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Merging quantum chemistry packages with B-splines for the multichannel scattering problem.

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Synopsis To study the photoionization of polyelectronic systems by attosecond pulses, we take advantage of existing quantum chemistry packages for the description of correlated electronic states, and of hybrid Gaussian-B-splines basis for the representation of continuum orbitals. In our approach, a short-range region, which can host all the interacting electrons and is described by commercial packages, is matched to a long-range region which describes single-ionization states in terms of a close-coupling expansion. We validate this approach showing multichannel ionization results for He.

Recent breakthroughs in ultrafast-laser technology, and more specifically the generation of extreme ultraviolet (XUV) and x-ray attosecond pulses [1,2], have made it possible to study electron dynamics at its natural time scale. Since such pulses can ionize the atom or molecule with which they interact, the theoretical description of the observables in attosecond pump-probe experiments requires a good representation of the system's ionization continua in a wide energy range. While this is possible for very small systems such as He and H_2 [3–6], in more complex systems this is still a challenge, due to the complicate short-range structure of polyelectronic functions. Indeed, whereas sophisticated methods to compute the electronic structure of bound molecular states are implemented in commercial quantum chemistry packages (QCP) (e.g., MOLCAS [7]), comparable tools for the continuum are not really available.

To tackle this problem, we are developing a merge between existing QCPs and current numerical scattering methods. To do so, we separate the electronic configuration space in a short-range region, which can host all the interacting electrons, and a long-range region in which one outer electron interacts with a finite number of correlated parent ions. This outer electron is expressed in terms of a hybrid Gaussian-B-spline basis (GABS) which combines short-range Gaussian functions, compatible with standard QCPs, with B-splines [8], which are appropriate to represent the continuum.

To illustrate the viability of our approach, here we present the results for the multichannel ionization of He, which is a necessary step towards the study of more complex systems. The eigenphases above the N=2 threshold and the photoionization cross section we obtain are in excellent agreement with state-of-the-art benchmarks [9]. The good results obtained together with the great flexibility of QCPs position our method as a strong candidate for the theoretical study of the ionization of poly-electronic systems.

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