Algorithm for calculating Bethe logarithm and adiabatic correction for atoms and two-centered molecules

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Our calculations based on NRDEQ expansion over $\alpha = \frac{1}{c}$.

$$\mathrm{E} = \mathrm{E}_{\mathrm{nr}} + \alpha^2 \mathrm{E}^{(2)} + \alpha^3 \mathrm{E}^{(3)} + \alpha^4 \mathrm{E}^{(4)} + \dots$$

The approach we developed is based on the general method for calculating matrix elements of an analytic function $f(\mathrm{A})$ of an known operator A.

Bethe logarithm and **adiabatic correction** are defined as

$$\ln k_0 = \frac{\langle \Psi \mid \mathbf{p}\left[(\mathrm{H}_0 - \mathrm{E}_0)\ln\left(2(\mathrm{H}_0 - \mathrm{E}_0)\right)\right]\ \mathbf{p}\mid \Psi\rangle}{\frac{1}{2}\langle \Psi \mid [\mathbf{p},[\mathrm{H}_0,\mathbf{p}]]\ \mid \Psi\rangle}$$

$$\delta E_{ad} = -\frac{1}{M}\ \langle \Psi\mid (\nabla_{\mathbf{R}}\mathrm{V})(\mathrm{E}_0 - \mathrm{H}_0)^{-1}(\mathrm{E}_0 - \mathrm{H}_0)^{-1}(\nabla_{\mathbf{R}}\mathrm{V})\mid \Psi\rangle - \frac{1}{4M}\ \langle \Psi\mid \nabla^2_{\mathbf{r}}\mid \Psi\rangle.$$

We use the **identity operator** I expressed in terms of non-ortogonal basis set.
It has following spectral representation:

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

where φ_b^p is the function describes states of p symmetry;

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

where φ_a^Σ and φ_a^Π are the sets of functions with Σ and Π symmetry respectively.