`molsturm`: Modular electronic structure theory framework

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The talk gives an overview of our recent efforts to simplify the investigation of novel types of basis functions for quantum-chemical calculations [1]. Motivated by Coulomb-Sturmians as basis functions for quantum-chemistry simulations the design of the flexible and light-weight quantum-chemical method development framework `molsturm` [2, 3] is outlined, where new discretisation methods for electronic structure theory calculations can be easily implemented and tested.

First a list of desirable properties for a basis in the context of quantum chemistry is reviewed. Amongst other aspects an ideal basis would be able to (1) accurately represent the physics of a chemical system, and (2) allow for systematic improvements aided by error estimates, whilst it (3) gives rise to numerically feasible discretised problems. The predominant basis function type in electronic structure theory, namely contracted Gaussian-type orbitals (cGTO) [4, 5], leads to comparatively simple discretised problems as well as an acceptable accuracy for most applications. These functions do, however, not satisfy the first two aforementioned criteria perfectly. For example, they are not able to properly describe the region of a state where electron and nucleus are close, see figure 1.

Our recent research has looked into so-called Coulomb-Sturmians (CS) as an alternative. These exponentially decaying functions are isoenergetic, analytical solutions to a partial differential equation, which is related to the Schrödinger equation for a single-electron system by scaling the nuclear attraction potential [6, 7]. They form a complete basis for $H^1(\mathbb{R}^3)$ and are able to correctly reproduce the physical features of the wave function, i.e. both the nuclear cusp as well as proper exponential decay [8]. Figure 1 displays the local energy for the hydrogen atom at small electron-proton distances if selected cGTO and CS basis sets are used for the discretisation. For cGTO discretisations the large fluctuations of the local energy at small distances are indicative of deviations of the obtained approximate eigensolution from being a true eigensolution. This is not improved much for distances less than 0.1 Bohr if a larger cc-pV6Z basis is used. In contrast for CS-based discretisations the behaviour is more uniform and the larger $(4, 1, 1)$ basis has local energies closer to -0.5 than $(3, 1, 1)$ over the full depicted range.

Ideally one would not need to restart development from scratch for each new type of basis function, but would be able to utilise already existing quantum-chemistry programs as much as possible. A direct implementation of a new basis function type into an existing quantum chemistry programs is, however, typically challenging, since the numerical properties differ substantially between discretisation methods. To give an illustration, figure 2 shows the sparsity as well as the size of the Fock matrices resulting from different discretisation approaches applied to a Hartree-Fock (HF) self-consistent field (SCF) calculation of beryllium. In some cases, like CS-based discretisations, unusual angular-momentum selection rules

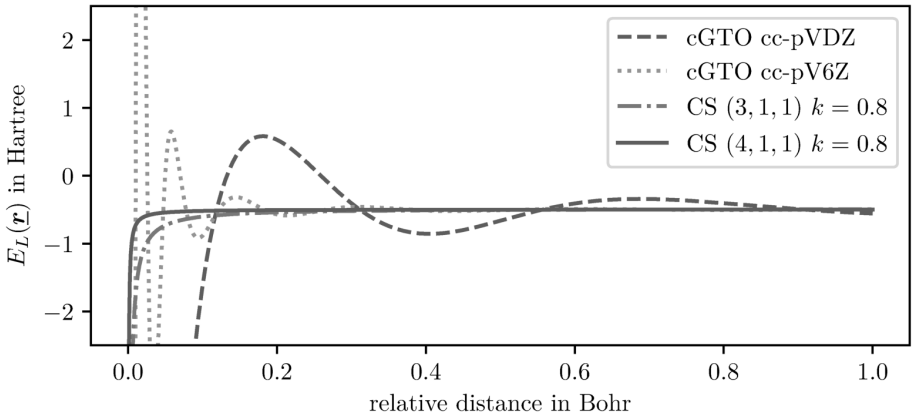

FIGURE 1. Plot of local energy $E_L(\underline{\boldsymbol{r}})$ versus radial distance of electron and proton for the hydrogen atom. Shown is the region where electron and proton are close. The exact local energy is -0.5 and deviations can be understood as the relative error of the discretised solution to being a true eigensolution of the Schrödinger equation [1, 7].

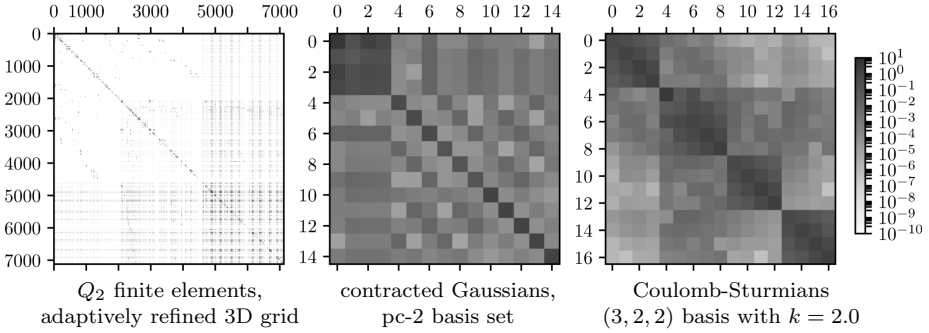

FIGURE 2. Examples of Fock matrices in a Hartree-Fock self-consistent field calculation for beryllium, discretised using finite elements, contracted Gaussians or Coulomb-Sturmians [1, 3].

can reduce computational effort for obtaining the Fock matrix elements further, provided that appropriate evaluation schemes can be used, see [1].

Such deviating numerical demands of different discretisations can be supported by so-called contraction-based methods [1, 3]. In this well-established approach one avoids to store the problem matrices in memory and instead uses matrix-vector product expressions as the algorithmic basis. Employing a concept called lazy matrices, where all matrix operations are subject to lazy evaluation, `molsturm` [2, 3]

features an SCF algorithm, which is completely separated from the code dealing with the discretisation. In `molsturm` it is thus possible to add a new type of discretisation or basis function in a plug and play fashion, i.e. just by implementing the link to the code performing the integral evaluations. Conversely a new algorithm — like an SCF scheme — only needs to be programmed once and immediately can be used with all basis function types available. Thus `molsturm` facilitates employing new mathematical approaches in practice and comparing them on a common setting to the methods already implemented. Lazy matrices are not necessarily limited to the SCF step or the context of quantum chemistry. The library `lazyten` [9] allows them to be used in the context of other physical problems as well.

It is explicitly *not* the goal of `molsturm` to become yet another complete quantum-chemistry package. Much rather the package focuses on solving SCF problems in the most general way possible and handing the results over to third-party packages or other user-provided algorithms building on top. For this reason `molsturm` offers a readily applicable `python` interface, where all relevant quantities can be easily obtained for post-processing. Due to the basis-function-independent nature of the SCF algorithm any novel basis function type implemented in `molsturm` immediately becomes available to algorithms built on top of this framework. Therefore `molsturm` can be thought of as a mediator between low-level developments with respect to novel algorithms and discretisation schemes for solving the HF problem on the one hand and high-level quantum-chemical method development: Both ends are abstracted from each other, but can still benefit from mutual progress.

References

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