First-quantized relativistic geminal-based many-particle quantum mechanics

M. Reiher[1*]

[1]*ETH Zurich, Lab. f. Phys. Chem., Vladimir-Prelog-Weg 2, 8093 Zurich, Switzerland*
[*]*Corresponding author:* markus.reiher@phys.chem.ethz.ch

We elaborate on the variational solution of the Schrödinger and Dirac equations of few-body, i.e., small atomic and molecular systems without relying on the Born–Oppenheimer paradigm [1]. The all-particle equations of motion are solved in a numerical procedure that relies on the variational principle, Cartesian coordinates, parameterized explicitly correlated Gaussian functions with polynomial prefactors, and the global vector representation. A stochastic variational optimization of the basis function parameters facilitates the calculation of accurate energies and wave functions for ground and excited states.
We developed a simple strategy for the elimination of the translational kinetic energy contamination of the total energy in such pre-Born–Oppenheimer calculations carried out in laboratory-fixed Cartesian coordinates [2]. The simple expressions for the coordinates and the operators are then preserved throughout the calculations, while the mathematical form and the parametrization of the basis functions are chosen such that translational and rotational invariance are respected.
For semi-classical (first-quantized) relativistic calculations we devised a kinetic-balance condition for explicitly correlated basis functions [3]. We demonstrate that the kinetic-balance condition can be obtained from the row reduction process commonly applied to solve systems of linear equations. The resulting form of kinetic balance establishes a relation between all components of the spinor of an N-fermion system to the non-relativistic limit, which is in accordance with exact-decoupling methods in relativistic orbital-based many-electron theory.

The talk will discuss these developments in the light of spectroscopic results and qualitative concepts such as molecular structure.

[1] E. Matyus, M. Reiher, J. Chem. Phys. **137**, 024104 (2012)
[2] B. Simmen, E. Matyus, M. Reiher, Mol. Phys. **111**, 2086 (2013)
[3] B. Simmen, E. Matyus, M. Reiher, J. Phys. B **48**, 245004 (2015)