APPOXIMATE SCALING OF MATRIX ELEMENTS FOR MULTIDIMENSIONAL ANHARMONIC VIBRATIONAL POTENTIALS

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The intermediate vibrational energy regime - well above the zero point, yet below the dissociation limit - plays an important role in many molecular processes, such as radiationless transitions or intramolecular vibrational relaxation (IVR). For molecules with N>6 vibrational degrees of freedom, the calculation of matrix elements, energy levels, and spectra of the fully anharmonic vibrational Hamiltonian at high energies presents a formidable problem. Here we derive an asymptotic formula based on the global topology of molecular potentials: under certain very general conditions the potential can be exactly factorized as N approaches infinity. Applying corrections derived from the N=1 limit yields several simple models for high-order force fields and matrix elements, which rely only on input parameters such as vibrational frequencies and cubic anharmonicities. Comparison of the models with numerical force fields derived from curvilinear model potentials and with Monte-Carlo sampled $ab-initio$ calculations for several small molecules shows that they are useful asymptotic approximations for N as low as 3 or 6. Implications of these simple yet physically reasonable force fields for several recently developed models for IVR are discussed, in particular threshold effects of high order force-constants on energy redistribution.