Variational Dirac–Coulomb approach with explicitly correlated basis functions

Péter Jeszenszki and Edit Mátyus
ELTE, Eötvös Loránd University, Institute of Chemistry, Pázmány Péter sétány 1/A, Budapest, H-1117, Hungary

The no-pair Dirac–Coulomb(–Breit) equation is solved with high-accuracy [1, 2, 3, 4] to provide a starting point for a new alternative theoretical method in relation with high-resolution atomic and molecular spectroscopy [5]. The sub-parts-per-billion convergence of the energy is achieved by considering the relativistic symmetry with an LS coupling scheme and expanding the relativistic wave function with an explicitly correlated Gaussian (ECG) basis set. The ECG significantly improves the description of the electron correlation compared to *e.g.,* a determinant basis set, but the positive-energy projection is more complicated due to the lack of the underlying one-electron picture. Therefore, several positive-energy projectors are examined to achieve and justify the parts-per-billion convergence of the energy. The no-pair Dirac–Coulomb energy is compared with perturbative results for atomic and molecular systems with small nuclear charge numbers and it reproduces the perturbative expressions [6] up to $\alpha^3 E_\mathrm{h}$ order.

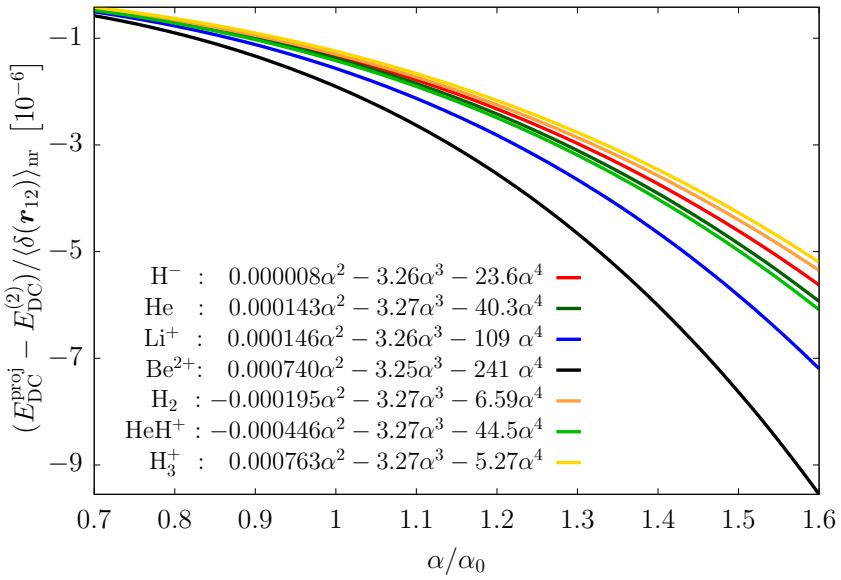

Figure 1: The dependence of the Dirac–Coulomb no-pair energy, ($E_\mathrm{DC}^\mathrm{proj}$) on the fine-structure constant (α). The non-relativistic energy and the α^2 perturbative energy correction ($E_\mathrm{DC}^{(2)}$) are extracted to highlight the agreement with the $\alpha^3 E_\mathrm{h}$ perturbative corrections, $\epsilon_{CC}^{++} \approx -3.24\langle\delta(\mathbf{r}_{12})\rangle_\mathrm{nr}\alpha^3 E_\mathrm{h}$ [6].

[1] P. Jeszenszki, D. Ferenc, and E. Mátyus, *J. Chem. Phys.* (2021), **154**, 224110. arXiv
[2] P. Jeszenszki, D. Ferenc, and E. Mátyus, *J. Chem. Phys.* (2022), **156**, 084111. arXiv
[3] D. Ferenc, P. Jeszenszki, and E. Mátyus, *J. Chem. Phys.* (2022), **156**, 084110. arXiv
[4] P. Jeszenszki and E. Mátyus, *J. Chem. Phys.* **158**, 054104 (2023). arXiv
[5] E. Mátyus, D. Ferenc, P. Jeszenszki, and Á. Margócsy, *ACS Phys. Chem. Au* (2023). arXiv
[6] J. Sucher, *Ph. D. Thesis* (1958), Columbia University.