

AB INITIO DENSITY FUNCTIONAL THEORY

RODNEY J. BARTLETT, STANISLAV IVANOV, SO HIRATA, IRENEUSZ GRABOWSKI

There is a fundamental dilemma in current density functional theory (DFT) methods, in that there is no way to converge to the right answer. This is contrary to the well-known paradigm of correlated ab initio methods. In this respect, DFT is a 'semi-empirical' theory and does not have systematic ways for improvement. We propose ab initio DFT to help resolve this problem. Taking functional derivatives with respect to density of exchange and correlation energy expressions, we introduce local, multiplicative one-particle operators that account for these terms. We have developed an exact exchange theory for molecules and are developing correlation potentials that can be tied to MBPT(2), MBPT(3), or even coupled-cluster theory. Even at the exchange only level (order of magnitude larger than correlation), many interesting, and more accurate results occur.

*Rodney J. Bartlett