

VARIATIONAL DIRAC–COULOMB APPROACH WITH EXPLICITLY CORRELATED BASIS FUNCTIONS

P. JESZENSZKI and **E. MÁTYUS**,

ELTE, Eötvös Loránd University, Institute of Chemistry, Budapest, Hungary

The no-pair Dirac–Coulomb(–Breit) equation is solved with high-accuracy [1, 2, 3, 4, 5, 6] to provide a starting point for a new alternative theoretical method in relation with high-resolution atomic and molecular spectroscopy [7]. 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 [8] up to $\alpha^3 E_h$ order.

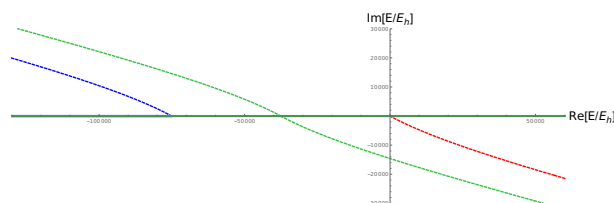


Figure 1: Visualization of the complex scaling technique to select the positive-energy states of the non-interacting two-electron system: unbound two-particle energies for $\theta = 0$ (solid) and for some finite $\theta > 0$ (dashed) value. The red, green, and blue colors indicate the electron-electron, electron-positron (or Brown–Ravenhall), and positron-positron states, respectively.

References

- [1] P. Jeszenszki, D. Ferenc, and E. Mátyus, *J. Chem. Phys.* (2021), **154**, 224110.
- [2] P. Jeszenszki, D. Ferenc, and E. Mátyus, *J. Chem. Phys.* (2022), **156**, 084111.
- [3] D. Ferenc, P. Jeszenszki, and E. Mátyus, *J. Chem. Phys.* (2022), **156**, 084110.
- [4] D. Ferenc, P. Jeszenszki, and E. Mátyus, *J. Chem. Phys.* **157**, 094113 (2022).
- [5] P. Jeszenszki and E. Mátyus, *J. Chem. Phys.* **158**, 054104 (2023).
- [6] D. Ferenc and E. Mátyus, *Phys. Rev. A* **107**, 052803 (2023).
- [7] E. Mátyus, D. Ferenc, P. Jeszenszki, Á. Margócsy, *ACS Phys. Chem. Au* **3**, 222 (2023).
- [8] J. Sucher, *Ph. D. Thesis* (1958), Columbia University.