

Maximally-localized Wannier Functions in Compressed Molecular Hydrogen

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We have constructed maximally-localized Wannier functions (WFs) for compressed solid hydrogen, starting from the LDA Bloch functions. Each occupied WF can be associated with two paired protons, defining a “Wannier molecule” in the bulk. The sum of the dipole moments of these “molecules” always gives the correct bulk polarization, even at high pressures when the charge density is non-zero everywhere in the unit cell and the overlap between neighboring WFs is non-negligible. We study the behavior of the dipoles and the spread of the WFs as a function of pressure and crystal structure. Contrary to often-used models of molecular solids, in which the molecules become smaller as the pressure increases, the “Wannier molecules” become more extended. We find that at megabar pressures the contribution to the dipoles arising from the tails of the WFs in the overlapping region is very significant. The strong vibron infrared absorption at high pressures is analyzed in terms of the change in the WFs due to the vibronic motion.