

Prediction of 1P Rydberg energy levels of beryllium based on calculations with explicitly correlated Gaussians

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Benchmark variational calculations are performed for the seven lowest $1s^22snp$ (1P), $n = 2 \dots 8$, states of the beryllium atom. The calculations explicitly include the effect of finite mass of ^9Be nucleus and account perturbatively for the mass-velocity, Darwin, and spin-spin relativistic corrections. The wave functions of the states are expanded in terms of all-electron explicitly correlated Gaussian functions. Basis sets of up to 12 500 optimized Gaussians are used. The maximum discrepancy between the calculated nonrelativistic and experimental energies of $1s^22snp$ (1P) \rightarrow $1s^22s^2$ (1S) transition is about 12 cm^{-1} . The inclusion of the relativistic corrections reduces the discrepancy to below 0.8 cm^{-1} . © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4858275>]

I. INTRODUCTION

High-precision calculations of energy levels for small atoms and atomic ions have been a subject of fruitful interplay between the experiment and theory, as has been evident from the works concerning the lithium atom.^{1–13} The most accurate calculations have included leading relativistic and quantum electrodynamics (QED) corrections of orders $\mathcal{O}(\alpha^4 mc^2)$, $\mathcal{O}(\alpha^5 mc^2)$, $\mathcal{O}(\frac{m}{M}\alpha^4 mc^2)$, and $\mathcal{O}(\frac{m}{M}\alpha^5 mc^2)$, where α is the fine structure constant, c is the speed of light, and m and M are the electron and nuclear mass, respectively. Particularly accurate have been the calculations involving Hylleraas basis functions. The form of these basis functions allows to describe very well both the electron correlation and the behavior of the wave function at short and long ranges of the electron-electron and electron-nucleus distances.

More recently, the experimental-theoretical interplay has started to focus on beryllium-like atoms, as both theoretical tools and experimental techniques have started to deliver higher accuracy results for transition energies of these four-electron systems. As extending the application of the Hylleraas basis functions to calculating states of atoms with four electrons has not been accomplished yet, other types of variational expansions have been used. One of the most popular and, arguably, the most effective among them have been all-electron explicitly correlated Gaussian functions (ECGs).^{14–16} Although Gaussian functions do not correctly describe interparticle cusps and the long-distance behavior of the wave function, if many of them are included in the basis set and their nonlinear parameters are well optimized, the accuracy of the computed results can be very high as evidenced by recent publications.^{17–26} In this work we continue to apply ECGs to study atomic excited states. The targeted states are the seven lowest $1s^22snp$ (1P), $n = 2 \dots 8$, states of the beryllium atom. The calculations involve two steps. In the first step performed at the nonrelativistic level of theory a ECG basis set for expanding the wave function of each considered state

is generated and the total energy of the state is calculated. The approach directly involves accounting for the final mass of the beryllium ^9Be nucleus. The second step involves the calculations of the largest relativistic corrections, namely, the mass-velocity (MV), Darwin (D), and spin-spin (SS) interaction corrections. The total nonrelativistic energies augmented with the corresponding relativistic corrections are used to determine the transition energies for the considered states with respect to the ground $1s^22s^2$ (1S) state.

The NIST Atomic Spectra Database^{27,28} lists six energy levels corresponding to $1s^22snp$ (1P), $n = 2 \dots 6$ Rydberg states of ^9Be . The energy of these six states expressed in wave numbers and determined with respect to the ground state are known to two figures after the decimal point. There are also some higher 1P states listed ($n = 7 \dots 13$), but the energy levels of those states are known less precisely—one figure after the decimal point or less. As the results of the present work indicate, theoretical calculations can yield more accurate values for the transition energies involving those higher states and, thus, may provide some guidance for their remeasurement at higher accuracy.

High accuracy in the ECG calculations can only be achieved if very large basis sets are employed and the nonlinear parameters of ECGs are extensively optimized. In this work the ECG basis is generated independently for each considered state. The optimization relies on a procedure that involves the analytic energy gradient determined with respect to the parameters. The use of the analytic gradient has a very notable effect on the efficiency of the optimization and makes calculations with very extended basis sets feasible.

II. THE HAMILTONIAN

The nonrelativistic Hamiltonian for the beryllium atom describing the intrinsic motion of the system (“intrinsic Hamiltonian,” \hat{H}_{int}) is obtained by separating out the

center-of-mass motion from the laboratory-coordinate-system Hamiltonian (for more details see, for example, Refs. 29 and 15). The separation is rigorous and leads to the following form of \hat{H}_{int} expressed in atomic units:

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

where $n = 4$, \mathbf{r}_i is the distance between the i th electron and the nucleus, m_0 is the nuclear mass (16424.2037 m_e for ${}^9\text{Be}$, where $m_e = 1$ is the electron mass), $q_0 = +4$ is the nuclear charge, $q_i = -1$ are electron charges, and $\mu_i = m_0 m_i / (m_0 + m_i)$ are electron reduced masses.

The internal Hamiltonian (1) explicitly depends on the mass of the nucleus. Thus, the calculated energy levels for different isotopes are slightly shifted with respect to each other. The shifts can be directly determined from the variational calculations without resorting to perturbation theory, which is typically employed in atomic structure calculations. The mass of the nucleus can also be set to infinity, in which case in the present calculations one obtains the energy spectrum of ${}^\infty\text{Be}$. Such calculations can be directly compared with the available reference data.

III. THE BASIS SET

The all-electron explicitly correlated Gaussians used in this work to describe the seven 1P states of the beryllium atom have the following form:

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

where z_{i_k} is the z -coordinate of the i_k th electron (i_k is an adjustable integer parameter in our calculations), A_k 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. The prime symbol indicates the matrix/vector transpose.

Gaussians (2) are square integrable if the A_k matrix is positive definite. To assure this requirement is always met we use the following Cholesky-factored form of A_k : $A_k = L_k L_k'$, where L_k is a lower triangular matrix. In this form the A_k matrix is always positive definite regardless of the values of the L_k matrix elements. Thus these values can be varied from ∞ to $-\infty$. In our calculations the elements of the L_k matrices replace the elements of the A_k matrix as the variational parameters and their optimization is carried out without any constraints.

In the approach employed in the present calculations we use the spin-free formalism to ensure the correct permutational symmetry properties. In this formalism, an appropriate symmetry projector is applied to the elementary basis functions (2). The symmetry projector can be constructed using the standard procedure involving Young operators as described, for example, in Ref. 30. For singlet 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 (particle 0 is the nucleus). As the Hamiltonian of the system commutes with all electron permutations, in the calculation of the overlap and Hamiltonian matrix elements, \hat{Y} may be applied to either *bra* or *ket* only (as $\hat{Y}^\dagger \hat{Y}$). More technical details on basis functions (2) and the evaluation of matrix elements with them can be found in Ref. 31.

As mentioned, the basis set optimization has been carried out separately for each of the seven 1P states considered in this work. The optimization was only done for the ${}^9\text{Be}$ isotope. In the calculations for ${}^\infty\text{Be}$, the ${}^9\text{Be}$ basis sets are used without reoptimization of the nonlinear parameters. Only the linear expansion coefficient of the wave function is readjusted by solving the secular equation. This simplification has virtually no effect on the accuracy of the ${}^\infty\text{Be}$ results as the change of the wave function upon varying the nuclear mass from 16424.2037 m_e to infinity is rather small.

The final basis set for each of the states considered in this work has been generated in a multistep process. It starts with a small set of randomly chosen functions and involves incremental addition of new functions. The new functions are added to the basis set one by one and their nonlinear L_k parameters are optimized using the procedure employing the analytic gradient of the energy. The initial guesses of these parameters are generated based on random sampling from a distribution that is defined by the parameters of the functions that are already in the basis. The random candidate, which lowers the energy the most, is then added to the basis. After a certain number of functions (10 in this particular calculation) is added to the basis set, the entire basis is reoptimized. The reoptimization involves cycling over all functions, one by one, several times and tuning their nonlinear parameters. As basis functions are added and optimized certain steps have to be taken to prevent the occurrence of linear dependencies between the basis functions, which may have a destructive effect on the numerical stability and efficiency of the calculations. As in most cases only pairs of basis functions develop strong linear dependencies, after each new function is added to the basis set and its exponential parameters are optimized, it is checked for possible linear dependence with every other function in the basis set. If linear dependency appears, the function is rejected and replaced by another function.

IV. CALCULATION OF THE RELATIVISTIC CORRECTIONS

While relativistic effects in atoms with small nuclear charge are weak, their inclusion provides considerable better agreement with the spectroscopic data. These effects can be accounted for by means of perturbation theory based on the expansion of the total energy in powers of the fine-structure constant.³² In this work we restrict ourselves only to the largest relativistic contributions due to the mass-velocity, Darwin, and spin-spin interaction effects.³³ The smaller orbit-orbit interaction correction, as well as higher order QED corrections, are not included. The operators representing the MV, D, and SS relativistic corrections can be written in the internal

coordinates \mathbf{r}_i as follows:

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

$$H_D = -\frac{\pi}{2} \left(\sum_{i=1}^n \frac{q_0 q_i}{m_i^2} \delta(\mathbf{r}_i) + \sum_{i \neq j}^n \frac{q_i q_j}{m_j^2} \delta(\mathbf{r}_{ij}) \right), \quad (4)$$

and

$$H_{SS} = -\frac{8\pi}{3} \sum_{i < j}^n \frac{q_i q_j}{m_i m_j} \mathbf{s}_i \cdot \mathbf{s}_j \delta(\mathbf{r}_{ij}). \quad (5)$$

Here \mathbf{s}_i is the spin operator for the i th electron. The spin-averaged value of $\mathbf{s}_i \cdot \mathbf{s}_j$ is equal to $-3/4$.

The corrections are computed as expectation values of the above operators with the zero-order wave functions that correspond to the 1P states. The calculations are performed for both ^9Be and $^\infty\text{Be}$ isotopes. In the former case the recoil effects are automatically included in all relativistic corrections (MV, D, and SS) calculated in this work.

V. CALCULATIONS OF THE ENERGIES OF THE 1P STATES FOR ^9Be

A thorough optimization of an ECG basis set is a very demanding computational task even if the analytic energy gradient is used in the calculation. As the number of nodes in higher excited states increases, more basis functions are needed to achieve a comparable accuracy as achieved for lower-lying states. In Table I the convergence of the total energy of ^9Be isotope with the number of ECG basis functions is shown for all seven 1P states considered in this work. As one can see for the lowest $1s^2 2s 2p$ state at the level of 10 700 ECGs the energy changes only by one in the ninth figure after the decimal point after the basis set is increased by 300 functions, while for the highest $1s^2 2s 8p$ state the increase by 300 functions from 12 200 to 12 500 changes the energy by three in the eighth figure after the decimal point.

As the experimental values expressed in wave numbers for the $1s^2 2s^2 (^1S) \rightarrow 1s^2 2s n p (^1P)$, $n = 2 \dots 6$, are given with two significant figures after the decimal point, this is the target accuracy we aim for in the present calculations. The analysis of the data presented in Table II suggests that the transition energy for the lowest $1s^2 2s 2p$ state is converged to about 0.001–0.002 cm^{-1} , while the convergence for the highest $1s^2 2s 8p$ state is about 0.03–0.05 cm^{-1} .

The components of the relativistic correction for all seven 1P states of ^9Be are shown in Table III. They are calculated using the largest basis set generated for each state. In Table III we also show the total energy for each state calculated as a sum of the total nonrelativistic energy and the corresponding relativistic corrections. The same set of data is also shown for the beryllium atom with an infinite mass of the nucleus ($^\infty\text{Be}$). Our $^\infty\text{Be}$ nonrelativistic energy for the lowest $1s^2 2s 2p (^1P)$ state can be compared with the recent result of Puchalski *et al.*²⁶ of $-14.473\,451\,334$ hartree. Our variational

TABLE I. The convergence of the total variational nonrelativistic finite-nuclear-mass energies (in hartree) of the $1s^2 2s n p (^1P)$, $n = 2 \dots 8$, states of ^9Be with the number of the Gaussian basis functions.

| Basis | $1s^2 2s 2p$ | $1s^2 2s 3p$ | $1s^2 2s 4p$ | $1s^2 2s 5p$ | $1s^2 2s 6p$ | $1s^2 2s 7p$ | $1s^2 2s 8p$ |
|--------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|
| 9500 | -14.472 543 744 99 | | | | | | |
| 9800 | -14.472 543 746 24 | | | | | | |
| 10 100 | -14.472 543 747 37 | | | | | | |
| 10 400 | -14.472 543 748 36 | | | | | | |
| 10 700 | -14.472 543 749 32 | | | | | | |
| 11 000 | | -14.392 242 869 62 | -14.361 037 782 92 | -14.346 975 836 50 | -14.339 569 857 26 | -14.335 215 369 91 | -14.332 444 624 24 |
| 11 300 | | -14.392 242 870 83 | -14.361 037 784 25 | -14.346 975 838 31 | -14.339 569 861 50 | -14.335 215 382 99 | -14.332 444 663 24 |
| 11 600 | | -14.392 242 871 87 | -14.361 037 785 48 | -14.346 975 840 02 | -14.339 569 865 90 | -14.335 215 394 59 | -14.332 444 698 49 |
| 11 900 | | -14.392 242 872 88 | -14.361 037 786 63 | -14.346 975 841 66 | -14.339 569 870 23 | -14.335 215 405 95 | -14.332 444 729 56 |
| 12 200 | | -14.392 242 873 82 | -14.361 037 787 68 | -14.346 975 843 26 | -14.339 569 874 04 | -14.335 215 414 36 | -14.332 444 757 96 |
| 12 500 | | | | | | | |

TABLE II. The convergence of the nonrelativistic transition energies expressed in cm^{-1} of the $1s^2 2snp$ (1P), $n = 2 \dots 8$, states of ^9Be with the number of the Gaussian basis functions. The transition energies are determined with respect to the ground $1s^2 2s^2$ (1S) state.

| Basis | $1s^2 2s2p$ | $1s^2 2s3p$ | $1s^2 2s4p$ | $1s^2 2s5p$ | $1s^2 2s6p$ | $1s^2 2s7p$ | $1s^2 2s8p$ | $1s^2 2s\infty p$ |
|--------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------------|
| 9800 | 42 554.3223 | | | | | | | |
| 9800 | 42 554.3221 | | | | | | | |
| 10 100 | 42 554.3218 | | | | | | | |
| 10 400 | 42 554.3216 | 60 178.3274 | | | | | | |
| 10 700 | 42 554.3214 | 60 178.3271 | 67 027.0523 | | | | | |
| 11 000 | | 60 178.3269 | 67 027.0520 | 70 113.2928 | | | | |
| 11 300 | | 60 178.3266 | 67 027.0517 | 70 113.2924 | 71 738.7173 | 72 694.4168 | 73 302.5252 | |
| 11 600 | | 60 178.3264 | 67 027.0514 | 70 113.2920 | 71 738.7164 | 72 694.4140 | 73 302.5167 | |
| 11 900 | | | 67 027.0512 | 70 113.2916 | 71 738.7154 | 72 694.4114 | 73 302.5089 | |
| 12 200 | | | | 70 113.2913 | 71 738.7145 | 72 694.4089 | 73 302.5021 | |
| 12 500 | | | | | 71 738.7136 | 72 694.4071 | 73 302.4959 | |
| 8000 | | | | | | | | 75 185.8656 |

upper bound, $-14.473\,451\,378(10)$ hartree, yields somewhat more converged value.

Table III also lists the transition energies for the seven 1P states calculated with respect to the ground 1S state using the corresponding total energies calculated with and without the relativistic corrections. The transition energies are calculated for both ^9Be and $^\infty\text{Be}$. The results for ^9Be are shown against the experimental transition energies.²⁷ Here, the following observations can be made. First, the comparison of the nonrelativistic ^9Be and $^\infty\text{Be}$ transition energies shows that the finite-nuclear-mass effect provides a noticeable contribution to the energies, which increases in magnitude from about -3 cm^{-1} for the lower states to about -5 cm^{-1} for the highest states. Second, the comparison of the calculated and experimental transition energies shows that, while at the non-

relativistic level the energy differs by about 11 cm^{-1} for the $1s^2 2s2p$ state and by about 7 cm^{-1} for the $1s^2 2s6p$ state, the differences are significantly reduced by including the relativistic corrections to only about 0.2 cm^{-1} for the lowest state and to 0.8 cm^{-1} for the $1s^2 2s5p$ state (for this state the difference with the experiment is the highest).

Finally, in Table IV some expectation values calculated for the seven 1P states obtained with the largest basis sets generated in the calculation are shown. Among the results it is interesting to examine the expectation values that demonstrate the increasing diffuseness of the electron density as the p electron becomes excited to higher Rydberg states. These expectation values are the average nucleus-electron distance, $\langle r_i \rangle$, and the average electron-electron distance, $\langle r_{ij} \rangle$. As one can see both $\langle r_i \rangle$ and $\langle r_{ij} \rangle$, as expected, rapidly increase with

TABLE III. Total nonrelativistic energies (E_{NR}) of $1s^2 2snp$ (1P), $n = 2 \dots 8$, states of the beryllium atom (^9Be), the mass-velocity, Darwin, and spin-spin interaction relativistic corrections, and the total energies that include relativistic corrections ($E_{\text{tot}} = E_{\text{NR}} + \alpha^2(E_{\text{MV}} + E_{\text{D}} + E_{\text{SS}})$) and their values with respect to the ground $1s^2 2s^2$ (1S) state ($\Delta E_{\text{NR}} = E_{\text{NR}} - E_{\text{NR}}^{\text{ground}}$, $\Delta E_{\text{tot}} = E_{\text{tot}} - E_{\text{tot}}^{\text{ground}}$). NIST denotes the experimental data from NIST Atomic Spectra Database.²⁷ All entries are in hartree, except the last three columns. Values in parentheses are estimates of uncertainty due to finite length of the basis.

| State | Basis | E_{NR} | E_{MV} | E_{D} | E_{SS} | E_{tot} | $\Delta E_{\text{NR}} (\text{cm}^{-1})$ | $\Delta E_{\text{tot}} (\text{cm}^{-1})$ | NIST (cm^{-1}) |
|---------------------|--------|-----------------|-----------------|----------------|-----------------|------------------|---|--|---------------------------|
| ^9Be | | | | | | | | | |
| $1s^2 2s^2$ Ref. 23 | 10 000 | -14.666 435 504 | -270.625 15 | 217.133 37 | 10.087 17 | -14.668 746 858 | | | |
| $1s^2 2s2p$ | 10 700 | -14.472 543 749 | -266.586 96 | 214.292 90 | 9.850 90 | -14.474 803 905 | 42 554.32(0) | 42 565.56(0) | 42 565.35 |
| $1s^2 2s3p$ | 11 600 | -14.392 242 874 | -267.378 65 | 214.901 05 | 9.887 24 | -14.394 510 868 | 60 178.33(0) | 60 187.84(0) | 60 187.34 |
| $1s^2 2s4p$ | 11 900 | -14.361 037 788 | -267.877 82 | 215.277 88 | 9.913 30 | -14.363 310 909 | 67 027.05(0) | 67 035.44(0) | 67 034.70 |
| $1s^2 2s5p$ | 12 200 | -14.346 975 843 | -268.057 86 | 215.413 82 | 9.922 32 | -14.349 250 833 | 70 113.29(0) | 70 121.27(0) | 70 120.49 |
| $1s^2 2s6p$ | 12 500 | -14.339 569 874 | -268.121 11 | 215.457 11 | 9.926 07 | -14.341 845 726 | 71 738.71(0) | 71 746.51(1) | 71 746.09 |
| $1s^2 2s7p$ | 12 500 | -14.335 215 414 | -268.134 37 | 215.461 89 | 9.930 71 | -14.337 491 471 | 72 694.41(1) | 72 702.15(1) | 72 701.8 |
| $1s^2 2s8p$ | 12 500 | -14.332 444 758 | -268.130 43 | 215.445 82 | 9.933 20 | -14.334 721 328 | 73 302.50(2) | 73 310.13(2) | 73 309.7 |
| $1s^2 2s\infty p$ | 2500 | -14.323 863 494 | -268.242 79 | 215.560 22 | 9.929 58 | -14.326 140 149 | 75 185.87(0) | 75 193.48(0) | 75 192.64(6) |
| $^\infty\text{Be}$ | | | | | | | | | |
| $1s^2 2s^2$ Ref. 23 | 10 000 | -14.667 356 486 | -270.692 12 | 217.173 60 | 10.088 85 | -14.669 669 175 | | | |
| $1s^2 2s2p$ | 10 700 | -14.473 451 378 | -266.653 39 | 214.332 98 | 9.852 57 | -14.475 712 848 | 42 557.25(0) | 42 568.49(0) | |
| $1s^2 2s3p$ | 11 600 | -14.393 143 528 | -267.444 90 | 214.940 94 | 9.888 89 | -14.395 412 838 | 60 182.79(0) | 60 192.31(0) | |
| $1s^2 2s4p$ | 11 900 | -14.361 938 388 | -267.944 00 | 215.317 69 | 9.914 95 | -14.364 212 825 | 67 031.52(0) | 67 039.92(0) | |
| $1s^2 2s5p$ | 12 200 | -14.347 876 275 | -268.124 05 | 215.453 63 | 9.923 97 | -14.350 152 582 | 70 117.80(0) | 70 125.79(0) | |
| $1s^2 2s6p$ | 12 500 | -14.340 470 145 | -268.187 31 | 215.496 91 | 9.927 72 | -14.342 747 315 | 71 743.26(0) | 71 751.05(1) | |
| $1s^2 2s7p$ | 12 500 | -14.336 115 562 | -268.200 56 | 215.501 69 | 9.932 36 | -14.338 392 936 | 72 698.98(1) | 72 706.73(1) | |
| $1s^2 2s8p$ | 12 500 | -14.333 344 814 | -268.196 62 | 215.485 61 | 9.934 85 | -14.335 622 702 | 73 307.09(2) | 73 314.73(2) | |
| $1s^2 2s\infty p$ | 2500 | -14.324 763 176 | -268.309 00 | 215.600 04 | 9.931 22 | -14.327 041 149 | 75 190.54(0) | 75 198.16(0) | |

TABLE IV. Expectation values for the $1s^2 2snp (^1P)$, $n = 2 \dots 8$, states of ^9Be . All values are in a.u.

| State | $\langle 1/r_i^2 \rangle$ | $\langle 1/r_{ij}^2 \rangle$ | $\langle 1/r_i \rangle$ | $\langle 1/r_{ij} \rangle$ | $\langle r_i \rangle$ | $\langle r_{ij} \rangle$ | $\langle r_i^2 \rangle$ | $\langle r_{ij}^2 \rangle$ | $\langle \delta(\mathbf{r}_i) \rangle$ | $\langle \delta(\mathbf{r}_{ij}) \rangle$ |
|-------------|---------------------------|------------------------------|-------------------------|----------------------------|-----------------------|--------------------------|-------------------------|----------------------------|--|---|
| $1s^2 2s2p$ | 14.214 77 | 1.542 322 | 2.069 045 | 0.693 271 | 1.775 941 | 2.976 695 | 6.518 197 | 12.922 95 | 8.722 421 | 0.261 303 |
| $1s^2 2s3p$ | 14.224 12 | 1.500 597 | 2.028 640 | 0.612 292 | 3.193 052 | 5.810 123 | 29.295 17 | 59.434 79 | 8.747 341 | 0.262 267 |
| $1s^2 2s4p$ | 14.237 29 | 1.489 304 | 2.012 288 | 0.579 089 | 5.492 002 | 10.361 00 | 104.1756 | 208.8678 | 8.762 854 | 0.262 958 |
| $1s^2 2s5p$ | 14.242 16 | 1.485 790 | 2.005 075 | 0.564 542 | 8.562 863 | 16.481 36 | 277.4885 | 555.3129 | 8.768 442 | 0.263 198 |
| $1s^2 2s6p$ | 14.244 31 | 1.484 375 | 2.001 303 | 0.556 952 | 12.392 36 | 24.129 91 | 610.9444 | 1222.125 | 8.770 239 | 0.263 297 |
| $1s^2 2s7p$ | 14.245 40 | 1.483 701 | 1.999 091 | 0.552 505 | 16.976 61 | 33.292 71 | 1181.383 | 2362.942 | 8.770 521 | 0.263 420 |
| $1s^2 2s8p$ | 14.246 01 | 1.483 341 | 1.997 686 | 0.549 680 | 22.315 32 | 43.966 70 | 2081.007 | 4162.150 | 8.769 931 | 0.263 486 |

the excitation. While the $\langle r_i \rangle$ expectation value for the lowest of the seven states is about 1.78 a.u., it increases to 22.31 a.u. for the seventh state. A similar increase is observed for the $\langle r_{ij} \rangle$ expectation value.

VI. SUMMARY

Very accurate quantum-mechanical variational calculations are performed for the lowest seven $1s^2 2snp (^1P)$, $n = 2 \dots 8$, states of the beryllium atom, ^9Be . Using a very extended set of all-electron explicitly correlated Gaussian functions a new nonrelativistic variational energy upper bound is obtained for each state. The optimization of nonlinear parameters of the basis functions takes advantage of the analytic gradient determined with respect to these parameters. After augmenting the nonrelativistic energies with a set of most significant relativistic corrections, namely, the mass-velocity, Darwin, and spin-spin corrections, the transition energies with respect to the beryllium ground $1s^2 2s^2 (^1S)$ state are calculated and compared with the experimental data. The discrepancy of the calculated transition energies with the experiment does not exceed 0.8 cm^{-1} . It is found that the relativistic and finite-nuclear-mass effects provide contributions similar in magnitude (of several wave numbers), but opposite in sign, to the transition frequencies. The results of this work lie foundation for further progress towards achieving truly spectroscopic accuracy in theoretical calculations of small atoms. Such calculations complemented with highly accurate experimental measurements and with understanding of the underlying atomic theory may allow precision tests of QED and determination of nuclear properties.

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