Realizing the importance of exchange-correlation potential in Density Functional Theory.

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Density Functional Theory (DFT) has emerged as a workhorse of computational chemistry due to its computational simplicity and ability to embed many-body effects into an effective single correlated particle operator. How to fold all the many-body effects into an effective single particle operator is not known in exact analytical form, thus many approximations have been proposed with a fair share of successes and failures. Depending on molecular properties, DFT results could be quite sensitive to the choice of exchange-correlation (xc) functionals, and as a consequence DFT results are subjected to distrust and considered not systematically improvable. In order to increase the predictability of DFT, a consistent DFT framework has been proposed. In a consistent DFT method, the xc potential ($Vxc[\varrho] = \partial EXC[\varrho]/\partial\varrho$) is required to demonstrate comparable accuracy, as the corresponding functional does, by satisfying Bartlett's IP theorem: i.e. the negative of the KS eigenvalues should be a good approximation to vertical ionization energies for all electrons in the system. Such behavior is formally expected from time dependent DFT considerations and observed in ab initio correlated optimized effective potentials. To demonstrate the consequence of Bartlett's IP theorem, an IP corrected model xc potential QTP(0,0) is introduced. QTP(0,0) is an explicit density dependent, local hybrid functional, where a variable amount of non–local exact exchange is included at all inter-electronic distances. The functional parameters involved in constructing QTP(0,0) are obtained by requiring that the occupied KS eigenvalues provide all of the vertical principal ionization energies to within an electron volt accuracy for just the water molecule. For forty other molecules, the IP's of QTP(0,0) were also found to show the same mean absolute error of ≈ 0.8 eV as those for the fitted water molecule. QTP(0,0) does an excellent job for problems where traditional xc functionals have difficulties, such as activation energies, core excitation energies, and charge transfer energies. IP corrected potential provides improved performance for various other kinds of molecular properties such as dispersion interaction, magnetic properties, electron affinities, etc.

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