Ab Initio Study of Atomic and Molecular Polarizabilities

IGOR VASILIEV, New Mexico State University, JAMES R. CHELIKOWSKY, The University of Texas at Austin — We calculate the static electric dipole polarizabilities for a variety of atoms and molecules using a finite field method implemented in the framework of an ab initio density functional formalism. Our calculations employ several different representations of the exchange-correlation potential, including the local density approximation, generalized gradient approximation, and asymptotically correct functionals introduced by Leeuwen-Baerends [1] and Casida-Salahub [2]. We observe that the computed values of polarizabilities are strongly influenced by the asymptotic behavior of the density functional exchange-correlation potential. The accuracy of theoretical atomic and molecular polarizabilities is substantially improved by the use of asymptotically correct exchange-correlation functionals. This result can be explained in terms of electronic excitation energies and the polarizability sum rule.


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