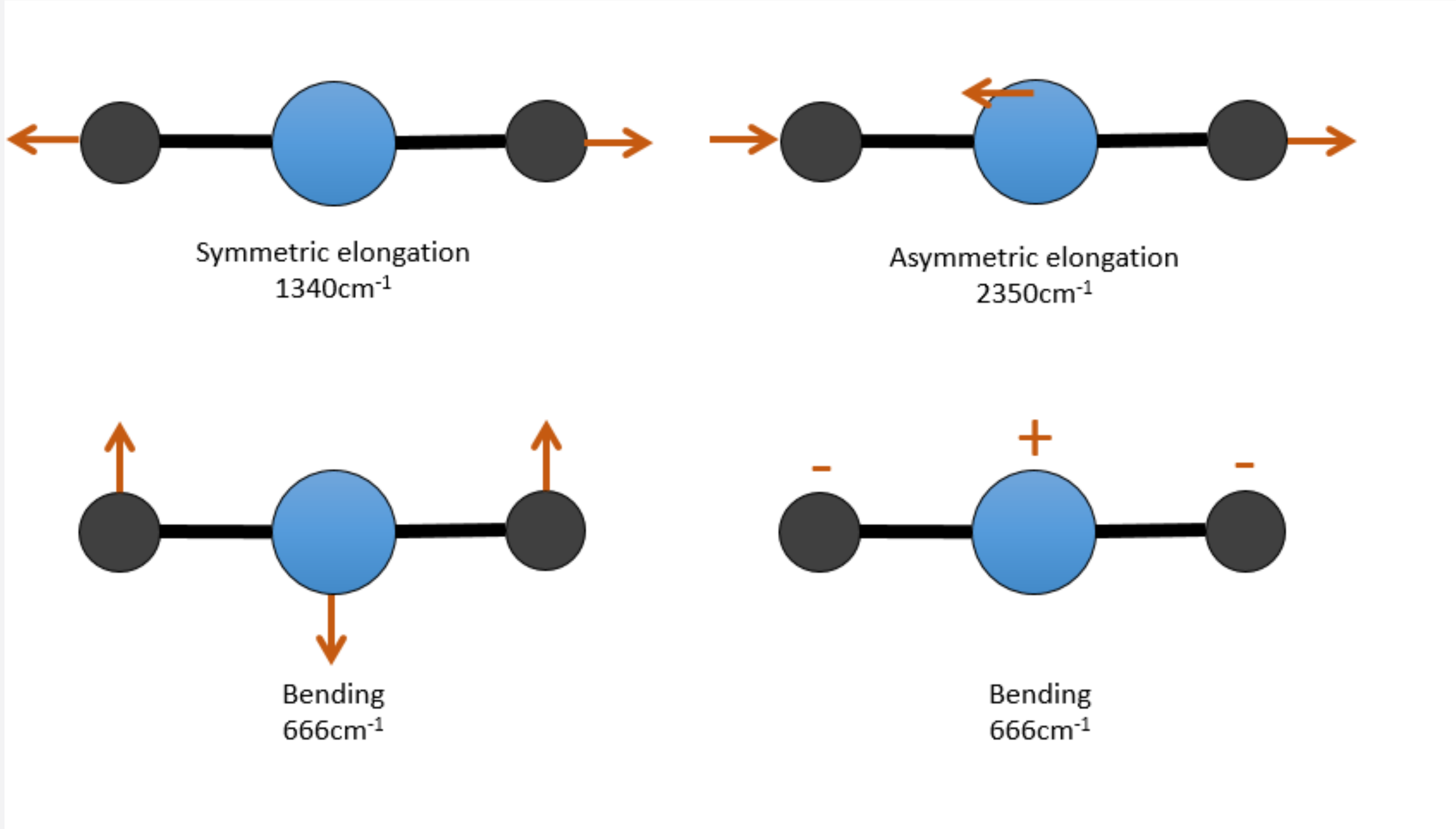
4.2 Vibronic Coupling

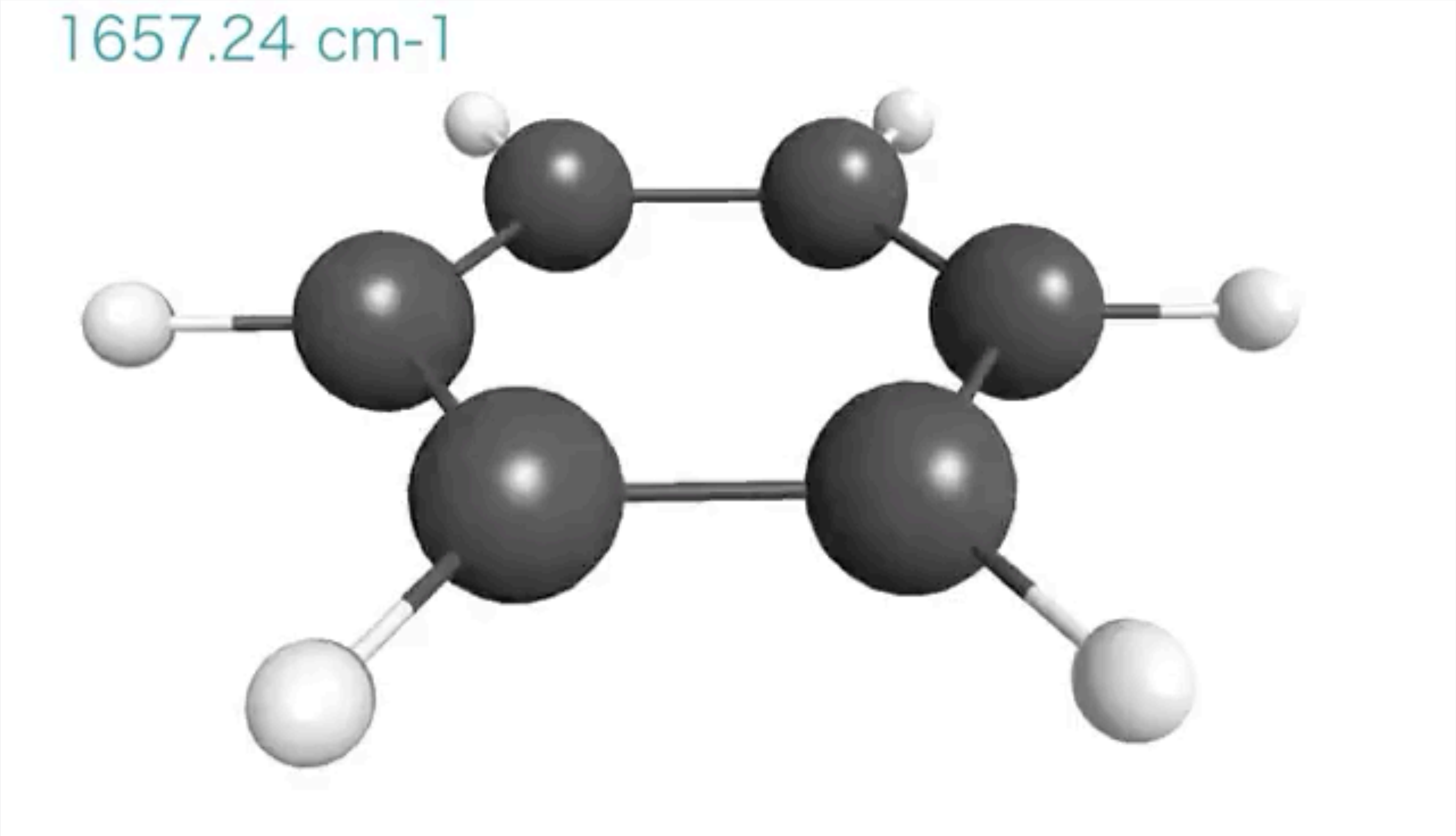
Molecular Normal Modes of Vibration

- in reality, nuclei in molecules vibrate around their equilibrium positions
- molecules with *N* atoms have 3*N* degrees of freedom (vibrations, translations, rotations)
- normal modes are linearly independent patterns of coupled vibrations of a sinusoidally oscillating system at a fixed (natural / resonant) frequency and with a fixed phase relation

3*N*–5 modes in linear molecules



3*N*–6 modes in cyclic molecules



- **normal mode vibrations are relevant for the details of electronic transitions**

Separation of Electronic and Nuclear Motions

- Born-Oppenheimer approximation: for sets of electron positions q and nuclei positions Q

$$|\Psi\rangle = |\phi^{\mathbf{e}}\rangle|\phi^{\mathbf{nu}}\rangle \quad \rightarrow \quad \Psi(q,Q) = \phi^{\mathbf{e}}(q,Q)\phi^{\mathbf{nu}}(Q)$$

- the time-independent Schrödinger equation becomes

$$[\hat{T}_{\mathbf{nu}} + \hat{T}_{\mathbf{e}} + \hat{V}(q,Q)]\phi^{\mathbf{e}}(q,Q)\phi^{\mathbf{nu}}(Q) = E\phi^{\mathbf{e}}(q,Q)\phi^{\mathbf{nu}}(Q)$$

$$\frac{\phi^{\mathbf{e}}(q,Q)}{\phi^{\mathbf{nu}}(Q)}\hat{T}_{\mathbf{nu}}\phi^{\mathbf{nu}}(Q) \; + \; [\hat{T}_{\mathbf{e}} + \hat{V}(q,Q)]\phi^{\mathbf{e}}(q,Q) = E\phi^{\mathbf{e}}(q,Q)$$

  - electronic equation (large nuclear masses, QN n): $\hat{H}_{\mathbf{e}}\phi^{\mathbf{e}}_n(q,Q) = E^{\mathbf{e}}_n(Q)\phi^{\mathbf{e}}_n(q,Q)$
  - nuclear equation (multiplication $\phi^{\mathbf{nu}}/\phi^{\mathbf{e}}$, QN ν): $[\hat{T}_{\mathbf{nu}} + E^{\mathbf{e}}_n(Q)]\phi^{\mathbf{nu}}_{n,\nu}(Q) = E^{\mathbf{tot}}_{n,\nu}\phi^{\mathbf{nu}}_{n,\nu}(Q)$

- **nuclear / electronic motion separation still valid because 30–300 vibrations and 10^3–10^5 electronic “revolutions” per molecular rotation**

Vibration in Diatomic Molecules

- **diatomic molecules only have one normal mode of vibration** and a configuration Q can be described by the variable $x = R - R_0$ (R interatomic distance with equilibrium position R_0)
- Taylor series of $E_n^{\mathbf{e}}(x)$ at the equilibrium $x = 0$ for small amplitude vibrations, in equlibrium:

$$E_n^{\mathbf{e}} \approx E_n^{\mathbf{e}} + \underbrace{(\frac{dE_n^{\mathbf{e}}}{dx})}_{=0}{}_0 x + \frac{1}{2}(\frac{d^2E_n^{\mathbf{e}}}{d^2x})_0 x^2$$

- the time-independent nuclear Schrödinger equation becomes

$$[-\frac{\hbar^2}{2\mu}\frac{d^2}{d^2x} + \frac{1}{2}(\frac{d^2E_n^{\mathbf{e}}}{d^2x})_0 x^2]\phi_{n,\nu}^{\mathbf{nu}}(x) = [E_{n,\nu}^{\mathbf{tot}} - E_n^{\mathbf{e}}(x=0)]\phi_{n,\nu}^{\mathbf{nu}}(x)$$

$$[-\frac{\hbar^2}{2\mu}\frac{d^2}{d^2x} + \frac{1}{2}\mu_m\omega^2x^2]\phi_{n,\nu}^{\mathbf{nu}}(x) = E_\nu^{\mathbf{vib}}\phi_{n,\nu}^{\mathbf{nu}}(x)$$

with reduced mass μ_m of the molecule and **frequency of resonance ω**.

- **for small amplitude vibrations, nuclear movement in diatomic molecules can be described as quantum harmonic oscillator**

Quantum Harmonic Oscillator

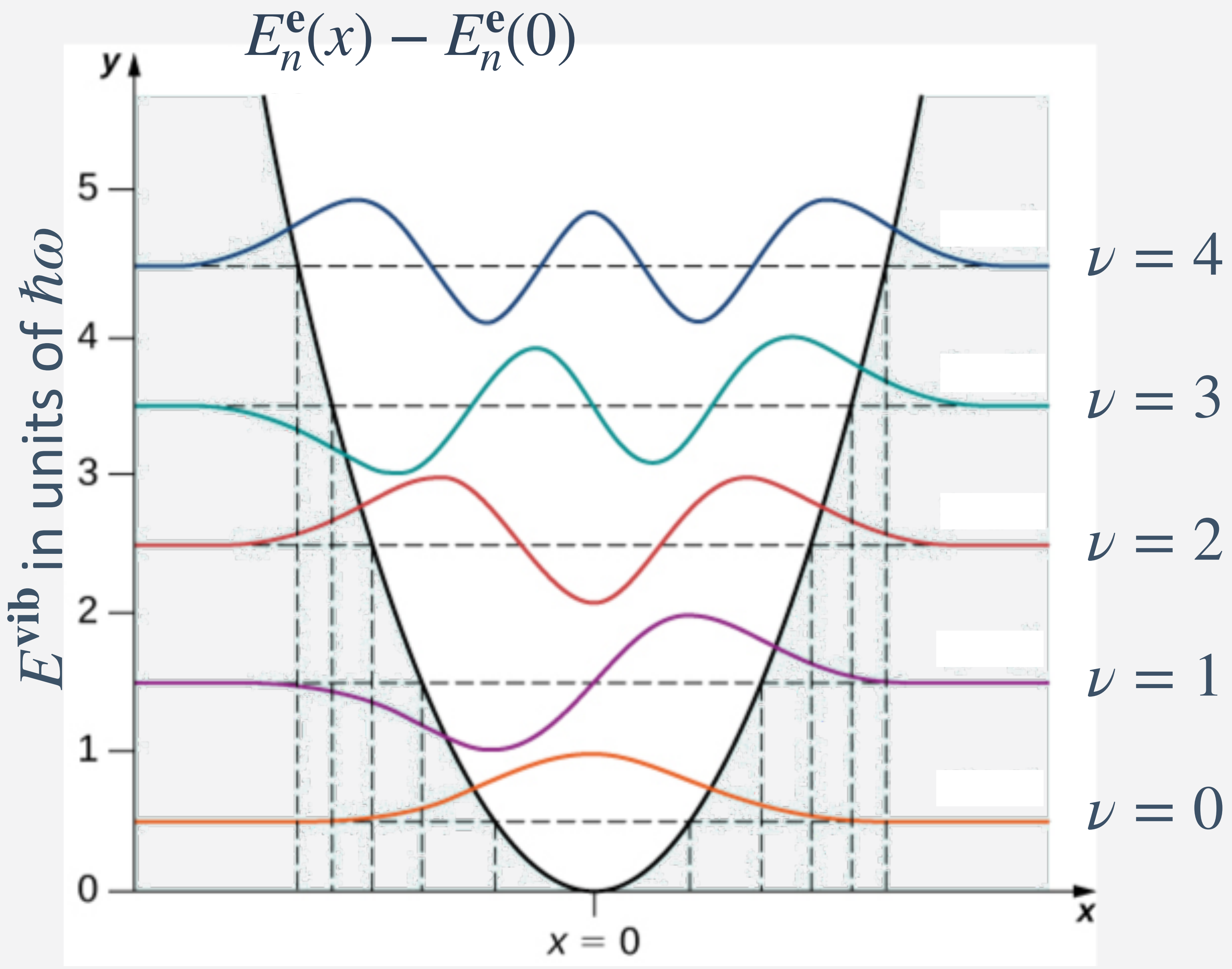
- vibrational wave functions represent the amplitude of probability for the bond length deviation compared to the equilibrium distance to be x

- vibrational energy levels from the Eigenvalues of the Schrödinger equation:

$$E_\nu^{\mathbf{vib}} = (\nu + \frac{1}{2})\hbar\omega$$

- vibrational energy in the ground state:

$$E_0^{\mathbf{vib}} = \frac{1}{2}\hbar\omega > 0$$

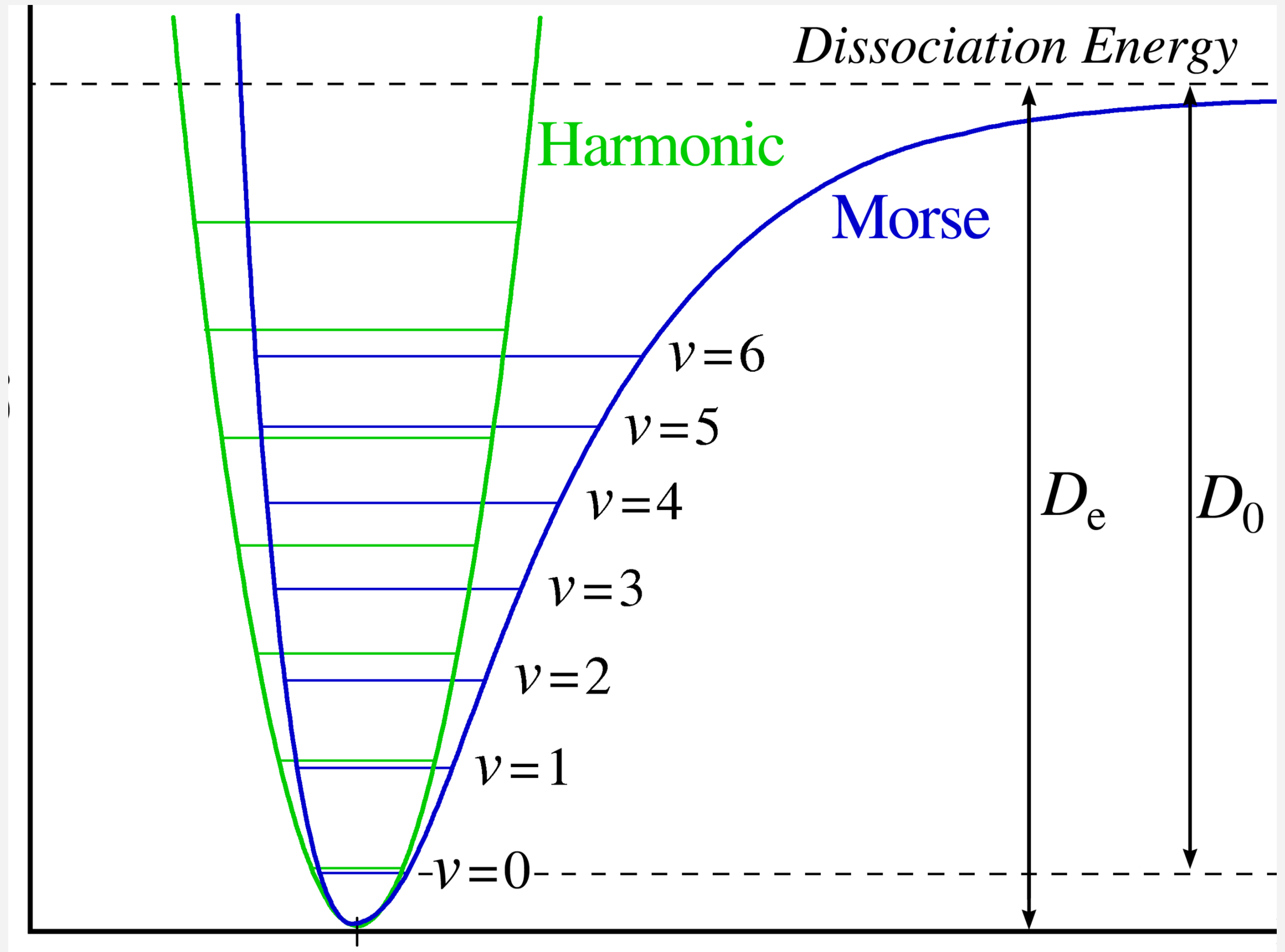


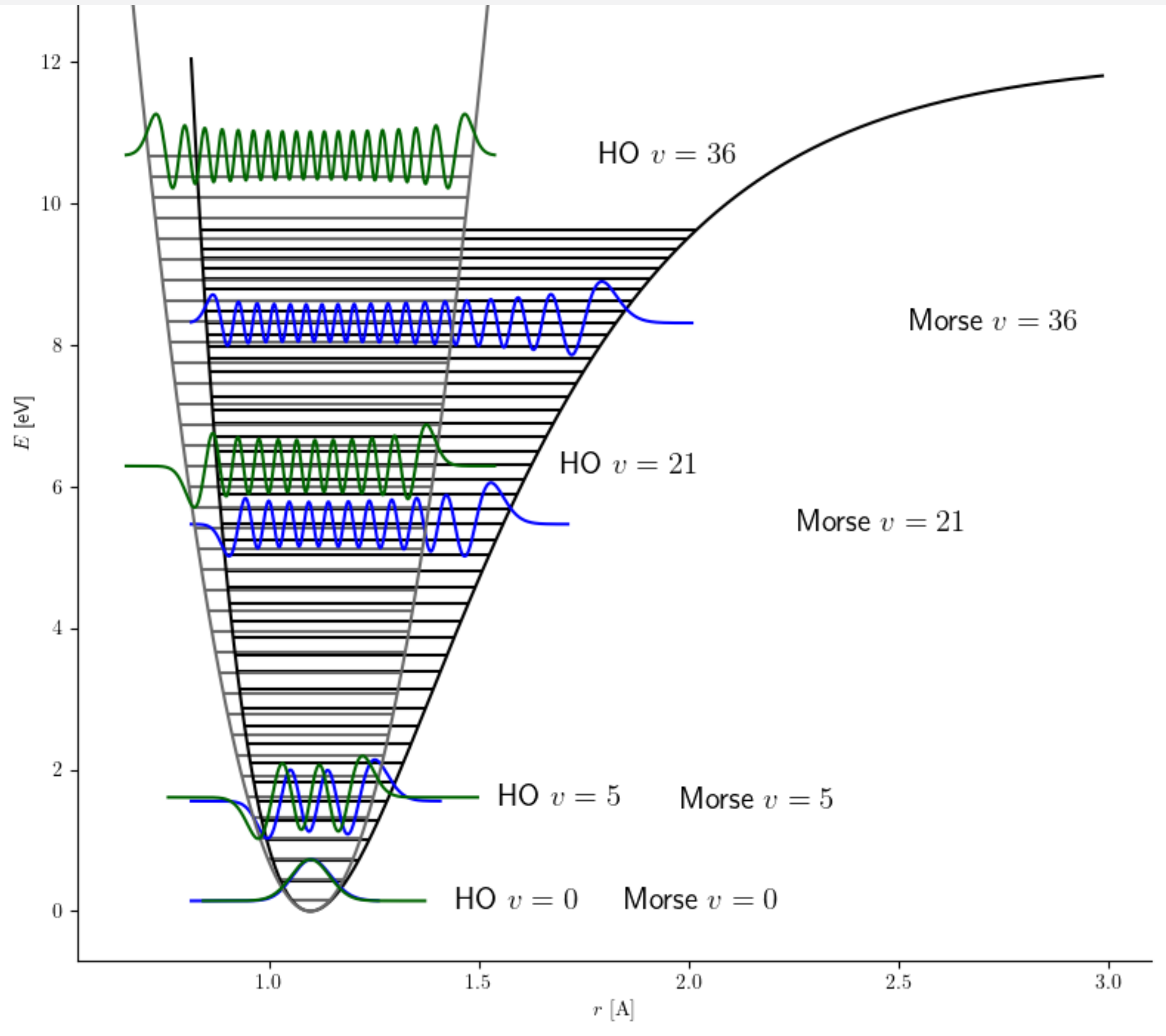
- the fact that there is “zero point” vibrational energy in the ground state is a reflection of the Heisenberg uncertainty principle (momentum is known, hence position is not)

Quantum Morse Oscillator

- electronic states more accurately described by a Morse potential for a variation of nuclear positions around the equilibrium molecular geometry

$$V'(r) = D_e(1 - e^{-a(r-r_0)})^2 \qquad E_n = h\nu_0(n + 1/2) - \frac{\left[h\nu_0(n + 1/2)\right]^2}{4D_e}$$

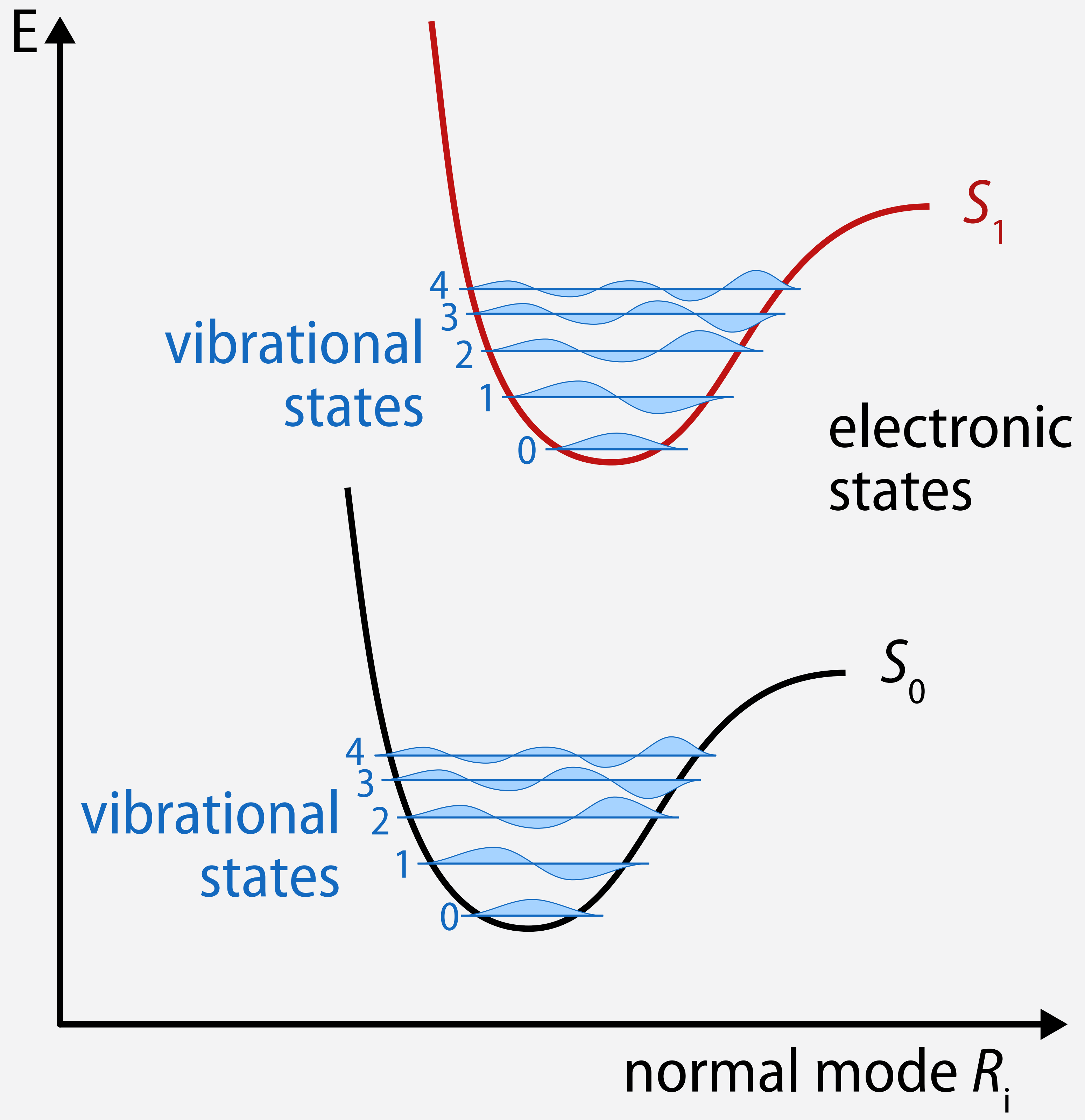


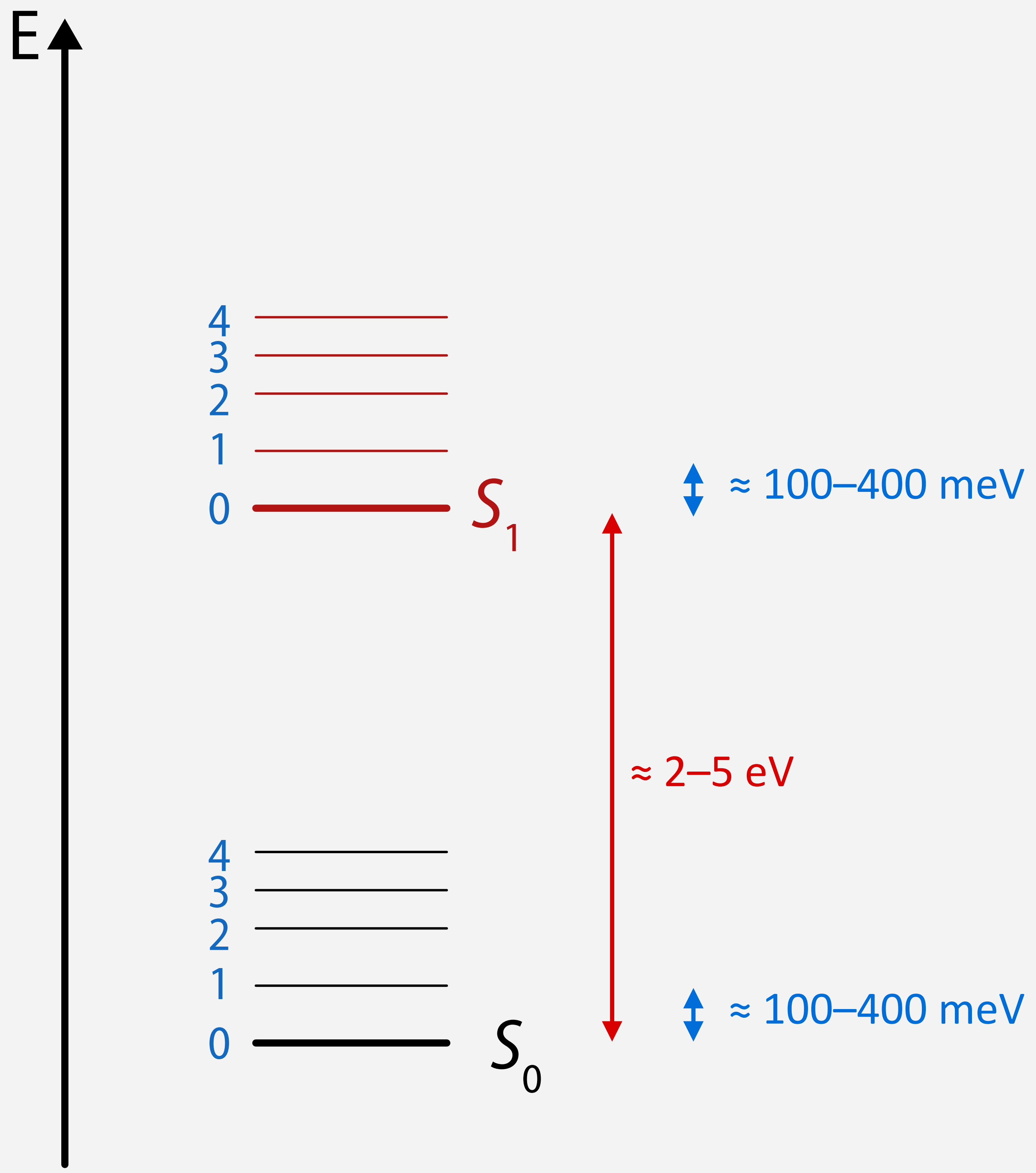


- **energy levels not equidistant but become closer toward the dissociation limit**
- **wave functions biased for the potential well *r* values, particularly for the large *r* boundary**

Superposition of Electronic and Vibrational States

- electronic and vibrational states can be combined into state diagrams
- again, state energy represents the sum of all electronic/vibrational energies of given state





- **for accurate solutions, this analysis has to be done for every normal mode vibration**
- **sufficient approximation for spectroscopy to assume one single “effective mode”**

Learning Outcome

- nuclei move in molecules according to their normal modes
- separation of the nuclear and electronic motion in the wave function still valid
- nuclear vibration can be treated with quantum harmonic oscillator model
- nuclear vibration split each electronic state in several vibronic states