

# An algorithm for calculating the Bethe logarithm and the adiabatic correction for atoms and two-center molecules

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Bethe logarithm  $\ln k_0$  is one of the leading quantum-electrodynamics energy corrections of the order of  $\alpha^3$ . A method for calculating this correction, which is an alternative to the method of Schwartz et al. [1], is presented. An effective algorithm for selecting a basis set to be used in the  $\ln k_0$  calculation is also shown. This work is based on the previous paper by Stanke et al. [2]. The approach proposed by Stanke et al. in that paper is extended for calculating multi-electron atoms and two-center molecules. The proposed algorithm employs a spectral representation of a function of an operator and its spectral decomposition. The calculations are done within the Born-Oppenheimer approximation using explicitly correlated Gaussian functions with shifted centers. In both cases, the atomic and the molecular, one of the main problems is the choice of appropriate basis sets.

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## 1. Background

The most convenient theoretical method for calculating bound states of light atoms and molecules is the expansion of the total energy of the system in powers of the fine-structure constant  $\alpha$ :

$$E = E^{(0)} + \alpha^2 E^{(2)} + \alpha^3 E^{(3)} + \alpha^4 E^{(4)} + \dots,$$

where

- $E^{(0)}$  is the nonrelativistic energy (a solution of the Schrödinger equation),
- $\alpha^2 E^{(2)}$  is the expectation value of the Breit-Pauli Hamiltonian, and
- $\alpha^3 E^{(3)}, \alpha^4 E^{(4)}, \dots$  are QED corrections.

The QED energy correction proportional to the third power of  $\alpha$  is given by:

$$E_3 = \frac{4}{3} \frac{Z}{m^2} \sum_i \left[ \ln \alpha^{-2} + \frac{19}{30} - \ln k_0 \right] \langle \delta(\mathbf{r}_i) \rangle + \\ + \sum_{i>j} \sum_j \left[ \left( \frac{164}{15} + \frac{14}{3} \ln \alpha \right) \frac{1}{m^2} \langle \delta(\mathbf{r}_{ij}) \rangle - \frac{14}{3} \frac{m}{4\pi} \left\langle P \left( \frac{1}{r_{ij}^3} \right) \right\rangle \right],$$

where

- $\ln k_0$  is the Bethe logarithm,
- $P(r^{-3})$  is a distribution (so-called Araki-Sucher correction), And
- $\alpha$  is the fine-structure constant.

## 2. Method

The approach developed in this work is based on the general method for calculating matrix elements of an analytic function,  $f(\mathbf{A})$ , of operator  $\mathbf{A}$ .

Bethe logarithm is defined as:

$$\ln k_0 = \frac{\langle \Psi | \mathbf{p} [(\mathbf{H}_0 - E_0) \ln(2(\mathbf{H}_0 - E_0))] \mathbf{p} | \Psi \rangle}{\frac{1}{2} \langle \Psi | [\mathbf{p}, [\mathbf{H}_0, \mathbf{p}]] | \Psi \rangle}.$$

The adiabatic correction is defined as:

$$\delta E_{ad} = -\frac{1}{M} \langle \Psi | \nabla_{\mathbf{R}}^2 | \Psi \rangle - \frac{1}{4M} \langle \Psi | \nabla_{\mathbf{r}}^2 | \Psi \rangle = \\ -\frac{1}{M} \langle \Psi | (\nabla_{\mathbf{R}} \mathbf{V})(E_0 - \mathbf{H}_0)^{-1} (E_0 - \mathbf{H}_0)^{-1} (\nabla_{\mathbf{R}} \mathbf{V}) | \Psi \rangle - \frac{1}{4M} \langle \Psi | \nabla_{\mathbf{r}}^2 | \Psi \rangle,$$

where  $E_0$  is the non-relativistic ground-state energy.

Let  $n$  denote the number of electrons in the system. The wave function of a systems bound state can be written as:

$$|\Psi\rangle = \sum_{i=1}^n c_i |\varphi_i\rangle,$$

where  $c_i$  are linear expansion coefficients and  $\varphi_i$  are basis functions.

We use the identity operator,  $\mathbf{I}$ , expressed in terms of a non-ortogonal basis set. This operator has the following spectral representation:

$$\mathbf{I}^p = \sum_{a,b} c_a^p |\varphi_a^p\rangle \langle c_b^p \varphi_b^p| = \sum_{a,b} |\varphi_a^p\rangle c_a^p c_b^{p\dagger} \langle \varphi_b^p| \quad - \text{ for atoms,}$$

where  $\varphi_b^p$  are basis function which are used to expand wave functions of states with the  $p$  symmetry.

$$\mathbf{I} = \sum_{a,b} |\varphi_a^\Sigma\rangle c_a^\Sigma c_b^{\Sigma\dagger} \langle \varphi_b^\Sigma| + \sum_{a,b} |\varphi_a^\Pi\rangle c_a^\Pi c_b^{\Pi\dagger} \langle \varphi_b^\Pi| \quad - \text{ for molecules,}$$

where  $\varphi_a^\Sigma$  and  $\varphi_a^\Pi$  are sets of basis functions with the  $\Sigma$  and  $\Pi$  symmetries, respectively.

### 3. Basis functions

The all-electron explicitly correlated Gaussian functions with shifted centers (ECGs) used to expand the spatial part of the wave function for the ground state have the following form:

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

for molecules and a similar form for atoms but without the shifts. In the above equation

- $\underline{\mathbf{A}}_k$  is a real  $3n \times 3n$  symmetric positive-definite matrix of variational exponential parameters,
- $\underline{\mathbf{A}}_k = \mathbf{A}_k \otimes \mathbf{I}_3$ , where  $\mathbf{I}_3$  is the  $3 \times 3$  unit matrix,
- $\mathbf{A}_k = \mathbf{L}_k \mathbf{L}_k^T$ , where  $\mathbf{L}_k$  is an  $n \times n$ , rank  $n$ , lower triangular matrix,
- $\mathbf{s}_k$  is a  $3n$  vector of the coordinates of the Gaussian centers (shifts).

Gaussian function  $\varphi_k^{(0)}$  are used to construct (by applying to them the  $\nabla_{\mathbf{r}}$  operator) new basis functions  $\varphi_k^{(x)}$ ,  $\varphi_k^{(y)}$ , and  $\varphi_k^{(z)}$  which are used to expand the special parts of wave functions of excited states. Those new basis functions have following form:

$$\begin{aligned} \varphi_k^{(z)} &= (z_{m_k} - s_{m_k}) \exp [ -(\mathbf{r} - \mathbf{s}_k)^T \underline{\mathbf{A}}_k (\mathbf{r} - \mathbf{s}_k) ], \\ \varphi_k^{(x)} &= (x_{m_k}) \exp [ -(\mathbf{r} - \mathbf{s}_k)^T \underline{\mathbf{A}}_k (\mathbf{r} - \mathbf{s}_k) ], \\ \varphi_k^{(y)} &= (y_{m_k}) \exp [ -(\mathbf{r} - \mathbf{s}_k)^T \underline{\mathbf{A}}_k (\mathbf{r} - \mathbf{s}_k) ]. \end{aligned}$$

In the calculation of the wave function expanded in terms of ECGs each Gaussian function is transformed with the appropriate permutational symmetry operator which is a sum of operators permuting the electron labels multiplied by appropriate linear coefficient.

#### 4. Numerical tests

The numerical results obtained using the algorithm described above are presented for the hydrogen atom in Table 1 and for the helium atom in Table 2. The results agree to within 2-4 significant digits with the literature data for all tested systems (the H, He, and Li atoms and the H<sub>2</sub>, H<sub>2</sub><sup>+</sup> molecules).

$N$	$\ln k_0$	$E_{nr}$		$\ln k_0$
30	2.98198	-0.49999999999021074	[3]	2.811 769 883
35	2.98342	-0.499999999996865	[4]	2.984 128 555 765 498
40	2.98369	-0.499999999999554	[5]	2.984 128 555 765 497 6107
45	2.98400	-0.499999999999861	[2]	2.984 003
50	2.98410	-0.499999999999874		
$\infty$		-0.5		

**Table 1:** Hydrogen atom. Values of the Bethe logarithm,  $\ln k_0$ , and the non-relativistic energy,  $E_{nr}$ , obtained in the basis set of  $N$  ECGs functions.

$N$	$E_{nr}$	$\ln k_0$		$\ln k_0$
200	-2.90372437193343912	4.408	[3]	4.374 0(4)
400	-2.90372437685818471	4.397	[6]	4.370 157 9(5)
600	-2.90372437699588535	4.389	[8]	4.370 160 218 (3)
800	-2.90372437702652771	4.384	[5]	4.370 160 223 06(2)
1000	-2.90372437703109238	4.384		
[6]	-2.90372437703411959			

**Table 2:** Helium atom. Values of the Bethe logarithm,  $\ln k_0$ , and the non-relativistic energy,  $E_{nr}$ , obtained in the basis set of  $N$  ECGs functions.

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