Three lowest S states of $^9Be^+$ calculated with including nuclear motion and relativistic and QED corrections

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(Received 8 February 2008; published 12 June 2008)

We have performed high-accuracy quantum mechanical calculations for the three lowest S states of the beryllium ion ($^9Be^+$). The nonrelativistic part of the calculations was done with the variational approach and explicitly included the nuclear motion (i.e., the finite-nuclear-mass approach). The nonrelativistic wave functions were expanded in terms of explicitly correlated Gaussian functions. These nonrelativistic functions were subsequently used to calculate the leading α^2 relativistic corrections ($\alpha=1/c$) and the α^3 and α^4 QED (quantum electrodynamics) corrections. In the α^4 QED correction we only accounted for its dominant component typically contributing about 80% of the correction. With those the present results are the most accurate ever obtained for $^9Be^+$. They also agree with the experimentally measured transitions within less than 0.1 cm^{-1}.

DOI: 10.1103/PhysRevA.77.062509 PACS number(s): 31.30.J−, 31.15.ac

I. INTRODUCTION

This work is a continuation of our interest in very accurate calculations of energy states of atomic systems with the use of explicitly correlated Gaussian (ECG) basis functions. In recent works [1–4] we showed that for atoms with three and four electrons these types of functions can produce results that agree very well with the most accurate experiments. In the atomic calculations we have employed an approach where the motion of electrons was not separated from the motion of the finite-mass nucleus (the finite-nuclear-mass approach or the FNM approach for short) [5–10]. In such an approach the electrons and the nucleus are treated on equal footing. This necessitates the use of basis functions that explicitly depend on the interparticle distances in expanding the wave function as the motions of the electrons and the nucleus are correlated (coupled). The explicitly correlated Gaussians are these kinds of functions. In general, however, Gaussians are less effective than the Hylleraas-type or Slater-type functions in describing the cusps and the long-range behavior of the wave function. However, the use of the Gaussians leads to much easier integrals that can be analytically calculated using standard procedures. Also, the total energy obtained with a wave function expanded in terms of ECGs can be analytically differentiated with respect to the Gaussian exponential parameters and the energy gradient can be determined. Since an extensive optimization of those parameters is very important in obtaining high-accuracy results with Gaussians, the availability of the analytic gradient is the key in efficiently performing this optimization.

Very accurate calculations on small atomic systems have been carried out for many years. Initially, the primary target has been the helium atom, but more recently the scope of the studied systems has been extended to three and four electron atoms. For example, the recent works on the Li atom [11–15] show the high level of sophistication that has been achieved in atomic calculations.

In order for the theoretical calculations to reproduce high-accuracy experimental results they not only need to include a very well converged nonrelativistic part but they also need to account for even the smallest relativistic and QED (quantum electrodynamics) effects. An effective approach to account for the QED effects in light atoms was developed by Pachucki [16,17]. In his approach the total energy of the system is expanded in powers of the fine structure constant α:

$$E(\alpha) = E_{\mathrm{NR}} + \alpha^2 E_{\mathrm{REL}} + \alpha^3 E_{\mathrm{QED}} + \alpha^4 E_{\mathrm{HQED}} + \cdots . \quad (1)$$

This enables including increasingly higher-order effects in a systematic way in the calculations. The leading terms of the expansion (1), i.e., the nonrelativistic energy E_{NR}, the relativistic correction $\alpha^2 E_{\mathrm{REL}}$, and the highest-order radiative correction $\alpha^3 E_{\mathrm{QED}}$, are well known since early works of Bethe and Salpeter [18], Araki [19], and Sucher [20]. Quite recently formulas for the radiative correction of the order of α^4 ($\alpha^4 E_{\mathrm{HQED}}$) were presented by Pachucki [17]. The expansion (1) provides the theoretical framework for the calculations performed in this work.

The most recent development of our FNM approach with Gaussians for very accurate atomic calculation has been the addition of procedures for calculating relativistic α^2 corrections [1–3]. Those include the mass-velocity and Darwin terms, as well as terms due to magnetic orbit-orbit, spin-spin, and Fermi contact interactions. These corrections, as well as the QED (quantum electrodynamics) corrections of the order of α^3 and α^4, were included in the atomic calculations performed using correlated Gaussians in the works of Pachucki and co-workers [12,21–23]. In the present work we combine the FNM approach for calculating the nonrelativistic energy and α^2 relativistic corrections developed in the Adamowicz group with the infinite-nuclear-mass (INM) approach for calculating the QED corrections developed by Pachucki *et al.* in very accurate calculations of the three lowest S states of the $^9Be^+$ ion.

II. METHOD USED IN THE CALCULATIONS

We consider here a four particle system, the ^{9}Be nucleus and three electrons. Let us denote the masses of the particles by M_i and their charges by Q_i $(i=1,\ldots,4)$. Here, particle 1 is the ^{9}Be nucleus and particles 2, 3, and 4 are the electrons. A transformation of the total nonrelativistic laboratory frame Hamiltonian of the system by separating the center-of-mass motion reduces the four particle problem to a three pseudoparticle problem described by the internal Hamiltonian $H_{\rm INT}$. In this transformation the laboratory Cartesian coordinates, $\mathbf{R}_i$, $i=1,2,3,4$, are replaced by three laboratory coordinates of the center of mass, $\mathbf{r}_0$, plus nine internal coordinates, $\mathbf{r}_i$, $i=1,2,3$, describing the positions of the pseudoparticles. These internal coordinates are coordinates in a Cartesian coordinate system whose origin is placed at the nucleus. The internal Hamiltonian $H_{\rm INT}$ for ^{9}Be$^+$ is

$$H_{\rm INT}=-\frac{1}{2}\left(\sum_{i=1}^{3}\frac{1}{\tilde{\mu}_i}\nabla_{\mathbf{r}_i}^2+\sum_{i=1}^{3}\sum_{j\neq i}^{3}\frac{1}{m_0}\boldsymbol{\nabla}_{\mathbf{r}_i}\cdot\boldsymbol{\nabla}_{\mathbf{r}_j}\right)+\sum_{i=1}^{3}\frac{q_0q_i}{r_i}+\sum_{i=1}^{3}\sum_{i<j}^{3}\frac{q_iq_j}{r_{ij}},\tag{2}$$

where in atomic units $q_0=Q_1=4$, $q_1=Q_2=-1$, $q_2=Q_3=-1$, $q_3=Q_4=-1$, $m_0=M_1=16\,424.2037$, $\tilde{\mu}_i$ are reduced masses: $\tilde{\mu}_i=m_0m_i/(m_0+m_i)$, where $m_1=m_2=m_3=1$. The internal Hamiltonian (2) describes the three "pseudoelectrons" moving in the central potential of the charge of the Be nucleus.

The calculations have been carried out with both the finite and infinite masses of the Be nucleus. The calculations with the infinite mass are equivalent to the INM calculations.

All four particles comprising the ^{9}Be$^+$ ion are fermions: three electrons with spin 1/2 and the nucleus with spin 3/2. Their magnetic moments are: $\boldsymbol{\mu}_i=g_iq_i/(2m_i)\mathbf{S}$, where g is the so-called g factor for the particle. The above relation assumes that the electron g factor is positive. While this is consistent with the convention used by some [24,25], it is different from the one used by others [26]. The reason for using the positive value of the g factor for the electron in this work is related to the use of the expressions for the nucleus-electron Darwin and spin-spin corrections from the works of Khriplovich *et al.* and Lee *et al.* [27,28] where the g factor for the electron has the positive sign.

To describe the relativistic effects in this system, we use the Dirac-Breit Hamiltonian in the Pauli approximation [18,29]. In the Pauli approximation for states with the S symmetry and after the transformation to the internal coordinate system, the Dirac-Breit-Pauli Hamiltonian ($H_{\rm REL}$) describing the leading α^2 relativistic corrections for S states of Be$^+$ is a sum of the mass-velocity (MV), Darwin (D), orbit-orbit (OO), and spin-spin (SS) terms:

$$H_{\rm REL}=H_{\rm MV}+H_{\rm D}+H_{\rm OO}+H_{\rm SS},\tag{3}$$

where

$$H_{\rm MV}=-\frac{1}{8}\left[\frac{1}{m_0^3}\Big(\sum_{i=1}^{3}\nabla_{\mathbf{r}_i}\Big)^4+\sum_{i=1}^{3}\frac{1}{m_i^3}\nabla_{\mathbf{r}_i}^4\right],\tag{4}$$

$$H_{\rm D}=-\frac{1}{2}\pi\left[\sum_{i=1}^{3}\frac{q_0q_i(2\kappa_i+1)}{m_i^2}\delta^3(\mathbf{r}_i)+\sum_{i=1}^{3}\sum_{j\neq i}^{3}\frac{q_iq_j(2\kappa_i+1)}{m_i^2}\delta^3(\mathbf{r}_{ij})\right],\tag{5}$$

$$H_{\rm OO}=-\frac{1}{2}\sum_{i=1}^{3}\frac{q_0q_i}{m_0m_i}\left[\frac{1}{r_i}\boldsymbol{\nabla}_{\mathbf{r}_i}\cdot\boldsymbol{\nabla}_{\mathbf{r}_i}+\frac{1}{r_i^3}\mathbf{r}_i\cdot(\mathbf{r}_i\cdot\boldsymbol{\nabla}_{\mathbf{r}_i})\nabla_{\mathbf{r}_i}\right]-\frac{1}{2}\sum_{i=1}^{3}\sum_{j=1,j\neq i}^{3}\frac{q_0q_i}{m_0m_i}\left[\frac{1}{r_i}\boldsymbol{\nabla}_{\mathbf{r}_i}\cdot\boldsymbol{\nabla}_{\mathbf{r}_j}+\frac{1}{r_i^3}\mathbf{r}_i\cdot(\mathbf{r}_i\cdot\boldsymbol{\nabla}_{\mathbf{r}_i})\nabla_{\mathbf{r}_j}\right]+\frac{1}{2}\sum_{i=1}^{2}\sum_{j>i}^{3}\frac{q_iq_j}{m_im_j}\left[\frac{1}{r_{ij}}\boldsymbol{\nabla}_{\mathbf{r}_i}\cdot\boldsymbol{\nabla}_{\mathbf{r}_j}+\frac{1}{r_{ij}^3}\mathbf{r}_{ij}\cdot(\mathbf{r}_{ij}\cdot\boldsymbol{\nabla}_{\mathbf{r}_i})\nabla_{\mathbf{r}_j}\right],\tag{6}$$

$$H_{\rm SS}=-\frac{2}{3}\pi\sum_{i=1}^{3}\sum_{j>i}^{3}\frac{q_iq_j(\kappa_i+1)(\kappa_j+1)}{m_im_j}\delta^3(\mathbf{r}_{ij})(\mathbf{S}_i\cdot\mathbf{S}_j)-\frac{2}{3}\pi\sum_{i=1}^{3}\frac{q_0q_i(\kappa_0+1)(\kappa_i+1)}{m_0m_i}\delta^3(\mathbf{r}_i)(\mathbf{S}_0\cdot\mathbf{S}_i),\tag{7}$$

where the κ for the electron is $\kappa_i=\kappa_e=1.159\,652\,181\,107\,5\times10^{-3}$ [in agreement with the relation $\kappa_e=(|g_e|-2)/2$ used by Mohr and Taylor [26], where $|g_e|=2.002\,319\,304\,371\,8$ [30]]. The value of κ for the ^{9}Be$^+$ nucleus is (in the above equations the symbols with subscript 0 correspond to the ^{9}Be$^+$ nucleus) $\kappa_0=-1.877\,71$ and it was obtained from the following relation between κ_0, the magnetic moment (μ_0), the mass (m_0), the charge (q_0), and the spin (S_0) of the ^{9}Be$^+$ nucleus: $2\kappa_0+2=\mu_0\frac{2m_0}{q_0}\frac{1}{S_0}$, where the magnetic moment for the ^{9}Be$^+$ nucleus in nuclear magnetons is $\mu_0=-1.177\,49\frac{q_p}{2m_p}$, with q_p and m_p denoting the proton charge and mass, respectively [31].

The high-precision-spectroscopy experiments performed on atoms [32,33] have shown that the Darwin interaction of the nucleus with the electromagnetic field generated by the electrons provides a small contribution to the transition energies. This interaction was theoretically studied by Khriplovich *et al.* [27] and Lee *et al.* [28]. They discussed the Born amplitude for the scattering of a particle with an arbitrary spin in an external electromagnetic field and showed that in the case of an atomic nucleus with spin S_N, mass M_N, and magnetic moment anomaly κ, the Darwin term ($\delta H_{\rm D}$) can, in general, be written as $\delta H_{\rm D}=-\frac{2}{3}\pi\frac{Q_NQ_e}{M_N^2}(2\kappa_N+1)S_N(1+\xi)\delta^3(\mathbf{r})$, where $\xi=0$ when the spin of the nucleus is expressed as a whole number and $\xi=\frac{1}{4S_N}$ when the spin of the nucleus is expressed as a half number. For ^{9}Be$^+$ $S_N=\frac{3}{2}$, and $\delta H_{\rm D}=-\frac{7}{6}\pi\frac{Q_NQ_e}{M_N^2}(2\kappa_N+1)\delta^3(\mathbf{r})$. Thus in the notation used in this work, the operator representing the Darwin nucleus-electron interaction in ^{9}Be$^+$ has the following form:

TABLE I. A comparison of the spin-spin electron-electron $[\langle H_{SS}(ee)\rangle]$ and nucleus-electron $[\langle H_{SS}(ne)\rangle]$ interaction effects calculated for the lowest three S states of the $^9Be^+$ ion with different sizes of the basis set. All values are in a.u.

State	Basis	$\langle H_{SS}(ee)\rangle$	$\langle H_{SS}(ne)\rangle$
$2S$	6000	9.95373	-7.19693×10^{-3}
	7000	9.95312	-7.19721×10^{-3}
	8000	9.95304	-7.19722×10^{-3}
$3S$	6000	9.68272	-7.57758×10^{-3}
	7000	9.68270	-7.57769×10^{-3}
	8000	9.68267	-7.57769×10^{-3}
$4S$	6000	9.62827	-7.65527×10^{-3}
	7000	9.62672	-7.65533×10^{-3}
	8000	9.62672	-7.65542×10^{-3}

$$\delta H_D = -\frac{7}{6}\pi\sum_{i=1}^{3}\frac{q_0 q_i(2\kappa_0+1)}{m_0^2}\delta^3(\mathbf{r}_i). \tag{8}$$

This form was used in the calculations. We should add that in our FNM approach the δH_D term appears naturally as a result of treating the nucleus and the electrons on equal footing. This term is analogical to the term describing the Darwin electron-electron interaction. A similar origin has the last term in the spin-spin interaction Hamiltonian H_{SS}. It arises from accounting for the magnetic interactions between the particles involved in $^9Be^+$. Also, similarly to δH_D, this term has a negligible contribution to the total relativistic correction, but was included for consistency with our FNM model. The evidence of the much smaller magnitude of the spin-spin nucleus-electron interaction in comparison with the spin-spin electron-electron interaction is presented in Table I. As one can see, the former effect is more than three orders of magnitude smaller than the latter and it has very little effect on the transition energies. However, since it determines the hyperfine splitting of the energy levels and can be measured we included the results included in Table I.

In this work the α^2 relativistic corrections have been calculated as the expectation value of the H_{REL} operator with the nonrelativistic FNM wave function, i.e., the wave function obtained in the calculation with the finite mass of the Be nucleus (Ψ_{FNM}). The calculation of the QED corrections of the order of α^3 and α^4 were performed using the INM wave functions Ψ_{INM}. In general, Ψ_{FNM} (and also Ψ_{INM}) is an antisymmetrized product of a function of the internal coordinates $\mathbf{r}$ and a function of the spin coordinates σ:

$$\Psi_{FNM} = \hat{A}[\Phi(\mathbf{r})\Omega_{S,M_S}(\sigma)]. \tag{9}$$

The spin function $\Omega_{S,M_S}(\sigma)$ is a product of the electronic spin function and the nuclear spin function: $\Omega_{S,M_S}=\Omega^e\Omega^N$. For the three states of $^9Be^+$ considered in this work we used $\Omega^e = \frac{1}{\sqrt{6}}[2\alpha(1)\beta(2)\alpha(3)-\beta(1)\alpha(2)\alpha(3)-\alpha(1)\alpha(2)\beta(3)]$.

The leading QED correction, which accounts for the effects due to the two-photon exchange, the vacuum polarization, the electron self-energy, etc., has the following form (it was taken from the work of Pachucki *et al.* [21] on the lithium atom):

$$E_{QED} = \sum_{i=1}^{3}\sum_{j>i}^{3}\left\{\left[\frac{164}{15}+\frac{14}{3}\ln\alpha\right]\langle\Psi_{INM}|\delta^3(\mathbf{r}_{ij})|\Psi_{INM}\rangle - \frac{14}{3}\langle\Psi_{INM}|\frac{1}{4\pi}P\left(\frac{1}{r_{ij}^3}\right)|\Psi_{INM}\rangle\right\} + \sum_{i=1}^{3}\left[\frac{19}{30}-2\ln\alpha-\ln k_0\right]\frac{4q_0}{3}\langle\Psi_{INM}|\delta^3(\mathbf{r}_i)|\Psi_{INM}\rangle, \tag{10}$$

where the recoil contributions were omitted. The above expression contains the so-called Araki-Sucher distribution P [19,20,34,35], which is defined as the following limit:

$$\langle\Psi|P\left(\frac{1}{r^3}\right)|\Psi'\rangle = \lim_{a\to0}\int\Psi^*(\mathbf{r})\Psi'(\mathbf{r})\left[\frac{1}{r^3}\Theta(r-a) + 4\pi\delta^3(\mathbf{r})(\gamma+\ln a)\right]d\mathbf{r}, \tag{11}$$

where Θ is the step function and γ is the Euler constant. Because of a highly singular character of $P(1/r_{ij}^3)$ a special technique based on an expectation-value identity approach, which accelerates the convergence, has been employed [36]. Another difficult to calculate quantity in Eq. (10) is the many-electron Bethe logarithm $\ln k_0$ defined as

$$\ln k_0 = -\frac{1}{D}\langle\Psi_{INM}|\nabla(H_0-E_0)\ln[2(H_0-E_0)]\nabla|\Psi_{INM}\rangle, \tag{12}$$

where for Be^+

$$\nabla = \sum_{i=1}^{3}\nabla_i \tag{13}$$

and

$$D = 2\pi q_0\langle\Psi_{INM}|\sum_{i=1}^{3}\delta^3(\mathbf{r}_i)|\Psi_{INM}\rangle. \tag{14}$$

Until recently $\ln k_0$ has been known with a high precision only for one- and two-electron systems (see, e.g., [37–39]). A few years ago Yan and Drake [40] and Pachucki *et al.* [21] reported high quality results including $\ln k_0$ for the ground and the first excited state of the lithium atom and later also for the ground state of Be^+ and Li^- and for the ground and the first excited state of Be [12,22]. The evaluation of $\ln k_0$ in those works was based on the integral representation used by Schwartz [41] and reformulated in a more concise form by Pachucki *et al.* [22]. In the calculation of $\ln k_0$ in the present work we used the procedure of Pachucki *et al.* [22]. More details concerning the computational implementation of the procedure can be found that work.

The α^4 QED term can be approximated by its dominant component that typically accounts for about 80% of the total value of the correction. This dominant component can be calculated as correction [22]:

$$E_{\mathrm{HQED}} \simeq 4\pi q_0^2 \left(\frac{139}{128} + \frac{5}{192} - \frac{\ln 2}{2} \right) \langle \Psi_{\mathrm{INM}} | \sum_{i=1}^{3} \delta^3(\mathbf{r}_i) | \Psi_{\mathrm{INM}} \rangle. \quad (15)$$

The remaining α^4 contributions, neglected here, involve singular terms which are more difficult to calculate [42,43].

The nonrelativistic wave functions for the three S states of $^9Be^+$ have been expanded in terms of the following ECG basis functions:

$$\phi_k = \exp[-\mathbf{r}'(A_k \otimes I_3)\mathbf{r}] = \exp[-\mathbf{r}'(L_k L_k' \otimes I_3)\mathbf{r}], \quad (16)$$

where $\otimes$ is the Kronecker product symbol, $\mathbf{r}$ is a vector of the internal Cartesian coordinates, $\mathbf{r}_1$, $\mathbf{r}_2$, and $\mathbf{r}_3$, of the three pseudoelectrons ($\mathbf{r}$ is a 9×1 vector), L_k is lower triangular matrix of nonlinear variational parameters (L_k is a 3×3), and I_3 is the 3×3 identity matrix. To ensure the proper permutational symmetry of the two electrons, the appropriate symmetry projectors were applied to the basis functions.

To calculate the nonrelativistic energies and to obtain the corresponding wave functions we used the variational method. For a given basis size K and a corresponding set of nonlinear parameters $\{L_k, k=1,\ldots,K\}$, the nonrelativistic energy of a particular state, E^i $(i=1,2,3,\ldots)$, was obtained as a solution of the secular equation:

$$H(\{L_k\})c^i = E^i S(\{L_k\})c^i, \quad (17)$$

where H and S are the $K\times K$ Hamiltonian and overlap matrices, respectively, and where c^i is a column vector whose components c_k^i are the linear coefficients of the basis functions. In order to get highly accurate energies and wave functions it is necessary to minimize the energy with respect to the elements of the $\{L_k\}$ matrices. We employed the analytic gradient in this task. The calculation of the analytic gradient requires the knowledge of the analytic derivatives of the $H(\{L_k\})$ and $S(\{L_k\})$ matrix elements with respect to the elements of $\{L_k\}$. The use of the analytic gradient significantly accelerates the optimization process and allows us to achieve higher accuracy at a lower computational cost.

The nonrelativistic, variational, FNM calculations have been performed separately for each state of the three states of Be^+, i.e., the nonlinear parameters $\{L_k\}$ were optimized independently for each state. Since the FNM and INM wave functions differ very little, there was no need to reoptimize the nonlinear parameters for the INM wave function Ψ_{INM}. Our experience from the previous atomic calculations shows that it is sufficient to only reoptimize the linear expansion coefficients c_k^i by solving the secular equation for the infinitely heavy mass of the nucleus in the Hamiltonian. This results in a slight adjustment of the linear coefficients that fully accounts for the difference between the INM and FNM wave functions.

III. RESULTS

In the first step of the calculations we determined the nonrelativistic FNM variational wave functions for the three lowest S states of the Be^+ ion considered in this work using the internal Hamiltonian (2). As mentioned above, the calculations for each state have been done separately, and for each state the basis set was grown to the size of up to 8000 functions. This was performed by 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 (again, one function at a time). The new functions added to the basis set were chosen using a stochastic selection procedure. In this procedure the exponential parameters of the added Gaussian were selected from a set of randomly generated candidates. The distribution of the nonlinear parameters of those randomly selected candidates was based on the distribution of the nonlinear parameters of the functions that were already included in the basis set. In Table II we show how the total nonrelativistic FNM energy for each state changed in the basis-set growing process. The energies are shown for each 1000 functions added. As one can see, for all three states with 8000 functions the nonrelativistic energy is converged to a relative accuracy of 10^{-10}, if not higher.

TABLE II. The convergence of the total nonrelativistic FNM energy E_{NR} for the $2S$, $3S$, and $4S$ states of $^9Be^+$ with the basis set size. All energies are in a.u.

Basis	E_{NR}		
	$2S$	$3S$	$4S$
1000	−14.3238634235	−13.9219152482	−13.7978498156
2000	−14.3238634780	−13.9219154758	−13.7978505778
3000	−14.3238634866	−13.9219154966	−13.7978506819
4000	−14.3238634903	−13.9219155033	−13.7978507025
5000	−14.3238634923	−13.9219155066	−13.7978507121
6000	−14.3238634933	−13.9219155085	−13.7978507155
7000	−14.3238634939	−13.9219155095	−13.7978507173
8000	−14.3238634944	−13.9219155102	−13.7978507185

In the next step the nonrelativistic FNM wave functions generated with the procedure described above were used to calculate the leading relativistic corrections, i.e., the mass-velocity (MV), the Darwin (D), the spin-spin interaction (SS), and the orbit-orbit interaction (OO) correction. In Table III we show the values of the relativistic corrections calculated with the 6000-term, 7000-term, and 8000-term wave functions. We also show the total relativistic correction multiplied by α^2. The reason for showing the results for the three basis sets is to compare the convergence of the total energy for each state with the convergence of the correction. Since some of the relativistic corrections involve singular operators, such as the fourth powers of the linear momentum operator (MV) and three-dimensional (3D) Dirac delta functions dependent on the interparticle distances (the D and SS corrections), a slower and nonmonotonic convergence in calculating their expectation values is usually observed. However, comparing the values for the total relativistic correction obtained for the 6000-term, 7000-term, and 8000-term wave functions shows that the convergence of this quantity is sufficiently tight. The absolute convergence is about $10^{-7}-10^{-8}$ a.u. for all three states considered in this work. The results shown in Table III also include the relativistic

TABLE III. The lowest three S states of the Be^+ ion. Total nonrelativistic energy (E_{NR}) and mass-velocity ($\langle H_{MV}\rangle$), Darwin ($\langle H_D\rangle$), spin-spin ($\langle H_{SS}\rangle$), and orbit-orbit ($\langle H_{OO}\rangle$) relativistic corrections, and the total α^2 correction ($\alpha^2 E_{REL}$) calculated with 6000, 7000, and 8000 Gaussian basis functions. Infinite-mass ($^\infty Be^+$) and finite-mass ($^9Be^+$) results are shown. All values are in a.u.

	State	Basis	E_{NR}	$\langle H_{MV}\rangle$	$\langle H_D\rangle$	$\langle H_{SS}\rangle$	$\langle H_{OO}\rangle$	$\alpha^2 E_{REL}$
$^\infty Be^+$								
	$2S$	6000	−14.3247631754	−268.30768	216.09786	9.95538	−0.90990	-2.2985597×10^{-3}
		7000	−14.3247631760	−268.31022	216.10054	9.95477	−0.90990	-2.2985849×10^{-3}
		8000	−14.3247631764	−268.31024	216.10068	9.95469	−0.90990	-2.2985825×10^{-3}
	$3S$	6000	−13.9227892657	−263.53423	212.90947	9.68433	−0.88718	-2.2273769×10^{-3}
		7000	−13.9227892667	−263.53554	212.91069	9.68431	−0.88718	-2.2273826×10^{-3}
		8000	−13.9227892674	−263.53557	212.91085	9.68429	−0.88718	-2.2273771×10^{-3}
	$4S$	6000	−13.7987166062	−262.48949	212.23359	9.62988	−0.88212	-2.2103649×10^{-3}
		7000	−13.7987166082	−262.49367	212.23788	9.62833	−0.88212	-2.2104414×10^{-3}
		8000	−13.7987166092	−262.49579	212.23894	9.62832	−0.88212	-2.2104987×10^{-3}
$^9Be^+$								
	$2S$	6000	−14.3238634933	−268.24146	216.05795	9.94653	−0.93630	-2.2990355×10^{-3}
		7000	−14.3238634939	−268.24400	216.06063	9.94592	−0.93630	-2.2990607×10^{-3}
		8000	−14.3238634944	−268.24402	216.06077	9.94584	−0.93630	-2.2990584×10^{-3}
	$3S$	6000	−13.9219155085	−263.46920	212.87015	9.67514	−0.91304	-2.2278742×10^{-3}
		7000	−13.9219155095	−263.47051	212.87137	9.67512	−0.91304	-2.2278799×10^{-3}
		8000	−13.9219155102	−263.47054	212.87153	9.67510	−0.91304	-2.2278744×10^{-3}
	$4S$	6000	−13.7978507155	−262.42472	212.19439	9.62062	−0.90786	-2.2108668×10^{-3}
		7000	−13.7978507173	−262.42890	212.19868	9.61907	−0.90786	-2.2109433×10^{-3}
		8000	−13.7978507185	−262.43102	212.19974	9.61906	−0.90786	-2.2110005×10^{-3}

corrections obtained with the INM wave functions. These values are shown as a reference for future calculations on Be^+ that may be performed within the INM approximation.

The next step of the calculations involved determination of the leading α^3 and α^4 QED corrections. The QED results are shown in Table IV. Apart from the values of the corrections we also show in Table IV the values of $P(1/r_{ij}^3)$ and $\ln k_0$, which 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 where the approach employed here was used in the calculations of the lowest excitation energy in the Be atom [44]. As one can see from the results presented in Table IV, the α^3 and α^4 corrections are by an order of magnitude smaller and two orders of magnitude smaller, respectively, than the α^2 relativistic correction. Also, with the increasing excitation level the α^3 correction becomes increasingly more similar. The same is the case for the α^2 and α^4 corrections. This converging trend is related to the fact the $2S$, $3S$, and $4S$ states considered here are the first members of a Rydberg series of states resulting from one of the valence electrons being excited to increasingly higher state with the S symmetry.

Next, the total nonrelativistic FNM energies and the relativistic and QED corrections were added and used to calculate the transition energies, which are shown in Table V in cm^{-1}. The calculated transition energies are compared with the experimental transitions. The comparison shows that only after adding all three relativistic and QED corrections, the two calculated transitions (i.e., $3S\rightarrow2S$ and $4S\rightarrow3S$) start to agree with the experimental values [45] within 0.1 cm^{-1}. For the first transition ($3S\rightarrow2S$) we get 88 231.842 cm^{-1} vs 88 231.915 cm^{-1} from the experiment, and for the second transition ($4S\rightarrow3S$) we get 27 232.601 cm^{-1} vs 27 232.525 cm^{-1} from the experiment. Thus for the first transition our calculations underestimated the transition energy by 0.073 cm^{-1} while for the second transition the calculations overestimated the transition by 0.076 cm^{-1}.

TABLE IV. α^3 and α^4 QED corrections ($\alpha^3 E_{QED}$ and $\alpha^4 E_{HQED}$) for the three lowest S states of Be^+ obtained in the infinite-mass calculations. The Araki-Sucher term, Eq. (11), and the Bethe logarithm, Eq. (12), are also shown. All values are in a.u.

State	$\langle P(1/r_{ij}^3)\rangle/(4\pi)$	$\ln k_0$	$\alpha^3 E_{QED}$	$\alpha^4 E_{HQED}$
$2S$	−0.597979	5.75167	3.37258×10^{-4}	1.5320×10^{-5}
$3S$	−0.603146	5.75409	3.32137×10^{-4}	1.5090×10^{-5}
$4S$	−0.603704	5.75032	3.31372×10^{-4}	1.5042×10^{-5}

TABLE V. *S-S* transition frequencies of $^9Be^+$ calculated: as differences of the total nonrelativistic energies (ΔE_{NR}), as differences of the total energies that include the α^2 relativistic corrections (ΔE_{REL}), as differences of the total energies that include the α^2 relativistic and α^3 QED corrections (ΔE_{QED}), and as differences of the total energies that include all α^2, α^3, and α^4 corrections (ΔE_{HQED}). Except for α^3 and α^4 corrections all other quantities were obtained in the finite-mass calculations. 8000-term wave functions were used in the calculations. All values are in cm^{-1}.

	$3S \rightarrow 2S$	$4S \rightarrow 3S$
ΔE_{NR}	88217.385	27229.074
ΔE_{REL}	88233.008	27232.778
ΔE_{QED}	88231.884	27232.610
ΔE_{HQED}	88231.834	27232.599
Experiment [45]	88231.915	27232.525

IV. SUMMARY

In this work we have presented a series of calculations aimed to determine the lowest two *S-S* transition frequencies in the Be^+ ion. The calculations have been performed using the nonrelativistic Schrödinger equation and the variational method to obtain the nonrelativistic wave function and the perturbation theory to obtain the relativistic and QED corrections. The nonrelativistic wave function was expanded in terms of explicitly correlated one-center Gaussian functions. The calculations were performed including the nuclear motion, i.e., without assuming the Born-Oppenheimer approximation regarding the separability of the electronic and nuclear motions. In this we differ from the conventional approach where the nonrelativistic infinite-nuclear-mass energy is calculated first and then corrections due to the finite nucleus mass are determined using the perturbation theory. The sum of the nonrelativistic FNM energy and the relativistic and QED corrections constituted the final total energy for each state that was used to calculate the $3S \rightarrow 2S$ and $4S \rightarrow 3S$ transition energies. Those energies agree with the corresponding experimental energies to less than 0.1 cm^{-1}.

The lowest electronic transition of a three electron atom—the Li atom—was calculated before by two groups [11,15,46,47]. The calculations included the relativistic and QED effects up to α^4 as well as the effects due to finite size of the nucleus and nuclear polarizability. Their results differ from the experiment in the seventh and eighth significant figures for ^6Li and ^7Li, respectively. Our results for the two lowest transitions of Be^+, which is isoelectronic with Li, differ from the experiment in the seventh significant figure. This is quite encouraging, considering that our goal is to use Gaussians and the approach presented here to perform very accurate calculations on atomic systems with more than three electrons. At present, Gaussians are the only choice of the basis functions for such calculations because the Hylleraas-type and Slater-type functions have not yet been implemented for atomic systems with more than three electrons. If we manage to converge the total nonrelativistic FNM energies of ground and excited states for such systems to the level achieved in the present work for Be^+, it should be also possible to reach the accuracy of seven significant figures in the transition energies for those systems.

ACKNOWLEDGMENTS

This work has been supported by the National Science Foundation. We would like to thank Professor Krzysztof Pachucki, Professor Michael Eides, and Dr. Peter Mohr for valuable discussion concerning the *g* factors. We are grateful to the University of Arizona Center of Computing and Information Technology for the use of their supercomputer resources.

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