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Research paper

An algorithm for calculating the Bethe logarithm for small molecules with all-electron explicitly correlated Gaussian functions

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HIGHLIGHTS

- Implementation of a new method for calculating the Bethe logarithm.
- The method is applicable to systems with an arbitrary number of electrons.
- The approach employs all-electron explicitly correlated Gaussian functions.
- The method enables to obtain more accurate predictions of atomic and molecular spectra.
- The first calculation of the Bethe logarithm for the LiH molecule was done.

ABSTRACT

An algorithm for calculating the Bethe logarithm, which is a part of the leading quantum electrodynamics energy correction, for the ground states of light molecules with an arbitrary number of electrons is derived and tested. The tests concern small atoms and one- and two-electron dihydrogen molecular systems. All-electron explicitly correlated Gaussian functions are used in the calculations. Next, the approach is employed to calculate the Bethe logarithm for the LiH molecule. These are the first calculations of the logarithm for a four-electron system. The method developed in this work allows to extend the Bethe-logarithm calculations to a wider range of molecules.

1. Introduction

In the description of an atomic system using the quantum-electrodynamics (QED) theory, charged particles emit and absorb photons. In quantum-mechanical calculations, these effects are included in the form of radiation corrections that provide the leading QED contribution to the energy. This contribution is of the order of α^3 (where α is the fine-structure constant). The first estimate of the atomic QED effects was done by Bethe [1] for the hydrogen atom. More complete calculations of these effects were subsequently performed by French and Weisskopf [2] and by Kroll and Lamb [3]. In high-precision calculations of multi-particle systems, besides the effects due to vacuum polarization, electron self-energy, and anomaly of the electron magnetic moment (the effect called the radiative correction), the α^3effect due the photon exchange has to be also included in the calculation. The correction that accounts for these latter effects is called the Salpeter correction [4,5]. This correction is small when the difference between the masses of the interacting particles is large. Thus, it can be neglected in the calculations of bound states of the hydrogen atom. The subsequent works, where the effect was calculated, pertained to the helium atom. Among the works one should, in particular, mention the works of Araki [6] and Sucher [7]. Most calculations concerning atoms with more than two electrons employ a generalized version of the procedure introduced by these authors.

The total contribution of one- and two-particle QED corrections of the order of α^3 to the Hamiltonian of multi-electron atoms and molecules can be derived based on the non-relativistic QED (NRQED) [8]. The contribution derived this way can be expressed as a sum of two parts. Both parts are of the order of α^3. The first part includes an average value of some effective potential and the second part includes the Bethe logarithm $\ln k_0$ defined as:

$$\ln k_0 = \frac{\langle \Psi_0 \,|\, \mathbf{j}\,(\mathrm{H}_0 - E_0)\ln|2(\mathrm{H}_0 - E_0)|\,\mathbf{j}\,|\Psi_0\rangle}{\frac{1}{2}|\langle\Psi_0|\,[\mathbf{j},\ [\mathrm{H}_0,\mathbf{j}]]\,|\,\Psi_0\rangle|} \equiv \frac{\mathcal{L}}{\mathcal{D}}, \tag{1}$$

where H_0 is the non-relativistic Hamiltonian of the system, E_0 is the ground state energy and Ψ_0 is the ground state wave function. In the above equation $\mathbf{j} = -\sum_{i=1}^{ne}\frac{\mathbf{p}_i}{m_e} + \sum_{\alpha=1}^{nn}\frac{\mathbf{p}_\alpha}{m_\alpha}$ is the operator representing the currents of the electrons and the nuclei. Within the Born-Oppenheimer approximation, we can assume that $\mathbf{j} = -\sum_{i=1}^{ne}\frac{\mathbf{p}_i}{m_e}$. In the atomic

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units used in this work $\mathbf{j} = \mathbf{p}$, where $\mathbf{p} = \sum_{i=1}^{ne} \mathbf{p}_i$ is a sum over the linear momenta of the electrons.

Numerical calculations of the Bethe logarithm are only straightforward for the hydrogen atom because the complete spectrum of states is known. For larger atomic and molecular systems, the calculations of the Bethe logarithm present on a larger challenge. The difficulty is due to the infinite sum over excited states that appears in the expression for . The level of difficulty of the calculation is exemplified by the fact that the value of the Bethe logarithm calculated for the ground state of the helium atom by Schwartz [9] in 1961 had remained unchallenged for over 30 years. In late 1990 there were some groundbreaking works on increasing the accuracy of the calculation of the Bethe logarithm. Three groups working independently used three different approaches to performed calculations of the logarithm that exceeded the previously achieved accuracy by three to five orders of magnitude [10–12].

Two methods are currently the most frequently used to calculate the Bethe logarithm. The first method, so-called integral representation technique, was introduced by Schwartz [9] and the second method was introduced by Drake and Goldman [11].

Numerical calculation of the Bethe logarithm for the smallest multielectron atom, the helium atom, has remained for a very long time a difficult problem [12,13]. The problem has been solved relatively recently by introduction of new procedures [10,11,14]. The recent progress has been so remarkable that the value of the Bethe logarithm is now calculated for the helium atom with an accuracy of 14 significant digits (by Korobov in Ref. [15]). It should be also noted that recently a promising method for calculating the Bethe logarithm using B-spline functions was developed Yang et al. [16] and Tang et al. [17].

In the case of the lithium atom, the calculations of the Bethe logarithm are much less accurate compared to hydrogen or helium. The reason for this is the lack of complete results for higher QED corrections and not so accurate results for the corrections in the order of α^3. The most precise estimation of the Bethe logarithm for the lithium atom was made by Pachucki and Komasa [18] and Yan and Drake [19]. The former authors used explicitly-correlated Gaussian basis functions and achieved an accuracy of six significant digits in the value of the logarithm.

Recently the most accurate Bethe-logarithm result for the ground state of the beryllium atom was obtained by Puchalski, Komasa, and Pachucki [20]. Also recently the first calculations of the QED corrections containing the Bethe logarithm for the boron atom were done by the same group [21]. The Bethe logarithm was also calculated for other atomic systems: antiprotonic helium atom [22], hydrogen-like atoms [23], helium-like atoms (i.e. Li^+, Be^{2+}, Ne^{+8}, Ps^-, and H^-) [11,14,24].

In the case of molecules, the values of the Bethe logarithm are only known for the hydrogen molecular ions, HD^+ and H_2^+ [25–28] and for the hydrogen molecule [29]. The molecular calculations are more complicated than the atomic calculation.

2. The method

The Bethe logarithm is calculated in the present work using an approach which is a generalization of the method introduce by Stanke et al. for the hydrogen atom [30]. The main contribution of the present work is the extension of the method to calculate the logarithm to multielectron atoms and diatomic molecules with more than two electrons. The extension involves a transformation of the numerator in the $\mathcal{L}$ algorithm to a form that is more convenient for a numerical implementation. The transformation involves three steps. In the first step numerator $\mathcal{L}$ is written in terms of a function of an operator. Next, the numerator is expressed in terms of a spectral identity. In the last step, an expression for a matrix representation of $\ln k_0$ is presented in the form of an expectation value.

The method employs a procedure to calculate an arbitrary function of a Hermitian operator, f(A). Matrix elements of operator f(A), $\langle\Psi|f(A)|\Psi\rangle$, are expressed in terms of eigenvalues of operator A. These matrix elements are calculated in the basis set of wave functions representing excited states. The matrix elements are then included in the numerator of the expression for the Bethe logarithm, $\mathcal{L}$, by inserting the spectral identity in the expression.

The starting point for developing the algorithm to calculate the $\ln k_0$ expectation value is the theorem for calculating a function of an operator. If the eigenvalue problem for operator A is solved:

$$\mathrm{A}\,|\psi_a\rangle = a\,|\psi_a\rangle, \tag{2}$$

where a and $|\psi_a\rangle$ are the eigenvalues and the corresponding eigenfunctions of operator A, respectively, an arbitrary analytical function of A satisfies the following eigenvalue equation:

$$\mathrm{f(A)}\,|\psi_a\rangle = \mathrm{f}(a)\,|\psi_a\rangle. \tag{3}$$

In this work, the total Hamiltonian, H, consists of nonrelativistic Schrödinger Hamiltonian, H_0, and a perturbation H′ (in the present case this operator is an operator consisting of terms of the order of α^2 and α^3) that provides a small contribution to the energy of the system.

We assume that the eigenvalue problem for H_0:

$$\mathrm{H}_0|\,\Psi_0\rangle = E_0\,|\,\Psi_0\rangle,$$

is solved. The ground-state energy of the perturbed Hamiltonian is written as:

$$E = E_0 + \Delta E, \tag{4}$$

where, to the first order,

$$\Delta E = \langle\Psi_0\,|\,\mathrm{H}'\,|\,\Psi_0\rangle. \tag{5}$$

Now, recalling the theorem of a function of an operator, the expression that appears in the numerator of $\ln k_0$ is represented as a function of H_0:

$$\mathrm{f}(\mathrm{H}_0) \equiv (\mathrm{H}_0 - E_0)\ln|2(\mathrm{H}_0 - E_0)|. \tag{6}$$

We now determine the expectation values of the above operator function. The expectation value of $f(H_0)$ is determined for the ground state wave function, Ψ_0. We assume that the special part of Ψ_0, which is an eigenfunction of H_0, can be represented as a linear combination of basis functions $\{\varphi_i\}$as:

$$|\,\Psi_0\rangle = \sum_{m=1}^{n} c_{m1}|\,\varphi_m\rangle, \tag{7}$$

where c_{m1} are linear expansion coefficients. The sum in (7) runs over basis functions used to expand the ground-state wave function. Let the number of the basis functions be n. Assuming that the basis set is complete, the matrix form of the eigenvalue problem for the unperturbed Hamiltonian, (II), is found from the following equation:

$$\begin{aligned}\sum_{i=1}^{n}\langle\varphi_m\,|\,\mathrm{H}_0\,|\varphi_i\rangle\langle\varphi_i\,|\,\Psi_0\rangle &= \sum_{i=1}^{n} E_0\,\langle\varphi_m\,|\,\varphi_i\rangle\langle\varphi_i\,|\,\Psi_0\rangle,\\ \sum_{i=1}^{n}(\mathrm{H}_{0mi} - E_0\,S_{mi})\,c_{i1} &= 0.\end{aligned} \tag{8}$$

In the matrix notation, the above equation can be written as:

$$\underline{\mathbf{H}}_0\,\underline{\mathbf{C}} = \underline{\mathbf{S}}\,\underline{\mathbf{C}}\,\underline{\mathbf{E}}_0, \tag{9}$$

where $\underline{\mathbf{S}}$ and $\underline{\mathbf{H}}_0$ are the overlap and nonrelativistic-Hamiltonian matrices, respectively, determined in the basis set of the $\{\varphi_i\}$ functions, $\underline{\mathbf{E}}_0$ is the diagonal matrix of the eigenvalues of H_0, and $\underline{\mathbf{C}}$ is the matrix of the linear expansion coefficients of the eigenfunctions in terms of the basis functions.

In the next step we transform Eq. (9) to obtain an expression for the matrix of Hamiltonian $\underline{\mathbf{H}}_0$:

$$\underline{\mathbf{H}}_0 = \underline{\mathbf{S}}\,\underline{\mathbf{C}}\,\underline{\mathbf{E}}_0\,\underline{\mathbf{C}}^{\dagger}(\underline{\mathbf{C}}\,\underline{\mathbf{C}}^{\dagger})^{-1}. \tag{10}$$

In the resulting equation, (10), we replace $(\underline{\mathbf{C}}\,\underline{\mathbf{C}}^{\dagger})^{-1}$ using the overlap matrix. To do that we use the expression resulting from the normalization condition for the eigenfunctions of $\underline{\mathbf{H}}_0$:

$$\underline{\mathbf{C}}^{\dagger}\,\underline{\mathcal{S}}\,\underline{\mathbf{C}} = \underline{\mathbf{1}}. \tag{11}$$

From that we get:

$$\underline{\mathcal{S}} = (\underline{\mathbf{C}}^{\dagger})^{-1}\underline{\mathbf{C}}^{-1} = (\underline{\mathbf{C}}\,\underline{\mathbf{C}}^{\dagger})^{-1}. \tag{12}$$

Using the above, (10) is written as:

$$\underline{\mathbf{H}}_0 \;=\; \underline{\mathbf{S}}\,\underline{\mathbf{C}}\,\underline{\mathbf{E}}_0\,\underline{\mathbf{C}}^{\dagger}\,\underline{\mathcal{S}}, \tag{13}$$

where $\underline{\mathcal{S}} = (\underline{\mathbf{C}}\,\underline{\mathbf{C}}^{\dagger})^{-1}$(this notation is used to simplify the expression and to emphasize that overlap matrices $\underline{\mathbf{S}}$ and $\underline{\mathcal{S}}$ do not need to be identical). The expansion coefficients, $\underline{\mathbf{C}}$, are obtained by solving the eigenvalue problem.

The resulting equation, Eq. (13), allows us to write the function of operator $\underline{\mathbf{H}}_0$ in a matrix form as:

$$\mathrm{f}(\underline{\mathbf{H}}_0) = \mathrm{f}(\,\underline{\mathbf{S}}\,\underline{\mathbf{C}}\,\underline{\mathbf{E}}_0\,\underline{\mathbf{C}}^{\dagger}\underline{\mathcal{S}}) = \;\underline{\mathbf{S}}\,\underline{\mathbf{C}}\,\mathrm{f}(\underline{\mathbf{E}}_0)\,\underline{\mathbf{C}}^{\dagger}\underline{\mathcal{S}}, \tag{14}$$

where $\mathrm{f}(\underline{\mathbf{E}}_0)$ is a diagonal matrix with the diagonal elements equal to the energies obtained from solving the eigenvalue equation for operator H_0. Expression (14), according to Eq. (6), is equivalent to the following equation:

$$\mathrm{f}(\underline{\mathbf{H}}_0) = \underline{\mathbf{S}}_{-}(\underline{\mathbf{H}}_0 - E_0)\ln\,|2(\underline{\mathbf{H}}_0 - E_0)|\,\underline{\mathbf{C}}^{\dagger}\underline{\mathcal{S}}. \tag{15}$$

2.1. Basis functions

The spatial part of the atomic ground-state wave function with the S symmetry is represented as a linear combination of the following one-center all-electron explicitly correlated Gaussian functions:

$$\phi_k^{(0)}(\mathbf{r}) = \exp[-\mathbf{r}^T\underline{\mathbf{A}}_k\mathbf{r}], \tag{16}$$

and the spatial part of the molecular ground-state wave function is represented as a linear combination of the following all-electron explicitly correlated Gaussian functions with shifted centers:

$$\phi_k^{(0)}(\mathbf{r}) = \exp[-(\mathbf{r} - \mathbf{s}_k)^T\underline{\mathbf{A}}_k(\mathbf{r} - \mathbf{s}_k)], \tag{17}$$

where $\mathbf{s_k}$is a $3n_e$-long vector of the shifts of the Gaussian centers and $\underline{\mathbf{A}}_k$ is a positive-definite real symmetric square matrix with the dimensions $3n_e \times 3n_e$ (where n_e is the number of the electrons in the system). The Cartesian coordinates of the electrons form $3n_e$-dimensional vector $\mathbf{r}$ given as:

$$\mathbf{r} = \begin{pmatrix}\mathbf{r}_1\\ \mathbf{r}_2\\ \vdots\\ \mathbf{r}_{n_e}\end{pmatrix} = \begin{pmatrix}x_1\\ y_1\\ z_1\\ \vdots\\ x_{n_e}\\ y_{n_e}\\ z_{n_e}\end{pmatrix}. \tag{18}$$

Matrix $\underline{\mathbf{A}}_k$ is rotationally invariant and can be written as a Kronecker product of $n_e \times n_e$-dimensional symmetric matrix $\mathbf{A}_k$ with a unit 3×3 matrix, $\mathbf{I}_3$: $\underline{\mathbf{A}}_k = \mathbf{A}_k \otimes \mathbf{I}_3$, where $\otimes$ denotes the Kronecker product. To ensure square integrability of function $\phi_k^{(0)}$, matrix $\mathbf{A}_k$ must also be positive definite. This happens automatically if $\mathbf{A}_k$ is represented in the following Cholesky factored form as: $\mathbf{A}_k = \mathbf{L}_k\mathbf{L}_k^T$, where $\mathbf{L}_k$ is an $n_e \times n_e$, rank n_e, lower triangular matrix. ϕ_k is automatically square-integrable for the $\mathbf{L}_k$ matrix elements being any real numbers. Elements of the shift vector, $\mathbf{s_k}$, and the matrix elements of $\mathbf{L}_k$ are optimized in the calculations using the variational method.

The proper permutational symmetry consistent with the permutational symmetry of the state of the system considered in the calculation has to be implemented through an appropriate symmetry projection represented by a linear combination of operators involving permutations of electron indices. Let $\underline{\mathbf{P}}$ be the permutation matrix with dimension $3n_e \times 3n_e$ that represents the permutation operator P. The following convention is used to represent the kl matrix element of an arbitrary operator O:

$$\langle \mathrm{P}\phi_k \mid \mathrm{O} \mid \mathrm{P}\,\phi_l\rangle = \langle \phi_k \mid \mathrm{P}^{\dagger}\mathrm{OP} \mid \phi_l\rangle = \langle \phi_k \mid \mathrm{O} \mid \mathrm{P}\,\phi_l\rangle. \tag{19}$$

By acting with the permutation operator P on basis functions $\phi_l^{(0)}$, $\phi_l^{(x)}$, and $\phi_l^{(z)}$ we get:

$$\begin{aligned}\mathrm{P}\phi^{(0)} = \mathrm{Pexp}[-(\mathbf{r} - \mathbf{s}_l)^T\underline{\mathbf{A}}_l(\mathbf{r} - \mathbf{s}_l)] &= \exp[-(\underline{\mathbf{P}}\mathbf{r} - \mathbf{s}_l)^T\underline{\mathbf{A}}_l(\underline{\mathbf{P}}\mathbf{r} - \mathbf{s}_l)] = \\ &= \exp[-(\mathbf{r} - \widetilde{\mathbf{s}}_l)^T\widetilde{\underline{\mathbf{A}}}_l(\mathbf{r} - \widetilde{\mathbf{s}}_l)] \equiv \widetilde{\phi}_l^{(0)},\end{aligned} \tag{20}$$

where $\widetilde{\underline{\mathbf{A}}}_l = \underline{\mathbf{P}}^T\underline{\mathbf{A}}_l\underline{\mathbf{P}}$ and $\widetilde{\mathbf{s}}_l = \underline{\mathbf{P}}^{-1}\mathbf{s}_l$.

2.2. Spectral identity

The next important transformation used in the present approach is the inclusion of a spectral identity, I, into the expression for the Bethe logarithm. I is constructed using a set of eigenfunctions. The selection of the basis functions for expanding the eigenfunctions used to construct I depends on the spatial symmetry of the considered state of the system (see further discussion).

The spectral identity, I, is inserted in two places in the expression for function $\mathrm{f}(\mathrm{H}_0)$ of operator H_0:

$$\mathcal{L} = \langle\, \nabla_{\mathbf{r}}\Psi_0 \mid \mathrm{I}\,\mathrm{f}(\mathrm{H}_0)\,\mathrm{I} \mid \nabla_{\mathbf{r}}\Psi_0\rangle. \tag{21}$$

From (21) it is clear that operator I has to be constructed using excited-state wave functions orthogonal to the wave function of the state under consideration (e.g. the ground-state in the present work) that have non-zero coupling matrix-elements with this wave function through operator $\nabla_{\mathbf{r}}$.

2.2.1. Atomic case

In the atomic case, if the ground-state wave function has S symmetry, the wave functions of excited states used in I have to have the P symmetry (denoted as $\{\phi^p\}$). According to the procedure introduced in Ref. [30], basis functions $\{\phi^p\}$can be formed from basis functions $\{\varphi\}$, which are employed to expand the wave function of the ground state, by multiplying them by the z coordinate (z_1 in the one-electron case and z_i, $i = 1, \ldots, n_e$ in the n_e electron case). Due to the spherical symmetry of the S ground-state wave function, one only needs to use basis functions $\{z\varphi\}$ in calculating the exited-state wave functions to be used in constructing the identity:

$$\phi^p \in \{z\varphi\}, \quad \text{where} \quad \{\varphi\} \quad \text{representing the ground state.} \tag{22}$$

Let us denote by n_p the number of the ϕ^p functions. This number is equal to:

$$n_p = n{\cdot}n_e,$$

where n in the number of the basis functions used to expand the wave function of the ground state and n_e in the number of electrons in the system.

The spectral identity constructed using the $\{\phi^p\}$ functions is denoted as I^p and it has the following form:

$$\mathrm{I}^p = \sum_{a=1}^{n_p} |\Psi_a^p\rangle\langle\Psi_a^p| = \sum_{a=1}^{n_p}\sum_{\alpha,\beta=1}^{n_p} C_{a\alpha}^p \mid \phi_\alpha^p\rangle\,\langle C_{a\beta}^p\,\phi_\beta^p \mid \;= \sum_{a=1}^{n_p}\sum_{\alpha,\beta=1}^{n_p} \mid \phi_\alpha^p\rangle\, C_{a\alpha}^p\, C_{a\beta}^{p\dagger}\,\langle\,\phi_\beta^p|, \tag{23}$$

where Ψ_a^p are eigenfunctions of H_0 with the P symmetry and $C_{a\alpha}^p$ are the linear expansion coefficients of these eigenfunctions in terms of the ψ_α^p basis functions.

2.2.2. Molecular case

In the case of diatomic molecules, the construction of the identity is more complicated. The basis functions used to construct the spectral identities used in $\ln k_0$ depend on the molecular symmetry. If the bond axis of the molecule is the z axis, OZ, the symmetry group is C_{∞}. The molecule can have a σ_h symmetry plane, an infinite number of C_2 axes (in the case of a homonuclear molecule) and a σ_v plane. What follows is that the excited states that couple with the Σ ground state can have either Σ or Π symmetry:

- $\phi^{\Sigma} \in \{z\varphi\}$,
- $\phi^{\Pi} \in \{x\varphi + y\varphi\}$.

The numbers of functions ϕ^{Σ} and ϕ^{Π} are denoted as n_{Σ} and n_{Π}, respectively. These numbers are:

- $n_{\Sigma} = n \cdot n_e - 1$,
- $n_{\Pi} = 2n \cdot n_e$,

where n is the number of basis functions used for expanding the wave function for the ground state and n_e is the number of electrons in the system. The reduction of the Σ basis set by one is due to removal of the ground-state wave function. The size of the Π basis set is $n \cdot n_e$ since the contributions from the $x\varphi$ and $y\varphi$ functions are the same, we only need to calculate one of them.

Thus, the spectral identity in this case is a sum of the Σ and Π identities:

$$\mathrm{I} = \mathrm{I}^{\Sigma} + \mathrm{I}^{\Pi}, \tag{24}$$

where

$$\mathrm{I}^{\Sigma} = \sum_{a=1}^{n_{\Sigma}} |\Psi_a^{\Sigma}\rangle\langle\Psi_a^{\Sigma}| = \sum_{a=1}^{n_{\Sigma}} \sum_{\alpha\beta=1}^{n_{\Sigma}} C_{\alpha a}^{\Sigma} \, |\phi_{\alpha}^{\Sigma}\rangle\langle C_{\beta a}^{\Sigma} \, \phi_l^{\Sigma}| = \sum_{a=1}^{n_{\Sigma}} \sum_{\alpha\beta=1}^{n_{\Sigma}} |\phi_{\alpha}^{\Sigma}\rangle \, C_{\alpha a}^{\Sigma} C_{\beta a}^{\Sigma\,\dagger} \, \langle\phi_{\beta}^{\Sigma}| \tag{25}$$

and

$$\mathrm{I}^{\Pi} = \sum_{a=1}^{n_{\Pi}} |\Psi_a^{\Pi}\rangle\langle\Psi_a^{\Pi}| = \sum_{a=1}^{n_{\Pi}} \sum_{\alpha\beta=1}^{n_{\Pi}} C_{\alpha a}^{\Pi} \, |\phi_{\alpha}^{\Pi}\rangle\langle C_{\beta a}^{\Pi} \, \phi_l^{\Pi}| = \sum_{a=1}^{n_{\Pi}} \sum_{\alpha\beta=1}^{n_{\Pi}} |\phi_{\alpha}^{\Pi}\rangle \, C_{\alpha a}^{\Pi} C_{\beta a}^{\Pi\,\dagger} \, \langle\phi_{\beta}^{\Pi}|. \tag{26}$$

2.3. Matrix form

2.3.1. Atomic case

The spectral identity, I, is introduced to expression $\mathcal{L}$ in the algorithm for the Bethe logarithm:

$$\mathcal{L} = \langle \nabla_{\mathbf{r}}\Psi_0 \,|\, \mathrm{I}\, \mathrm{f}(\mathrm{H}_0)\, \mathrm{I} \,|\, \nabla_{\mathbf{r}}\Psi_0\rangle. \tag{27}$$

The ground-state wave function, Ψ_0, is now expanded in terms of basis functions φ according to (14):

$$\mathcal{L} = \langle \nabla_{\mathbf{r}}\Psi_0 \,|\, \mathrm{I}\, \mathrm{f}(\mathrm{H}_0)\, \mathrm{I} \,|\, \nabla_{\mathbf{r}}\Psi_0\rangle = \sum_{l,d=1}^{n} \sum_{l,d,\alpha,\beta,\gamma,\xi=1}^{n_p} C_{l1}^{\dagger} \langle \nabla_{\mathbf{r}}\varphi_l \,|\phi_{\alpha}^{p}\rangle \, C_{\alpha a}^{p} C_{\beta a}^{p\,\dagger}$$
$$\langle\phi_{\beta}^{p}\,|\,\mathrm{f}(\mathrm{H}_0)\,|\phi_{\gamma}^{p}\rangle \, C_{\gamma b}^{p} C_{\xi b}^{p\,\dagger} \, \langle\phi_{\xi}^{p}\,|\,\nabla_{\mathbf{r}}\varphi_d\rangle \, C_{d1}. \tag{28}$$

The matrix elements of operator function $\mathrm{f}(\mathrm{H}_0)$ is calculated as:

$$\langle\phi_{\beta}^{p}\,|\,\mathrm{f}(\mathrm{H}_0)\,|\phi_{\gamma}^{p}\rangle = [\, \underline{\mathbf{S}}^{p} \, \underline{\mathbf{C}}^{p} \, (\mathrm{H}_0 - \underline{\mathbf{E}}_0) \ln 2(\mathrm{H}_0 - \underline{\mathbf{E}}_0) \, \underline{\mathbf{C}}^{p\dagger} \, \underline{\mathbf{S}}^{p} \,]_{\beta\gamma} =$$
$$\equiv \sum_{q,t,w,r=1}^{n_p} \underline{\mathbf{S}}_{\beta q}^{p} \, \underline{\mathbf{C}}_{qt}^{p} \, \mathrm{f}(\underline{\mathbf{E}}_0^{p})_{tw} \, \underline{\mathbf{C}}_{wr}^{p\,\dagger} \, \underline{\mathbf{S}}_{r\gamma}^{p}, \tag{29}$$

where $\underline{\mathbf{C}}^{p}$ is the matrix of the linear expansion coefficients of the P eigenvectors, $\underline{\mathbf{E}}_0$ is a diagonal matrix with all diagonal elements equal to the ground-state energy, E_0, and $\underline{\mathbf{E}}_0^{p}$ is a diagonal matrix with the diagonal elements being differences between the energies of the exited states used to construct the spectral identity, I^{p}, and the ground-state energy.

The expression for the numerator of the Bethe logarithm can be now written in a matrix form as:

$$\mathcal{L} = \underline{\mathbf{C}}^{T} \underline{\mathbf{X}}^{p\,T} \underline{\mathbf{S}}^{-1p} \underline{\mathbf{S}}^{p} \underline{\mathbf{C}}^{p} \mathrm{f}(\underline{\mathbf{E}}_0) \underline{\mathbf{C}}^{p\dagger} \underline{\mathbf{S}}^{p} \underline{\mathbf{S}}^{-1p} \underline{\mathbf{X}}^{p} \underline{\mathbf{C}}, \tag{30}$$

where matrix elements of X^{p} are defined as:

$$X_{ab}^{p} = \langle \varphi_a \,|\, \nabla_{\mathbf{r}}\, \phi_b \rangle. \tag{31}$$

The way the spectral identity is constructed in the present approach is different than it was done by Drake and Goldman [11]. While in the present work the identity is formed based on functions used to expand the ground-state wave function, in the approach of Drake and Goldman the identity was formed only with functions that provide good representation of high excited states. According to these authors, such states should contribute the most to the value of the Bethe logarithm.

The difference in the way the wave functions for the p states are constructed in the Drake and Goldman and Stanke et al. approaches rests in limiting the powers of r in the latter approach to 0 and 2, while in the former approach the number of different powers is equal to $\Omega - 1$. Drake and Goldman [11] argued that it is important for their p basis set to include functions with multipliers $\frac{z}{r}$ that guarantee fast convergence of the $\ln k_0$ value. In Ref. [30] some test calculations were performed with different p basis functions to show which functions are capable of reproducing very well the accurate value of $\ln k_0$ for the hydrogen atom when similar number of the basis functions as used by Drake and Goldman is employed. The calculations showed that the condition of Drake and Goldman for faster convergence of the calculations may not be strictly applicable to the Gaussian functions. Naturally, the Gaussian calculations are not as accurate as the calculations of Drake and Goldman, as the Gaussians do not fulfill the Kato cusp condition at the nucleus and their long-range behavior is also deficient. In Ref [30] a simple alternative way for constructing p functions for the Bethe logarithm calculations was proposed. It involves multiplying the basis functions variationally optimized for the ground-state wave function of the hydrogen atom by the z coordinate. According to the authors of Ref. [30], the p basis set constructed this way should be sufficient to reproduce a few significant figures of the accurate value of $\ln k_0$ for larger atoms and molecules.

2.3.2. Molecular case

To construct the matrix form of the expression to calculate $\ln k_0$ for a molecule we use an analogical procedure as that used for atoms. However, as atomic symmetries are different from molecular symmetries, different basis functions need to be used in the calculations. For a diatomic molecule there are two types of the $\nabla_{\mathbf{r}}$ operators (i.e. the derivative can be calculated wither with respect to either parallel or perpendicular coordinate relative to the bond axis):

$$\nabla_{\mathbf{r}} = \nabla_{\mathbf{r}}^{\perp} + \nabla_{\mathbf{r}}^{\parallel}. \tag{32}$$

These operators acting on Ψ_0 generate functions Ψ^{Σ} and Ψ^{Π} which are mutually orthogonal:

$$\begin{aligned} \nabla_{\mathbf{r}}^{\perp}\Psi_0 &\rightarrow \Psi^{\Pi}, \\ \nabla_{\mathbf{r}}^{\parallel}\Psi_0 &\rightarrow \Psi^{\Sigma}, \end{aligned} \tag{33}$$

placing them in the numerator of $\ln k_0$ gives rise to two independent contributions:

$$\begin{aligned} \mathcal{L} &= \langle \nabla_{\mathbf{r}}\Psi_0 \,|\, \mathrm{I}\, \mathrm{f}(\mathrm{H}_0)\, \mathrm{I} \,|\, \nabla_{\mathbf{r}}\Psi_0\rangle = \langle (\nabla_{\mathbf{r}}^{\perp} + \nabla_{\mathbf{r}}^{\parallel})\Psi_0 \,|\, \mathrm{I}\, \mathrm{f}(\mathrm{H}_0)\, \mathrm{I} \,|\, (\nabla_{\mathbf{r}}^{\perp} + \nabla_{\mathbf{r}}^{\parallel})\Psi_0\rangle = \\ &= \langle \nabla_{\mathbf{r}}^{\perp}\Psi_0 \,|\, \mathrm{I}^{\Pi}\, \mathrm{f}(\mathrm{H}_0)\, \mathrm{I}^{\Pi} \,|\, \nabla_{\mathbf{r}}^{\perp}\Psi_0\rangle + \langle \nabla_{\mathbf{r}}^{\parallel}\Psi_0 \,|\, \mathrm{I}^{\Sigma}\, \mathrm{f}(\mathrm{H}_0)\, \mathrm{I}^{\Sigma} \,|\, \nabla_{\mathbf{r}}^{\parallel}\Psi_0\rangle. \end{aligned} \tag{34}$$

The spectral identities corresponding to the Σ and Π symmetries are constructed using basis functions $\{\phi^{\Sigma}\}$ and $\{\phi^{\Pi}\}$, respectively. The linear expansion coefficients of the excited-state wave functions in terms of basis functions are obtained by solving the corresponding eigenvalue problems for H_0. Now, expanding the ground-state wave function, Ψ_0, using basis functions φ_l we obtain:

$$\begin{aligned} \mathcal{L} &= \sum_{l,d=1}^{n} \sum_{a,b\alpha,\beta,\gamma,\xi=1}^{n_{\Sigma}} C_{l1}^{\dagger} \langle \nabla_{\mathbf{r}}^{\perp}\varphi_l \,|\phi_{\alpha}^{\Sigma}\rangle \, C_{\alpha a}^{\Sigma} C_{\beta a}^{\Sigma\,\dagger} \, \langle\phi_{\beta}^{\Sigma}\,|\,\mathrm{f}(\mathrm{H}_0)\,|\phi_{\gamma}^{\Sigma}\rangle \\ &\quad C_{\gamma b}^{\Sigma} C_{\xi b}^{\Sigma\,\dagger} \, \langle\phi_{\xi}^{\Sigma}\,|\,\nabla_{\mathbf{r}}^{\perp}\varphi_d\rangle C_{d1} + \\ &\quad + \sum_{l,d=1}^{n} \sum_{a,b,\alpha,\beta,\gamma,\xi=1}^{n_{\Pi}} C_{l1}^{\dagger} \langle \nabla_{\mathbf{r}}^{\parallel}\varphi_l \,|\phi_{\alpha}^{\Pi}\rangle \, C_{\alpha a}^{\Pi} C_{\beta a}^{\Pi\,\dagger} \, \langle\phi_{\beta}^{\Pi}\,|\,\mathrm{f}(\mathrm{H}_0)\,|\phi_{\gamma}^{\Pi}\rangle \\ &\quad C_{\gamma b}^{\Pi} C_{\xi b}^{\Pi\,\dagger} \, \langle\phi_{\xi}^{\Pi}\,|\,\nabla_{\mathbf{r}}^{\parallel}\varphi_d\rangle C_{d1}, \end{aligned} \tag{35}$$

where the summation over the functions used to construct the spectral identity runs only over the Σ functions.

The expectation value of the function of operator H_0 is calculated

according to (14) as a sum of two parts:

$$\begin{aligned}\langle\phi_\beta^\Sigma \mid \mathrm{f}(\mathrm{H}_0)\mid\phi_\gamma^\Sigma\rangle &= \sum_{q,t,w,r=1}^{n_\Sigma} S_{\beta q}^\Sigma\, C_{qt}^\Sigma\, \mathrm{f}(\underline{\mathbf{E}}_0^\Sigma)_{tw}\, C_{wr}^{\Sigma\,\dagger}\, S_{r\gamma}^\Sigma,\\ \langle\phi_\beta^\Pi \mid \mathrm{f}(\mathrm{H}_0)\mid\phi_\gamma^\Pi\rangle &= \sum_{q,t,w,r=1}^{n_\Pi} S_{\beta q}^\Pi\, C_{qt}^\Pi\, \mathrm{f}(\underline{\mathbf{E}}_0^\Pi)_{tw}\, C_{wr}^{\Pi\,\dagger}\, S_{r\gamma}^\Pi.\end{aligned} \tag{36}$$

Analogically to the atomic case, expression $\mathcal{L}$ for diatomic molecules with the ground-state wave functions with Σ symmetry can be written in the matrix form as:

$$\begin{aligned}\mathcal{L}=&\underline{\mathbf{C}}^T\underline{\mathbf{X}}^{\Sigma T}\underline{\mathbf{S}}^{-1\Sigma}\underline{\mathbf{S}}^\Sigma\underline{\mathbf{C}}^\Sigma\mathrm{f}(\underline{\mathbf{E}}_0)\underline{\mathbf{C}}^{\Sigma\dagger}\underline{\mathbf{S}}^\Sigma\underline{\mathbf{S}}^{-1\Sigma}\underline{\mathbf{X}}^\Sigma\underline{\mathbf{C}}+\\ &+\underline{\mathbf{C}}^T\underline{\mathbf{X}}^{\Pi T}\underline{\mathbf{S}}^{-1\Pi}\underline{\mathbf{S}}^\Pi\underline{\mathbf{C}}^\Pi\mathrm{f}(\underline{\mathbf{E}}_0)\underline{\mathbf{C}}^{\Pi\dagger}\underline{\mathbf{S}}^\Pi\underline{\mathbf{S}}^{-1\Pi}\underline{\mathbf{X}}^\Pi\underline{\mathbf{C}},\end{aligned} \tag{37}$$

where $\underline{\mathbf{C}}$ is the vector of the linear expansion coefficients of the ground-state wave function in terms of the basis functions. $\underline{\mathbf{C}}^\Sigma$ and $\underline{\mathbf{C}}^\Pi$ are the matrices of the corresponding expansion coefficients obtained for excited-state wave functions by solving the eigenvalue problem in the Σ and Π basis sets, respectively.

The matrix elements of matrices X^Σ and X^Π are:

$$\begin{aligned}X_{ab}^\Sigma &= \langle\varphi_a^\Sigma \mid \nabla_{\mathbf{r}}^\perp\,\phi_b\rangle,\\ X_{ab}^\Pi &= \langle\varphi_a^\Pi \mid \nabla_{\mathbf{r}}^\parallel\,\phi_b\rangle.\end{aligned} \tag{38}$$

3. Basis set reduction

In this section we describe a method for reducing the size of the basis set of excited-state wave functions used for constructing the spectral identity. The reduction is necessary in order to carry out $\ln k_0$ calculations for larger systems.

Due to long computational time required to calculate the expectation value of the Bethe logarithm when a large basis set describing excited states is used, a method has been developed for reducing the number of p (Σ and Π for diatomic molecules) basis functions. For example, in the case of the beryllium atom, a good-quality wave function for the ground state requires the use of at least 5000 explicitly correlated Gaussian functions. This number of functions, when multiplied by z_i, $i = 1, ...,4$, gives 20,000 functions (minus the functions eliminated due to linear dependencies) for constructing the wave functions of the p excited states. Diagonalization of the Hamiltonian matrix calculated for the basis set of 20,000 functions, which is needed to obtain all p eigenvalues and eigenfunctions, is not currently possible within the CPU time and memory allocations available to us at present time.

The goal of limiting the number of the p basis functions is to generate a subset of these functions which is manageable and relatively small yet gives values of the Bethe logarithm with an acceptable accuracy. Two approaches to perform the reduction of the set of the p basis functions are considered in this work (we describe the approaches using the atomic case; the approach for molecules is analogical). Both of the approaches use parameter λ as the cutoff parameter for truncating the basis set. In each method the contribution of a single function (more precisely, of the set of p functions generated from a single s function) to the value of the Bethe logarithm is calculated and compared with λ to determine if the function should be included in the p-function basis set.

To determine the contribution of a particular p basis function to the Bethe logarithm in the first method, the value of $\ln k_0(k;\Psi_0)$ is calculated using the complete ground-state wave function, Ψ_0, but with the spectral identity constructed only using n_e functions $\phi_k^{(p)}$ obtained by multiplying function $\phi_k^{(0)}$ by z_i, $i = 1, ...,n_e$. In the second method, the value of the Bethe logarithm is calculated with the ground-state wave function expanded only in terms of one function, i.e. function $\phi_k^{(0)}$, and with the p functions used to expand the spectral identity being the same as in the first method. Whether the $\phi_k(p)$ functions generated based on the $\phi_k^{(0)}$ function include or not included in the p basis set is determined by comparing the absolute value of the Bethe logarithm obtained with each method (i.e. the $\ln k_0(k, \Psi_0)$ value in the first method and the $\ln k_0(k)$ in the second method) with the cutoff value, λ. If the absolute value of the Bethe-logarithm is greater than the cutoff, the functions are included in the p subset. The choice of the most optimal value of λ is still an open problem that is investigated. However, the analysis performed so far has resulted in working out an effective way of how this value can be selected.

Our calculations of the Bethe logarithm performed so far confirm the conclusion reached by Drake and Goldman [11] that the largest contributions to the logarithm come from basis functions representing high-excited states. However, in order to obtain a very accurate logarithm value, one needs to also include more diffuse Gaussian functions with small exponents. In the analysis of the contributions of individual functions to the Bethe logarithms, it is established that Gaussians with small exponents are functions for which the individual $\ln k_0(k;\Psi_0)$ or $\ln k_0(k)$ contributions are usually small. In accepting or rejecting a particular subset of functions $\psi_k^{(p)}$ generated from the $\psi_k^{(0)}$ function to the p basis set, which is subsequently used to construct the spectral identity, the following criterion is used:

$$|\ln k_0(k;\Psi_0)| > \lambda \tag{39}$$

and

$$|\ln k_0(k)| > \lambda \tag{40}$$

in the first and the second method, respectively.

4. Results

The above-described reduction methods do not allow to obtain a value of the Bethe logarithm accurate to many significant digits, but is provides a relatively simple and efficient way to construct a compact basis set for expanding excited-state wave functions used in the spectral identity in the expression for the Bethe logarithm. The methods allow to extended the calculations of the Bethe algorithm, at a low cost, to larger atomic and molecular systems.

Both methods for reducing the basis-set size lead to similar results for the Bethe logarithm. However, due to the significant amount of time needed to solve the ground-state eigenvalue problem in the full basis set in the first method, the second method is more practical and significantly faster. We have also considered a method where the basis functions used for expanding the wave functions of excited states are selected based on the magnitude of their contributions to the wave function of the ground state. However, that approach was deemed inadequate because it resulted in significant decrease of the accuracy of the ground-state energy and, consequently, to much lower accuracy of the Bethe logarithm.

The results for excite-state basis sets with large number of functions, for which the calculations of $\ln k_0$ for the complete basis sets, are obtained by extrapolating the results obtained with reduced basis sets. The curves obtained for ground-state basis sets with different lengths as functions of different values on λ are nearly parallel (i.e. shifted with respect to each other by a constant value). Thus, having a few values of $\ln k_0(k)$ or $\ln k_0(\Psi_0, k)$ one can estimate the value of the logarithm for the whole basis set.

The purpose of performing atomic calculations in this work is to test the performance of the proposed approach vis-a-vis the results presented in the literature and calculated with methods more accurate than the present method. The comparison will show how many significant figures in the value of the Bethe logarithm calculated with the present method can be considered reliable.

4.1. Hydrogen atom

For the hydrogen atom it is possible to directly determine which basis functions provide more significant contributions to the value of the Bethe logarithm. Both reduction methods give consistent results showing that Gaussians with small exponents always contribute little to the logarithm, but the contributions of the Gaussians with large exponents may be either relatively large or small. In the case of the first reduction method, where a contribution of a given basis function is calculated using the ground-state wave function expanded using all functions in the basis set, more

Table 1
The convergence of the ground-state energy E_0 and the first P excited state of the hydrogen atom with the number (n) of Gaussians in the basis set. The values of the Bethe logarithm, $\ln k_0$, and a comparison with the most precise previous calculations are shown. All values are given in a.u.

$\ln k_0$		n	$\ln k_0$	E_0	E_{p1}
2.811 769 883(28)	[13]	30	2.98198	−0.49999999999021074	−0.12421530728341865
2.984 128 555 765 498	[31]	35	2.98342	−0.49999999999996865	−0.12499892298399225
2.984 125 555 765 497 6107	[14]	40	2.98369	−0.49999999999999554	−0.12490299272327426
2.984 003 384 0	[30]	45	2.98400	−0.49999999999999861	−0.12499788897296360
		50	2.98410	−0.49999999999999874	−0.12499999901708187

Gaussians with larger exponents remain in the basis set than when the second method is used. In the case of the second method, the contributions of the Gaussians with moderate and large exponents are similar. The results for the hydrogen atom are presented in Table 1. Interestingly, they are somewhat better than those obtained by Stanke et al. [30] in quadruple precision (in this work we used the double precision).

It is shown that in order to reproduce three significant figures of the reference values, one can reduce the basis set for expending the excited states by about 30 percent, when the first reduction method is used, and by about a half, when the second reduction method is used. The values of $\ln k_0(k;\Psi_0)$ and $\ln k_0(k)$ for different values of the cut-off parameter, λ, for the hydrogen atom are shown in Table 2.

4.2. Helium atom

The results obtained in analogical calculations performed for the helium atom are presented in Tables 3 and 4. The results in Table 3 are compared with the original results of Schartz [9], Bhatia and Drachman [24], and Korobov [14], as well as with the most recent results of Korobov [15] and Yang et al. [16] (who had used the B-spline functions).

For the helium atom, we also show a comparison of the results obtained in the basis set of 2000 functions with the results obtained by extrapolating the values obtained employing the second reduction method in the calculations where the basis set for expanding the P excited states is reduced to 1300, 1600, and 2000 functions. All these values are shown in Table 4.

Calculations are also performed for the Bethe logarithm for the lowest nine ^{1}S states of the helium atom. The value of 4.37 a.u. obtained in the calculations (within the estimated accuracy of the calculations of three significant figures) agree for the lowest seven states with the results of Korobov [15].

4.3. Lithium atom

For atoms with more than two electrons i.e. for the lithium and beryllium atoms, as well as for the boron atom that will be considered in future calculations, it is impossible to perform calculations using the full basis set for expanding the wave functions of excited states used to construct the spectral identity. The results marked with ^{e} denote values obtained using extrapolation in terms of the parameter λ of the results obtained using smaller basis sets. The procedure described earlier in this work is used in the extrapolation. In Table 5 one can find two extrapolated values for the basis sets of 5000 and 6000 functions.

Table 2
The Bethe logarithm calculations for the ground state of the hydrogen atom obtained in the reduced excited states basis sets made from the full base of 50 Gaussians ($\lambda = 0.0$). All values are given in a.u.

λ	n_λ	$\ln k_0(k;\Psi)$	λ	n_λ	$\ln k_0(k)$
0.1	30	3.08641	1000.0	18	3.04931
0.5	34	3.00400	50.0	27	2.98491
0.01	38	2.98338	10.0	32	2.98350
0.05	40	2.98368	2.0	36	2.98532
0.001	46	2.98402	1.0	40	2.98505
0.0001	48	2.98407	0.5	46	2.98438
0.0	50	2.98410	0.0	50	2.98410

Table 3
The Bethe-logarithm ($\ln k_0$) calculations and the value of the non-relativistic energy, E_{nr}, for the ground-state of the helium atom with the number n of Gaussians in the basis. All values are given in a.u.

n	E_{nr}	$\ln k_0$	$\ln k_0$	
600	−2.90372437699588586	4.390	4.370(4)	[9]
1200	−2.90372437703296022	4.385	4.370 159(2)	[12]
1400	−2.90372437703410139	4.376	4.370 160 218(3)	[11]
1600	−2.90372437703410776	4.373	4.370 160 223 06(2)	[14]
1800	−2.90372437703411172	4.373	4.370 160 022(5)	[16]
2000	−2.90372437703411408	4.373	4.370 160 223 0703(3)	[15]
[10]	−2.90372437703411959			

Table 4
The Bethe logarithm calculations for the ground state of the helium atom obtained in the reduced excited-state basis sets obtained from the base of 2000 Gaussians ($\lambda = 0.0$). All values are given in a.u.

λ	n_λ	$\ln k_0(k;\Psi_0)$	λ	n_λ	$\ln k_0(k)$	λ	n_λ	$\ln k_0(k)$
160.0	556	4.452	2.0	355	5.138	2.0	265	5.426
155.0	622	4.391	1.0	670	4.394	1.0	507	4.418
150.0	700	4.389	0.5	925	4.388	0.5	696	4.389
100.0	861	4.387	0.4	1001	4.367	0.4	743	4.376
5.0	1948	4.373	0.1	1383	4.367	0.1	989	4.369
4.0	1959	4.373	0.05	1513	4.370	0.05	1063	4.372
3.0	1968	4.373	0.01	1712	4.372	0.01	1169	4.371
0.0	2000	4.373	0.0	2000	4.373	0.0	1300	4.375
							2000	4.369^e

The values for 5000 and 6000 basis functions are estimated based on the curve obtained for smaller basis sets; among them there are those taken from Table 7. The second reduction method is employed for generating the data for the extrapolation. This method is used because it allows for a more significant reduction of the size of the basis set used for constructing of the excited-state spectral identity than the first method (as it is evident from the results shown in Table 6).

In the case of the lithium and beryllium atoms, our approach reproduces only two significant digits of the reference results, but the calculations are performed with the excited-state basis sets very significantly reduced in comparison used in the reference calculations.

4.4. Beryllium atom

Tables 8 and 9 present the results obtained in the present work for the beryllium atom. Here also, only two significant digits of the reference results are reproduced.

4.5. H_2^+ and H_2 molecules

The calculations of the Bethe logarithm for molecules are important because the accuracy of determining energies of molecular ground and excited states for small systems is primarily limited by the uncertainty

Table 5
The Bethe-logarithm ($\ln k_0$) calculations and the value of the non-relativistic energy, E_{nr}, for the ground state of the lithium atom with the number of Gaussians in the basis, n. All values are given in a.u.

n	$\ln k_0$	E_{nr}
1000	5.261	−7.4780528771
2000	5.258	−7.4780592852
5000	5.239[e]	−7.4780600463
6000	5.236[e]	−7.4780603072
[32]	5.176 82	
[19]	5.178 15(3)	
[18]	5.178 17(3)	

Table 6
The Bethe-logarithm calculations for the ground state of the lithium atom obtained in the reduced excited-state basis sets made from the full base of 2000 Gaussians ($\lambda = 0.0$). All values are given in a.u.

λ	n_λ	$\ln k_0(k;\Psi_0)$	λ	n_λ	$\ln k_0(k)$
2.0	338	5.627	6.0	208	5.202
1.0	675	5.245	4.0	215	5.203
0.5	948	5.226	3.0	241	5.225
0.3	1137	5.239	2.0	300	5.227
0.2	1256	5.239	1.0	323	5.242
0.1	1452	5.250	0.5	795	5.258
0.0	2000	5.258	0.0	2000	5.258

Table 7
The Bethe logarithm calculations for the ground state of the lithium atom obtained in the reduced excited-state basis sets generated from the full base of 1000, 2000 or 5000 Gaussians ($\lambda = 0.0$). All values are given in a.u.

λ	n_λ	$\ln k_0(k)$	λ	n_λ	$\ln k_0(k)$	λ	n_λ	$\ln k_0(k)$
6.0	208	5.211	6.0	208	5.202	6.0	2016	5.197
4.0	215	5.215	4.0	215	5.203	4.0	214	5.193
3.0	259	5.232	3.0	241	5.225	3.0	242	5.220
2.0	303	5.232	2.0	300	5.227	2.0	299	5.219
1.0	339	5.249	1.0	323	5.242	1.0	323	5.233
0.5	642	5.259	0.5	795	5.258	0.5	1489	5.251
0.0	1000	5.261	0.0	2000	5.258	0.0	5000	5.239[e]

of the values of the leading QED corrections, in particular, the correction involving the logarithm. As mentioned, there only two molecular systems for which the Bethe-logarithm values were determined with high accuracy. These systems are ions of diatomic hydrogen, H_2^+ and HD^+ [25–27], and the hydrogen molecule, H_2. Probably the first calculations of the Bethe logarithm for H_2 were done by Wolniewicz [34] using the approximate method introduced by Garcia [35] and by Bishop and Cheung [36]. More accurate results were presented in 2009 by Piszczatowski et al. [29]. Their approach employed the adiabatic approximation to the expression for $\ln k_0$ and took advantage the integration method of Schwartz. The approach applied to the H_2^+ ion produced results that agreed very well with the very accurate results of Korobov.

Our results for $\ln k_0$ for H_2^+ and H_2 obtained with the approach described in this work are shown in the left column in Table 10. The results for H_2^+ are compared with the results of Korobov [27] and, as one can see, the agreement is very good (of the order of 3–5 permilles). The results for the H_2 molecule presented in Table 10 are compared with the results of Piszczatowski [29].

A comparison of the $\ln k_0$ results for the H_2^+ ion with the results of Korobov is also shown in Fig. 1. As one can see, the deviation of the results for the internuclear distances shorter than the equilibrium distance of $R = 2.0$ a.u. is about 3 permilles, but increases to about 5

Table 8
The Bethe-logarithm ($\ln k_0$) calculations and the value of the non-relativistic energy, E_{nr}, for the ground state of the beryllium atom with the number of Gaussians in the basis, n. All values are given in a.u.

n	$\ln k_0$	E_{nr}
100	5.85	−14.64919377
1000	5.84	−14.66649481
2000	5.83	−14.66716806
3000	5.83	−14.66724877
5000	5.81[e]	
6500	5.79[e]	
[33]	5.75 034(3)	−14.667355627
[20]	5.75 046(2)	−14.667356498(3)

Table 9
The Bethe-logarithm calculations for the ground state of the beryllium atom performed in the reduced excited-state basis sets obtained from the full base of 1000, 2000, and 5000 Gaussians (the full basis set result corresponds to $\lambda = 0.0$). All values are given in a.u.

λ	n_λ	$\ln k_0(k)$	λ	n_λ	$\ln k_0(k)$	λ	n_λ	$\ln k_0(k)$
4.0	66	6.35	4.0	82	6.09	3.5	35	6.52
3.5	163	5.98	3.5	186	5.84	3.0	138	5.83
3.0	252	5.84	3.0	253	5.82	2.5	252	5.82
2.5	329	5.83	2.5	351	5.82	2.4	281	5.80
2.3	372	5.83	2.2	462	5.81	2.3	307	5.80
2.0	496	5.85	2.0	710	5.84	2.2	327	5.79
1.8	699	5.84	1.8	1069	5.83	2.1	347	5.80
1.5	885	5.84	1.5	1667	5.83	2.0	496	5.83
0.0	1000	5.84	0.0	2000	5.83	0.0	5000	5.81[e]

permilles for distances larger than the equilibrium distance. The discrepancy can be related to an uneven quality of the basis sets optimized for different points on the potential energy curve. In the case of the hydrogen molecule, H_2, the relative error is larger and, while it is about 3 permille for large internuclear distance ($R = 6.0$ a.u. and larger), it increases to above 2 percent near the equilibrium distance of $R = 1.4$ a.u.

4.6. LiH molecule

In Table 11 the results obtained for the Bethe logarithm employing the present approach for the LiH molecule are shown. The calculations are done is the basis set of 2400 explicitly correlated Gaussians. The Gaussians are taken from our previous calculations where the non-relativistic energies and the leading relativistic corrections were determined for the whole LiH potential energy curve [37,38]. We estimate that the Bethe-logarithm results shown in Table 11 are accurate to three significant digits. This may not sound impressive, but these are the first ever $\ln k_0$ calculations performed for the LiH molecule.

Table 10
The Bethe-logarithm ($\ln k_0$) calculations for the ground state of H_2^+ and H_2 molecules as a function of internuclear distance R. All values are given in a.u.

H_2^+			H_2		
R	$\ln k_0$	$\ln k_0$ [27]	R	$\ln k_0$	$\ln k_0$ [29]
0.5	3.2071	3.215803070	0.6	3.157	3.15960
1.0	3.0541	3.062912414	0.8	3.070	3.09331
1.5	3.0137	3.023052703	1.0	3.013	3.05490
2.0	3.0008	3.012508830	1.2	2.975	3.03215
2.5	2.9922	3.009486203	1.4	2.958	3.01855
3.0	2.9904	3.007520064	1.6	2.943	3.01040
4.0	2.9845	3.001853814	2.0	2.943	3.00240
5.0	2.9778	2.995328425	5.0	2.973	2.98848

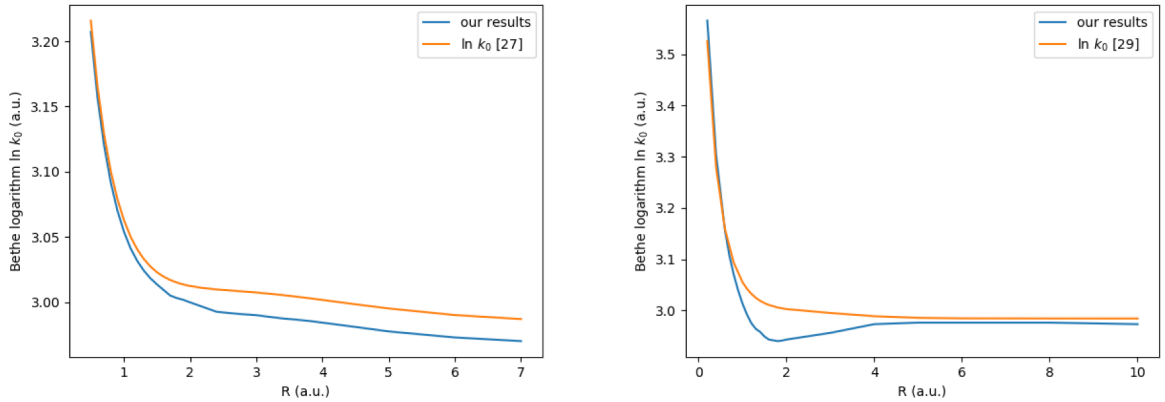

Fig. 1. Comparison between the two curves of the Bethe logarithm values (in a.u.) for H_2^+ (left figure) and H_2 (right figure) molecules obtained using the presented method (blue curves) and calculated in [27] for H_2^+ and in [29] for H_2 (orange curves). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

5. Summary

The aim of the present work is the development of a method for calculating the Bethe logarithm for molecules. The method is tested in the calculations of the logarithm performed for atoms from hydrogen to beryllium and for the H_2^+ and H_2 molecules. Explicitly correlated all-electron Gaussian functions are used in the calculations. As an example of the application of the method, we perform calculations for the ground state of the LiH molecule. The derived algorithm for calculating the Bethe logarithm is implemented using Fortran90 and the MPI protocol. The algorithm involves a spectral identity generated using excited-state wave functions that have non-zero matrix elements with the wave function of the ground state for which the Bethe logarithm is calculated. For atoms with S ground states, these wave functions have P symmetry. For diatomic molecules with Σ ground-states, the excited-state wave functions have either Σ or Π symmetry. It is shown that an effective basis set for expanding the excited-state spectral identity for atoms with S ground states can be generated by multiplying the S Gaussians used for expanding the ground-state wave function by the z_i coordinate, where index i varies from one to the number of electrons in the system. For diatomic molecules with Σ ground states, an effective basis set for expanding the excited-state spectral identity can be generated my multiplying the Σ Gaussians of the ground-state basis set by $(z_i s_{z_i})$ and $(x_i s_{x_i})$ or $(y_i s_{y_i})$, where s_{x_i}, s_{y_i}, and s_{z_i} are coordinates of the Gaussian shifts. The results obtained for the Bethe logarithm presented here are not as precise as those obtained by Schwarz or by Drake and Goldman, but they agree with those results to 2–4 significant digits. In this work we also describe an approach that can be used to reduce the basis set for expanding excited-state wave functions employed generating the spectral identity in the calculation of the Bethe-logarithm. The reduction is used to generate relatively small basis sets that shorten the calculations of the Bethe logarithm and enables consideration of larger and more complex atomic and molecular systems. An example of such a system is the LiH molecule. Bethe-logarithm calculations for this system have not been done before.

A question can be asked how to increase the accuracy of the present approach. There are two possible reasons for the not-so-impressive accuracy of the present results, particularly for atoms with more than two electrons. The first reason is related to the known deficiencies of the Gaussian functions in representing the cusp and tail behavior of wave functions of atomic bound states. The second reason is related to the construction of the spectral identity that is being inserted into the algorithm used to calculate the Bethe logarithm. This spectral identity is constructed using excited-state wave functions that have non-zero matrix elements with the wave function of the considered state of the system. The matrix elements involve a ∇-containing operator that appears in the expression for the logarithm. The basis set used to generate the excited states is formed by taking the basis functions variationally optimized for the ground state and multiplying them by electron coordinates. The spectral identity constructed this way is likely not optimal for calculating the Bethe logarithm, as it is not optimized for this use. Perhaps, a functional can be constructed to perform optimization of the basis functions used in the spectral identity. We will consider constructing such a functional in future work.

Table 11
The Bethe-logarithm ($\ln k_0$) calculations and the value of the non-relativistic energy, E_{nr}, for the ground state of the LiH molecule with 2400 Gaussians. All values are given in a.u.

R	E_{nr}	$\ln k_0$
2.0	−8.0007611686	5.29
2.5	−8.0582624519	5.30
3.0	−8.0705406298	5.30
3.5	−8.0647231889	5.31
4.0	−8.0522494037	5.31
5.0	−8.0244067293	5.30
6.0	−8.0019762699	5.29
10.0	−7.9785051124	5.24

CRediT authorship contribution statement

Ewa Palikot: Conceptualization, Methodology, Software, Data curation, Writing - original draft, Visualization, Investigation, Validation, Writing - review & editing. **Monika Stanke:** Conceptualization, Methodology, Software, Data curation, Writing - original draft, Supervision. **Ludwik Adamowicz:** Conceptualization, Methodology, Software, Data curation, Writing - original draft, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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