**PIB**

1 Particle
Potential was zero
\( N \rightarrow 0 \)

As \( n \uparrow \), \( \Delta E \uparrow \)

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**Harmonic Oscillator**

2 particles reduced to one particle eq

\( n \) Can be zero (ZPE)

\( \Delta E = \hbar \nu \) for all \( n \)

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**Anharmonic Oscillator**

Potential is parabolic close to equilibrium but quickly deviates from parabolic as bond length moves away from equilibrium.

As \( n \uparrow \), \( \Delta E \downarrow \)

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**Harmonic Oscillator**

Bond between particles is analogous to a classical spring ⇒ bond does not break.

1. **Boundary Conditions**:
   - \( x \) ranges from \(-\infty \) to \( +\infty \)
   - Since \( \psi(x) \) is a state function, \( \psi(\pm \infty) = 0 \)

2. **Potential**:
   - \( V = V(x) = \frac{1}{2} k x^2 \)
   - \( k \) = force constant
   - \( \nu \) = frequency of vibration
   - \( \omega = \frac{\nu}{\sqrt{\mu}} \) (Hz)
   - \( \omega = \frac{1}{2 \pi} \sqrt{\frac{k}{\mu}} \) (cm\(^{-1}\))

3. **Hamiltonian**:
   - \( H = \hat{\mathbf{r}} + \hat{\mathbf{p}} = -\hbar^2 \frac{d^2}{dx^2} + \frac{1}{2} k x^2 \)

4. **Schrodinger Eq**:
   - \[ -\hbar^2 \frac{d^2 \psi(x)}{dx^2} + \frac{1}{2} k x^2 \psi(x) = E \psi(x) \]

5. **Energies**:
   - \( E_n = \hbar \nu \left( n + \frac{1}{2} \right) \)
   - \( E(n) - E(\infty) = h \nu \left( \frac{n}{2} - \frac{1}{2} \right) = h \nu \)
7. Wavefunctions
\[\psi_n(x) = N_n H_n(\alpha^{1/2} x) e^{-\frac{\alpha x^2}{2}}\]
\(\alpha \approx \frac{1}{2}\) as \(x \to \infty\)

Where: \(N_n\) is the normalization constant,
\(H_n(\alpha^{1/2} x)\) is the Hermite polynomial,
\(\alpha^2 = \frac{k_B T}{\hbar^2}\)

E.g.: \(\psi_0(x) = (\frac{\alpha}{\pi})^{1/4} e^{-\frac{\alpha x^2}{2}}\)
\(\psi_1(x) = (\frac{4\alpha^3}{\pi})^{1/4} x e^{-\frac{\alpha x^2}{2}}\)

All spectroscopic observations must obey selection rules.

E.g.) **Harmonic Oscillator** — Only transitions between adjacent energy states are allowed \((\Delta E = h\nu)\)

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**Anharmonic Oscillator**

- \(D_e\): Dissociation Energy
- \(D_0\): Potential well depth

\[V(x) = \frac{1}{2} k x^2 + \frac{1}{2} \delta_3 x^3 + \frac{1}{24} \delta_4 x^4 + \cdots\]

**Potential**

**Enthalpies**

\[\Delta H_n = E(n) = \tilde{\omega}_0 (n + \frac{1}{2}) - \frac{\hbar \tilde{\omega}_0}{2} (n + \frac{1}{2})^2\]

\(n = 0, 1, 2, \ldots\) 
\(\tilde{\omega} = \) fundamental frequency in wavenumbers
\(\zeta = \) anharmonicity constant

**Selection Rules for anharmonic oscillator**

\(\Delta n \text{ is allowed to be } \pm 1, \pm 2, \pm 3\)