Going beyond Kohn and Sham (KS): determining accurate ground and first excited states LUIZ FERREIRA, Universidade de Sao Paulo, MARCELO MARQUES, LARA TELES, RONALDO PELA, Instituto Tecnologico de Aeronautica — The Total energy in KS is written as

\[ E = \frac{1}{2} \sum \int \nabla \psi^* \cdot \nabla \psi + \frac{1}{2} \int \sum \frac{\psi^* \psi(r) \sum \psi^* \psi(r')}{(r - r')} + \int \sum \psi^* \psi V_{\text{nuclei}} + \text{Exc} \]

The KS procedure continues by minimizing the energy with respect to the wavefunctions \( \psi \). The equation for the wave functions is similar to the one-particle Schrödinger equation. In our talk we will present results obtained in the following way: we add an external potential \( V_{\text{add}} \) to the nuclei potential \( V_{\text{nuclei}} \) and, after the calculation is completed, we subtract what we added, namely. \(- \int \sum \psi^* \psi V_{\text{add}}\). The result is a calculation according to the Eq. above but with wavefunctions not satisfying the KS equations. If the exchange-correlation term were reliable one would expect that the calculated energy would be larger than the KS energy. The added potential \( V_{\text{add}} \) is what is being used in the LDA-1/2 method and is dependent on a cut-off parameter \( C \). Making the extremization of the total energy with respect to \( C \) we obtain (1) a point of maximum, which frequently will be shown to be the first excited state, (2) a minimum, with an energy lower than the KS (\( C = 0 \)) ground state and with improved lattice parameter.