Abstract

The rectangular collocation approach allows solving the Schrödinger equation, electronic or nuclear, without converging integrals. The rectangular nature of the matrix equation facilitates basis optimization and, when applying the kinetic energy operator (KEO) numerically [1], it is easy to use any basis functions, even non-integrable [2]. As a result, the approach can handle problems which pose difficulties with the traditional variational approach such as calculation of vibrational spectra at interfaces, where potential energy surfaces (PES) are usually unavailable and ab initio calculations are costly [3].

The absence of the requirement to converge integral allows reducing the volume of space sampled by the collocation points and to use relatively small point sets which could be computed ab initio, obviating the need for a PES. At the same time, numeric application of the exact KEO much simplifies calculations without introducing approximations. As the method solves the Schrödinger equation directly, it does not require potential representations over orders of coupling like VSCF (vibrational self-consistent field) and does not break down at resonances like perturbation theory.

I will review the basics of the methods, results of previous applications of rectangular collocation to free and adsorbed molecules present recent advances in the method, such as sampling only selected parts of the configuration space [4] or machine learning optimization of the collocation point set [5] as well as the applications to the electronic Schrödinger equation and the Kohn-Sham equation [5, 6].

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