

# Lowest ten $^1P$ Rydberg states of beryllium calculated with all-electron explicitly correlated Gaussian functions

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Received 13 March 2019, revised 9 May 2019

Accepted for publication 28 May 2019

Published 16 July 2019



CrossMark

## Abstract

In this work we report very accurate calculations of the ten lowest  $^1P$  ( $L = 1$ ) bound states of the beryllium atom performed with the finite-nuclear-mass (FNM) approach and with all-electron explicitly correlated Gaussian functions. The FNM non-relativistic variational energies of the states are augmented with the leading relativistic and quantum-electrodynamics (QED) corrections. The latter include the Araki–Sucher QED correction whose implementation for the  $L = 1$  states is featured in this work. The calculated energies for interstate transition energies are compared with the experimental results.

Keywords: Rydberg spectrum of beryllium atom, explicitly correlated all-electron Gaussian functions, finite-nuclear-mass approach

## 1. Introduction

One of the major challenges of the quantum theory of atoms is to determine the energy levels corresponding to bound ground and excited states and the frequencies of the transitions between these levels with the spectroscopic accuracy (i.e. below  $1 \text{ cm}^{-1}$ ). As such determination involves the calculation of the corresponding wave functions representing the computed states, various properties of the states can also be determined. That involves, for example, the transition intensities, the average distances of the electrons to the nucleus and between the electrons, etc. As the amount of computations required grows very rapidly with the number of electrons (this growth is proportional to the factorial of the number of electrons), even for atoms with a few electrons this becomes a computationally very demanding task. Thus, in undertaking calculations of an atomic spectrum a balance needs to be achieved between the accuracy one aims for in the

calculations and the amount of resource these calculations are expected to take.

One of the many challenges involved in atomic calculations is to target not only a few lowest lying states but to extend the calculations to a wider spectrum of states. For both helium and lithium atoms calculations exist where nearly ten lowest states were calculated with very high accuracy [1, 2]. For the beryllium atoms only the lowest five  $^1S$  states [3] and one  $^1P$  state [4] were calculated. Recently, very accurate calculations were also performed for the lowest four  $^2S$  states of the boron atom [5]. The capabilities now exist to extend the calculations for the beryllium and boron atoms to ten states and beyond. This is being done in the present work where very accurate calculations are performed for the lowest ten  $^1P$  states of the beryllium atom.

The electronic structure of the beryllium atom is of great relevance to various problems arising in different areas of modern science. Stellar astrophysics and plasmas research, as well as studies in high-temperature physics and applied nuclear physics,

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relay on precise knowledge and understanding of the beryllium spectrum.

Precise determination of atomic energy levels and other properties is an involved undertaking because the strong Coulombic interaction between electrons leads to rather large contribution due the electron correlation, which needs to be accurately described in the calculations. Moreover, there are some subtle effects due to relativity, quantum-electrodynamics (QED), and finite nuclear mass and size that need to be also described. To accurately represent the correlated motion of the electrons in an atom one needs to make the wave function explicitly dependent on the inter-electron distances. This can be, for example, accomplished by expanding the wave function in terms of basis functions that depend on these distances. All-electron explicitly correlated Gaussian functions (ECGs) are such functions. They have been used in atomic calculations since they were first introduced to the field by Boys [6]. For example, for the beryllium atom calculations involving ECGs [7] resulted in the determination of the  $3^1S \rightarrow 2^1S$  transition energy within the experimental error bar from the value measured by Johansson [8, 9]. ECGs were also used to calculate the lowest  $S \rightarrow P$  transitions of beryllium [4]. While the latter beryllium calculations were performed with the infinite-nuclear-mass (INM) approach and the finite-mass effects were obtained using the perturbation theory, the finite-nuclear-mass (FNM) approach was used in the former calculations. Thus, the FNM effects (adiabatic and non-adiabatic) were explicitly included in the nonrelativistic energies, as well as in the leading relativistic corrections, as those corrections were calculated as expectation values of the corresponding relativistic operators with the wave functions obtained in the FNM calculations. Thus, the relativistic corrections explicitly include the so-called recoil effects that in the INM approach are determined in a more complicated way using the perturbation-theory approach.

In this work we report first large-scale applications of the algorithms for calculating the leading relativistic corrections for singlet states with  $L = 1$  (the  $P$  states) recently implemented by our group [10]. We also report the derivation and implementation of the Araki–Sucher QED correction calculated using the FNM wave function expanded in terms of all-electron ECGs.

In recent years we have used various types of ECG basis functions in accurate atomic and molecular calculations performed with an approach where the Born–Oppenheimer approximation has not assumed [11–13]. The standard variational method and large ECG basis sets have been employed in the calculations and the nonlinear parameters of the Gaussians have been extensively optimized to obtain very well converged non-relativistic energies of the considered states. As the expression for the total energy obtained using the various forms ECGs can be easily analytically differentiated with respect to the Gaussian exponential parameters, the energy gradient in an analytical form can be determined [11, 14]. The implementation of the gradient in our atomic and molecular calculations has been of critical importance. The variational optimization of the Gaussian nonlinear parameters is much more effective when the energy gradient is made available to the subroutine that runs the energy minimization. Thus, even

though the Gaussians less efficient in describing the cusps and the long-range behavior of the wave function in comparison with, for example, explicitly-correlated Slater functions, this deficiency can be effectively remediated with the use of sufficiently large and well optimized basis sets. Due to the implementation of the gradient, the very accurate results we have generated for ground and excited states of some atomic systems with more than three electrons have been unmatched in accuracy by calculations performed by others.

## 2. Method used in the calculations

We first write the total non-relativistic Hamiltonian of an  $n$ -electron atom in the laboratory Cartesian coordinate system without the Born–Oppenheimer approximation. This Hamiltonian describing a  $n + 1$ -particle system consisting of a nucleus and  $n$  electrons is dependent on  $3(n + 1)$  coordinates. Next separation of the motion of the center of mass [12] is performed that effectively reduces the  $(n + 1)$ -particle problem to an  $n$ -particle problem. The separation is accomplished by transforming the laboratory coordinate system to a new system of coordinates of which the first three are the laboratory Cartesian coordinates of the center of mass and the remaining  $3n - 3$  are internal Cartesian coordinates. To define the internal coordinates the nucleus is placed in the center of the internal coordinates system and vectors  $\mathbf{r}_i$  are used to define the positions the electrons ( $i = 1, \dots, n$ ) with respect to the nucleus. When the total Hamiltonian is transformed from the laboratory coordinate system to the new system of coordinates, it separates into the Hamiltonian representing the kinetic energy of the center-of-mass motion (dependent only on the center-of-mass coordinates) and the so-called internal Hamiltonian (dependent only on the internal  $\mathbf{r}_i$ ,  $i = 1, \dots, n$ , coordinates). The separation is rigorous. The internal Hamiltonian,  $H_{\text{nr}}$ , which has the following form (in a.u.):

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

where  $q_0$  is the nuclear charge,  $q_i = -1$ ,  $i = 1, \dots, n$ , are charges of the electrons,  $m_0$  is the mass of the nucleus ( $16\,424.205\,5m_e$  for  $^9\text{Be}$ , where  $m_e$  is the mass of an electron),  $m_i = 1$ ,  $i = 1, \dots, n$  are the electron masses, and  $\mu_i = m_0 m_i / (m_0 + m_i)$ ,  $i = 1, \dots, n$  are the reduced masses of the electrons. ‘T’ denotes the transposition. The finite-nuclear-mass effects are represented by the mass-polarization term and by the reduced masses  $\mu_i$ .

The most convenient way to account for the leading relativistic and QED effects is to expand the total energy in powers of the fine structure constant [15, 16]

$$E_{\text{tot}} = E_{\text{nr}}^{(0)} + \alpha^2 E_{\text{rel}}^{(2)} + \alpha^3 E_{\text{qed}}^{(3)} + \dots,$$

where  $E_{\text{nr}}^{(0)}$  is an eigenvalue of the nonrelativistic Hamiltonian (1),  $\alpha^2 E_{\text{rel}}^{(2)}$  represents the leading relativistic corrections, and

$E_{\text{qed}}^{(3)}$  represents the leading QED corrections ( $\alpha$  is the fine structure parameter;  $\alpha = 7.297\,352\,569\,8 \cdot 10^{-3}$  [17]). In this work  $E_{\text{qed}}^{(3)}$  only includes the Araki–Sucher term. In appendix we show the derivation of this term for the basis functions used in this work to expand the wave functions of the  $n$  electron  $^1P$  states.

The  $E_{\text{rel}}^{(2)}$  corrections are evaluated in this work in the framework of the perturbation theory using the non-BO nonrelativistic wave function corresponding to  $E_{\text{nr}}^{(0)}$  as the zero-order solution. These corrections are expectation values of the respective effective Dirac–Breit Hamiltonians in the Pauli approximation [18, 19]. For the singlet  $^1P$  states of beryllium considered in this work the relativistic Hamiltonian contains the following terms:

$$\hat{H}_{\text{rel}} = \hat{H}_{\text{MV}} + \hat{H}_{\text{D}} + \hat{H}_{\text{OO}} + \hat{H}_{\text{SS}}, \quad (2)$$

which represent the mass–velocity (MV), Darwin (D), orbit–orbit (OO), and spin–spin (SS) interactions (the spin–orbit interaction does not appear as it is zero for singlet states). The explicit form of these terms is given in [12]. The terms are:

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

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

$$\begin{aligned} H_{\text{OO}} = & -\frac{1}{2} \sum_{i=1}^4 \frac{q_0 q_i}{m_0 m_i} \left( \frac{1}{r_i} \nabla_{\mathbf{r}_i} \cdot \nabla_{\mathbf{r}_i} + \frac{1}{r_i^3} \mathbf{r}_i \cdot (\mathbf{r}_i \cdot \nabla_{\mathbf{r}_i}) \nabla_{\mathbf{r}_i} \right) \\ & - \frac{1}{2} \sum_{\substack{i,j=1 \\ j \neq i}}^4 \frac{q_0 q_i}{m_0 m_i} \left( \frac{1}{r_i} \nabla_{\mathbf{r}_i} \cdot \nabla_{\mathbf{r}_j} + \frac{1}{r_i^3} \mathbf{r}_i \cdot (\mathbf{r}_i \cdot \nabla_{\mathbf{r}_i}) \nabla_{\mathbf{r}_j} \right) \\ & + \frac{1}{2} \sum_{\substack{i,j=1 \\ j > i}}^4 \frac{q_i q_j}{m_i m_j} \left( \frac{1}{r_{ij}} \nabla_{\mathbf{r}_i} \cdot \nabla_{\mathbf{r}_j} + \frac{1}{r_{ij}^3} \mathbf{r}_{ij} \cdot (\mathbf{r}_{ij} \cdot \nabla_{\mathbf{r}_i}) \nabla_{\mathbf{r}_j} \right), \end{aligned} \quad (5)$$

and

$$H_{\text{SS}} = -\frac{8\pi}{3} \sum_{\substack{i,j=1 \\ j > i}}^4 \frac{q_i q_j}{m_i m_j} (\mathbf{s}_i \cdot \mathbf{s}_j) \delta(\mathbf{r}_{ij}), \quad (6)$$

where  $\delta(\mathbf{r})$  is the Dirac delta function and  $\mathbf{s}_i$  are spin operators for individual electrons. For the states considered in this work  $\mathbf{s}_i \cdot \mathbf{s}_j = -\frac{3}{4}$ .

The leading QED correction for the beryllium atom that accounts for the two-photon exchange, the vacuum polarization, and the electron self-energy effects are expressed as:

$$\begin{aligned} H_{\text{QED}} = & \sum_{\substack{i,j=1 \\ j > i}}^4 \left[ \left( \frac{164}{15} + \frac{14}{3} \ln \alpha \right) \delta(\mathbf{r}_{ij}) - \frac{7}{6\pi} P(r_{ij}^{-3}) \right] \\ & + \sum_{i=1}^4 \left( \frac{19}{30} - 2 \ln \alpha - \ln k_0 \right) \frac{4q_0}{3} \delta(\mathbf{r}_i). \end{aligned} \quad (7)$$

Here the last term is the Araki–Sucher distribution [20–24] and the expectation value of  $P(r_{ij}^{-3})$  is:

$$\langle P(r_{ij}^{-3}) \rangle = \lim_{a \rightarrow 0} \langle r_{ij}^{-3} \Theta(r_{ij} - a) + 4\pi(\gamma + \ln a) \delta(\mathbf{r}_{ij}) \rangle, \quad (8)$$

where  $\Theta$  is the Heaviside step function and  $\gamma = 0.577\,2\dots$  is the Euler–Mascheroni constant. The derivation of the  $kl$  matrix element of  $\langle P(r_{ij}^{-3}) \rangle$  for the basis functions used in this work to expand the spatial parts of the wave functions of the considered  $^1P$  states is presented in appendix. The numerical values of the conversion factor from a Hartree to a wavenumber and of the fine structure constant used in present work are:  $1\text{hartree} = 2.194\,746\,313\,705 \times 10^5 \text{ cm}^{-1}$  and  $\alpha = 7.297\,352\,537\,6 \times 10^{-3}$ , respectively.

In the calculations for all  $^1P$  states considered in this work we use a single value of the Bethe logarithm,  $\ln k_0 = 5.752\,32$ , which was calculated for the  $2^1P$  state of beryllium atom by Puchalski *et al* [4]. Obviously, this is an approximation. It can be justified by almost constant values of  $\ln k_0$  for the lowest  $^1S$  states of beryllium calculated in our previous work [3].

The HQED correction is calculated using the following approximate formula developed by Pachucki *et al* [25, 26]:

$$H_{\text{HQED}} = \pi q_0^2 \left( \frac{427}{96} - 2 \ln 2 \right) \sum_{i=1}^4 \delta(\mathbf{r}_i). \quad (9)$$

It corresponds to the dominant part of the so-called one-loop term.

### 3. Basis functions

The spatial parts of the wave functions of the ten lowest  $^1P$  states of beryllium considered in this work are expanded in terms of following ECGs:

$$\phi_k = z_{m_k} \exp[-\mathbf{r}^T \underline{\mathbf{A}}_k \mathbf{r}]. \quad (10)$$

Here  $m_k$  is an integer that depends on  $k$  with a value from 1 to  $n$ ,  $\underline{\mathbf{A}}_k$  is  $3n \times 3n$  symmetric matrix, and  $\mathbf{r}$  is a  $3n$  vector of the internal Cartesian coordinates of the electrons (for the Be atoms  $\mathbf{r}$  has the length of 12).

As basis functions (10) are used to expand wave functions of bound atomic states, they need to be square integrable. This only happens if the  $\underline{\mathbf{A}}_k$  matrix is positive definite. To make it positive definite we represent it in the Cholesky-factored form as  $\underline{\mathbf{A}}_k = (L_k L_k^T) \otimes I_3$ , where  $L_k$  is a  $n \times n$  lower triangular matrix,  $I_3$  is a 3 unit matrix, and  $\otimes$  denotes the Kronecker product. With the  $L_k$  matrix elements being any real numbers,  $\underline{\mathbf{A}}_k$  is positive definite. This is an important feature because it allows to use the  $L_k$  matrix elements as the variational optimization parameters which can be varied without any restrictions in the range from  $-\infty$  to  $+\infty$ . The optimization of these parameters through the variational energy minimization is performed in our calculations.

The proper permutational symmetry in the present calculations is implemented with the use of the spin-free formalism. In this formalism, an appropriate symmetry projector is constructed and applied to the spatial parts of the wave function to

impose the desired symmetry properties. The projector, which introduces the desired symmetry properties, is constructed using the standard procedure involving Young operators [27]. For the  $^1P$  states of the beryllium atom the symmetry projector can be chosen as:  $P = (1 - P13)(1 - P24)(1 + P12)(1 + P34)$ , where  $P_{ij}$  permutes the spatial coordinates of the  $i$ th and  $j$ th electrons. In the calculations of the Hamiltonian and overlap matrix elements, as well as in the operators representing the relativistic corrections, the projector is placed only in the ‘ket’ ( $|\tilde{\phi}\rangle = P|\phi\rangle$ ) part of the integrals because the operators are symmetric with respect to permutations of the electron labels. As in the beryllium calculations the projector contains  $4! = 24$  terms, each matrix element is a sum of 24 different terms.

The variational calculations are performed separately and independently for each state and for each state a different basis set is generated. In the calculations the linear expansion coefficients,  $c_k$ , of the wave function in terms of basis functions are obtained in the standard way by solving the secular equation. The nonlinear parameters (i.e. the  $L_k$  matrix elements) are optimized through the variational minimization of the total nonrelativistic energy. The analytic energy gradient determined with respect to these parameters is used in the minimization [12].

The growing of the basis set for each state is a multistep process. It involves choosing a small starting set of ECGs (for the lowest state this set is generated using a orbital guess obtained using a standard AO basis set; for a higher state a basis set generated for the next lower state is used as the initial guess). After the initial basis set is optimized the updating of the set starts. It involves addition of small groups of functions, optimizing them, and reoptimizing the whole set. All this is done using the one-function-at-the-time approach. The initial guesses for the added functions are generated by selecting a set of most contributing functions already included in the basis set, randomly perturbing their nonlinear parameters, and choosing the functions which lower the energy the most. At this stage, the  $m_k$  indices involved in the angular components of the basis functions are also optimized. After a certain number of functions (100 in the present calculations) is added to the basis set, the entire basis is reoptimized. The reoptimization involves cycling over all functions, one by one, several times and reoptimizing their nonlinear parameters. In the calculations performed before for other systems it was determined that the above strategy is efficient and numerically stable. The stability of the calculations is also enhanced by checking if the optimization generates any linear dependencies between the basis functions. Such dependencies may lead to numerical inaccuracies and destabilization of the optimization process. If during the optimization of a basis function it becomes linearly dependent with other functions already included in the basis set, the function is reset to what it was before the optimization. The use of the analytic gradient is crucial in making the optimization efficient.

The variational optimization of the nonlinear parameters of the Gaussians is carried out using the FNM approach. Thus, the total energies obtained in the calculations include the adiabatic and non-adiabatic effects resulting from the finite mass of nucleus of  $^7\text{Be}$ . The same basis are used to perform the INM energy calculations ( $^\infty\text{Be}$ ) without

reoptimization of the nonlinear parameters. As our previous calculations of atomic isotopomers have shown, no reoptimization of the nonlinear variational parameters is needed when states of different isotopes are calculated. The adjustment of the linear coefficients,  $c_k$ , through re-diagonalization of the Hamiltonian and overlap matrices is quite sufficient for describing the relatively small changes in the wave function and the energy caused by the change of the nuclear mass.

## 4. Results

The  $L = 1$  atomic code written in Fortran90 and employing the MPI (message passing interface) used in the present calculations has been updated to include the algorithm to calculate the Araki–Sucher QED correction. The lowest ten  $^1P$  states of the beryllium atom are calculated. The optimization of the nonlinear parameters of the basis functions has been by far the most time consuming part of the calculations that had lasted for several months. The INM energy of the lowest  $^1P$  state obtained in the present calculations of  $-14.473\,451\,388\,2$  hartree can be compared the value of  $-14.473\,451\,37(4)$  reported by Puchalski *et al* [4]. Our value is slightly lower than theirs.

The results for the ten states that include the nonrelativistic energies and the expectation values which appear in the leading relativistic and QED corrections are shown in table 1. For  $^9\text{Be}$  the results include values obtained for 14 600, 15 500, and 16 400 ECGs (15 000, 16 000, and 16 400 ECGs for state  $11p$ ), as well as the results obtained with the basis set of 16 400 ECGs where several additional optimization cycles of the nonlinear parameters are performed to further lower the total energies of each of the considered states. While the first several additional optimization cycles are performed using the standard double-precision computer arithmetic (with 8 bytes per a floating-point number), the last cycles are performed with an extended precision (with 10 bytes per a floating-point number). As the results presented in table 1 show, the additional optimization cycles are particularly important for the upper states whose energies are noticeably lowered by carrying out the additional optimization. Undoubtedly, further optimization and/or increasing the size of the basis sets would produce further improvement of the energies, but with the computer capabilities available to us, this would not be practical. For  $^\infty\text{Be}$  only the results obtained with 16 400 ECGs are shown.

The  $^9\text{Be}$  results allow to examine the convergence of the results in terms of the number of the basis functions. As one can see, for the lowest five states the total energies are converged within nine digits after the decimal point. Beyond the sixth state the convergence becomes progressively worse. For the  $11s$  state only six digits after the decimal point are converged. Also, in the calculations for the higher states switching from the double computer precision to the extended precision results in more significant energy lowering. The calculations of the expectation values of the quantities used to determine the relativistic and QED corrections for all states are also carried out using the extended precision.

**Table 1.** Convergence of the total nonrelativistic energies,  $E_{nr}$ , and expectation values which appear in the leading relativistic and QED corrections with the number of basis functions for the lowest ten  $^1P$  states of  $^9\text{Be}$ . The nonrelativistic infinite-nuclear mass energies of beryllium ( $^\infty\text{Be}$ ) is also shown. Superscript  $a$  after the basis size indicates that several additional optimization cycles have been performed for the whole basis set. All values are given in a.u.

State	Isotope	Basis	$E_{nr}$	$\langle \hat{H}_{mv} \rangle$	$\langle \delta(\mathbf{r}_i) \rangle$	$\langle \delta(\mathbf{r}_{ij}) \rangle$	$\langle \hat{H}_{oo} \rangle$	$\langle P(1/r_{ij}^3) \rangle$
$2^1P$	$^9\text{Be}$	14 600	-14.472 543 756 8	-266.592 68	8.722 635 0	0.261 300 3	-0.838 224 7	-0.565 745
	$^9\text{Be}$	15 500	-14.472 543 757 6	-266.592 67	8.722 636 5	0.261 299 7	-0.838 224 7	-0.565 715
	$^9\text{Be}$	16 400	-14.472 543 758 4	-266.592 67	8.722 637 9	0.261 299 6	-0.838 224 7	-0.565 710
	$^9\text{Be}$	16 400 <sup>a</sup>	-14.472 543 759 8	-266.592 59	8.722 636 9	0.261 299 6	-0.838 224 6	-0.565 709
	$^\infty\text{Be}$	16 400 <sup>a</sup>	-14.473 451 388 2	-266.659 02	8.724 264 8	0.261 343 9	-0.812 091 5	-0.565 917
$3^1P$	$^9\text{Be}$	14 600	-14.392 242 880 2	-267.380 49	8.747 414 7	0.262 265 9	-0.882 080 4	-0.585 898
	$^9\text{Be}$	15 500	-14.392 242 881 7	-267.381 52	8.747 449 3	0.262 265 6	-0.882 080 4	-0.585 885
	$^9\text{Be}$	16 400	-14.392 242 882 6	-267.381 56	8.747 455 6	0.262 265 8	-0.882 080 4	-0.585 899
	$^9\text{Be}$	16 400 <sup>a</sup>	-14.392 242 884 4	-267.381 59	8.747 457 1	0.262 265 7	-0.882 080 4	-0.585 892
	$^\infty\text{Be}$	16 400 <sup>a</sup>	-14.393 143 538 5	-267.447 85	8.749 077 4	0.262 309 6	-0.855 811 5	-0.586 099
$4^1P$	$^9\text{Be}$	14 600	-14.361 037 794 5	-267.880 92	8.762 978 1	0.262 933 7	-0.913 549 6	-0.594 291
	$^9\text{Be}$	15 500	-14.361 037 796 0	-267.882 04	8.763 029 5	0.262 933 1	-0.913 549 6	-0.594 266
	$^9\text{Be}$	16 400	-14.361 037 797 2	-267.882 15	8.763 031 4	0.262 923 4	-0.913 549 5	-0.593 773
	$^9\text{Be}$	16 400 <sup>a</sup>	-14.361 037 799 9	-267.882 15	8.763 032 1	0.262 923 3	-0.913 549 5	-0.593 766
	$^\infty\text{Be}$	16 400 <sup>a</sup>	-14.361 938 399 8	-267.948 34	8.764 649 0	0.262 967 0	-0.887 204 0	-0.593 972
$5^1P$	$^9\text{Be}$	14 600	-14.346 975 854 0	-268.058 27	8.768 476 8	0.263 197 0	-0.924 932 3	-0.598 223
	$^9\text{Be}$	15 500	-14.346 975 856 7	-268.058 18	8.768 507 5	0.263 196 2	-0.924 932 2	-0.598 189
	$^9\text{Be}$	16 400	-14.346 975 859 3	-268.057 76	8.768 510 2	0.263 196 1	-0.924 932 2	-0.598 186
	$^9\text{Be}$	16 400 <sup>a</sup>	-14.346 975 863 8	-268.057 72	8.768 510 4	0.263 196 0	-0.924 932 2	-0.598 183
	$^\infty\text{Be}$	16 400 <sup>a</sup>	-14.347 876 295 3	-268.123 91	8.770 127 0	0.263 239 7	-0.898 561 4	-0.598 388
$6^1P$	$^9\text{Be}$	14 600	-14.339 569 896 9	-268.130 65	8.770 602 0	0.263 288 9	-0.929 839 3	-0.598 777
	$^9\text{Be}$	15 500	-14.339 569 904 7	-268.130 79	8.770 614 4	0.263 288 4	-0.929 839 3	-0.598 763
	$^9\text{Be}$	16 400	-14.339 569 911 0	-268.134 10	8.770 670 6	0.263 288 2	-0.929 839 3	-0.598 758
	$^9\text{Be}$	16 400 <sup>a</sup>	-14.339 569 924 2	-268.134 20	8.770 674 1	0.263 287 9	-0.929 839 3	-0.598 743
	$^\infty\text{Be}$	16 400 <sup>a</sup>	-14.340 470 194 4	-268.200 39	8.772 290 7	0.263 331 6	-0.903 457 8	-0.598 948
$7^1P$	$^9\text{Be}$	14 600	-14.335 215 466 8	-268.137 94	8.770 693 8	0.263 374 2	-0.932 286 6	-0.600 765
	$^9\text{Be}$	15 500	-14.335 215 483 5	-268.144 00	8.770 931 4	0.263 373 8	-0.932 286 6	-0.600 749
	$^9\text{Be}$	16 400	-14.335 215 510 8	-268.146 90	8.771 066 0	0.263 369 1	-0.932 286 5	-0.600 572
	$^9\text{Be}$	16 400 <sup>a</sup>	-14.335 215 559 2	-268.151 07	8.771 204 6	0.263 366 8	-0.932 286 5	-0.600 471
	$^\infty\text{Be}$	16 400 <sup>a</sup>	-14.336 115 706 0	-268.217 26	8.772 821 0	0.263 410 6	-0.905 899 7	-0.600 677
$8^1P$	$^9\text{Be}$	14 600	-14.332 444 940 2	-268.136 69	8.770 230 8	0.263 475 5	-0.933 641 1	-0.604 013
	$^9\text{Be}$	15 500	-14.332 445 006 9	-268.136 56	8.770 266 7	0.263 473 2	-0.933 640 9	-0.603 936
	$^9\text{Be}$	16 400	-14.332 445 100 9	-268.137 02	8.770 327 8	0.263 471 4	-0.933 641 1	-0.603 880
	$^9\text{Be}$	16 400 <sup>a</sup>	-14.332 445 263 5	-268.136 89	8.770 342 7	0.263 470 9	-0.933 641 1	-0.603 864
	$^\infty\text{Be}$	16 400 <sup>a</sup>	-14.333 345 316 8	-268.203 08	8.771 959 1	0.263 514 7	-0.907 251 0	-0.604 071
$9^1P$	$^9\text{Be}$	14 600	-14.330 575 377 2	-268.149 13	8.770 190 0	0.263 576 8	-0.934 452 1	-0.607 244
	$^9\text{Be}$	15 500	-14.330 575 490 2	-268.149 45	8.770 226 5	0.263 572 7	-0.934 452 7	-0.607 110
	$^9\text{Be}$	16 400	-14.330 575 614 3	-268.149 70	8.770 283 9	0.263 557 8	-0.934 453 0	-0.606 524
	$^9\text{Be}$	16 400 <sup>a</sup>	-14.330 575 973 2	-268.150 47	8.770 308 5	0.263 555 9	-0.934 453 0	-0.606 464
	$^\infty\text{Be}$	16 400 <sup>a</sup>	-14.331 475 953 7	-268.216 68	8.771 924 9	0.263 599 7	-0.908 060 7	-0.606 671
$10^1P$	$^9\text{Be}$	14 600	-14.329 251 944 5	-268.094 62	8.765 868 7	0.263 925 9	-0.934 974 9	-0.618 801
	$^9\text{Be}$	15 500	-14.329 252 437 4	-268.093 83	8.766 008 6	0.263 919 1	-0.934 976 7	-0.618 630
	$^9\text{Be}$	16 400	-14.329 252 920 6	-268.094 17	8.766 171 3	0.263 874 7	-0.934 974 3	-0.617 224
	$^9\text{Be}$	16 400 <sup>a</sup>	-14.329 255 009 9	-268.096 76	8.766 291 3	0.263 871 8	-0.934 974 5	-0.617 144
	$^\infty\text{Be}$	16400 <sup>a</sup>	-14.330 154 912 7	-268.162 95	8.767 907 3	0.263 915 6	-0.908 577 6	-0.617 352
$11^1P$	$^9\text{Be}$	15 000	-14.328 274 732 2	-267.843 75	8.756 435 5	0.264 362 0	-0.935 344 4	-0.630 531
	$^9\text{Be}$	16 000	-14.328 276 605 0	-267.842 22	8.756 697 1	0.264 320 6	-0.935 341 3	-0.629 488
	$^9\text{Be}$	16 400	-14.328 277 315 8	-267.847 23	8.756 894 4	0.264 312 9	-0.935 342 6	-0.629 292
	$^9\text{Be}$	16 400 <sup>a</sup>	-14.328 285 422 3	-267.850 13	8.757 096 2	0.264 306 9	-0.935 344 2	-0.629 147
	$^\infty\text{Be}$	16 400 <sup>a</sup>	-14.329 185 241 1	-267.916 26	8.758 711 0	0.264 350 7	-0.908 940 3	-0.629 355

The results from table 1 are used to calculate excitation energies corresponding to  $2p \rightarrow np$ ,  $n = 3, \dots, 11$ , transitions. The results obtained at the non-relativistic FNM level, with including the leading relativistic corrections, with including the

leading relativistic and QED corrections, and with additionally including higher-order QED corrections are shown in table 2. For each state, values obtained with various numbers of basis functions are presented to enable assessing the basis-set

**Table 2.** Convergence of the  $2p \rightarrow np$  transition energies and their extrapolated values calculated using the FNM nonrelativistic energies ( $\Delta E_{nr}$ ), FNM energies that include the leading relativistic corrections ( $\Delta E_{nr+rel}$ ), and FNM energies that include the leading relativistic and QED corrections ( $\Delta E_{nr+rel+qed}$ ,  $\Delta E_{nr+rel+qed+hqed}$ ). The transition energies are compared to the experimentally derived values from [28]. The values in parentheses shown after the experimental transition energies are uncertainties derived from the level uncertainties reported in [28]. All transitions are given in  $\text{cm}^{-1}$ . The values in parentheses shown after the transition energies extrapolated to the complete basis set provide an estimate of the order of magnitude of the extrapolation error.

Transition	Basis	$\Delta E_{nr}$	$\Delta E_{nr+rel}$	$\Delta E_{nr+rel+qed}$	$\Delta E_{nr+rel+qed+hqed}$	Experiment
$2^1P \rightarrow 3^1P$	14 600	17 624.005	17 621.777	17 621.988	17 621.997	17 621.99(0.20)
	15 500	17 624.005	17 621.774	17 621.985	17 621.995	
	16 400	17 624.005	17 621.775	17 621.986	17 621.996	
	16 400 <sup>a</sup>	17 624.005	17 621.775	17 621.986	17 621.995	
	$\infty$	17 624.005(0)	17 621.772(5)	17 621.983(5)	17 621.993(5)	
$2^1P \rightarrow 4^1P$	14 600	24 472.730	24 469.004	24 469.346	24 469.361	24 469.35(0.20)
	15 500	24 472.730	24 469.005	24 469.347	24 469.363	
	16 400	24 472.730	24 469.001	24 469.344	24 469.359	
	16 400 <sup>a</sup>	24 472.730	24 469.001	24 469.343	24 469.359	
	$\infty$	24 472.729(0)	24 468.996(10)	24 469.339(10)	24 469.354(10)	
$2^1P \rightarrow 5^1P$	14 600	27 558.969	27 554.710	27 555.098	27 555.116	27 555.14(0.20)
	15 500	27 558.969	27 554.719	27 555.108	27 555.125	
	16 400	27 558.968	27 554.724	27 555.113	27 555.130	
	16 400 <sup>a</sup>	27 558.968	27 554.724	27 555.112	27 555.130	
	$\infty$	27 558.967(2)	27 554.728(10)	27 555.117(10)	27 555.134(10)	
$2^1P \rightarrow 6^1P$	14 600	29 184.389	29 179.871	29 180.277	29 180.296	29 180.74(0.20)
	15 500	29 184.387	29 179.871	29 180.277	29 180.296	
	16 400	29 184.386	29 179.847	29 180.254	29 180.272	
	16 400 <sup>a</sup>	29 184.385	29 179.845	29 180.252	29 180.270	
	$\infty$	29 184.383(6)	29 179.819(50)	29 180.227(50)	29 180.245(50)	
$2^1P \rightarrow 7^1P$	14 600	30 140.076	30 135.490	30 135.897	30 135.915	30 136.45(0.20)
	15 500	30 140.072	30 135.485	30 135.894	30 135.912	
	16 400	30 140.067	30 135.483	30 135.893	30 135.912	
	16 400 <sup>a</sup>	30 140.063	30 135.470	30 135.882	30 135.900	
	$\infty$	30 140.057(15)	30 135.459(25)	30 135.873(25)	30 135.891(25)	
$2^1P \rightarrow 8^1P$	14 600	30 748.136	30 743.435	30 743.838	30 743.856	30 744.35(2.0)
	15 500	30 748.122	30 743.432	30 743.835	30 743.853	
	16 400	30 748.101	30 743.423	30 743.827	30 743.845	
	16 400 <sup>a</sup>	30 748.088	30 743.415	30 743.819	30 743.837	
	$\infty$	30 748.069(50)	30 743.407(50)	30 743.812(50)	30 743.830(50)	
$2^1P \rightarrow 9^1P$	14 600	31 158.458	31 153.612	31 154.015	31 154.033	31 144.05(2.0)
	15 500	31 158.433	31 153.593	31 153.996	31 154.014	
	16 400	31 158.406	31 153.577	31 153.980	31 153.998	
	16 400 <sup>a</sup>	31 158.364	31 153.532	31 153.935	31 153.953	
	$\infty$	31 158.353(80)	31 153.534(80)	31 153.938(80)	31 153.957(80)	
$2^1P \rightarrow 10^1P$	14 600	31 448.918	31 443.511	31 443.876	31 443.893	31 443.85(2.0)
	15 500	31 448.810	31 443.451	31 443.818	31 443.834	
	16 400	31 448.704	31 443.379	31 443.747	31 443.764	
	16 400 <sup>a</sup>	31 448.578	31 443.257	31 443.626	31 443.643	
	$\infty$	31 448.431(400)	31 443.173(400)	31 443.544(400)	31 443.561(400)	
$2^1P \rightarrow 11^1P$	15 000	31 663.391	31 658.237	31 658.521	31 658.534	31 655.75(2.0)
	16 000	31 662.980	31 657.912	31 658.198	31 658.211	
	16 400	31 662.824	31 657.753	31 658.041	31 658.054	
	16 400 <sup>a</sup>	31 662.210	31 657.162	31 657.452	31 657.465	
	$\infty$	31 661.976(1200)	31 657.017(1200)	31 657.313(1200)	31 657.327(1200)	

convergence and extrapolate the results to the basis set limit. The transition frequencies are compared the experimental results. The following conclusions can be drawn by examining the results shown in the table. The transition energies for the lowest six states are very well converged at the non-relativist level. Beyond the sixth state the convergence is noticeably slowing down, but the results obtained with the largest basis sets are still within  $0.1\text{--}0.2\text{ cm}^{-1}$  from the extrapolated basis-set-limit values. The contribution from the leading relativistic corrections to the transition energies varies from about  $2\text{ cm}^{-1}$  for lower states to about  $5\text{ cm}^{-1}$  for the higher states. This is by far the largest correction. The QED corrections contribute only  $0.2\text{--}0.4\text{ cm}^{-1}$ . The comparison of the transition frequencies calculated at the highest level of theory with the experimental values shows perfect agreement for the lowest three transitions. For higher transitions the deviation from the experimental values does not exceed  $0.5\text{ cm}^{-1}$ . However, for the  $2p \rightarrow 9p$  transition the difference between the experiment and the theory suddenly rises to  $10\text{ cm}^{-1}$ . This is likely due to a typo in the experimental value which instead of the reported  $31\,153.561\text{ cm}^{-1}$  [28] should be  $31\,143.561\text{ cm}^{-1}$ . Also, there is a more substantial difference between the calculated and the experimental results for the highest  $2p \rightarrow 11p$  transition of about  $1.7\text{ cm}^{-1}$ . This difference is likely caused by inaccuracy in the non-relativistic energy which is not as well converged with the number of basis functions as the energies of other states. Inaccuracies in the experiment may also contribute to this difference.

## 5. Summary

In summary, high-accuracy calculations are performed for the  $^1P$  Rydberg spectrum of the beryllium atom. Ten lowest  $^1P$  are considered. The approach used involves expanding the wave functions of the states in terms of explicitly correlated Gaussian functions whose nonlinear parameters are extensively optimized by the variational minimization of the total energies of the states. The non-relativistic Hamiltonian used to calculate the energies and the wave functions explicitly depend on the mass of the nucleus. Subsequently, the wave functions are used to calculate the leading relativistic and QED corrections. The energies corrected for the relativistic and QED effects are used to calculate the  $2p \rightarrow np$ ,  $n = 3, \dots, 11$ , transition energies, which are compared with the experimental values. For the lowest transition the calculated values agree very well with experiment. For higher transitions (except for the top transition) the deviation never exceeds  $0.5\text{ cm}^{-1}$ .

The present work provides the first ever comprehensive study of an extended spectral range of Rydberg states of a four-electron atomic system performed using the highest available level of theory. It represents a large undertaking involving many months of computing. The most time-consuming part of the calculations is the variational optimization of the nonlinear parameters of the non-relativistic wave functions of the considered states. The result show that, for

lower excited states, the approach used in this work is capable of reproducing the experimental values well within the experimental error bar. For higher states, the agreement is good, but not as good as for lower states. Not sufficiently large basis set of Gaussians and limitations of the model can contribute to the discrepancies.

## Acknowledgments

This work of MS has been supported by the Polish National Science Centre, grant DEC-2013/10/E/ST4/00033. SB acknowledges funding from MES RK state-targeted program BR05236454 and NU faculty development grant 090118FD5345. The authors are grateful to Professor Gordon W F Drake (University of Windsor) for useful discussions. The authors are also grateful to the University of Arizona Research Computing and Nazarbayev University Library and IT Services for providing computational resources for this work.

## Appendix

Following the approach described by Bethe and Salpeter [18] Araki [20], and Sucher [21] the matrix element,  $Q_{kl}$ , of the Araki–Sucher QED correction involving the  $\psi_k$  and  $\psi_l$  basis functions can be expressed as follows:

$$Q_{kl} = \langle \psi_k | P \left( \frac{1}{r_{ij}^3} \right) | \psi_l \rangle = \lim_{\alpha \rightarrow 0} \int d\mathbf{r} \psi_k^*(\mathbf{r}) \psi_l(\mathbf{r}) \times \left[ \frac{1}{r^3} \Theta(r - \alpha) + 4\pi \delta^3(\mathbf{r}_{ij}) (\gamma_E + \ln \alpha) \right] \equiv \quad (11)$$

$$\equiv \lim_{\alpha \rightarrow 0} \left[ \left\langle \frac{1}{r^3} \Theta(r - \alpha) \right\rangle + 4\pi \langle \delta^3(\mathbf{r}_{ij}) \rangle (\gamma_E + \ln \alpha) \right], \quad (12)$$

where

- $\Theta$  is the step function and
- $\gamma_E$  is the Euler constant.

Let us first consider the two-electron contribution to the matrix element of the Araki–Sucher correction. We use the following expansion in terms of the Dirac delta function:

$$Q_{kl} = \langle \psi_k | P \left( \frac{1}{r_{ij}^3} \right) | \psi_l \rangle = \lim_{\alpha \rightarrow 0} [ \langle \chi(\mathbf{r}_{ij}) \rangle + 4\pi \langle \delta^3(\mathbf{r}_{ij}) \rangle (\gamma_E + \ln \alpha) ], \quad (13)$$

where

$$\langle \chi(\mathbf{r}_{ij}) \rangle = \int_{-\infty}^{\infty} d\xi \chi(\xi) \langle \psi_k | \delta(\mathbf{r}_{ij} - \xi) | \psi_l \rangle. \quad (14)$$

In this case we have:

$$\left\langle \phi_k \left| \frac{1}{r_{ij}^3(\alpha)} \right| \tilde{\phi}_l \right\rangle = \lim_{\alpha \rightarrow 0} \int_{\alpha}^{\infty} d\xi \frac{1}{|\xi|^3} \langle \phi_k | \delta(\mathbf{r}_{ij} - \xi) | \tilde{\phi}_l \rangle. \quad (15)$$

Detailed leads can be found at work [29].

The  $Q_{kl}$  matrix element is calculated for the following basis functions:

$$\begin{aligned} \phi_k &= z_{m_k} \exp[-\mathbf{r}^T \mathbf{A}_k \mathbf{r}] \\ &= \frac{\partial}{\partial \alpha_k} \exp[-\mathbf{r}^T \mathbf{A}_k \mathbf{r} + \alpha_k \mathbf{v}^{kT} \mathbf{r}], \\ \text{where } \mathbf{v}^k &= v^k \otimes \epsilon^z, \quad \epsilon^z = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} \end{aligned}$$

and where  $\mathbf{v}^k$  is a  $n$  dimensional vector whose elements are all zeros except for the  $m_k$  element, which is equal to one. We now use the following [30]:

$$\begin{aligned} \langle \phi_k | \delta((a \otimes I_3)^T \mathbf{r} - \xi) | \tilde{\phi}_l \rangle &= \langle \phi_k | \tilde{\phi}_l \rangle \pi^{-3/2} (a^T A_{kl}^{-1} a)^{-3/2} \\ &\times \left[ 1 + \frac{1}{(a^T A_{kl}^{-1} a)} \frac{v^{kT} A_{kl}^{-1} a}{v^{kT} A_{kl}^{-1} v^l} \left( 2 \frac{(\epsilon^z T \xi)^2}{a^T A_{kl}^{-1} a} - 1 \right) \right] \\ &\times \exp \left[ -\frac{\xi^T \xi}{a^T A_{kl}^{-1} a} \right]. \end{aligned} \quad (16)$$

For  $a = j^j - j^i$ , where  $j^i$  is an  $n$ -component vector whose  $i$ th element is one while all others are zeros, we have:

- $a^T a = J_{ij}$  and
- $a^T A_{kl}^{-1} a = \text{Tr} [A_{kl}^{-1} J_{ij}]$ .

It is worth noting that vectors  $j^i$  and  $j^j - j^i$  have the following direct relation to matrices  $J_{ii}$  and  $J_{ij}$ :

$$j^i (j^i)^T = J_{ii}, \quad (j^j - j^i)(j^j - j^i)^T = J_{ij}. \quad (17)$$

$J_{ii}$  replaces  $J_{ij}$  in the calculations of the one-electron contribution to the  $Q_{kl}$  matrix element the Araki–Sucher correction.

With the above we have:

$$\begin{aligned} \langle \phi_k | \delta(\mathbf{r}_{ij} - \xi) | \tilde{\phi}_l \rangle &= \langle \phi_k | \tilde{\phi}_l \rangle \pi^{-3/2} \text{Tr} [A_{kl}^{-1} J_{ij}]^{-3/2} \\ &\times \left[ 1 + \frac{1}{\text{Tr} [A_{kl}^{-1} J_{ij}]} \frac{v^{kT} A_{kl}^{-1} J_{ij} A_{kl}^{-1} v^l}{v^{kT} A_{kl}^{-1} v^l} \right. \\ &\times \left. \left( 2 \frac{(\epsilon^z T \xi)^2}{\text{Tr} [A_{kl}^{-1} J_{ij}]} - 1 \right) \right] \exp \left[ -\frac{\xi^T \xi}{\text{Tr} [A_{kl}^{-1} J_{ij}]} \right], \end{aligned} \quad (18)$$

where

$$\xi = \begin{pmatrix} \xi_x \\ \xi_y \\ \xi_z \end{pmatrix},$$

is a vector with the length of  $3n$ . Introducing the following quantities:

- $\beta = 1 / \text{Tr} [A_{kl}^{-1} J_{ij}]$  and
- $\eta = v^{kT} A_{kl}^{-1} J_{ij} A_{kl}^{-1} v^l / v^{kT} A_{kl}^{-1} v^l$

we have:

$$\begin{aligned} \langle \phi_k | \delta(\mathbf{r}_{ij} - \xi) | \tilde{\phi}_l \rangle &= \langle \phi_k | \tilde{\phi}_l \rangle \frac{\beta^{3/2}}{\pi^{3/2}} \\ &\times [1 + \beta \eta (2\beta (\epsilon^z T \xi)^2 - 1)] \exp[-\beta \xi^T \xi] \\ &= \langle \phi_k | \tilde{\phi}_l \rangle \frac{\beta^{3/2}}{\pi^{3/2}} [1 + 2\eta \beta^2 (\epsilon^z T \xi)^2 - \beta \eta] \exp[-\beta \xi^T \xi]. \end{aligned} \quad (19)$$

According to equations (14) and (15) er have:

$$\begin{aligned} \left\langle \phi_k \left| \frac{1}{r_{ij}^3} \right| \tilde{\phi}_l \right\rangle &= \langle \phi_k | \chi(\mathbf{r}_{ij}) | \tilde{\phi}_l \rangle \\ &= \int_{-\infty}^{\infty} d\xi \chi(\xi) \langle \phi_k | \delta(\mathbf{r}_{ij} - \xi) | \tilde{\phi}_l \rangle \\ &= \langle \phi_k | \tilde{\phi}_l \rangle \frac{\beta^{3/2}}{\pi^{3/2}} \int_{-\infty}^{\infty} d\xi |\xi|^{-3} [1 + 2\eta \beta^2 (\epsilon^z T \xi)^2 - \beta \eta] \\ &\times \exp[-\beta \xi^T \xi]. \end{aligned} \quad (20)$$

Now, we transform the above integral to the spherical coordinates:

$$z = R \cos \theta, \quad \varphi|_0^{2\pi}, \quad \theta|_0^{\pi}$$

and using the volume element  $J = R^2 \sin \theta$ , we have

$$\epsilon^T \cdot \xi = R \cos \theta, \quad (21)$$

$$\xi^T \cdot \xi = R^2, \quad (22)$$

$$d\xi = 2\pi R^2 dR \sin \theta d\theta, \quad (23)$$

$$\begin{aligned} 2\eta \beta^2 (\epsilon^z T \xi)^2 &= 2\eta \beta^2 R^2 \cos^2 \theta \equiv \gamma R^2 \cos^2 \theta, \\ \gamma &= 2\eta \beta^2. \end{aligned} \quad (24)$$

Using the above we now determine the matrix element:

$$\begin{aligned} \left\langle \phi_k \left| \frac{1}{r_{ij}^3(\alpha)} \right| \tilde{\phi}_l \right\rangle &= 2\pi \langle \phi_k | \tilde{\phi}_l \rangle \frac{\beta^{3/2}}{\pi^{3/2}} \lim_{\alpha \rightarrow 0} \int_{\alpha}^{\infty} dR R^2 \\ &\times \int_0^{\pi} \sin \theta d\theta \frac{1}{R^3} [1 + \gamma R^2 \cos^2 \theta - \beta \eta] \\ &\times \exp[-\beta R^2] \\ &= 2\pi \langle \phi_k | \tilde{\phi}_l \rangle \frac{\beta^{3/2}}{\pi^{3/2}} \lim_{\alpha \rightarrow 0} \int_{\alpha}^{\infty} dR \frac{1}{R} \\ &\times \exp[-\beta R^2] 2 \left( 1 - \beta \eta + \frac{1}{3} \gamma R^2 \right) \\ &= 4\pi \langle \phi_k | \tilde{\phi}_l \rangle \frac{\beta^{3/2}}{\pi^{3/2}} \frac{1}{6} \left( \frac{\gamma}{\beta} \right. \\ &\left. + 6(1 - \beta \eta) \lim_{\alpha \rightarrow 0} \frac{1}{2} \Gamma[0, \alpha^2 \beta] \right). \end{aligned} \quad (25)$$

We now use the above determined quantities in (13) and obtained the final equation for the two-electron  $Q_{kl}$  matrix element:

$$\begin{aligned}
 Q_{kl} &= \left\langle \phi_k \left| P \left( \frac{1}{r_{ij}^3(\alpha)} \right) \right| \phi_l \right\rangle = \lim_{\alpha \rightarrow 0} [\langle \chi(\mathbf{r}_{ij}(\alpha)) \rangle \\
 &+ 4\pi \langle \delta^3(\mathbf{r}_{ij}) \rangle (\gamma_E + \ln \alpha)] \\
 &= \langle \phi_k | \tilde{\phi}_l \rangle \frac{4\beta^{3/2}}{\pi^{1/2}} \lim_{\alpha \rightarrow 0} \left[ \frac{1}{6} \left( \frac{\gamma}{\beta} + 6(1 - \beta\eta) \frac{1}{2} \Gamma[0, a^2\beta] \right) \right. \\
 &\left. + (1 - \beta\eta)(\gamma_E + \ln \alpha) \right] \\
 &= \langle \phi_k | \tilde{\phi}_l \rangle \frac{4\beta^{3/2}}{\pi^{1/2}} \left[ \frac{1}{6} \frac{\gamma}{\beta} + (1 - \beta\eta) \right. \\
 &\left. \frac{1}{2} (-\gamma_E - \ln(a^2\beta) + a^2\beta + \dots) + (1 - \beta\eta)(\gamma_E + \ln \alpha) \right] \\
 &= \langle \phi_k | \tilde{\phi}_l \rangle \frac{2\beta^{3/2}}{\pi^{1/2}} \left[ \frac{1}{3} \frac{\gamma}{\beta} + (1 - \beta\eta)(\gamma_E - \ln \beta) \right] \\
 &= \langle \phi_k | \tilde{\phi}_l \rangle \frac{2}{\pi^{1/2} \text{Tr}[A_{kl}^{-1} J_{ij}]^{3/2}} \\
 &\times \left[ \frac{2}{3} \frac{v^{kT} A_{kl}^{-1} J_{ij} A_{kl}^{-1} v^l}{\text{Tr}[A_{kl}^{-1} J_{ij}](v^{kT} A_{kl}^{-1} v^l)} \right. \\
 &\left. + \left( 1 - \frac{v^{kT} A_{kl}^{-1} J_{ij} A_{kl}^{-1} v^l}{\text{Tr}[A_{kl}^{-1} J_{ij}](v^{kT} A_{kl}^{-1} v^l)} \right) \right. \\
 &\left. \times (\gamma_E + \ln \text{Tr}[A_{kl}^{-1} J_{ij}]) \right]. \tag{26}
 \end{aligned}$$

To obtain the one-electron  $Q_{kl}$  matrix element we replace  $J_{ij}$  in the above equation with  $J_{ii}$ .

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### References

[1] Drake G W F and Yan Z-C 1992 *Phys. Rev. A* **46** 2378  
 [2] Puchalski M, Kędziera D and Pachucki K 2010 *Phys. Rev.* **82** 062509

[3] Stanke M, Komasa J, Bubin S and Adamowicz L 2009 *Phys. Rev. A* **80** 022514  
 [4] Puchalski M, Pachucki K and Komasa J 2014 *Phys. Rev. A* **89** 012506  
 [5] Bubin S and Adamowicz L 2017 *Phys. Rev. Lett.* **118** 043001  
 [6] Boys S F 1960 *Proc. R. Soc. A* **258** 402  
 [7] Stanke M, Kędziera D, Bubin S and Adamowicz L 2007 *Phys. Rev. Lett.* **99** 043001  
 [8] Johansson L 1963 *Ark. Fys.* **23** 119  
 [9] Kramida A and Martin W C 1997 *J. Phys. Chem. Ref. Data* **26** 1185  
 [10] Stanke M, Bralin A, Bubin S and Adamowicz L 2018 *Phys. Rev. A* **97** 012513  
 [11] Kinghorn D B and Adamowicz L 1999 *Phys. Rev. Lett.* **83** 2541  
 [12] Bubin S, Pavanello M, Tung W-C, Sharkey K L and Adamowicz L 2013 *Chem. Rev.* **113** 36  
 [13] Mitroy J, Bubin S, Horiuchi W, Suzuki Y, Adamowicz L, Cencek W, Szalewicz K, Komasa J, Blume D and Varga K 2013 *Rev. Mod. Phys.* **85** 693  
 [14] Kozłowski P M and Adamowicz L 1992 *J. Chem. Phys.* **96** 9013  
 [15] Caswell W E and Lepage G P 1986 *Phys. Lett. B* **167** 437  
 [16] Pachucki K 1997 *Phys. Rev. A* **56** 297  
 [17] Mohr P J, Taylor B N and Newell D B 2012 *Rev. Mod. Phys.* **84** 1527  
 [18] Bethe H A and Salpeter E E 1977 *Quantum Mechanics of One- and Two-Electron Atoms* (New York: Plenum)  
 [19] Akhiezer A I and Berestetskii V B 1965 *Quantum Electrodynamics* (New York: Wiley)  
 [20] Araki H 1957 *Prog. Theor. Phys.* **17** 619  
 [21] Sucher J 1958 *Phys. Rev.* **109** 1010  
 [22] Kabir P K and Salpeter E E 1957 *Phys. Rev.* **108** 1256  
 [23] Yan Z-C and Drake G W F 1998 *Phys. Rev. Lett.* **81** 774  
 [24] Pachucki K 1998 *J. Phys. B: At. Mol. Opt. Phys.* **31** 5123  
 [25] Pachucki K and Komasa J 2004 *Phys. Rev. Lett.* **92** 213001  
 [26] Pachucki K 2006 *Phys. Rev. A* **74** 022512  
 [27] Hamermesh M 1962 *Group Theory and Its Application to Physical Problems* (Reading, MA: Addison-Wesley)  
 [28] NIST ASD Team, Kramida A E, Ralchenko Y and Reader J 2013 *NIST Atomic Spectra Database, ver. 5.1 (Online)* (Gaithersburg, MD: National Institute of Standards and Technology) (<https://doi.org/10.18434/T4W30F>)  
 [29] Stanke M, Jurkowski J and Adamowicz L 2017 *J. Phys. B: At. Mol. Phys.* **50** 065101  
 [30] Bubin S and Adamowicz L 2008 *J. Chem. Phys.* **128** 114107