

# Structural, electronic, and bonding properties of liquid water from first principles

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We study, from first principles, structural, electronic, and bonding properties of liquid water. Our system is twice as large as that used in previous *ab initio* simulations and our computed structural properties are in good agreement with the most recent neutron scattering experiments. Moreover, the use of a novel technique, based on the generation of maximally localized Wannier functions, allowed us to describe the molecular charge distribution and the polarization effects in liquid water with a degree of accuracy not previously possible. We find that, in the liquid phase, the water molecule dipole moment has a broad distribution around an average value of about 3.0 D. This value is 60% higher than that of the gas phase and significantly larger than most previous estimates. A considerable increase is also observed in the magnitude of the average eigenvalues of the quadrupole moment tensor. We also find that the anisotropy of the electronic charge distribution of the water molecule is reduced in the liquid. The relevance of these results for current modeling of liquid water is discussed. © 1999 American Institute of Physics. [S0021-9606(99)31132-6]

## I. INTRODUCTION

Due to its extraordinary importance liquid water has been studied by theoretical and experimental techniques more extensively than any other liquid. In spite of this intense research effort, molecular-level understanding of its structural and electronic properties remains incomplete.

One of the important changes which the water molecules undergo in passing from the gas to the liquid phase is due to the polarization effects produced by the electric fields of the surrounding molecules and the formation of an extended

on effective potentials, have been performed (the related literature is very extensive: see Refs. 8–28, and further references quoted therein, for a representative set of references). The quality of these simulations depends on the chosen model potential and is not always adequate (see, for instance, Ref. 24), as can be deduced by considering those properties of liquid water for which a direct comparison with accurate experimental data is possible. In particular, the change in the dipole moment, in passing from the gas to the condensed phase, cannot be reproduced by empirical models unless they

caused by the electric field induced by the surrounding molecules. In Fig. 6 we show the distribution of the modulus of the water dipole moment in the liquid. As can be seen the distribution is characterized by a relatively broad peak which reaches its maximum value at about 2.8 D and reveals the

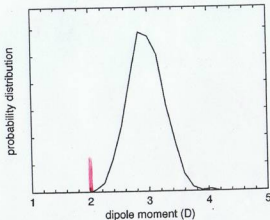


FIG. 6. Distribution of the modulus of the water molecule dipole moment in liquid water, obtained by considering 12 MD configurations of the 64-molecule system.