Equation of state and Raman frequency of diamond from quantum Monte Carlo

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Diamond is an important material with many technological applications, including a key role within high-pressure physics. Diamond anvil cells are used to study the structures of materials and phase transitions under pressure, and to synthesise new materials. Although there have been many experimental studies of the physical properties of diamond, in fact they are not well characterised under very high pressures.

The equations of state (EOS) of many materials can be described over a wide range of pressures by the values of the equilibrium volume V_0, the zero-pressure bulk modulus B_0, and the zero-pressure derivative of the bulk modulus B_0'. The values of V_0 and B_0 for diamond are well established, but there is considerable uncertainty about the value of B_0'. A recent study gave $B_0' = 3.0 \pm 0.1$,[1] although it has been argued that the ruby pressure calibration used should be revised. The most commonly cited value is $B_0' = 4.0 \pm 0.5$,[2] but the large error bar leads to considerable uncertainty in the EOS at high pressures. The Raman frequency of diamond is also of considerable interest, and the possibility of using its volume dependence as a pressure gauge in very-high-pressure diamond-anvil-cell studies has been widely discussed.

We use the variational quantum Monte Carlo (VMC) and the more accurate diffusion quantum Monte Carlo (DMC) methods to calculate the equation of state and Raman frequency of diamond. We make corrections for the effects of zero-point motion and finite temperature effects to enable proper comparison with experiment. DMC gives values of V_0 and B_0 in good agreement with experiment, while for B_0' we obtain 3.8±0.1, which is within error bars of the experimental value reported in Ref. [2], but well outside the error bars of the value reported in Ref. [1]. Our value is close to that obtained within density functional theory using the Perdew-Burke-Ernzerhof (PBE) Generalised Gradient Approximation (GGA).

The Raman frequency of diamond is calculated at several volumes using the frozen phonon method. Our DMC frequency of 1359±4 cm^{-1} calculated at the experimental equilibrium volume is in good agreement with the experimental value of 1333 cm^{-1}. At each volume the VMC and DMC Raman frequencies are a little higher than those obtained from the local density approximation (LDA) and the PBE-GGA.

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