Asymptotic Analysis of Atomic Pauli Potentials

Antonio C. Cancio,
Dept. of Physics and Astronomy, Ball State University
Jeremy Redd,
Department of Physics, Utah Valley University

In orbital-free density functional theory (OFDFT), the functional derivative of the Pauli contribution to the Kohn-Sham kinetic energy, the Pauli potential, is key to solving for the density. It can be expressed as the Pauli kinetic energy per particle, plus a response potential which describes the response of this quantity to a change in density. We have constructed the exact response and Pauli potentials for closed shell atoms, for which the former becomes an exact eigenvalue expression, extended to large Z atoms attainable only in theory. The asymptotic behavior of the core electrons in this limit is that of the semiclassical Fermi-electron gas, providing a disciplined way to develop a density functional approximation to it. In this limit and as radius approaches zero, we show that the Pauli potential tends to the magnitude of the lowest energy eigenvalue. We also test the utility of several gradient expansion-based approaches as orbital-free approximations to the response potential. We find that such approximations are very poor for the evanescent region far from the nucleus. These results should aid the construction of orbital-free approximations to the Pauli potential with proper scaling to high density and particle number, and ultimately better OFDFT models.