

## **On the Edge of Koopmans' Theorem**

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It is well known that the density of an atom falls off exponentially with increasing distance to the nucleus, with a falloff length inversely proportional to the square root of the ionization energy. It is less well known what happens when the ionization energy goes to zero, which is the case if the nuclear charge is artificially reduced to the critical value. At this critical value there is a normalizable state at the bottom of the continuum, but only falls off as an exponential of the square root of the radius. We calculate this state for the two-electron atom using the pseudospectral method, finding the critical value of the nuclear charge is 0.91102822495(6). This system provides the most extreme test of ground state density functional theory. We use the numerically exact wave function to extract the exact Kohn-Sham, correlation, and exchange potentials. These are compared with density functional theories.