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Calculations of low-lying ^1P states of the beryllium atom

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High-accuracy nonrelativistic variational calculations employing explicitly correlated Gaussian basis functions have been performed to determine the energies and the expectation values of some operators for the lowest four $^1P_1$ states of the beryllium atom. The states correspond to the electron configurations $1s^22s^1np^1$, where $n=2$, 3, 4, and 5. The calculations were performed for both finite and infinite mass of the Be nucleus. The basis set for each state was grown to the level of 5000 Gaussians. With that many functions we achieved a tight energy convergence. The reported values, to the best of our knowledge, are the most accurate ever obtained for the four states.

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I. INTRODUCTION

Explicitly correlated Gaussian functions (ECGFs) provide a powerful tool for very accurate calculations of bound states of small atomic and molecular systems. The explicit dependency of these functions on the interparticle distances allows an effective description of the correlation effects that are usually strong in the case of particles interacting with Coulombic forces. Perhaps the most attractive feature of the ECGFs is that all the necessary matrix elements involving the Hamiltonian, as well as other common operators, can be analytically evaluated relatively easily for an arbitrary number of particles and can be expressed with compact and closed formulas. This feature of the Gaussians has stimulated an interest in using these functions in very accurate atomic and molecular calculations.

In one of our previous works [1] we derived and implemented formulas for calculating atomic and molecular systems with one of the particles in a p state. As the approach was general and not based on the Born-Oppenheimer approximation, the particles could be electrons, nuclei, or any other type of particles. In fact, one of the numerical examples presented in that work was a system with a positron in a p state. In the formulas presented in Ref. [1] we used complex exponential parameters in the Gaussians that provides additional radial flexibility to those functions in describing the oscillatory behavior of the wave function. Apart from the formulas for the Hamiltonian matrix elements, we also presented expressions for calculating analytical derivatives (the gradient) of the energy with respect to complex Gaussian exponential parameters. In the variational optimization of the wave function the availability of the analytical gradient is key in generating very extended and well optimized basis sets that assure very good convergence of the calculations in terms of the total energy and other properties. A nontrivial aspect of the implementation of the ECGF method has always been an effective parallellization of the computer code. In an ideal case one would like to achieve a linear scaling of the calculation with the number of processors (for a large number of processors). Even though there are many parts of the variational optimization algorithm that scale very well, there are also parts that are more difficult to effectively parallelize. Also, the efficiency of the parallelization depends on the computer platform used for the calculation.

The aim of this paper is to describe a series of the four lowest singlet $^1P_1$ states of the beryllium atom corresponding to the electron configurations $1s^22s^1np^1$, $n=2$, 3, 4, and 5. The main question we are addressing is how well the nonrelativistic energies of the four states can be converged when a large number of ECGFs is used in expanding the wave function. In the previous paper [1] we used a relatively small basis set for the ground state ($1s^22s^12p^1$) calculation to test the algorithms and the computer code for calculating the Hamiltonian matrix elements and the energy gradient. We also tested the effectiveness of the code paralellization and the gradient-based optimization approach. In the present paper we employ the approach to carry out very accurate large-scale calculations of the four Be $^1P_1$ states to demonstrate the capability of the ECGF method to very accurately describe P states of a four-electron atomic system.

Although atomic calculations with ECGFs for states with non-zero total angular momentum have been done before by other authors (see, for example, Refs. [2,3]), neither of those calculations was carried to the level of accuracy achieved in the present paper. For example, the lowest ^1P state of beryllium was calculated by Komasa and Rychlewski [3] using the infinite-nuclear-mass (INM) and their best variational energy obtained with 1200 basis functions was $-14.473\,442\,016$ a.u. By applying the gradient-based minimization algorithm we were able to lower this value in Ref. [1] to $-14.473\,442\,537$ a.u. using only 800 ECGFs. Here we show that by increasing the basis set to 5000 function (while optimizing the nonlinear parameters to a somewhat lesser degree) we achieve a further significant improvement in lowering the energy.

The presentation of this paper includes the following. First we briefly review the approach used in the calculations and we describe the form of the variational wave function. Next we present the results that include the total energies calculated for the finite and infinite masses of the Be nucleus and some expectation values commonly determined in atomic calculations. In the last section we calculate some

$n\ {}^1P_1 \rightarrow m\ {}^1P_1$ and $n\ {}^1P_1 \rightarrow m\ {}^1S_0$ transition energies and we compare them with the experimental values.

II. HAMILTONIAN

The present calculations have been done with a scheme that directly takes into account the finite mass of the beryllium nucleus [the finite-nuclear-mass (FNM) approach]. Such calculations require a transformation of the Hamiltonian from the laboratory coordinate frame to an internal frame and an elimination of the center-of-mass motion from the consideration. In our approach such a transformation starts with the laboratory-frame Cartesian coordinates $\mathbf{R}_i$, describing the N particles forming the atom (these include the nucleus and the electrons) with masses M_i and charges Q_i. Next, the motion of the center-of-mass is separated out using a new set of Cartesian coordinates where the first three are the center-of-mass coordinates and the remaining $3N-3$ coordinates are internal coordinates. The center of the internal coordinate system is placed at the nucleus (the so-called reference particle). All other particles (electrons) are referred to the reference particle using the relative coordinates $\mathbf{r}_i=\mathbf{R}_{i+1}-\mathbf{R}_1$. These coordinates, together with the three coordinates describing the position of the center-of-mass $\mathbf{r}_0$, are our new coordinates. With the total mass of the system denoted as $M_{\rm tot}=\Sigma_{i=1}^N M_i$, the coordinate transformation has the following form:

$$\mathbf{r}_0 = \frac{M_1}{M_{\rm tot}}\mathbf{R}_1 + \frac{M_2}{M_{\rm tot}}\mathbf{R}_2 + \cdots + \frac{M_N}{M_{\rm tot}}\mathbf{R}_N,$$

$$\mathbf{r}_1 = -\mathbf{R}_1 + \mathbf{R}_2,$$

$$\mathbf{r}_2 = -\mathbf{R}_1 + \mathbf{R}_3, \ldots ,$$

$$\mathbf{r}_n = -\mathbf{R}_1 + \mathbf{R}_N. \tag{1}$$

Upon the transformation (1), the laboratory frame Hamiltonian separates into the Hamiltonian describing the motion of the center-of-mass of the system and the following "internal" Hamiltonian:

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

where $n=N-1$, the prime symbol denotes the matrix-vector transposition, $r_{ij}=|\mathbf{r}_j-\mathbf{r}_i|$, $m_i=M_{i+1}$, $q_i=Q_{i+1}$, and $\mu_i=m_0 m_i/(m_0+m_i)$ (for ^{9}Be nucleus we used 16 424.2037 for m_0). This Hamiltonian we used in the present calculations.

The Hamiltonian (2) describes the motion of n pseudoparticles with masses m_i and charges q_i in the central field generated by the charge of the nucleus located in the center of the coordinate system. We use the term pseudoparticles (or perhaps we should call them pseudoelectrons) because the charges of the particles described by $\hat{H}_{\rm int}$ are the same as the charges of the electrons, but their masses are slightly smaller. The motions of the pseudoelectrons are coupled through the mass polarization terms $\Sigma_{i\neq j}^n m_0^{-1}\nabla'_{\mathbf{r}_i}\nabla_{\mathbf{r}_j}$ and through the Coulombic interactions. By setting the nuclear mass to infinity $\hat{H}_{\rm int}$ becomes the Hamiltonian used in atomic calculations based on the INM approach.

III. BASIS FUNCTIONS

The general form of the basis functions for describing the $L=1$ atomic states used in this paper is

$$\phi_k = z_{p_k}\exp[-\mathbf{r}'(A_k\otimes I_3)\mathbf{r}]. \tag{3}$$

Here z_{p_k} is the z coordinate of pseudoparticle (pseudoelectron) p_k, A_k is an $n\times n$ real symmetric matrix of exponential parameters unique for each basis function, and $A_k\otimes I_3$ denotes the Kronecker product of A_k and the 3×3 identity matrix I_3. Notice that, in general, index p_k is not the same for all basis functions (which is denoted by including index k in z_{p_k}) and can range from 1 to n. In a general case of a system consisting of different types of particles index p_k can be considered as an integer variational parameter and should be optimized along with other basis function parameters. However, for atoms where all pseudoparticles are the same (indistinguishable), one can use the same value of p_k (say, $p_k=1$) for all basis functions. This does not lead to any incompleteness of the basis set.

As the basis functions (3) have to be square integrable, matrix A_k must be positive definite. A convenient way to assure this is to represent A_k in the form of the Cholesky decomposition $A_k=L_k L_k'$, where L_k is a triangular matrix (the so-called Cholesky factor). A matrix represented in the Cholesky factored form is automatically positive definite, regardless of the signs and magnitudes of the elements of L_k. There is a significant practical advantage of using the Cholesky-factored form of A_k. Since there is no need to impose any restrictions on the elements of L_k, the variational optimization of these elements can be performed with no constraints and they can be allowed to vary in the range $[-\infty,+\infty]$. For such an optimization very fast and efficient algorithms can be employed. This would not be the case, if the variational parameters were the elements of matrix A_k.

The trial wave function, and what follows the basis functions used in the wave function expansion, should possess a certain symmetry with respect to the permutations of the electrons involved in the system. This symmetry can be implemented by applying certain symmetry projectors, which are linear combinations of permutational operators $\hat{P}_\alpha$ to each basis function. For a specific state of the system the appropriate symmetry operator can be determined based on well known procedures [4]. Permutational operators $\hat{P}_\alpha$ are products of elemental transposition operators $\hat{P}_{ij}$. In its original form $\hat{P}_{ij}$ permutes electrons. In our approach it needs to be transformed to permute pseudoelectrons. As the $\mathbf{R}\rightarrow\mathbf{r}$ transformation is linear, the transformation of the internal coordinates (i.e., the coordinates of pseudoparticles) under the permutation of particles is also linear and can be described by a permutation matrix $\mathbf{P}_{ij}=P_{ij}\otimes I_3$. The action of permutational operators on the basis functions (3) was described in more details in Ref. [1].

IV. VARIATIONAL PROCEDURE

A variational calculation with explicitly correlated Gaussians can generate a very accurate energy and the corresponding wave functions provided that the Gaussian exponential parameters are well optimized. Such an optimization is by far the most time consuming step of the calculation. The optimization can be accelerated by utilizing the analytical energy gradient with respect to the exponential parameters of the basis functions. In our previous papers [5–8] we used the gradient in the variational energy minimization and we showed that this dramatically speeded up the calculations.

In the Rayleigh-Ritz variational scheme the wave function of the system, ψ, after the elimination of the spin variables, is approximated as a linear combination of K basis functions ϕ_k:

$$\psi(\mathbf{r}) = \sum_{k=1}^{K} \mathsf{c}_k \hat{Y} \phi_k(\mathbf{r}). \tag{4}$$

Here $\hat{Y}$ is some permutational symmetry projector (a linear combination of permutational operators $\hat{P}_\alpha$) and c_k are the linear variational parameters. The minimization of the energy functional with respect to the parameters c_k yields the secular equation

$$(\mathsf{H} - \varepsilon \mathsf{S})\mathsf{c} = 0, \tag{5}$$

where H and S are the Hamiltonian and overlap matrices, respectively, and c is the vector of the linear coefficients c_k. The solutions of Eq. (5) give upper bounds ε to the exact ground- and excited-state energies of the system. The corresponding sets of the linear parameters c define the wave functions.

By taking the differential of Eq. (5)

$$d(\mathsf{H} - \varepsilon \mathsf{S})\mathsf{c} = (d\mathsf{H})\mathsf{c} - (d\varepsilon)\mathsf{S}\mathsf{c} - \varepsilon(d\mathsf{S})\mathsf{c} + (\mathsf{H} - \varepsilon \mathsf{S})d\mathsf{c} \tag{6}$$

and multiplying by $\mathsf{c}^\dagger$ (the dagger stands for transposed and complex conjugated) from the left we obtain

$$d\varepsilon = \mathsf{c}^\dagger (d\mathsf{H} - \varepsilon d\mathsf{S})\mathsf{c}. \tag{7}$$

In the above equation we assumed that the wave function is normalized ($\mathsf{c}^\dagger \mathsf{S} \mathsf{c} = 1$). $d\mathsf{H}$ and $d\mathsf{S}$ are determined with respect to the variations of the L_k matrices and require calculations of the first derivatives of the H and S matrix elements with respect to the L_k matrix elements. We refer the reader to our previous paper [1] for more details regarding the algorithm for calculating the gradient of the energy with respect to the exponential matrices of the $L=1$ Gaussians.

In the calculations carried out in this paper each of the four $^1P_1$ states of Be has been determined separately. This involved variational optimization of the basis set for each state performed in a separate calculation using the FNM approach. In the calculations the basis set for each state has been grown to the size of 5000 functions in the following multistep scheme. First, a set of 100 functions was generated with a random selection procedure and the whole set was optimized using the gradient-based minimization procedure. In this step, the nonlinear parameters of all basis functions were optimized simultaneously. Next, the basis set was grown up to 5000 functions by successive additions of ten functions. These ten functions were generated based on the distribution of nonlinear parameters of the basis functions already included in the basis set. After each addition the basis set was reoptimized with the gradient-based procedure. Here, however, we did not optimize the parameters of all basis functions simultaneously. Instead, we reoptimized the entire basis set by varying the parameters of one function at a time. Optimizing the parameters of only one basis function at a time is somewhat less effective, but saves a significant amount of computer time, because at each step of the optimization cycle only one row and one column of matrices H and S need to be updated. The results obtained for basis sets with increasingly larger number of functions for each state are discussed next.

TABLE I. Convergence of the total energies (in a.u.) of ^{9}Be and $^\infty$Be for the four lowest $^1P_1$ states. The values obtained with the largest basis size include estimates of the remaining absolute uncertainty.

State	Basis Size	$E(^9\text{Be})$	$E(^\infty\text{Be})$
$2\ ^1P_1$	1000	−14.472 533 452	−14.473 441 083
	2000	−14.472 542 454	−14.473 450 082
	3000	−14.472 543 386	−14.473 451 014
	4000	−14.472 543 606	−14.473 451 234
	5000	−14.472 543 683(70)	−14.473 451 311(70)
$3\ ^1P_1$	1000	−14.392 231 761	−14.393 132 415
	2000	−14.392 241 460	−14.393 142 114
	3000	−14.392 242 494	−14.393 143 148
	4000	−14.392 242 724	−14.393 143 378
	5000	−14.392 242 802(70)	−14.393 143 456(70)
$4\ ^1P_1$	1000	−14.361 024 843	−14.361 925 442
	2000	−14.361 036 239	−14.361 936 839
	3000	−14.361 037 349	−14.361 937 948
	4000	−14.361 037 606	−14.361 938 206
	5000	−14.361 037 697(90)	−14.361 938 297(90)
$5\ ^1P_1$	1000	−14.346 955 516	−14.347 855 945
	2000	−14.346 973 552	−14.347 873 983
	3000	−14.346 975 179	−14.347 875 610
	4000	−14.346 975 562	−14.347 875 993
	5000	−14.346 975 695(130)	−14.347 876 126(130)

V. RESULTS

In Table I we show how the total nonrelativistic FNM and INM energies for each of the four states vary when the basis set size changes from 1000 to 5000 in increments of 1000. The INM calculations were performed with the basis sets generated in the FNM calculations with only the linear expansion coefficients being allowed to adjust through the solution of the secular equation (5). The nonlinear parameters

TABLE II. Some expectation values of ^{9}Be and $^\infty$Be. All values are in a.u.

State	Basis Size	$\langle r_i^{-2}\rangle$	$\langle r_{ij}^{-2}\rangle$	$\langle r_i^{-1}\rangle$	$\langle r_{ij}^{-1}\rangle$	$\langle r_i\rangle$	$\langle r_{ij}\rangle$	$\langle r_i^2\rangle$	$\langle r_{ij}^2\rangle$	$\langle \delta(\mathbf{r}_i)\rangle$	$\langle \delta(\mathbf{r}_{ij})\rangle$
2^1P_1	1000	14.2147053	1.54234409	2.06904279	0.693271378	1.77593076	2.97666084	6.51786078	12.9222351	8.71134	0.261726
^{9}Be	2000	14.2147582	1.54232602	2.06904453	0.693271514	1.77593949	2.97668912	6.51814856	12.9228338	8.71949	0.261479
	3000	14.2147638	1.54232353	2.06904468	0.693271442	1.77594111	2.97669413	6.51819031	12.9229286	8.72079	0.261397
	4000	14.2147653	1.54232287	2.06904474	0.693271472	1.77594087	2.97669410	6.51819054	12.9229311	8.72168	0.261345
	5000	14.2147658	1.54232263	2.06904475	0.693271467	1.77594101	2.97669453	6.51819446	12.9229399	8.72178	0.261323
3^1P_1	1000	14.2240391	1.50062424	2.02863857	0.612294358	3.19314412	5.81025657	29.2958482	59.4355440	8.73600	0.262822
^{9}Be	2000	14.2241073	1.50060140	2.02863977	0.612292485	3.19306527	5.81014368	29.2953221	59.4350157	8.74460	0.262474
	3000	14.2241144	1.50059822	2.02863991	0.612292347	3.19305529	5.81012840	29.2952052	59.4348347	8.74629	0.262359
	4000	14.2241159	1.50059743	2.02863993	0.612292281	3.19305333	5.81012570	29.2951853	59.4348114	8.74658	0.262322
	5000	14.2241166	1.50059718	2.02863994	0.612292268	3.19305277	5.81012502	29.2951846	59.4348160	8.74698	0.262314
4^1P_1	1000	14.2371907	1.48934122	2.01228307	0.579084396	5.49344954	10.3638224	104.232155	208.980861	8.74538	0.263741
^{9}Be	2000	14.2372763	1.48931011	2.01228781	0.579089214	5.49212160	10.3612331	104.179622	208.875870	8.75847	0.263241
	3000	14.2372861	1.48930562	2.01228815	0.579089408	5.49203685	10.3610715	104.176997	208.870687	8.76126	0.263057
	4000	14.2372883	1.48930466	2.01228820	0.579089386	5.49201402	10.3610277	104.176034	208.868770	8.76220	0.263028
	5000	14.2372890	1.48930405	2.01228821	0.579089358	5.49200963	10.3610198	104.175863	208.868447	8.76235	0.262972
5^1P_1	1000	14.2420035	1.48586006	2.00506958	0.564539312	8.56891753	16.4933331	277.922176	556.179701	8.75068	0.264408
^{9}Be	2000	14.2421410	1.48579863	2.00507474	0.564542158	8.56353641	16.4826765	277.537381	555.410331	8.76371	0.263521
	3000	14.2421538	1.48579184	2.00507503	0.564542075	8.56306390	16.4817516	277.501557	555.339002	8.76583	0.263332
	4000	14.2421573	1.48579113	2.00507531	0.564542436	8.56294208	16.4815127	277.494281	555.324466	8.76752	0.263327
	5000	14.2421584	1.48579081	2.00507537	0.564542479	8.56289731	16.4814253	277.490908	555.317765	8.76765	0.263324
2^1P_1	1000	14.2164802	1.54250579	2.06916812	0.693302984	1.77586108	2.97656492	6.51741211	12.9214805	8.71297	0.261770
$^\infty$Be	2000	14.2165327	1.54248744	2.06916979	0.693302984	1.77586982	2.97659333	6.51769616	12.9220704	8.72112	0.261523
	3000	14.2165382	1.54248490	2.06916992	0.693302866	1.77587169	2.97659901	6.51774086	12.9221730	8.72241	0.261442
	4000	14.2165398	1.54248423	2.06916997	0.693302882	1.77587147	2.97659912	6.51774082	12.9221765	8.72331	0.261390
	5000	14.2165402	1.54248398	2.06916998	0.693302871	1.77587165	2.97659968	6.51774506	12.9221867	8.72341	0.261368
3^1P_1	1000	14.2258022	1.50078444	2.02876260	0.612324848	3.19308420	5.81016537	29.2952947	59.4342942	8.73762	0.262866
$^\infty$Be	2000	14.2258702	1.50076145	2.02876377	0.612322938	3.19300378	5.81004944	29.2947254	59.4336779	8.74622	0.262518
	3000	14.2258773	1.50075822	2.02876391	0.612322766	3.19299360	5.81003357	29.2946041	59.4334830	8.74791	0.262403
	4000	14.2258788	1.50075740	2.02876391	0.612322664	3.19299197	5.81003157	29.2945900	59.4334740	8.74820	0.262366
	5000	14.2258795	1.50075715	2.02876392	0.612322647	3.19299135	5.81003079	29.2945859	59.4334718	8.74860	0.262357
4^1P_1	1000	14.2389493	1.48950158	2.01240734	0.579115561	5.49331769	10.3635987	104.228250	208.973068	8.74700	0.263785
$^\infty$Be	2000	14.2390343	1.48947028	2.01241212	0.579120491	5.49196642	10.3609625	104.174820	208.866256	8.76008	0.263285
	3000	14.2390441	1.48946575	2.01241247	0.579120681	5.49187631	10.3607897	104.171947	208.860555	8.76288	0.263101
	4000	14.2390462	1.48946477	2.01241250	0.579120634	5.49185365	10.3607462	104.171000	208.858675	8.76381	0.263072
	5000	14.2390470	1.48946414	2.01241250	0.579120581	5.49185026	10.3607405	104.170855	208.858414	8.76397	0.263016
5^1P_1	1000	14.2437620	1.48601999	2.00519317	0.564569081	8.56894055	16.4934202	277.924897	556.185184	8.75230	0.264452
$^\infty$Be	2000	14.2438987	1.48595851	2.00519870	0.564572686	8.56334369	16.4823329	277.525880	555.387334	8.76533	0.263565
	3000	14.2439112	1.48595171	2.00519911	0.564572839	8.56281337	16.4812930	277.486486	555.308872	8.76744	0.263376
	4000	14.2439146	1.48595101	2.00519942	0.564573277	8.56266930	16.4810098	277.477879	555.291678	8.76913	0.263371
	5000	14.2439157	1.48595068	2.00519949	0.564573351	8.56261583	16.4809051	277.473979	555.283923	8.76926	0.263368

were not reoptimized for the infinite-mass case. As our previous experience in atomic calculations has shown, there is no practical need for this costly reoptimization if the change of the inverse nuclear mass is very small (which was $1/16\,424.2037 \to 0$ in these calculations). The readjustment of only the linear coefficients fully recovers the shift of the total energy of the system in such a case. As one can see, for all four states with 5000 functions the nonrelativistic energy

TABLE III. $n\,^1P_1 \to m\,^1P_1$ transition energies (in cm^{-1}) for $^{\infty}$Be and ^{9}Be compared with the experimental transition energies [9]. Δ is the difference between the calculated transition for ^{9}Be and the experiment. The estimated uncertainties of calculated transitions due to finite size of the basis are given in parentheses.

Transition	$^{\infty}$Be	^{9}Be	Experiment	Δ
$5\,^1P_1 \to 2\,^1P_1$	27 560.57(2)	27 558.99(2)	27 555.14	3.85
$4\,^1P_1 \to 2\,^1P_1$	24 474.28(1)	24 472.74(1)	24 469.35	3.39
$3\,^1P_1 \to 2\,^1P_1$	17 625.54(1)	17 624.01(1)	17 621.99	2.02
$5\,^1P_1 \to 3\,^1P_1$	9935.03(2)	9934.98(2)	9933.15	1.83
$4\,^1P_1 \to 3\,^1P_1$	6848.74(1)	6848.73(1)	6847.36	1.37
$5\,^1P_1 \to 4\,^1P_1$	3086.29(1)	3086.25(1)	3085.79	0.46

is converged to the relative accuracy of at least 10^{-8} and likely even better than that. As expected, the convergence is somewhat better for the lowest state than for the fourth excited state. With the increase of the number of nodes in the wave function, the higher states become more difficult to describe and require more basis functions in order to reach the same accuracy as achieved for the lower states. The results shown in Table I allow a calculation of the finite-nuclear-mass effect on the total energy. This effect is slightly larger for the ground $2\,^1P_1$ state (0.000 907 628 a.u.; the result with 5000 basis functions) than for the fourth $5\,^1P_1$ state (0.000 900 432 a.u.).

In the next step we used the FNM and INM wave functions to calculate expectation values of some elementary operators. The results are shown in Table II for all four states and for the basis set sizes ranging from 1000 to 5000. Here are some comments that can be made upon examining the results.

The convergence of all the expectation values with the number of basis functions is very good. As expected, the expectation values of single powers of the interparticle distances converge faster than of the squares of the distances. For both Dirac delta functions $\langle \delta(\mathbf{r}_i) \rangle$ and $\langle \delta(\mathbf{r}_{ij}) \rangle$, four decimal figures are converged for all states.

As expected, the $\langle r_i \rangle$ and $\langle r_{ij} \rangle$ expectation values (as well as the $\langle r_i^2 \rangle$ and $\langle r_{ij}^2 \rangle$ expectation values) increase with the excitation level following the increase of the distance of the p electron from the core of the atom. The core contraction that occurs with the excitation does not offset this increase.

The contraction of the core electron density resulting from the outer p electron moving to larger distances due to the electron excitation results in a slight increase of the electron density at the nucleus which is manifested by an increase of the $\langle \delta(\mathbf{r}_i) \rangle$ expectation value. The same effect is seen in the $\langle \delta(\mathbf{r}_{ij}) \rangle$ expectation value.

For all four states, making the nucleus move along with the electrons by changing its mass from infinity to the finite mass in the calculations results in a slight increase of the average nucleus-electron distance ($\langle r_i \rangle$) and a small reduction of the electron density at the nucleus [the $\langle \delta(\mathbf{r}_i) \rangle$ expectation value].

In Table III we show transition energies between the $n\,^1P$ states calculated using the ^{9}Be and $^{\infty}$Be total energies obtained with 5000 basis functions and presented in Table I.

TABLE IV. $n\,^1P_1 \to m\,^1S_0$ transition energies (in cm^{-1}) for $^{\infty}$Be and ^{9}Be compared with the experimental transition energies [9]. Δ is the difference between the calculated transition for ^{9}Be and the experiment. The estimated uncertainties of calculated transitions due to finite size of the basis are given in parentheses.

Transition	$^{\infty}$Be	^{9}Be	Experiment	Δ
$5\,^1P_1 \to 2\,^1S_0$	70 117.83(3)	70 113.32(3)	70 120.49	−7.17
$4\,^1P_1 \to 2\,^1S_0$	67 031.54(2)	67 027.06(2)	67 034.70	−7.64
$3\,^1P_1 \to 2\,^1S_0$	60 182.79(2)	60 178.33(2)	60 187.34	−9.01
$2\,^1P_1 \to 2\,^1S_0$	42 557.26(2)	42 554.33(2)	42 565.35	−11.02
$5\,^1P_1 \to 3\,^1S_0$	15 443.14(3)	15 442.08(3)	15 443.23	−1.15
$4\,^1P_1 \to 3\,^1S_0$	12 356.85(2)	12 355.83(2)	12 357.44	−1.61
$3\,^1S_0 \to 2\,^1P_1$	12 117.43(2)	12 116.90(2)	12 111.91	4.99
$3\,^1P_1 \to 3\,^1S_0$	5508.11(2)	5507.10(2)	5510.08	−2.98

The calculated transition energies are compared with the transition energies determined from the experimental data taken from Ref. [9]. Let us first examine the transition $5\,^1P_1 \to 2\,^1P_1$. The calculated energy for this transition using the $^{\infty}$Be energies of 27560.57 cm^{-1} is 5.43 cm^{-1} off from the experimental value of 27 555.14 cm^{-1}. Including the FNM effect by using the ^{9}Be energies in the calculation lowers the transition energy to 27 558.99 cm^{-1} and reduces the discrepancy between the experiment and the calculations to 3.85 cm^{-1}. For the $4\,^1P_1 \to 2\,^1P_1$ and $3\,^1P_1 \to 2\,^1P_1$ transitions the discrepancy between the calculated ^{9}Be transition and the experiment is smaller, 3.39 and 2.02 cm^{-1}, respectively. This can be explained by the fact that relativistic effects, which are not accounted for in the present calculations, but which need to be included to achieve better agreement with the experiment, cancel out to a higher degree for these transitions than for the $5\,^1P_1 \to 2\,^1P_1$ transition. For the transitions that involve higher states the difference between the experiment and the calculations becomes even smaller. This is because the magnitude of the relativistic effects due to the excited p electron become progressively smaller, while the relativistic effects due to the inner electrons cancel out almost completely.

The same trends can be observed for $n\,^1P_1 \to m\,^1S_0$ transitions, which are shown in Table IV. To compute these transitions we used the total energies of −14.667356446($^{\infty}$Be) and −14.666 435 464(^{9}Be) a.u. and −14.418 240 230($^{\infty}$Be) and −14.417 335 005(^{9}Be) a.u. for $2\,^1S_0$ and $3\,^1S_0$ states of beryllium taken from our previous work [10]. To be consistent, we used the energies obtained with 5000 functions, though the convergence of these S state energies with 5000 basis functions is likely to be slightly better than the convergence of the P state energies with the same number of basis functions. In any event, the convergence of nonrelativistic energies for both the P and S states is quite high and for the purpose of determining the transition energies (shown in Tables III and IV) the values can be considered nearly exact. The $n\,^1P_1 \to m\,^1S_0$ transitions show somewhat larger difference between the computed values and the experimental ones than for the $m\,^1P_1 \to n\,^1P_1$ transitions. This is because the relativistic effects for S and P states are quite different and, thus, do not cancel out as much as in the case of $m\ {}^1P_1 \rightarrow n\ {}^1P_1$ transitions. Moreover, the largest discrepancy is observed in the transitions that involve the $2\ {}^1S_0$ state where the relativistic effects are largest as they usually are for the atomic ground states.

VI. SUMMARY

Very accurate nonrelativistic calculations with the finite nuclear mass have been performed for four lowest ${}^1P_1$ states of Be using large basis sets of explicitly correlated Gaussian functions. The variational nonrelativistic energies obtained in the calculations are by far the lowest obtained for these states. The total energies of the four lowest ${}^1P_1$ states computed in this study and the energies of the two lowest ${}^1S_0$ states obtained in our previous work were used to determine the $n\ {}^1P_1 \rightarrow m\ {}^1P_1$ and $n\ {}^1P_1 \rightarrow m\ {}^1S_0$ transition energies. The comparison of the results with the experimental transition energies shows that the calculations are off from the experiment by 0.5–11 cm^{-1}. While some very small additional improvement of the agreement can probably come from increasing the number of the basis functions beyond 5000, the most important improvement is expected to come from including the relativistic corrections in the calculations. We already calculated those corrections for S states of beryllium [10] and their inclusion, together with the inclusion of the leading quantum electrodynamic corrections computed previously by Komasa and Pachucki [11], brought the calculated transition energies for those states much closer to the experiment. It is our intent to now develop algorithms for calculating relativistic corrections with ECGFs for states with higher orbital angular momenta.

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