Lowest Excitation Energy of $^9$Be

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Variational calculations employing explicitly correlated Gaussian functions and explicitly including the nuclear motion [i.e., without assuming the Born-Oppenheimer (BO) approximation] have been performed to determine the lowest singlet transition energy in the $^9$Be atom. The non-BO wave functions were used to calculate the $\alpha^2$ relativistic corrections ($\alpha = 1/137.035 999 679$). With those corrections and with the $\alpha^3$ and $\alpha^4$ QED corrections determined previously by others, we obtained $54.677.35$ cm$^{-1}$ for the $3^1S \rightarrow 2^1S$ transition energy. This result falls within the error bracket for the experimental transition of $54.677.26 (10)$ cm$^{-1}$. This is the first time an electronic transition of Be has been calculated from first principles with the experimental accuracy.

The theoretical calculations on two- and three-electron atomic systems using Slater-type or Hylleraas-type explicitly correlated functions have achieved a very high level of precision matching and, in some instances, have exceeded the precision of the experiment [1–5]. Thus the challenge in very accurate atomic calculations is now shifted to achieving a similar level of accuracy in calculations on atoms with more than three electrons. Though the Slater-type or Hylleraas-type functions very effectively describe the most important features of atomic wave functions, in cases with more than three electrons they lead to difficulties in calculating the Hamiltonian matrix elements, which have not been resolved. In such a situation there has been a search for alternative basis functions for atomic calculations that are efficient in describing atomic states yet easy to use in practical implementations. One of the bases that has been tested are explicitly correlated Gaussian functions (ECGF). The simplicity of the matrix with these types of functions has motivated their use in atomic and molecular calculations since they were first introduced to the field by Boys [6] in the 1960s. However, since Gaussians, in general, are less effective than Slaters or Hylleraas-type functions in describing the cusp and long-range behaviors of the wave function, their use in calculations aiming at a subwave-number precision in determining atomic transition energies has not been fully successful. For example, the recent work of Pachucki and Komasa [7] on the lowest transition energy of the beryllium atom showed that, despite including several thousand Gaussian in the basis set, the results are still short of the experimental transition by about 0.2 cm$^{-1}$ [8].

In recent years we have also used various types of ECGFs in very accurate variational atomic and molecular calculations performed with an approach where the Born-Oppenheimer (BO) approximation is not assumed [9–14]. Without the BO approximation, the calculations treat the motions of the electrons and the nuclei on equal footing. Hence, the effect of the finite masses of the nuclei (the nucleus for an atomic system) is automatically included in the total energy, and it is not added as a perturbation as is usually done in precise atomic calculations, including those of Pachucki and Komasa for Be [7].

There are three differences in the present calculations in comparison to the standard approach used by others including Pachucki and Komasa. First, our approach includes putting the nuclear motion on equal footing with the electronic motion (the non-BO approach). Second, we use the analytical gradient of the energy calculated with respect to the Gaussian exponential parameters in the variational optimizations of the wave functions. Third, the non-BO wave functions are used to calculate the $\alpha^2$ relativistic corrections with the algorithms we have recently developed [15–19]; thus those corrections explicitly include the nuclear effects in addition to the electronic effects.

In our view, the significance of this work lies in showing that, with the above-described new features of the method, one can achieve in the calculations employing correlated Gaussians on a four-electron system an accuracy similar to that achieved before in the calculations for two- and three-electron atoms using Slater-type or Hylleraas-type explicitly correlated functions [1–5]. Thus the frontier of very accurate atomic calculations can now be extended, and such quantities as ionization potentials, electron affinities, and transition energies can be determined with the accuracy matching the accuracy of the present day experiment.

$^9$Be is a system consisting of five fermions, four electrons, and the nucleus with spin $3/2$. Let us start with the nonrelativistic Hamiltonian for $^9$Be after the motion of the center-of-mass motion has been separated out. With this separation, the five-particle problem is reduced to a four-particle problem described by the internal Hamiltonian, $H_{\text{int}}$ [9,10]. In our approach we use Cartesian coordinates to describe the internal states of the system. The origin of the internal coordinate system is placed at the nucleus...
(called the reference particle). The other particles (electrons) are referred to the reference particle using the Cartesian position vectors \( \mathbf{r}_i \). The internal Hamiltonian, \( H_{\text{int}} \), for \(^{9}\text{Be}\) is

\[
H_{\text{int}} = -\frac{1}{2} \left( \sum_{i=1}^{4} \frac{1}{\mu_i} \nabla_i^2 + \sum_{i=1}^{4} \sum_{j\neq i}^{4} \frac{1}{M_i} \nabla_i \cdot \nabla_j \right) + \frac{4}{3} \sum_{i=1}^{4} \frac{Q_0 Q_i}{r_i} + \frac{3}{4} \sum_{i=1}^{4} \sum_{j\neq i}^{4} \frac{Q_i Q_j}{r_{ij}},
\]

where \( Q_0 = +4 \) is the nuclear charge, \( Q_1 = Q_2 = Q_3 = Q_4 = -1 \) are charges of the electrons, \( \mu_i = M_0 M_i / (M_0 + M_i) \), \( i = 1, \ldots, 4 \) are the reduced masses, \( M_0 \) is the mass of the nucleus (\( M_0 = 16424.2037 \text{ a.u.} \)), and \( M_i = 1 \text{ a.u.} \), \( i = 1, \ldots, 4 \) are the electron masses. The separation of the internal Hamiltonian and the Hamiltonian of the motion of the center-of-mass is exact. The internal Hamiltonian (1) describes the motion of four pseudoparticles (pseudoelectrons) in the central potential of the charge of the nucleus.

To account for the relativistic effects in \(^{9}\text{Be}\), we use the Dirac-Breit Hamiltonian in the Pauli approximation, which suffices for light atoms where the velocities of the electrons are relatively small [20,21]. In this approximation, for states with the \( S \) symmetry (these are the states considered in this work for \(^{9}\text{Be}\)) and after the transformation to the internal coordinate system, the Dirac-Breit-Pauli Hamiltonian has the following form [15]:

\[
H_{\text{int}}^{\text{rel}} = H_{MV} + H_D + H_{OO} + H_{SS},
\]

where the mass-velocity term

\[
H_{MV} = -\frac{1}{8} \left[ \sum_{i=1}^{4} \frac{1}{M_i} (\sum_{j=1}^{4} \nabla_j^2) + \sum_{i=1}^{4} \frac{1}{M_i} \nabla_i^2 \right],
\]

the Darwin term

\[
H_D = -\frac{\pi}{2} \sum_{i=1}^{4} \frac{1}{M_i} Q_0 Q_i \nabla_i^3(r_i) + \sum_{i=1}^{4} \sum_{j=1}^{4} \frac{1}{M_i M_j} Q_i Q_j \nabla_i^3(r_{ij})
+ \frac{14\pi}{3} \sum_{i=1}^{4} \frac{1}{M_i} Q_0 Q_i \nabla_i^3(r_i),
\]

the orbit-orbit term

\[
H_{OO} = -\frac{1}{2} \sum_{i=1}^{4} \sum_{j=1}^{4} \frac{Q_0 Q_i}{M_i M_j} \left[ \frac{1}{r_i} \nabla_i \cdot \nabla_j + \frac{1}{r_{ij}} \mathbf{r}_i \cdot (\mathbf{r}_i \cdot \nabla_j) \nabla_j \right] + \frac{1}{2} \sum_{i=1}^{4} \sum_{j=1}^{4} \frac{Q_i Q_j}{M_i M_j} \left[ \frac{1}{r_{ij}} \nabla_{ij} \cdot \nabla_j + \frac{1}{r_{ij}} \mathbf{r}_{ij} \cdot (\mathbf{r}_{ij} \cdot \nabla_j) \nabla_j \right],
\]

and the spin-spin term is

\[
H_{SS} = -\frac{8\pi}{3} \sum_{i=1}^{4} \frac{Q_0 Q_i}{M_i M_j} (\mathbf{S}_i \cdot \mathbf{S}_j) \delta^3(r_i) - \frac{8\pi}{3} \sum_{i=1}^{4} \sum_{j=1}^{4} \frac{Q_i Q_j}{M_i M_j} (\mathbf{S}_i \cdot \mathbf{S}_j) \delta^3(r_{ij}).
\]

In the atomic Dirac-Breit-Pauli Hamiltonian, the Darwin correction describing the interaction of the nucleus (with charge \( Q \), spin \( I \), and mass \( M \)) with an electron has the following form [22]:

\[
\frac{2\pi}{3} \frac{Q}{M^2} (g - 1) I (1 + \zeta) \delta(\mathbf{r}),
\]

where \( g \) is gyromagnetic ratio (for the \(^{9}\text{Be}\) nucleus it is equal to 0.78507). Parameter \( \zeta \) is equal to zero for an integer spin and \( 1/(4I) \) for a half-integer spin. In this work we do not consider the electron-nucleus spin-spin interaction, because it is negligibly small in comparison with the electron-electron spin-spin interaction.

The Gaussian basis functions used in this work to calculate the \( 2^1S \) and \( 3^1S \) states of \(^{9}\text{Be}\) are

\[
\phi_k = \exp[-r^4(L_k L_k \otimes I_3) \mathbf{r}],
\]

where \( \otimes \) is the Kronecker product symbol, \( \mathbf{r} \) is a vector of the internal Cartesian coordinates of the four pseudoparticles (pseudoelectrons) for \(^{9}\text{Be}\) \( \mathbf{r} \) is a \( 12 \times 1 \) vector, \( L_k \) is lower triangular matrix of nonlinear variation parameters (for Be \( L_k \) is a \( 4 \times 4 \) rank 4 matrix), and \( I_3 \) is the \( 3 \times 3 \) identity matrix. To ensure the proper permutational symmetry of the electrons, the appropriate symmetry projections are applied to the basis functions.

The wave functions and the corresponding energies of the \( 2^1S \) and \( 3^1S \) states of \(^{9}\text{Be}\) have been obtained using the variational method by minimizing the energy

\[
E(\{L_k\}, \{c_k\}) = \min_{\{L_k\}, \{c_k\}} c^\ast H(\{L_k\}) c / S(\{L_k\}) c,
\]

with respect to both linear expansion coefficients, \( c_k \), and the nonlinear parameters of the basis functions, i.e., the basis set exponent matrices, \( L_k \). In the above expression, \( H(\{L_k\}) \) and \( S(\{L_k\}) \) are the Hamiltonian and overlap matrices, respectively. Both depend on the nonlinear parameters of the basis functions. \( c \) is a column vector whose components are \( c_k \). The variational calculations for the \( 2^1S \) and \( 3^1S \) states have been performed independently and, for each state, a different Gaussian basis set was generated. The use of the analytical gradient in optimizing the basis functions was key in achieving high accuracy and lowering the computational cost.

The results of the calculations are summarized in Tables I and II. The results in Table I show how the total energy of the ground and the first excited singlet state with the \( S \) symmetry (the \( 2^1S \) and \( 3^1S \) states) converges with the number of basis functions. The ground-state results have been taken from our recent work concerning the calculations of the ionization potential of \(^{9}\text{Be}\) [23]. For each state two sets of results are presented. The first set consists of finite-mass results corresponding for \(^{9}\text{Be}\) obtained using the variational minimization of the total energy with the nonrelativistic internal Hamiltonian (1). The second set of results was obtained by setting the mass of the Be nucleus to infinity. Such calculations are equivalent to calculations

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The infinite-mass calculations have been performed with 6000 basis functions. Upon examining the en-
nergies for the ground and the first excited 5s-state of the beryllium atom. MV, D, SS, and OO stand for
functions from 1000 to 6000. Upon examining the energy convergence, one can see that the ground state con-
verges faster than the first excited state. This can be ex-
pected since the excited-state wave function is more difficult to describe than the ground-state wave function
due to a radial node.

The infinite-mass energies obtained here can be directly compared with the recent BO results of Komasa and
Pachucki. Our best result for Be obtained with 6000 basis functions of $-14.667\,435\,548\,6$ a.u. is noticeably lower than their result of $-14.667\,355\,748$ a.u. However, the

table for the 2$^1 S^\pi$ and 3$^1 S^\pi$ states of Be in comparison with the experiment. All energies in

TABLE II. Nonrelativistic energies ($E_{\text{nonrel}}$), finite nuclear mass corrections ($E_{\text{FM}}$), relativistic ($\alpha^2 E_{\text{rel}}$) corrections, QED corrections ($\alpha^3 E_{\text{QED}}^{(3)}$ and $\alpha^4 E_{\text{QED}}^{(4)}$), and the total energies ($E_{\text{total}}$) for the 2$^1 S^\pi$ and 3$^1 S^\pi$ states of Be in comparison with the experiment. All energies in hartrees and transition energies in cm$^{-1}$.

<table>
<thead>
<tr>
<th>Quantity</th>
<th>2$^1 S^\pi$</th>
<th>3$^1 S^\pi$</th>
<th>$\Delta E^a$</th>
<th>2$^1 S^b$</th>
<th>3$^1 S^b$</th>
<th>$\Delta E^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{\text{nonrel}}$</td>
<td>$-14.667,435,477$</td>
<td>$-14.417,335,037$</td>
<td>54.671.227(50)</td>
<td>$-14.667,355,748$</td>
<td>$-14.418,236,555$</td>
<td>54.675.34(22)</td>
</tr>
<tr>
<td>$E_{\text{FM}}$</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>0.000,920,998</td>
<td>0.000,905,240</td>
<td>-3.459(0)</td>
</tr>
<tr>
<td>$\alpha^2 E_{\text{rel}}$</td>
<td>-0.002,360,112</td>
<td>-0.002,329,847</td>
<td>6.6424(200)</td>
<td>-0.002,360,312</td>
<td>-0.002,331,034</td>
<td>6.43(16)</td>
</tr>
<tr>
<td>$\alpha^3 E_{\text{QED}}^{(3)}$</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>0.000,339,785</td>
<td>0.000,337,520</td>
<td>-0.497(1)</td>
</tr>
<tr>
<td>$\alpha^4 E_{\text{QED}}^{(4)}$</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>0.000,815,435</td>
<td>0.000,815,330</td>
<td>-0.023(6)</td>
</tr>
<tr>
<td>$E_{\text{total}}$</td>
<td>$-14.668,440,368$</td>
<td>$-14.419,312,034$</td>
<td>54.677.349(320)</td>
<td>$-14.668,439,842$</td>
<td>$-14.419,309,499$</td>
<td>54.677.78(45)</td>
</tr>
<tr>
<td>Experiment$^d$</td>
<td>54.677.26(10)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
highest improvement was obtained for the first excited states where our infinite-mass energy is \(-14.418 \pm 240.261\) a.u. while their energy was \(-14.418 \pm 236.555\) a.u.

In Table I we also show the relativistic energy corrections in the order of \(\alpha^2\) calculated in this work and their sum multiplied by \(\alpha^2\) (the entry \(\alpha^2E_{\text{rel}}\) in the last column in the table). As one can see, the convergence of \(\alpha^2E_{\text{rel}}\) is quite good, however not as good as for the total non-relativistic energy. Our total \(\alpha^2\) relativistic corrections for the two states calculated with the 6000-term wave functions of \(-0.002360\) \(12\) a.u. and \(-0.002329\) \(847\) a.u., respectively, can be compared with the \(\alpha^2\) corrections of \(-0.002360\) \(312\) a.u. and \(-0.002331\) \(034\) a.u. obtained with the BO wave functions by Pachucki and Komasa [7]. The values are very similar.

In Table III we present the calculation of the \(3^1S \rightarrow 2^1S\) transition and a comparison with the results of Pachucki and Komasa [7]. Our final value of the transition energy of \(54.677.3494\) cm\(^{-1}\) was obtained by subtracting our non-relativistic \(2^1S\) and \(3^1S\) energies obtained with 6000 basis functions, adding the difference between \(\alpha^2\) relativistic corrections of the two states also obtained with the 6000-term wave functions, and adding the \(\alpha^3\) and \(\alpha^4\) QED corrections calculated by Pachucki and Komasa [7] to the result. Our result differs from the result of \(54.677.78\) cm\(^{-1}\) obtained by Pachucki and Komasa [7] by more than 0.4 cm\(^{-1}\). The difference is significant and can be mostly attributed to our nonrelativistic energies of the two states being much better converged than their energies. There is also a smaller contribution to this difference from the improved calculation of the relativistic corrections.

Pachucki and Komasa [7] used the experimental \(mP \rightarrow nS\) transitions obtained by Johansson [8] to estimate the \(3^1S \rightarrow 2^1S\) transition. This estimation gave them a value of \(54.677.26(10)\) cm\(^{-1}\). Our result matches this value within the experimental error.

It is interesting to examine the convergence of the transition energy value with the number of the basis functions as shown in Table III. As one can see, the convergence is very good, and the agreement between the calculations and the experiment improves when more functions are added to the basis set. However, at least 6000 functions are needed for the calculations and the experiment to agree within the experimental accuracy. This is the first time such an agreement has been obtained for an electronic transition of the Be atom. However, the calculations also show that a considerable computational effort is required to achieve such a result.

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References