Relativistic correction to the single-particle kinetic energy term

MARK PEDERSON, TUNNA BARUAH, Code 6392, Naval Research Laboratory, Washington DC — Evaluation of the relativistic kinetic energy, given by \( \sqrt{p^2c^2 + m^2c^4} \), is one strategy that may be promising from the standpoint of approximate scalar relativistic treatments. However the square root makes it cumbersome in quantum mechanical operator form. Chandra et al. [P. Chandra et al., Chem. Phys. 84, 1 (1984)] have shown that it is possible to derive a simplified method for evaluating the relativistic kinetic energy within a single-particle framework. In this method a finite basis set of the \( p^2 \) operator is used to evaluate the expectation values of the \( p^2 \) dependent operators. In our formulation, we use a complete basis set of the \( p^2 \) operator to determine a variational expression for the above operator that is useful for Gaussian-orbital-based calculations. We compare the results of the corrections to the kinetic energy obtained by our formulation with other methods such as the expansion of the kinetic energy operator method and an incomplete \( p^2 \) basis method. Comparison to the full Dirac equation is made for simple atoms and the importance of the Darwin term will also be discussed.