Fully Anharmonic Resonance Raman Spectra of Diatomic Systems Through Variation Quantum Monte Carlo Simulations

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Abstract: In this work, the time independent framework of the Resonance Raman (RR) effect was used to obtain pure vibrational (RR) spectra of diatomic systems within the Born-Oppenheimer approximation. The anharmonic correction was introduced by the vibrational Modified Variation Quantum Monte Carlo (MVQMC) method [1]. In order to improve the performance the method, three Random Numbers Generators (RNG) were accessed (MT19937, RANLUX 4 and the native RNG of GNU F77 compiler, version 4.8) for the calculations of the six low lying vibrational states of $X^1\Sigma^+_g$ and $B^1\Sigma^+_u$ electronic states of H$_2$. We found that the most cost effective RNG was the MT19937, which was adopted in the subsequent calculations, followed by the GNU F77 RNG. The Potential Energy Curves of the ground and excited states and the Electric Dipole Transition Moment Curve were computed at the CASSCF(124,2)/d-aug-cc-pVQZ level. In general, we found that the CASSCF/MVQMC vibrational energies of low-lying states are very accurate compared to experimental data [2] (Figure 1). Figure 2 shows harmonic intensities significantly higher than anharmonic ones and that the inclusion of Herzberg-Teller vibronic coupling correction increases the RR intensities relative to the Franck-Condon level. We found that anharmonic and vibronic corrections are relevant for other systems as well (e.g. O$_2$, not shown here), where the relative RR intensities changes with the inclusion of these corrections.
Figure 1: $\text{H}_2$ vibrational energies of states $X^1\Sigma_g^+$ and $B^1\Sigma_u^+$. 

Figure 2: Franck-Condon (FC) and Herzberg-Teller (FC+HT) RR spectra of $\text{H}_2$ from harmonic (HO) and fully anharmonic (ANA) wavefunctions.

Key-words: Resonance Raman Spectroscopy; Variation Quantum Monte Carlo; Anharmonicity; Ab initio methods.

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References: