

Quartic force field representation of the potential energy surface. Vibrational SCF, vibrational MP2 and vibrational CI methods.

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Abstract

The Born–Oppenheimer approximation results in a concept of the potential energy surface (PES) which governs the dynamics of nuclear motions. Solving the electronic Schrödinger equations for nuclear coordinates one can determine the PES. The accuracy of dynamics calculations is affected by the accuracy of the PES. Since the PES is a function of $3N-6$ internal coordinates, the problem of rapid growing of degrees of freedom appears. Thus, in the case of a general molecule it is difficult to determine the full-dimensional PES by *ab initio* electronic structure calculations. An approximation to the PES, which is a potential energy function (PEF), has to be used in dynamics calculations. The accuracy of the PEF is restricted to its analytical form.

Prof. Yagi and coworkers proposed the quartic force field approximation (QFF), which is an extremely efficient technique to represent the PES suitable e.g. for vibrational MP2 calculations and to account for anharmonic effects. The QFF can be generated in terms of second, third, and fourth potential energy derivatives with respect to normal coordinates at the equilibrium structure.¹ To further reduce the computational costs for multi-dimensional cases, Yagi proposed an *n*-mode coupling representation of QFF (*n*MR-QFF).² It includes up to *n* modes coupled to each other. It has been shown that *n*MR-QFF can be constructed with less computational effort.

3MR-QFF representation of the PES has been used in vibrational SCF, vibrational MP2 and vibrational CI calculations which have been applied to the proton sponges. The result has been compared to those obtained from vibrational Schrödinger equation.