Progress in material science and drug design is becoming increasingly dependent on the availability of numerical simulations that make it possible to obtain information about properties of atoms, molecules, polymers, and crystals without resorting to costly experimental measurements. In order to be competitive, such simulations, also known as molecular modeling, have to be both sufficiently accurate and computationally inexpensive. Quantum chemistry has a whole lot of such numerical methods at its disposal. However, despite over half a century of research, the factors that limit accuracy of some of these methods are still not fully understood.

One of such factors is the possible existence of the so-called unoccupied natural orbitals (UNOs) that derive from electronic wavefunctions of Coulombic systems (i.e. atoms, molecules, and ions). There is suspicion that several of quantum-chemical approaches to molecular modeling are negatively impacted by the presence of UNOs. These approaches include the extended Koopmans' theorem, which yields highly accurate predictions of ionization potentials and electron affinities, and the 1-matrix (a.k.a. the one-electron reduced density matrix or simply the density matrix) functional theory, which appears to be one of the promising novel electronic structure methods.

In this grant proposal, we describe ways of resolving this troublesome issue of UNOs. When completed, the proposed research will open the avenue to faster and more accurate molecular modeling that will benefit not only scientists but, by speeding up development of new medicines and materials, also people of all walks of life.