candidate functions were generated based on the parameters of the functions already included in the set. After a new function was selected, its i_k electron number index and the L_k parameters were optimized. Next the function was checked for any linear dependency with the functions already included in the basis set and, if such linear dependency appeared, the function was rejected and replaced by a new function. This new function was then subject to optimization. After a certain number of new functions (usually a hundred) were added to the basis set, the whole set was reoptimized by cycling over all functions one by one and reoptimizing their L_k parameters. After the parameters of a function were reoptimized, the function was again checked for any linear dependency with all other functions in the set and its parameters were reset to their original values if the linear dependency within a certain predefined threshold occurred. The cyclic optimization of all functions was repeated several times. The process of basis set growing continued until satisfactory convergence was reached for each state. The convergence threshold was set to be about 0.01 cm^{-1} for the transition energy determined with respect to the ground ^1S ($1s^22s^2$) state.

The convergence of the total energies of the the six states of ^{9}Be considered in the calculations with the number of the ECG basis functions is presented in Table I. The energy values are given for basis set sizes changing in increments of 300 starting from 5000. Upon examining the energies one notices that the convergence slows down as the excitation level increases. This is why the calculations for the lowest $1s^22s2p$ state were stopped after reaching the basis set size of 7400, but continued to 10 400 for the highest $1s^22s7p$. The energies obtained for $^\infty$Be are also shown in the table.

Using the total energies of the states from Table I we calculated the corresponding transition energies with respect to the ground ^1S ($1s^22s^2$) state. These transition energies obtained for basis sets with different sizes and their comparison with the experimental transition energies taken from Ref. 1 are shown in Table II. As one can see by examining the convergence of the calculated energies in the table, the target convergence of 0.01 cm^{-1} was reached for all states except perhaps for the last one (the $1s^22s7p$ state).

The difference between the experimental and the calculated relative energies shown in Table II is due to not including in the calculation the relativistic (REL) and quantum electrodynamics (QED) effects. Also one should also note that the experimental energies reported in Ref. 1 for the $^1P^o$ states of ^{9}Be are more accurate for the first five states than for the sixth state. Similar trend is also observed for other atoms. For example, for the lithium atom only first few energies in the ^2D Rydberg series are provided with the accuracy of 0.01 cm^{-1} and, as the excitation level increases, the reported energies become increasingly more inaccurate. We have performed very accurate non-relativistic finite-mass calculations of the ^2D series of lithium states and we showed that the calculated energies can be used to refine the experimental values for some higher states. The refinement was based on the realization that the REL+QED correction to the state energy becomes constant as the excitation level increases.[17] This makes it possible to very accurately estimate the energies of the states corresponding to those higher level excitations by adding this constant, whose value can be very well

TABLE I. The convergence of the total non-relativistic energies for the lowest ^1P states of ^{9}Be with the number of ECGs in the basis set. The energies of $^\infty$Be shown at the bottom of the table were calculated with the largest number of ECGs generated for the corresponding states of ^{9}Be. All values are in hartrees.

	Basis	$1s^22s2p$	$1s^22s3p$	$1s^22s4p$	$1s^22s5p$	$1s^22s6p$	$1s^22s7p$
^{9}Be	5000	−14.472 543 663	−14.392 242 763	−14.361 037 654	−14.346 975 658	−14.339 569 447	−14.335 213 783
	5300	−14.472 543 679	−14.392 242 782	−14.361 037 682	−14.346 975 689	−14.339 569 509	−14.335 213 960
	5600	−14.472 543 691	−14.392 242 796	−14.361 037 700	−14.346 975 712	−14.339 569 560	−14.335 214 123
	5900	−14.472 543 700	−14.392 242 809	−14.361 037 714	−14.346 975 731	−14.339 569 612	−14.335 214 251
	6200	−14.472 543 708	−14.392 242 818	−14.361 037 725	−14.346 975 747	−14.339 569 651	−14.335 214 378
	6500	−14.472 543 715	−14.392 242 828	−14.361 037 735	−14.346 975 760	−14.339 569 682	−14.335 214 496
	6800	−14.472 543 722	−14.392 242 835	−14.361 037 740	−14.346 975 770	−14.339 569 706	−14.335 214 637
	7100	−14.472 543 726	−14.392 242 840	−14.361 037 749	−14.346 975 780	−14.339 569 726	−14.335 214 745
	7400	−14.472 543 730	−14.392 242 845	−14.361 037 754	−14.346 975 788	−14.339 569 743	−14.335 214 841
	7700	...	−14.392 242 850	−14.361 037 758	−14.346 975 795	−14.339 569 758	−14.335 214 923
	8000	...	...	−14.361 037 758	−14.346 975 801	−14.339 569 771	−14.335 214 996
	8300	...	...	−14.361 037 765	−14.346 975 807	−14.339 569 782	−14.335 215 058
	8600	...	...	−14.361 037 768	−14.346 975 812	−14.339 569 793	−14.335 215 104
	8900	...	...	−14.361 037 770	−14.346 975 816	−14.339 569 802	−14.335 215 152
	9200	...	...	...	...	−14.339 569 809	−14.335 215 192
	9500	...	...	...	...	−14.339 569 820	−14.335 215 230
	9800	...	...	...	...	...	−14.335 215 259
	10100	...	...	...	...	...	−14.335 215 290
	10400	...	...	...	...	...	−14.335 215 315
$^\infty$Be		−14.473 451 358	−14.393 143 504	−14.361 938 370	−14.347 876 248	−14.340 470 090	−14.336 115 462

established if very accurate experimental energies are known for a sufficient number of lower lying states in the series, to the non-relativistic energy obtained from the calculations. Using this approach the experimental energies of several high-lying states in the ^2D Rydberg series of lithium were refined in Ref. 17. In this work we apply the procedure to the $^1P^o$ states of beryllium.

The first step of the procedure is to examine the convergence of the difference between the experimental and calculated non-relativistic (exp-calc) energies for the considered states. This can be done using the results in Table III. These results show the differences and how they converge with the number of ECGs used in the calculations. The following observations can be made upon examining the

TABLE II. The convergence of the relative non-relativistic energies of the lowest six ^1P ($1s^22snp$) states of ^{9}Be determined with respect to the ground ^1S ($1s^22s^2$) state ($E_{g.s.} = -14.666\,435\,504\,36$ hartree [11]). All values are in cm^{-1}.

Basis	$1s^22s2p$	$1s^22s3p$	$1s^22s4p$	$1s^22s5p$	$1s^22s6p$	$1s^22s7p$	$1s^22s\infty p$
5000	42 554.34	60 178.35	67 027.08	70 113.33	71 738.81	72 694.77	
5300	42 554.34	60 178.35	67 027.07	70 113.33	71 738.79	72 694.73	
5600	42 554.33	60 178.34	67 027.07	70 113.32	71 738.78	72 694.69	
5900	42 554.33	60 178.34	67 027.07	70 113.32	71 738.77	72 694.66	
6200	42 554.33	60 178.34	67 027.06	70 113.31	71 738.76	72 694.63	
6500	42 554.33	60 178.34	67 027.06	70 113.31	71 738.76	72 694.61	
6800	42 554.33	60 178.34	67 027.06	70 113.31	71 738.75	72 694.58	
7100	42 554.33	60 178.33	67 027.06	70 113.31	71 738.75	72 694.55	
7400	42 554.33	60 178.33	67 027.06	70 113.30	71 738.74	72 694.53	
7700		60 178.33	67 027.06	70 113.30	71 738.74	72 694.52	
8000			67 027.06	70 113.30	71 738.74	72 694.50	
8300			67 027.06	70 113.30	71 738.73	72 694.49	
8600			67 027.06	70 113.30	71 738.73	72 694.48	
8900			67 027.06	70 113.30	71 738.73	72 694.46	
9200					71 738.73	72 694.46	
9500					71 738.73	72 694.45	
9800						72 694.44	
10100						72 694.43	
10400						72 694.43	
Experiment[1]	42 565.35	60 187.34	67 034.70	70 120.49	71 746.09	72 701.8	75 192.64

TABLE III. The convergence of the difference between the experimental and calculated non-relativistic energies of the lowest six ^1P ($1s^2 2snp$) states of ^{9}Be determined with respect to the ground ^1S ($1s^2 2s^2$) state. All values are in cm^{-1}.

Basis	$1s^2 2s2p$	$1s^2 2s3p$	$1s^2 2s4p$	$1s^2 2s5p$	$1s^2 2s6p$	$1s^2 2s7p$	$1s^2 2s\infty p$
5000	11.01	8.99	7.62	7.16	(7.28)	(7.03)	
5300	11.01	8.99	7.63	7.16	(7.30)	(7.07)	
5600	11.02	9.00	7.63	7.17	(7.31)	(7.11)	
5900	11.02	9.00	7.63	7.17	(7.32)	(7.14)	
6200	11.02	9.00	7.64	7.18	(7.33)	(7.17)	
6500	11.02	9.00	7.64	7.18	(7.33)	(7.19)	
6800	11.02	9.00	7.64	7.18	(7.34)	(7.22)	
7100	11.02	9.01	7.64	7.18	(7.34)	(7.25)	
7400	11.02	9.01	7.64	7.19	(7.35)	(7.27)	
7700		9.01	7.64	7.19	(7.35)	(7.28)	
8000			7.64	7.19	(7.35)	(7.30)	
8300			7.64	7.19	(7.36)	(7.31)	
8600			7.64	7.19	(7.36)	(7.32)	
8900			7.64	7.19	(7.36)	(7.34)	
9200					(7.36)	(7.34)	
9500					(7.36)	(7.35)	
9800						(7.36)	
10100						(7.37)	
10400						(7.37)	
Refs. 11 and 18							6.77

data:

- The exp-calc difference is the highest for lowest $1s^2 2s2p$ state in the series (11.02 cm^{-1}) and it decreases to 9.00 cm^{-1} for the $1s^2 2s3p$ state, 7.64 cm^{-1} for the $1s^2 2s4p$ state, and 7.19 cm^{-1} for the $1s^2 2s5p$ state. The limit for this decreasing series can be very accurately determined because it is equal to exciting the atom to the $1s^2 2s\infty p$ state, which is equivalent to removing the electron from the atom. Thus, the exp-calc difference in this case can be determined by subtracting the experimental and calculated energies obtained for ^{9}Be$^+$. This yields the value of 6.77 cm^{-1}.[11,18]
- In the calculations of the ^{7}Li ^2S, $^2P^o$, and ^2D Rydberg series the exp-calc energy difference within each series monotonically converged to the exp-calc energy difference for ^{7}Li$^+$.[17,19,20] It is reasonable to assume that a similar trend should also be observed for the $^1P^o$ $1s^2 2snp$ Rydberg series of ^{9}Be. If this is the case and if we assume that the experimental energies of the four lowest states in the series, i.e., the $1s^2 2snp$, $n = 2, \ldots, 5$, states, are accurate within the reported number of significant digits, the experimental energy of the next state in the series, the $1s^2 2s6p$ state, reported as 71 746.09 cm^{-1}, is, in our view, likely to be somewhat off from the true value. This is because when this energy value is used in calculating the exp-calc energy difference for this state, one gets the value of 7.35 cm^{-1} while any reasonable interpolation (see below) of the 11.02, 9.01, 7.64, 7.19, and 6.77 cm^{-1} exp-calc energy differences corresponding to the $1s^2 2snp$, $n = 2, \ldots, 5$, and $1s^2 2s\infty p$ states gives a value below 7 cm^{-1}.
- If $f(n)$, the interpolant which gives an estimate of the exp-calc energy difference (in cm^{-1}) for a particular value of the quantum number n (assuming notation $1s^2 2snp$) is chosen in the form of an exponent, then the following expression can be obtained:

$$f(n) = 6.77 + 4.25 \exp\left[-0.771(n-1)\right]. \qquad (5)$$

Its values at $n = 5$ and 6 are 6.96 and 6.86 cm^{-1}, respectively. When added to the calculated state energies of 71 738.73 and 72 694.43 cm^{-1} they allow one to estimate what the experimental energies of the two states should be. The obtained values, 71 745.69 and 72 701.29 cm^{-1}, respectively, are nearly 0.5 cm^{-1} smaller than the energies reported in Ref. 1. It should be noted that this difference may vary somewhat depending on the choice of the interpolant's functional form. The variation, however, rarely exceeds 0.01–0.05 cm^{-1} (or 2–10% in relative terms).

IV. SUMMARY

The lowest six Rydberg $^1P^o$ states of the beryllium atom, ^{9}Be, are investigated with non-relativistic finite-nuclear-mass variational calculations which employ all-electron explicitly correlated Gaussian functions. The ECG basis set for each state is generated independently by incrementally increasing the number of functions and by optimizing their exponential parameters with the use of an approach utilizing the analytical energy gradient determined with respect to these parameters. While 7400 ECGs is more than sufficient to converge the energy of the lowest $1s^2 2s2p$ state with the accuracy higher than 0.01 cm^{-1}, 10 400 ECGs it is still not quite enough to reach this accuracy level for the highest $1s^2 2s7p$ state in the series. When the calculated non-relativistic energies of the four

lowest states in the series are compared with the experimental ones reported in Ref. 1, one notices that the differences become smaller and tend to monotonically converge to the difference between the experimental and the non-relativistic calculated energy of the ground state of $^9Be^+$. By approximating this converging series with an exponential function and by using this function to estimate the exp-calc energy difference for the two highest considered states in the series, i.e., the $1s^22s6p$ and $1s^22s7p$ states, one gets values 6.96 and 6.86 cm^{-1}, respectively. These values added to the best calculated energies provide energy estimates which we claim are more accurate than the experimental energies reported in Ref. 1.

Besides the very well converged non-relativistic energies of the six lowest ^1P states of ^9Be, which can provide a benchmark for future high-accuracy calculations of other four-electron atomic systems, the present work also introduces a refinement procedure for estimating the transition energies of high excited Rydberg states, which are usually measured not as accurately as the energies of the lowest states. If the predicted refined values of the $1s^22s6p$ and $1s^22s7p$ states of ^9Be are confirmed experimentally, the procedure will be applied to other atomic systems in our future works.

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