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Five lowest ^1S states of the Be atom calculated with a finite-nuclear-mass approach and with relativistic and QED corrections

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We have performed very accurate quantum mechanical calculations of the five lowest S states of the beryllium atom. In the nonrelativistic part of the calculations we used the variational method and we explicitly included the nuclear motion in the Schrödinger equation. The nonrelativistic wave functions of the five states were expanded in terms of explicitly correlated Gaussian functions. These wave functions were used to calculate the leading α^2 relativistic correction (α is the fine structure constant) and the α^3 quantum electrodynamics (QED) correction. We also estimated the α^4 QED correction by calculating its dominant component. A comparison of the experimental transition frequencies with the frequencies obtained based on the energies calculated in this work shows an excellent agreement.

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I. INTRODUCTION

In recent works [1–8] we have shown that explicitly correlated Gaussian (ECG) basis functions provide an excellent basis for performing very accurate calculations for ground and excited states of small atoms. We also showed that calculations on atoms with four electrons can be as accurate as for three-electron atoms. To reach such high accuracy the approach used in the calculations has to explicitly include the coupling between the motion of the electrons and the motion of the nucleus and has to account for the leading relativistic and quantum electrodynamics (QED) corrections. In our approach the electron-nucleus motion coupling is achieved by using the finite-nuclear-mass (FNM) approach [9–14] which treats the electrons and the nucleus on equal footing. Thus the Hamiltonian used in the calculations explicitly depends on the coordinates of the electrons and the nucleus. In order to calculate energies and the corresponding wave functions of such Hamiltonian with very high accuracy one needs to use basis sets for expanding the wave functions which explicitly depend on the interparticle distances (i.e., the distances between electrons and the distances between the electrons and the nucleus) and can effectively describe the correlation effects in the system. Explicitly correlated Gaussians we used in the calculations are such functions. The advantage of the correlated Gaussians in atomic and molecular calculations comes from the fact that the Hamiltonian matrix elements, as well as the matrix elements involved in calculating the relativistic and QED corrections, are expressed with relatively simple and compact formulas for these functions. Also, these formulas can be derived in a general form for an arbitrary number of particles. The Hylleraas-type or Slater-type functions do not have this property. However, the well known inability of Gaussians to properly describe the electron-electron and electron-nucleus cusps and somewhat worse efficiency in describing the long-range behavior of the wave function is a drawback inherent to the calculations with Gaussians. The deficiencies of the explicitly correlated Gaussians can be largely overcome by using a larger number of these functions in the wave function expansions.

As the formulas for the Hamiltonian matrix elements can be implemented in a general form for any number of particles in the system (the number of particles is a variable in the calculation), one can, in principle, calculate any atomic system. Naturally, proper angular components have to be included in the Gaussians when the calculation concerns a system with not only s electrons, but also p, d, etc. electrons. We recently implemented p explicitly correlated Gaussians in our atomic code [8] and an implementation of more general forms of the atomic Gaussians that can describe several non-s electrons is forthcoming [15]. The only factor that limits the size of the atomic system one can calculate with all-electron correlated Gaussian functions is the availability of the computer resources for the calculation. As such calculations to be meaningful have to be performed with very high accuracy, they usually require a considerable amount of computer time. The dependency of the calculation time on the number of particles is determined by the number of terms in the operator that needs to be applied to the wave function in order to impose the proper permutational symmetry. In calculations with fully correlated basis functions the number of the permutations is $N!$ (N is the number of identical particles, i.e., electrons) and its value rapidly increases as N becomes large. For a four-electron atom, such as the beryllium atom, $N!=24$ and such a system is certainly within the reach of present day computers. Even a system with six electrons where $N!=720$ can probably still be calculated even though it would require large amounts of computer time. It should be added that the amount of computational work increases not only due to the $N!$ permutations, but also due to progressively larger computational work required for calculating elementary matrix elements and due to a usually larger size of the basis necessary for describing a system containing a larger number of particles.

A very essential feature of Gaussians in atomic calculations is that the Hamiltonian matrix elements calculated with those functions can be easily analytically differentiated with respect to the Gaussian exponential parameters and the energy gradient can be determined. The implementation of the gradient for various types of correlated Gaussians in atomic and molecular calculations have allowed us to considerably improve the ability of the first-principle quantum mechanical calculations to produce results that match high-resolution experimental data [9,10]. The availability of the gradient considerably accelerates the optimizations of the Gaussian parameters which is key in high-accuracy calculations with explicitly correlated Gaussians. The modern experiments involving measurements of atomic electronic transitions are now reaching the relative accuracy of $10^{-8}-10^{-9}$. In our recent calculations of the lowest transition frequency of the Be atom [3] we were able to achieve the experimental accuracy. In the present work we further improved the accuracy of the result reported in [3] and we also performed calculations of three additional excited ^1S states of the Be atom. This allowed us to determine additional transition frequencies.

There are three steps in the present calculations. The first, which is the most time consuming, involves variational calculations of the nonrelativistic wave functions of the considered states with an approach that explicitly accounts for the coupling of the electron-nuclear motion. The second step involves calculations of the leading α^2 relativistic corrections. In the third step the α^3 and α^4 QED corrections are calculated. Both the relativistic and QED corrections were performed using the perturbation theory in the framework of the nonrelativistic QED (NRQED) method [16–18]. The zeroth-order level in this approach is the nonrelativistic Schrödinger equation employed in step one. The QED corrections of the order of α^3 are calculated using the procedure developed by Pachucki *et al.* [19–22] for the wave functions expanded in terms of explicitly correlated Gaussians, but obtained in infinite-nuclear-mass (INM) calculations. The α^4 was estimated using the procedure also developed in those works of Pachucki *et al.*

II. METHOD USED IN THE CALCULATIONS

In the nonrelativistic variational calculations we used the Hamiltonian obtained by separating the center-of-mass motion from the nonrelativistic laboratory frame Hamiltonian. This separation is rigorous and reduces the five-particle problem of the Be atom to a four pseudoparticle problem represented by the following "internal" Hamiltonian, $\hat{H}_{\text{int}}$, expressed in terms of internal Cartesian coordinates with the nucleus placed in the center of the internal coordinate system,

$$\hat{H}_{\text{int}} = -\frac{1}{2}\left(\sum_{i=1}^{4}\frac{1}{\mu_i}\nabla^2_{\mathbf{r}_i} + \sum_{i=1}^{4}\sum_{j\neq i}^{4}\frac{1}{m_0}\nabla_{\mathbf{r}_i}\cdot\nabla_{\mathbf{r}_j}\right) + \sum_{i=1}^{4}\frac{q_0 q_i}{r_i} + \sum_{i=1}^{4}\sum_{i<j}^{4}\frac{q_i q_j}{r_{ij}}, \quad (1)$$

where in atomic units $q_0=4$ (the charge of the nucleus), $q_1=q_2=q_3=q_4=-1$ (the charges of the electrons), $m_0=16424.2037$ (the mass of the ^{9}Be nucleus), μ_i are the reduced electron masses, $\mu_i=m_0 m_i/(m_0+m_i)$, where $m_1=m_2=m_3=m_4=1$. $\mathbf{r}_i$, $i=1,2,3,4$, are the position vectors of the electrons with respect to the nucleus (or the position vectors of the pseudoelectrons with respect to the center of the internal coordinate system), r_i are their lengths, and $r_{ij}=|\mathbf{r}_j-\mathbf{r}_i|$ are the distances between the electrons. The calculations with the $\hat{H}_{\text{int}}$ Hamiltonian have been carried out for finite and infinite masses of the Be nucleus. They yielded the nonrelativistic energies, E_{nonrel}, and the corresponding wave functions. Both sets of the results are reported.

A nonrelativistic atomic wave function is an antisymmetrized product of a spatial function of the internal Cartesian coordinates, $\mathbf{r}=(\mathbf{r}_1', \mathbf{r}_2', \mathbf{r}_3', \mathbf{r}_4')'$ of the four pseudoelectrons (the prime symbol denotes the vector/matrix transposition; $\mathbf{r}$ is a 12×1 vector), and a function the spin coordinates of all the particles in the system, σ,

$$\Psi(\mathbf{r},\sigma) = \hat{A}[\Phi(\mathbf{r})\Omega_{S,M_S}(\sigma)]. \quad (2)$$

The antisymmetrization operator, $\hat{A}$, acts only on the coordinates of the electrons. The spin function $\Omega_{S,M_S}(\sigma)$ is a product of the electronic spin function and the spin function of the nucleus, $\Omega_{S,M_S}=\Omega^e\Omega^N$. Ω^e for the Be states considered in this work is a singlet four-electron wave function. In practical calculations it is more convenient to use a spin-free formalism and apply the appropriate Young operators to the spatial wave function $\Phi(\mathbf{r})$ to implement the symmetry properties of the state under consideration [23].

For the spatial wave function $\Phi(\mathbf{r})$ we use an expansion in terms of the following explicitly correlated s-type Gaussians:

$$\phi_k = \exp[-\mathbf{r}'(A_k\otimes I_3)\mathbf{r}] = \exp[-\mathbf{r}'(L_k L_k\otimes I_3)\mathbf{r}], \quad (3)$$

where $\otimes$ is the Kronecker product symbol, L_k is a 4×4 lower triangular matrix of nonlinear variational parameters, and I_3 is the 3×3 identity matrix. The nonlinear parameters of the Gaussian (3) are represented in the Cholesky factored form, $A_k=L_k L_k'$, to make the function square-integrable for any values of the L_k matrix elements. With this, the optimization of L_k's can be carried out without restrictions (i.e., the L_k matrix elements can be varied in the range $[-\infty,+\infty]$).

In the nonrelativistic calculations in this work we used the variational method and each state was calculated separately. In order to obtain a highly accurate energy and a wave function, the L_k's matrices of the Gaussian basis functions for each state were extensively optimized by performing an energy minimization. In this minimization we employed the analytic gradient of the energy determined with respect to the L_k matrix elements. As we have shown [1–8], the use of the analytic gradient significantly accelerates the optimization process and considerably reduces its computational cost.

In calculating the relativistic effects we used the Dirac-Breit Hamiltonian in the Pauli approximation ($\hat{H}_{\text{rel}}$) [24,25] transformed to the internal coordinate system. For the states with the S symmetry considered in this work $\hat{H}_{\rm rel}$ includes the mass-velocity (MV), Darwin (D), orbit-orbit (OO), and spin-spin (SS) terms,

$$\hat{H}_{\rm rel} = \hat{H}_{\rm MV} + \hat{H}_{\rm D} + \hat{H}_{\rm OO} + \hat{H}_{\rm SS}. \tag{4}$$

In the internal coordinates these operators are

$$\hat{H}_{\rm MV} = -\frac{1}{8}\left[\frac{1}{m_0^3}\left(\sum_{i=1}^{4}\boldsymbol{\nabla}_{\mathbf{r}_i}\right)^4 + \sum_{i=1}^{4}\frac{1}{m_i^3}\boldsymbol{\nabla}^4_{\mathbf{r}_i}\right], \tag{5}$$

$$\hat{H}_{\rm D} = -\frac{1}{2}\pi\left[\sum_{i=1}^{4}\frac{q_0 q_i}{m_i^2}\delta^3(\mathbf{r}_i) + \sum_{i=1}^{4}\sum_{j\neq i}^{4}\frac{q_i q_j}{m_i^2}\delta^3(\mathbf{r}_{ij})\right], \tag{6}$$

$$\begin{aligned}\hat{H}_{\rm OO} = &-\frac{1}{2}\sum_{i=1}^{4}\sum_{j=1}^{4}\frac{q_0 q_i}{m_0 m_i}\left[\frac{1}{r_i}\boldsymbol{\nabla}_{\mathbf{r}_i}\cdot\boldsymbol{\nabla}_{\mathbf{r}_j} + \frac{1}{r_i^3}\mathbf{r}_i\cdot(\mathbf{r}_i\cdot\boldsymbol{\nabla}_{\mathbf{r}_i})\boldsymbol{\nabla}_{\mathbf{r}_j}\right]\\ &+\frac{1}{2}\sum_{i=1}^{2}\sum_{j>i}^{4}\frac{q_i q_j}{m_i m_j}\left[\frac{1}{r_{ij}}\boldsymbol{\nabla}_{\mathbf{r}_i}\cdot\boldsymbol{\nabla}_{\mathbf{r}_j} + \frac{1}{r_{ij}^3}\mathbf{r}_{ij}\cdot(\mathbf{r}_{ij}\cdot\boldsymbol{\nabla}_{\mathbf{r}_i})\boldsymbol{\nabla}_{\mathbf{r}_j}\right],\end{aligned} \tag{7}$$

$$\begin{aligned}\hat{H}_{\rm SS} = &-\frac{2}{3}\pi\sum_{i=1}^{4}\sum_{j>i}^{4}\frac{q_i q_j}{m_i m_j}\delta^3(\mathbf{r}_{ij})(\mathbf{s}_i\cdot\mathbf{s}_j) - \frac{2}{3}\pi\sum_{i=1}^{4}\frac{q_0 q_i}{m_0 m_i}\delta^3(\mathbf{r}_i)\\ &\times(\mathbf{s}_0\cdot\mathbf{s}_i).\end{aligned} \tag{8}$$

In the present calculations we have not included the magnetic anomaly factors for the electrons and the nucleus in the Darwin and spin-spin corrections. The relativistic correction calculations have been performed with the finite and infinite mass of the Be nucleus using the finite- and infinite-mass nonrelativistic wave functions.

The calculations of the α^2 relativistic corrections in this work have been performed by computing the expectation value of the $H_{\rm rel}$ operator with the nonrelativistic FNM wave function, i.e., the wave functions obtained in the calculations with the finite mass of the ^{9}Be nucleus ($\Psi_{\rm FNM}$). We also performed the calculations of the relativistic corrections with the wave function obtained in the infinite-mass calculation ($\Psi_{\rm INM}$). Since the procedure used in this work for calculating the α^3 and α^4 QED corrections was only developed for the infinite-mass wave function only this type of calculations have been performed.

In calculating the QED corrections we used the approach described in the work of Pachucki *et al.* [20]. The leading QED correction for the Be atom that accounts for the two-photon exchange, the vacuum polarization, and the electron self-energy effects can be expressed as [20]

$$\begin{aligned}E_{\rm QED} = &\sum_{i=1}^{4}\sum_{j>i}^{4}\left\{\left[\frac{164}{15}+\frac{14}{3}\ln\alpha\right]\langle\Psi_{\rm INM}|\delta^3(\mathbf{r}_{ij})|\Psi_{\rm INM}\rangle\right.\\ &\left.-\frac{14}{3}\langle\Psi_{\rm INM}|\frac{1}{4\pi}P\left(\frac{1}{r_{ij}^3}\right)|\Psi_{\rm INM}\rangle\right\}\\ &+\sum_{i=1}^{4}\left[\frac{19}{30}-2\ln\alpha-\ln k_0\right]\frac{4q_0}{3}\langle\Psi_{\rm INM}|\delta^3(\mathbf{r}_i)|\Psi_{\rm INM}\rangle.\end{aligned} \tag{9}$$

The above expression does not include the recoil contributions, which are usually much smaller than the leading contributions. The last term in expression (9) is the so-called Araki-Sucher distribution [26–29]. This contribution is determined as the following limit:

$$\begin{aligned}\langle\Psi|P\left(\frac{1}{r^3}\right)|\Psi'\rangle = \lim_{a\to 0}\int &\Psi^*(\mathbf{r})\Psi'(\mathbf{r})\\ &\times\left[\frac{1}{r^3}\Theta(r-a)+4\pi\delta^3(\mathbf{r})(\gamma+\ln a)\right]d\mathbf{r},\end{aligned} \tag{10}$$

where Θ is the step function and γ is the Euler constant. To overcome the usually slow convergence of the highly singular $P(1/r_{ij}^3)$ we used the so-called expectation value identity approach implemented by Pachucki *et al.* [30].

The term involving the so-called Bethe logarithm, $\ln k_0$, in expression (9) is more difficult to calculate for an atom with more than one electron. The Bethe logarithm can be expressed as

$$\begin{aligned}\ln k_0 = -\frac{1}{D}&\langle\Psi_{\rm INM}|\,\boldsymbol{\nabla}\,(\hat{H}_{\rm int}-E_{\rm nonrel})\\ &\times\ln[2(\hat{H}_{\rm int}-E_{\rm nonrel})]\,\boldsymbol{\nabla}\,|\Psi_{\rm INM}\rangle,\end{aligned} \tag{11}$$

where for Be

$$\boldsymbol{\nabla} = \sum_{i=1}^{4}\boldsymbol{\nabla}_i \tag{12}$$

and

$$D = 2\pi q_0\langle\Psi_{\rm INM}|\sum_{i=1}^{4}\delta^3(\mathbf{r}_i)|\Psi_{\rm INM}\rangle. \tag{13}$$

High precision calculations of $\ln k_0$ has been done for some one- and two-electron atoms by Drake [31] and Korobov [32], as well as for the three-electron lithium atom by Yan and Drake [33] and Pachucki *et al.* [20]. More recently values for the Bethe logarithm were also reported for the ground state of Be$^+$ and Li$^-$ and the ground and the first-excited state of the neutral Be atom by Pachucki *et al.* [19,21]. The procedure used to evaluate the Bethe logarithm in those works was based on the integral representation of $\ln k_0$ proposed by Schwartz [34] and refined by Pachucki *et al.* [21]. The procedure developed by Pachucki *et al.* [21] has been used in the present work.

TABLE I. Nonrelativistic energies and expectation values of the operators representing leading relativistic corrections for the lowest ^1S states of the beryllium atom. All values are given in a.u.

State	E_{nonrel}	E_{MV}	E_{D}	E_{SS}	E_{OO}	$\alpha^2 E_{\text{rel}}$	$E_{\text{nonrel}}+\alpha^2 E_{\text{rel}}$
$^\infty$Be, 2 ^1S	−14.667356486	−270.69212	217.17360	10.08885	−0.89182	−0.002360180	−14.669716666
$^\infty$Be, 3 ^1S	−14.418240328	−268.51887	215.71792	9.95185	−0.90013	−0.002329705	−14.420570033
$^\infty$Be, 4 ^1S	−14.370087876	−268.35953	215.61884	9.93707	−0.90594	−0.002327593	−14.372415469
$^\infty$Be, 5 ^1S	−14.351511654	−268.30536	215.58124	9.93522	−0.90777	−0.002326907	−14.353838561
$^\infty$Be, 6 ^1S	−14.342403552	−268.27117	215.54956	9.94361	−0.90854	−0.002326367	−14.344729920
^{9}Be, 2 ^1S	−14.666435504	−270.62515	217.13337	10.08717	−0.91846	−0.002360264	−14.668795768
^{9}Be, 3 ^1S	−14.417335103	−268.45255	215.67805	9.95019	−0.92654	−0.002329792	−14.419664895
^{9}Be, 4 ^1S	−14.369185452	−268.29328	215.57901	9.93542	−0.93234	−0.002327680	−14.371513132
^{9}Be, 5 ^1S	−14.350610346	−268.23914	215.54142	9.93357	−0.93417	−0.002326994	−14.352937341
^{9}Be, 6 ^1S	−14.341502798	−268.20496	215.50976	9.94195	−0.93493	−0.002326455	−14.343829254

The α^4 QED correction is smaller than the leading α^3 correction and can be determined more approximately without affecting the accuracy of the calculations. In the present work only the dominant component of the α^4 correction usually accounting for about 80% of its value was calculated using the following formula developed by Pachucki *et al.* [21],

$$E_{\text{HQED}} \simeq 4\pi q_0^2 \left(\frac{139}{128} + \frac{5}{192} - \frac{\ln 2}{2}\right) \langle \Psi_{\text{INM}} | \sum_{i=1}^{4} \delta^3(\mathbf{r}_i) | \Psi_{\text{INM}} \rangle. \tag{14}$$

The remaining α^4 QED contributions are more difficult to calculate because they involve some singular terms [35,36]. We neglected these contributions in the present calculations.

The numerical values of the fine structure constant and the Hartree-wave-number conversion factor used in this work were taken from [37]. They are: $\alpha = 7.297\,352\,537\,6 \times 10^{-3}$, 1 hartree$= 2.194\,746\,313\,705 \times 10^5$ cm^{-1}.

III. RESULTS

In the first step of the calculations we determined the nonrelativistic FNM variational wave functions and the total energy for the five lowest S states of the Be atom considered in this work. In the calculations the basis set for each state has been grown to the size of 10 000 functions. The growing of the basis set involved gradually adding subsets of 20 functions to the basis set and optimizing each function of the subset, one function at a time. After the addition of each 20 functions the entire basis set was reoptimized in a cyclic optimization where again the parameters of one function at a time were reoptimized using the gradient-based minimization procedure. A stochastic procedure was used to select the initial values of the nonlinear parameters of the added functions. The distribution of these values was chosen based on the parameters of the functions already included in the basis set. When basis size of 10 000 functions was reached for each state, several additional cyclic optimizations were performed of all the functions to generate the final basis set. The present calculations have required several months of continuous computing. The calculations for all five states have been carried out simultaneously on a parallel computer system using either eight or 16 processors per calculation.

In the next step the nonrelativistic FNM wave functions generated with the procedure described above were used to calculate the α^2 relativistic corrections, i.e., the mass-velocity, Darwin, spin-spin interaction, and orbit-orbit corrections. In Table I we show the total nonrelativistic and relativistic energies, and the relativistic corrections calculated with 10 000 Gaussian basis functions and with the finite and infinite mass of the Be nucleus. Increasing the number of the basis functions from 6000, used in our previous calculations for the two lowest S states of Be, to 10 000 resulted in the lowering of the ground state FNM energy from $-14.666\,435\,477$ to $14.666\,435\,504$ a.u. and of the first-excited state from $-14.417\,335\,037$ to $-14.417\,335\,103$ a.u. As expected, the energy gain is somewhat larger for the excited state than for the ground state, but both gains are small enough to assume that the two energies are very well converged with the number of the basis functions. The convergence of the energies for the 4 ^1S, 5 ^1S, and 6 ^1S states can also be expected to be quit good. Some more discussion concerning the convergence is included in the section where the calculated values of the transition energies are presented.

The next step of the calculations involved determination of the leading α^3 and α^4 QED corrections. The results are presented in Table II. Apart from the values of these correc-

TABLE II. α^3 and α^4 QED corrections ($\alpha^3 E_{\text{QED}}$ and $\alpha^4 \delta E_{\text{HQED}}$) for the lowest singlet S states of beryllium atom obtained in the infinite-mass calculations. The Araki-Sucher term, Eq. (10), and the Bethe logarithm, Eq. (11), are also shown. All values are in a.u.

State	$\langle P(1/r_{ij}^3)\rangle/(4\pi)$	$\ln k_0$	$\alpha^3 E_{\text{QED}}$	$\alpha^4 \delta E_{\text{HQED}}$
2 ^1S	−0.583045	5.75035	3.39796×10^{-4}	1.5435×10^{-5}
3 ^1S	−0.594604	5.75129	3.37492×10^{-4}	1.5330×10^{-5}
4 ^1S	−0.596727	5.75121	3.37348×10^{-4}	1.5323×10^{-5}
5 ^1S	−0.597337	5.75049	3.37362×10^{-4}	1.5321×10^{-5}
6 ^1S	−0.597578	5.74895	3.37460×10^{-4}	1.5320×10^{-5}

TABLE III. Transition energies between adjacent ^1S states of Be atom computed using infinite-nuclear mass nonrelativistic energies, and then gradually corrected with the inclusion of finite-nuclear mass, relativistic, and QED effects. All values are in cm^{-1}.

Transition	$2\ ^1S \leftarrow 3\ ^1S$	$3\ ^1S \leftarrow 4\ ^1S$	$4\ ^1S \leftarrow 5\ ^1S$	$5\ ^1S \leftarrow 6\ ^1S$
ΔE_{nonrel} (infinite-nuclear mass)	54674.677(2)	10568.242(3)	4077.009(6)	1998.997(30)
ΔE_{nonrel} (finite-nuclear mass)	54671.219(2)	10567.627(3)	4076.765(6)	1998.876(30)
ΔE_{rel}	54677.907(20)	10568.090(30)	4076.915(40)	1998.994(70)
ΔE_{QED}	54677.401(24)	10568.059(36)	4076.918(50)	1999.016(85)
ΔE_{HQED}	54677.378(30)	10568.057(38)	4076.918(50)	1999.015(85)
Experiment	54677.26(10)	10568.07(10)	4076.87(10)	1998.95(10)

tions we also show in the table the values of $P(1/r_{ij}^3)$ and $\ln k_0$, which, as mentioned, are the most difficult to compute. For the discussion on the accuracy of the procedure to calculate the QED corrections we refer the reader to the work of Pachucki and Komasa [22].

In the last step of this work we calculated the energies corresponding to the transitions between $2\ ^1S \leftarrow 3\ ^1S$, $3\ ^1S \leftarrow 4\ ^1S$, $4\ ^1S \leftarrow 5\ ^1S$, and $5\ ^1S \leftarrow 6\ ^1S$ states. In Table III we show the transition energy values obtained using the INM and FNM nonrelativistic energies, and with energies that include the relativistic and QED corrections. For each value we show the numerical uncertainty determined bases on the level of the convergence of the particular value with the number of basis functions and on other factors contributing to the numerical noise in the calculations.

In the table we also show the experimental transition energies taken from the review paper of Kramida and Martin [38], but originally measured by Johansson [39]. The accuracy of the experimental results can be estimated based on Johansson's statement, which can be found in his paper, that the error in his transition energy measurement should be less than ± 0.05 cm^{-1}. As each experimental transition included in Table III was determined indirectly from two $mP \leftarrow nS$ transitions, it is reasonable to assume the experimental uncertainty to be about 0.10 cm^{-1} (or less).

As one can see, the energies for the $2\ ^1S \leftarrow 3\ ^1S$, $3\ ^1S \leftarrow 4\ ^1S$, $4\ ^1S \leftarrow 5\ ^1S$, and $5\ ^1S \leftarrow 6\ ^1S$ transitions calculated using the FNM nonrelativistic energies augmented with the relativistic and QED corrections differ from the experimental results by 0.12, 0.01, 0.05, and 0.06 cm^{-1}, respectively. This shows that the accuracy level of the present calculations is very high. This is the first time higher excited states of a four-electron atom have been calculated with such an accuracy.

IV. SUMMARY

Explicitly correlated all-electron Gaussian functions have been employed to perform very accurate FNM calculations of the five lowest S states of the beryllium atom. The calculations yielded results that agree with the experimental values within the experimental inaccuracy. The results demonstrate that four-electron atomic systems can now be calculated nearly as accurate as three-electron systems.

As the timing of the variational calculations with all-electron correlated Gaussians scales as the factorial of the number of electrons, the method used in the present work can, at present, be only applied to smaller atomic systems (i.e., to the first row atoms). In an extension of the approach to larger system the $N!$ dependency will have to be reduced. One possibility of dealing with this problem is to use a nonvariational approach such as the coupled cluster method. Monkhorst in his work published in 1987 [40] described how this can be done in an approach that does not assume the Born-Oppenheimer approximation. Perhaps, this is the way to overcome the factorial dependency in the high-accuracy calculations of larger atomic systems.

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