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Excitation energy of ^{9}Be

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The high precision relativistic and radiative corrections to the energy of the excited $3\,^1S$ state of the beryllium atom are obtained. The nonrelativistic wave function, expanded in a basis of exponentially correlated Gaussian functions, yields the lowest upper bounds to the energy of $2\,^1S$ and $3\,^1S$ states. By means of the integral representation, a reference-quality Bethe logarithm has been obtained. The resulting theoretical $2\,^1S$ -$3\,^1S$ transition energy amounts to 54 677.78(45) cm^{-1} and differs from the known experimental value by about 0.5 cm^{-1}.

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I. INTRODUCTION

Theoretical predictions of the energy levels in many-electron atoms with an accuracy competitive to that achievable from measurements require two conditions to be fulfilled. First of all, the interparticle correlation has to be fully incorporated into the calculations. This goal can be achieved by using large expansions of the nonrelativistic wave function in the basis of explicitly correlated functions with optimized nonlinear parameters. For the helium atom, the best examples of the application of such functions are computations by Drake *et al.* [1], who employed the Hylleraas basis function and computations by Korobov [2] performed using a correlated exponential basis. The Hylleraas basis has been successfully employed also in the calculations on the lithium atom by Yan and Drake [3] and, most recently, by Puchalski and Pachucki [4] who predicted the nonrelativistic energy of the ground state with an accuracy exceeding 12 significant figures. For the beryllium atom, though, since the classical work by Sims and Hagstrom [5], some progress towards constructing an accurate wave function has been observed [6–10]; difficulties in computing matrix elements in the Hylleraas basis prevents one from a full utilization of this basis functions. Hitherto, the most accurate energy for the ground state of the berylliumlike atoms has been obtained using the exponentially correlated Gaussian (ECG) basis sets [11,12].

The second condition indispensable for obtaining accurate energy predictions is an adequate theoretical description of the beyond-nonrelativistic effects. For the many-electron atoms, the routinely used methods rely on the Dirac-Coulomb Hamiltonian which is a sum of the one-electron Dirac Hamiltonians with Coulomb interactions between electrons. This approach, though acceptable as the first approximation, cannot be used in high-accuracy calculations as it is inconsistent with quantum electrodynamics (QED). A very convenient and well-founded approach, valid for light systems with few electrons, relies on expansion of the total binding energy in powers of α—the fine structure constant. Each coefficient of this expansion can be expressed as the expectation value of some operator, to be called an effective Hamiltonian [13]. These operators are known for the leading relativistic and QED corrections [14–17]. An evaluation of these corrections for $3\,^1S$ excited state of a beryllium atom is the main subject of the present work.

II. THE METHOD

The total energy of a bound system can be represented by an expansion in powers of α:

$$E(\alpha) = E_{\rm NR} + \alpha^2 E_{\rm REL} + \alpha^3 E_{\rm QED} + \alpha^4 \delta E_{\rm QED} \qquad (1)$$

with the expansion coefficients having a transparent physical interpretation. A particular form of these coefficients, valid for the beryllium atom in the singlet S state, is described below. We use units where $m=\hbar=c=1$ and a common prefactor $m\alpha^2$ is pulled out from the binding energy. $E_{\rm NR}$ is a sum of E_0, the nonrelativistic energy of the atom corresponding to the clamped nuclei Hamiltonian

$$H_0 = -\sum_i \left(\frac{\nabla_i^2}{2} + \frac{Z}{r_i}\right) + \sum_{i>j} \frac{1}{r_{ij}}, \qquad (2)$$

and the finite nuclear mass correction $E_{\rm FM}$. This correction, given by

$$E_{\rm FM} = \frac{1}{2M}\langle\Psi|\Big(\sum_i \nabla_i\Big)^2|\Psi\rangle, \qquad (3)$$

where M is the nuclear mass, has been computed by summing up the normal, $E_{\rm NMS}=-E_0/M$, and the specific, $E_{\rm SMS}=\langle\Psi|\Sigma_{i>j}\nabla_i\cdot\nabla_j|\Psi\rangle/M$ mass shifts [18]. $E_{\rm REL}=\langle\Psi|H_{\rm REL}|\Psi\rangle$ is the leading relativistic correction expressed as the nonrelativistic expectation value of the Breit-Pauli Hamiltonian $H_{\rm REL}$, which for the closed shell atom in the nonrecoil limit reads

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$$H_{\mathrm{REL}} = \sum_i \left[-\frac{\nabla_i^4}{8} + \frac{Z\pi}{2}\delta(\boldsymbol{r}_i) \right] - \sum_{i>j} \left(1 + \tfrac{8}{3}\boldsymbol{s}_i \cdot \boldsymbol{s}_j\right) \pi \delta(\boldsymbol{r}_{ij}) + \sum_{i>j} \frac{1}{2} \left(\frac{1}{r_{ij}} \nabla_i \cdot \nabla_j + \frac{1}{r_{ij}^3} \boldsymbol{r}_{ij} \cdot (\boldsymbol{r}_{ij} \cdot \nabla_i) \nabla_j \right). \tag{4}$$

The third coefficient of the expansion (1), E_{QED}, represents the leading radiative correction

$$E_{\mathrm{QED}} = \sum_{i>j} \left\{ \left[\tfrac{164}{15} + \tfrac{14}{3} \ln \alpha \right] \langle \Psi | \delta(\boldsymbol{r}_{ij}) | \Psi \rangle - \frac{14}{3} \langle \Psi | \frac{1}{4\pi} P\left(\frac{1}{r_{ij}^3}\right) | \Psi \rangle \right\} + \sum_i \left[\tfrac{19}{30} + \ln(\alpha^{-2}) - \ln k_0 \right] \frac{4Z}{3} \langle \Psi | \delta(\boldsymbol{r}_i) | \Psi \rangle . \tag{5}$$

This expression, apart from the expectation value of the Dirac delta distributions δ, contains the Araki-Sucher term defined as

$$\langle \phi | P\left(\frac{1}{r^3}\right) | \psi \rangle \equiv \lim_{a \to 0} \int d\boldsymbol{r}\, \phi^*(\boldsymbol{r}) \psi(\boldsymbol{r}) \left[\frac{1}{r^3} \Theta(r - a) + 4\pi \delta(\boldsymbol{r}) (\gamma + \ln a) \right], \tag{6}$$

with Θ being the step function and γ—the Euler constant. Eq. (5) contains also the many-electron Bethe logarithm $\ln k_0$ defined by

$$\ln k_0 = -\frac{1}{D} \langle \Psi | \nabla (H_0 - E_0) \ln[2(H_0 - E_0)]\, \nabla | \Psi \rangle , \tag{7}$$

where the following symbols are incorporated

$$\nabla = \sum_i \nabla_i , \tag{8}$$

$$D = 2\pi Z \langle \Psi | \sum_i \delta(\boldsymbol{r}_i) | \Psi \rangle . \tag{9}$$

Since the last coefficient in Eq. (1), δE_{QED}, is quite complicated [13], we approximate it by its leading term

$$\delta E_{\mathrm{QED}} \approx 4\pi Z^2 \left(\frac{139}{128} + \frac{5}{192} - \frac{\ln(2)}{2} \right) \langle \Psi | \sum_i \delta(\boldsymbol{r}_i) | \Psi \rangle , \tag{10}$$

which is the known correction to the Lamb shift in hydrogenlike systems. The remaining α^4 contributions involve second-order terms which are relatively difficult to compute. The $\alpha^4 \delta E_{\mathrm{QED}}$ component gives a rough estimate of the error made by cutting off the expansion in Eq. (1).

III. EVALUATION OF MATRIX ELEMENTS

The nonrelativistic wave function employed in this project is represented as a K-term linear expansion in a four-electron spatial basis $\{\psi_l(\boldsymbol{r})\}$ multiplied by an appropriate singlet spin eigenfunction, Ξ_{S,M_S},

$$\Psi(\boldsymbol{r}, \boldsymbol{\sigma}) = \hat{\mathcal{A}} \left(\Xi_{S,M_S}(\boldsymbol{\sigma}) \sum_{l=1}^{K} c_l \psi_l(\boldsymbol{r}) \right). \tag{11}$$

The expansion is antisymmetrized by applying the four-electron projector $\hat{\mathcal{A}}$. As the basis functions $\psi_l(\boldsymbol{r})$ we used exponentially correlated Gaussian functions introduced by Singer [19]

$$\psi_l(\boldsymbol{r}) = \exp[-\boldsymbol{r}^T \mathbf{A}_l \boldsymbol{r}] \tag{12}$$

and

$$\tilde{\psi}_l(\boldsymbol{r}) = \boldsymbol{r}_i \exp[-\boldsymbol{r}^T \tilde{\mathbf{A}}_l \boldsymbol{r}] \tag{13}$$

of S and P symmetry, respectively. The positive definite matrices $\mathbf{A}_l$ are built of nonlinear parameters determined in a variational optimization process [20]. The quality of the final results depends primarily on the effectiveness of the optimization of these nonlinear parameters and this optimization is the most time consuming part of the project.

Some of the operators involved in the nonrelativistic expansion (1) are of a singular nature. Expectation values of such operators computed in the Gaussian type basis converge very slowly even if the wave functions are energetically of high quality. One way to circumvent this problem is a reformulation of the expectation values in terms of other, less singular operators. This idea, for the first time applied by Drachman [21], was already explored successfully in the atomic calculations reported in Refs. [11,22], where a detailed description of the method and numerical convergence results can be found. Such regularized calculations were performed for the expectation values of $\delta(\boldsymbol{r})$, p^4, and $P(1/r^3)$ operators. Convergence of the remaining operators, including the Breit operator, is less problematic and their expectation values were computed conventionally.

One of the most difficult quantities to be determined is the four-electron Bethe logarithm, Eq. (7). An efficient technique of evaluation of $\ln k_0$ for multielectron systems was described in Refs. [11,23]. In this approach the Bethe logarithm is represented as a one-dimensional integral over the variable $t = 1/\sqrt{1+2\omega}$

$$\ln k_0 = \frac{1}{D} \int_0^1 \frac{f(t) - f_0 - f_2 t^2}{t^3} dt , \tag{14}$$

where

$$f(t) = -\langle \Psi | \nabla \frac{\omega}{H_0 - E_0 + \omega} \nabla | \Psi \rangle , \tag{15}$$

and where ω is a frequency corresponding to the energy of a virtual photon. It is crucial that $f(t)$ is computed to a high accuracy. An important factor deciding on the final accuracy of $\ln k_0$ is the small t asymptotics of the integrand in Eq. (14). As shown by Schwartz [24], at very low values of t the integrand has the following expansion:

$$f(t) = f_0 + f_2 t^2 + f_3 t^3 + f_4 t^4 \ln(t) + o(t^4) , \tag{16}$$

in which the lowest-order coefficients are known to be $f_0 = -\langle \Psi | \nabla^2 | \Psi \rangle$, $f_2 = -2D$, $f_3 = 8ZD$, and $f_4 = 16Z^2 D$, and the higher-order coefficients were fit to $f(t)$ of Eq. (15). A feature of this approach which is not to be overestimated is that it can be applied to many-electron atoms as well as to molecules. To evaluate the Bethe logarithm in the integral form of Eq. (14) we need the first-order perturbation correction function $\tilde{\mathbf{\Psi}}$, which is a solution of the following equation:

$$(H_0 - E_0 + \omega)\tilde{\mathbf{\Psi}} = -\mathbf{\nabla}\Psi. \tag{17}$$

The $\mathbf{\nabla}$ operator defined in Eq. (8), couples the unperturbed S states with the intermediate P states, hence $\tilde{\mathbf{\Psi}}$ is to be expanded in the basis of the form (13). Assuming Ψ is known, the perturbation equation can be solved variationally by minimizing the Hylleraas functional at different ω:

$$\mathcal{J}_\omega[\tilde{\mathbf{\Psi}}] = \langle\tilde{\mathbf{\Psi}}|H_0 - E_0 + \omega|\tilde{\mathbf{\Psi}}\rangle + 2\langle\tilde{\mathbf{\Psi}}|\mathbf{\nabla}|\Psi\rangle. \tag{18}$$

It is important that the same $\tilde{\mathbf{\Psi}}$ minimizes the above functional in a broad range of ω, not only at the static case ($\omega=0$). To reach this effect, we separately optimize $\mathcal{J}_\omega$ in Eq. (18) using four 1200-term basis sets at four different frequencies ω=0, 10, 100, and 1000 and glue them together to form a final 4800-term basis set for $\tilde{\mathbf{\Psi}}$.

IV. RESULTS AND DISCUSSION

In this work, the wave functions for both $2\,^1S$ and $3\,^1S$ states were expanded in a common set of basis functions of type (12). The advantage of using a single set of basis functions for both states is that the eigenvectors obtained in a single diagonalization of the Hamiltonian are perfectly orthogonal. The final basis set was constructed from four smaller sets optimized separately with respect to eigenvalues of the four lowest states of the symmetry S. The subsets corresponding to the states $2\,^1S$ and $3\,^1S$ were composed of 1600 basis functions, whereas to the $4\,^1S$ and $5\,^1S$ states—of 600 and 800 functions, respectively, yielding a total of 4600 basis functions. The nonrelativistic wave functions obtained for the $2\,^1S$ and $3\,^1S$ states were subsequently employed to compute the expectation values of several operators appearing in the expressions (2)–(10). Numerical values of these expectation values are listed in Table I. We note that the $2\,^1S$ column of the table contains values corrected and slightly improved over those obtained from a smaller expansion ($K=3600$) and reported previously [11]. The nonrelativistic clamped nucleus energies $E_0=\langle\Psi|H_0|\Psi\rangle$ are the lowest upper bounds available to date. In particular, the new ground state energy is slightly improved with respect to the best previous energy estimate [11]. The new upper bound to $3\,^1S$ energy is lower by 14×10^{-6} a.u. than previous estimations obtained from the 3600-term ECG wave function in Ref. [25] and by 3.7×10^{-3} a.u. than the upper bound computed by Chung and Zhu [26]. It is worth noting that the extrapolated energy obtained by Chung and Zhu using their full-core plus correlation [27] method differs from our result by merely 5.6×10^{-7} a.u.

TABLE I. Expectation values (in a.u.) of various operators with nonrelativistic wave functions of a beryllium atom (K=4600) in the $2\,^1S$ and $3\,^1S$ states. The implicit summation over i and over pairs $i>j$ is assumed.

	$2\,^1S$	$3\,^1S$
$\langle\Psi\|H_0\|\Psi\rangle$	−14.667 355 748	−14.418 236 555
$\langle\Psi\|\mathbf{\nabla}^2\|\Psi\rangle$	−30.255 159(8)	−29.737 482(30)
$\langle\Psi\|\delta(\mathbf{r}_i)\|\Psi\rangle$	35.368 92(4)	35.127 90(12)
$\langle\Psi\|\delta(\mathbf{r}_{ij})\|\Psi\rangle$	1.605 302(4)	1.583 070(12)
$\langle\Psi\|\mathbf{p}_i\cdot\mathbf{p}_j\|\Psi\rangle$	0.460 224(4)	0.450 512(10)
$\langle\Psi\|p_i^4\|\Psi\rangle/8$	270.704 8(5)	268.562(13)
$\langle\Psi\|r_{ij}^{-3}\mathbf{r}_{ij}(\mathbf{r}_{ij}\cdot\mathbf{p}_i)\mathbf{p}_j$ $+r_{ij}^{-1}\mathbf{p}_i\cdot\mathbf{p}_j\|\Psi\rangle/2$	−0.891 825(1)	−0.900 470(4)
$\langle\Psi\|P(1/r_{ij}^3)\|\Psi\rangle/4\pi$	−0.583 03(5)	−0.594 08(13)
$\ln k_0$	5.750 48(6)	5.750 89(15)

The computed energy difference ΔE between the levels $3\,^1S$ and $2\,^1S$ is presented in Table II. The total value of ΔE is obtained as a sum of the components originating from Eq. (1). The finite mass correction together with the relativistic and radiative corrections are listed separately in Table II, which permits an assessment of the contributions coming from different physical effects. The total correction to the nonrelativistic excitation energy amounts to 2.45(23) cm^{-1} which is merely 45 ppm of the total ΔE. The uncertainties, given in the last column of the table, are transferred from the errors estimated for the $3\,^1S$ state. The final theoretical value ΔE=54 677.78(45) cm^{-1} can be confronted with the experimentally derived value of 54 677.26 cm^{-1}, which comes from the measurements performed in 1962 by Johansson [28]. His results were included in the compilation of energy levels of Be by Kramida and Martin [29]. The anticipated experimental uncertainty displayed in Table II is based on Johansson's opinion that "the estimated errors in the level values are, in general, less than ±0.05 cm^{-1}." Since the spacing between $3\,^1S$ and $2\,^1S$ levels has been determined indirectly from two $nS\rightarrow mP$ transitions, we get an experimental uncertainty of 0.10 cm^{-1}.

The difference between theory and experiment is close to the sum of both theoretical and experimental uncertainties. It

TABLE II. Components of the $2\,^1S\rightarrow3\,^1S$ excitation energy for the ^{9}Be atom. E_0 is the nonrelativistic clamped nucleus energy; E_{FM}, α^2E_{REL}, α^3E_{QED}, and $\alpha^4\delta E_{\mathrm{QED}}$ are the finite nuclear mass, the leading relativistic, the leading radiative, and the higher-order radiative corrections, respectively, defined by Eqs. (2)–(5), (10), and (3). The mass of the ^{9}Be nuclei M=16424.203m. Physical constants are from [30].

	Be($2\,^1S$) (a.u.)	Be($3\,^1S$) (a.u.)	ΔE (cm^{-1})
E_0	−14.667 355 748	−14.418 236 555	54675.34(22)
E_{FM}	0.000 028 019	0.000 027 428	−3.459(0)
α^2E_{REL}	−0.002 360 312	−0.002 331 034	6.43(16)
α^3E_{QED}	0.000 339 785	0.000 337 520	−0.497(1)
$\alpha^4\delta E_{\mathrm{QED}}$	0.000 015 435	0.000 015 330	−0.023(6)
Total	−14.669 332 811	−14.420 187 320	54677.78(45)
Experiment[a]			54677.26(10)
Diff.			0.52(55)

[a] References [28,29]

is a justification of our computational approach, which is based on explicitly correlated Gaussian functions and the perturbative expansion of energy in Eq. (1). However, the theoretical uncertainty is still 4–5 times larger than the experimental one. The main contribution to the theoretical uncertainty in ΔE comes from the the nonrelativistic energy of the $3\,^1S$ state. This can be improved by using the Hylleraas basis set, although computational difficulties with four-electron integrals have not yet been resolved. A relatively large uncertainty in the relativistic correction to ΔE is due to the relativistic kinetic energy of the $3\,^1S$ state. In spite of five significant figures of $\langle\Psi|p_i^4|\Psi\rangle$ being obtained, the cancellation between one-electron contributions in $\langle\Psi|H_{\mathrm{REL}}|\Psi\rangle$ and contributions coming from $3\,^1S$ and $2\,^1S$ levels results in about 2% uncertainty of the total relativistic correction.

This work, as well as our previous work on the ionization potential of Be [11], illustrate the present possibilities of ECG functions in predicting the energy levels of four-electron atoms. We can conclude that the main factor limiting the accuracy of the present day theoretical predictions of atomic levels is the nonrelativistic energy.

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