A mixed B-splines and Gaussian basis for the accurate description of continuum states.

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With the advent of sub-femtosecond extreme ultraviolet light pulses, provided by high-harmonic generation **[1]** and of femtosecond intense x-ray sources **[2]** it is now possible to study fragmentation processes of atoms and molecules under the action of controlled driving fields, most prominently photoionization and Auger decay, with unprecedented sensitivity and time resolution. The theoretical description of these processes for polyelectronic molecules represents a challenge due to two conflicting requirements. On the one hand, the polycentric multi-reference character of the short-range component of molecular electronic states is best expressed in terms of Gaussian functions, a standard in all modern quantum chemistry packages. Due to the rapid build-up of linear dependencies, however, Gaussian functions are unsuited to reproduce the characteristic multi-channel oscillatory behavior in the mid and asymptotic radial range. On the other hand, scattering states are optimally reproduced by B-splines, a robust numerical basis extensively used to compute the electronic continuum in atoms and small hydrides **[3]** which, in turn, are not easily integrated in existing quantum-chemistry code.

Here we show that a mixed basis, comprising a short-range diffuse set of gaussian functions and a large set of B-splines provides the advantages of both sets. In particular, the B-spline set supplements the gaussian set so that a uniformly accurate representation of continuum orbitals can be achieved across a wide radial and energy range. As a result, such basis could conceivably be used to build unbound states appropriate for molecular ionization with high-energy photons. We illustrate the performance of the new constructed basis by presenting preliminary results of several tests calculations for the interaction of hydrogenic ions with external pulses in perturbative and non-perturbative conditions, either in terms of transition matrix elements in the dipole approximation or by directly solving the Time Dependent Schrödinger Equation.

References:
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