PHOT 222: Quantum Photonics

LECTURE 15

Michaël Barbier, Spring semester (2024-2025)

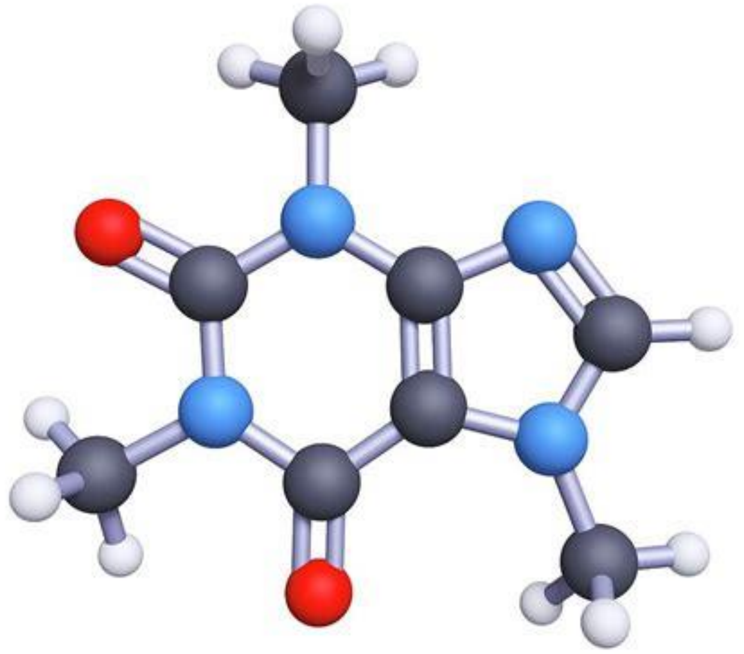
OVERVIEW OF THE COURSE

week	topic	Serway 9th	Young
Week 1	Relativity	Ch. 39	Ch. 37
Week 2	Waves and Particles	Ch. 40	Ch. 38-39
Week 3	Wave packets and Uncertainty	Ch. 40	Ch. 38-39
Week 4	The Schrödinger equation and Probability	Ch. 41	Ch. 39
Week 5	**Midterm exam 1**		
Week 6	Quantum particles in a potential	Ch. 41	Ch. 40
Week 7	Bayram		
Week 8	Harmonic oscillator	Ch. 41	Ch. 40
Week 9	Tunneling through a potential barrier	Ch. 41	Ch. 40
Week 10	**Midterm exam 2**		
Week 11	Bohr’s hydrogen atom, absorption/emission spectra	Ch. 42	Ch. 41
Week 12	Quantum mechanical model of the hydrogen atom	Ch. 42	Ch. 41
Week 13	Exercises		
Week 14	Spin / Many-electron atoms	Ch. 42	Ch. 41
Week 15	**Molecules**	**Ch. 43**	**Ch. 42**
Week 16	Crystalline materials & energy band structure	Ch. 43	Ch. 42

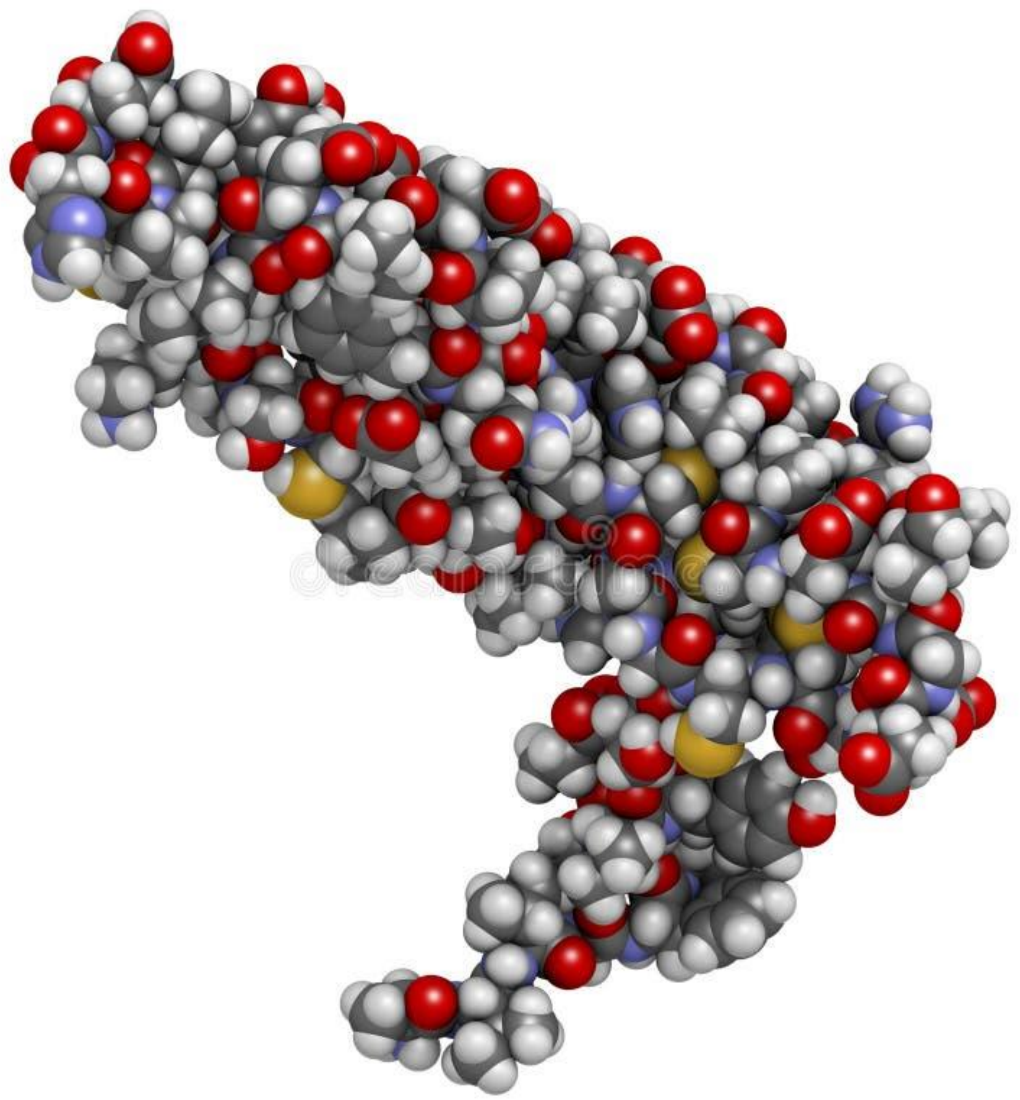
Molecules

MOLECULES

- Materials:
  - single atoms,
  - molecules,
  - crystalline materials,
  - amorphous materials
- Materials can consist of many atoms
- Describing electrons in matter:
  - (Relative) positions of the nuclei
  - Positions of the electrons
  - Interactions between all nuclei and all electrons



Caffeine
$C_8H_{10}N_4O_2$



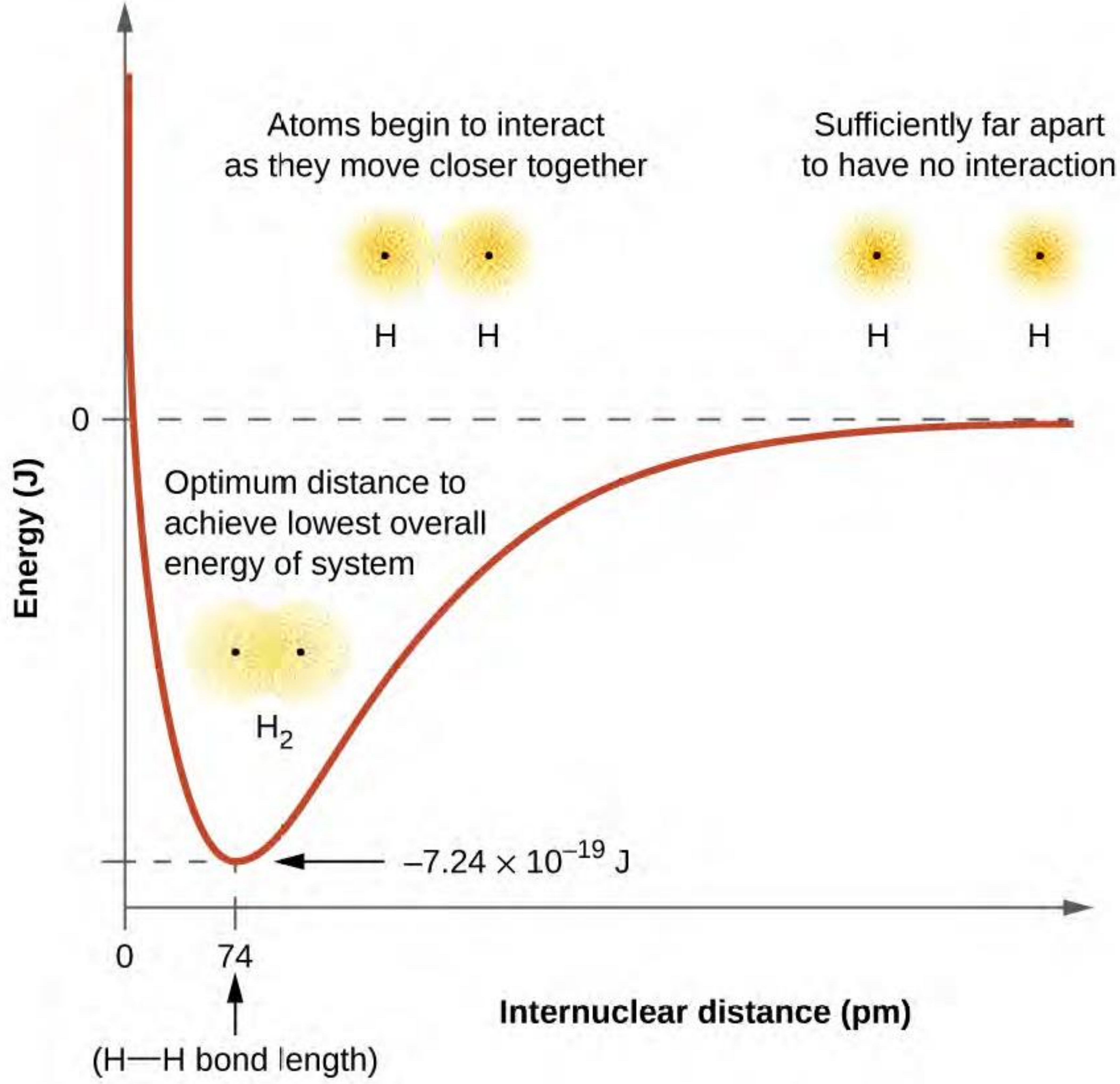
MOLECULAR BOND

- Bonding of atoms in a molecule
  - Electric forces between atoms
  - Coulomb force is conservative

  →Potential landscape --> minima

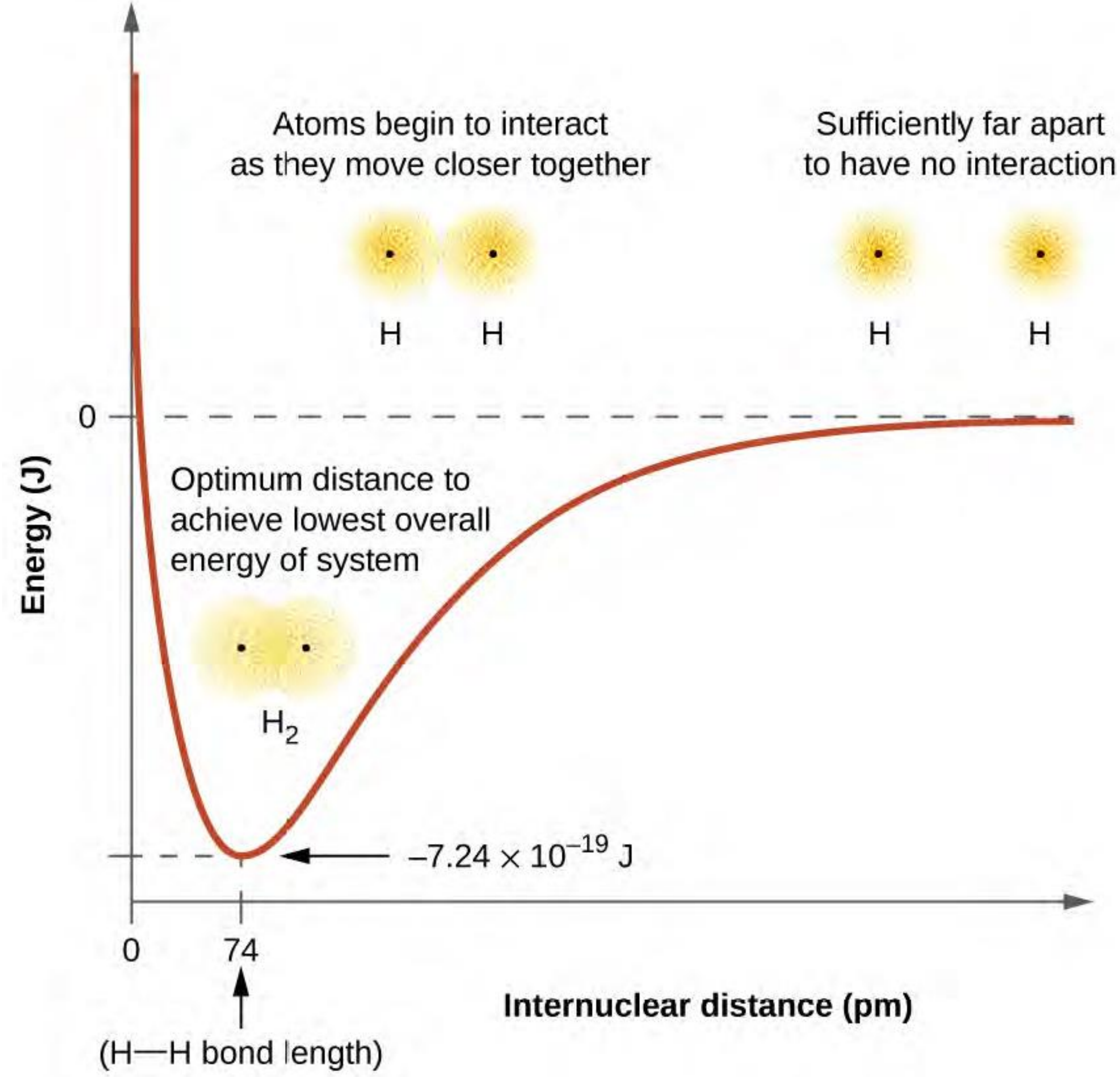
- Potential energy function of a molecule:

1. Repulsive force
2. Attractive force when orbitals share electron



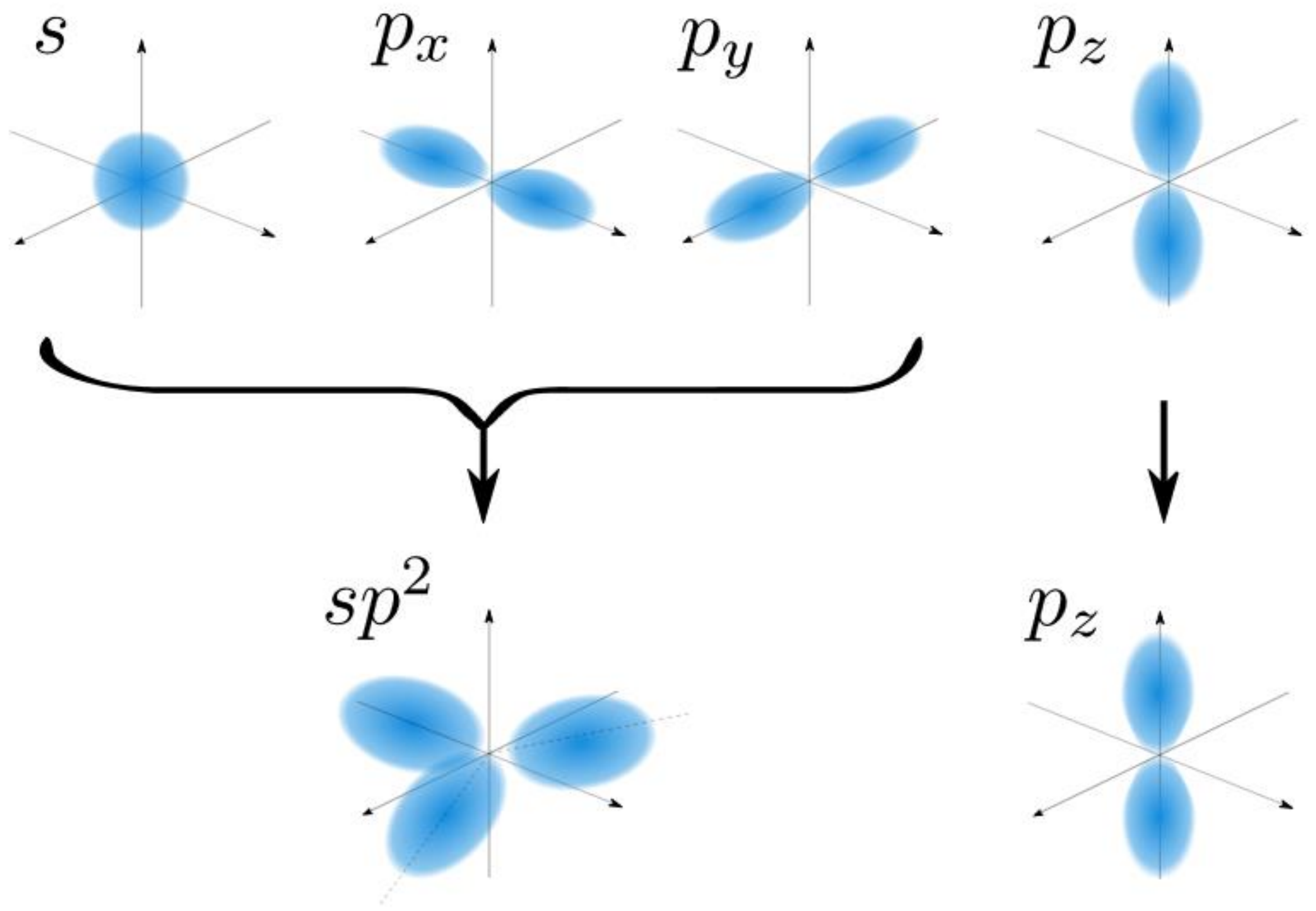
MOLECULAR BOND

- Molecular bond between atoms
- Different types of bonds
  - Ionic bonds
  - Covalent bonds
  - Vanderwaals bonds
  - Hydrogen bonds

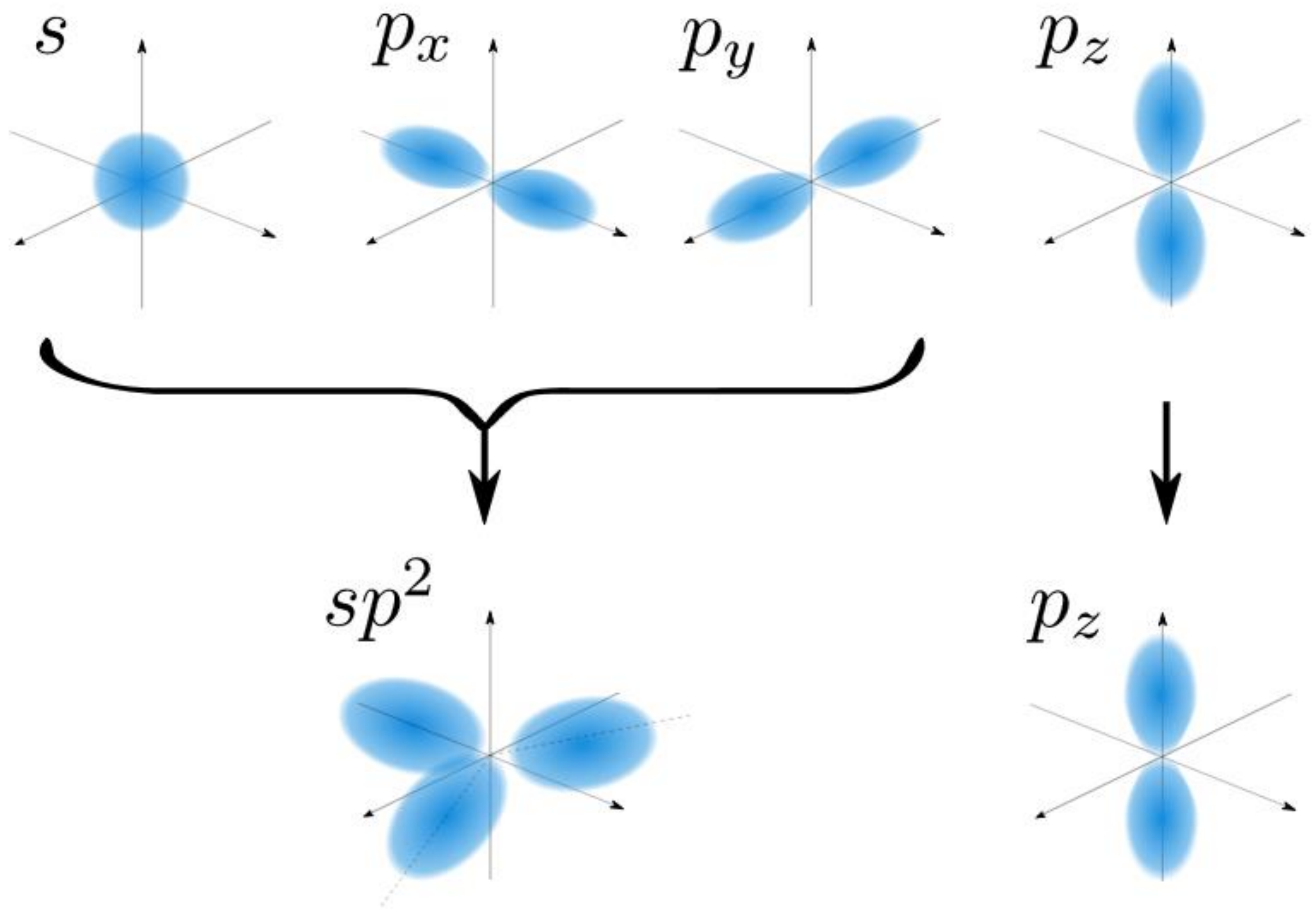


COVALENT BONDS: HYBRIDIZATION

- Superposition of orbitals: sp^2-hybridization
  - Orbitals in the plane
  - s-orbital is now symmetric with p-orbitals
- Improved orbital overlap/access to all electrons



COVALENT BONDS: HYBRIDIZATION



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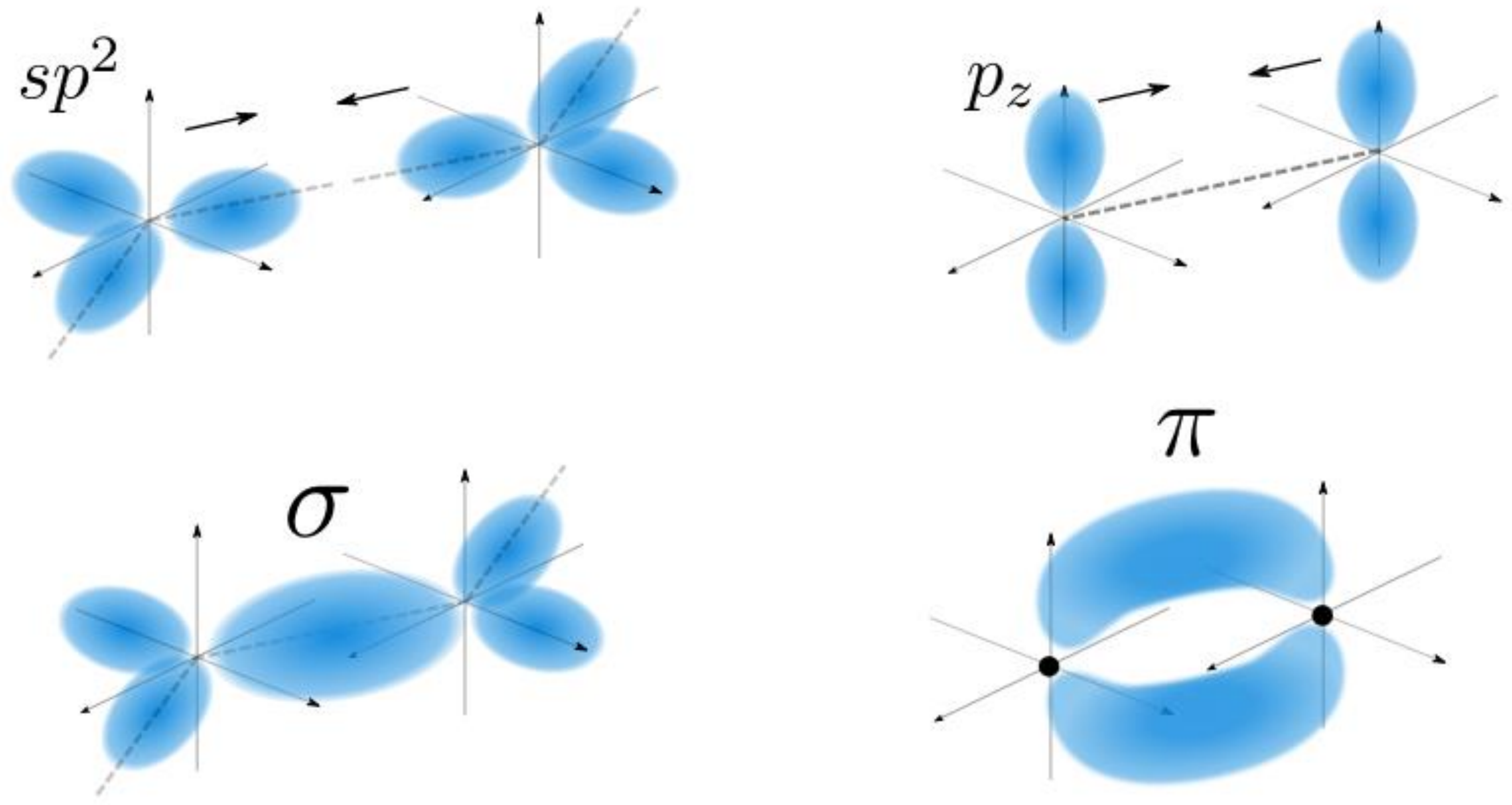


σ - bonds: Strong overlap between sp^2 hybridized orbitals

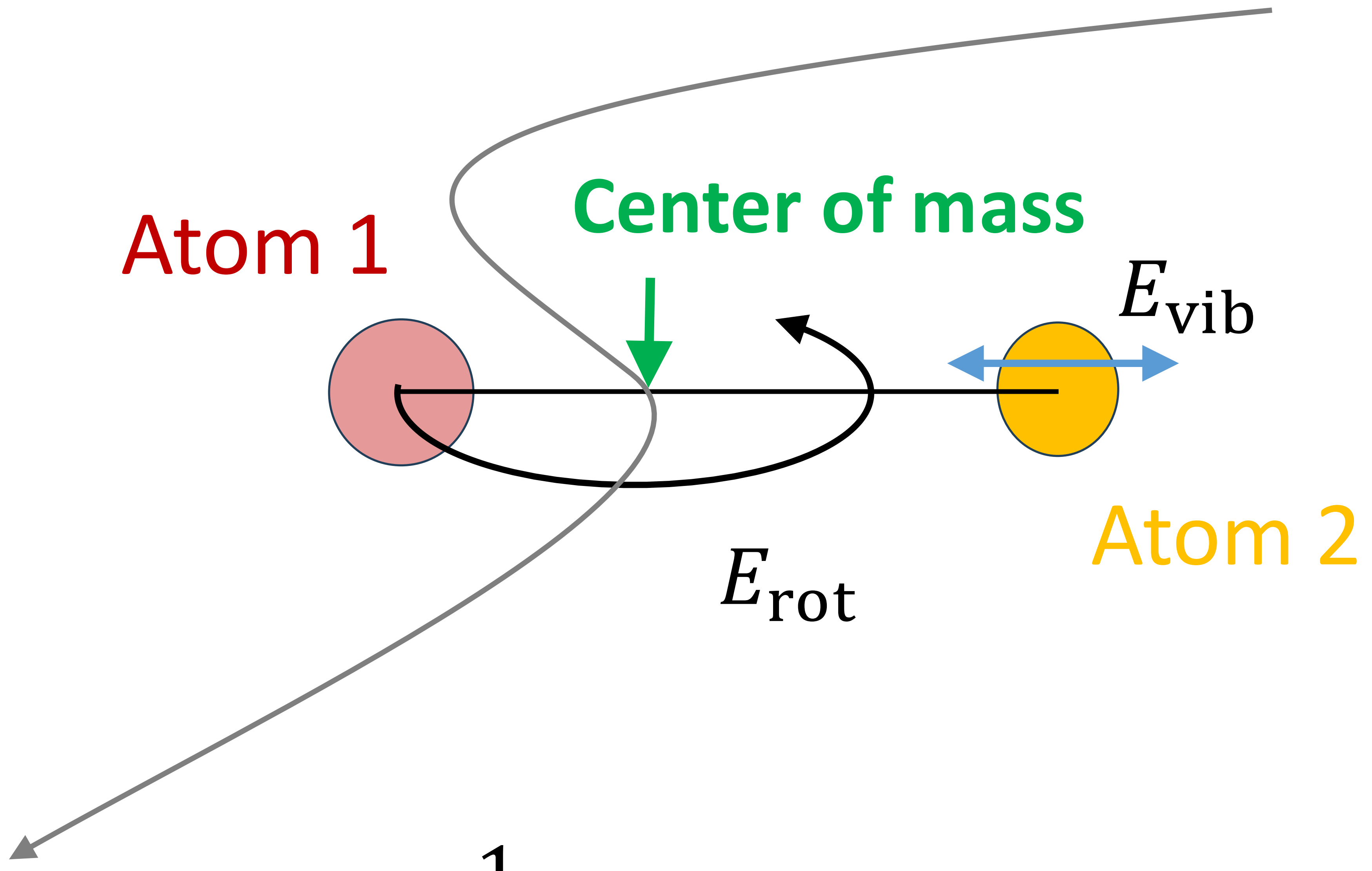
π - bonds: Less overlap between p_z–orbitals (but also in the plane)

Molecular Spectra – Rotations & Vibrations

MOLECULAR SPECTRA

- Assume diatomic molecule
- Energy states:

$$E = E_{\mathrm{electron}} + E_{\mathrm{trans}} + E_{\mathrm{rot}} + E_{\mathrm{vib}}$$



$$E_{\mathrm{trans}} = \frac{1}{2}(m_1+m_2)v^2$$

- **Electronic energy** levels: complex
- **Translation** of whole molecule
- **Rotation** of whole molecule
- **Vibrations** in bonds

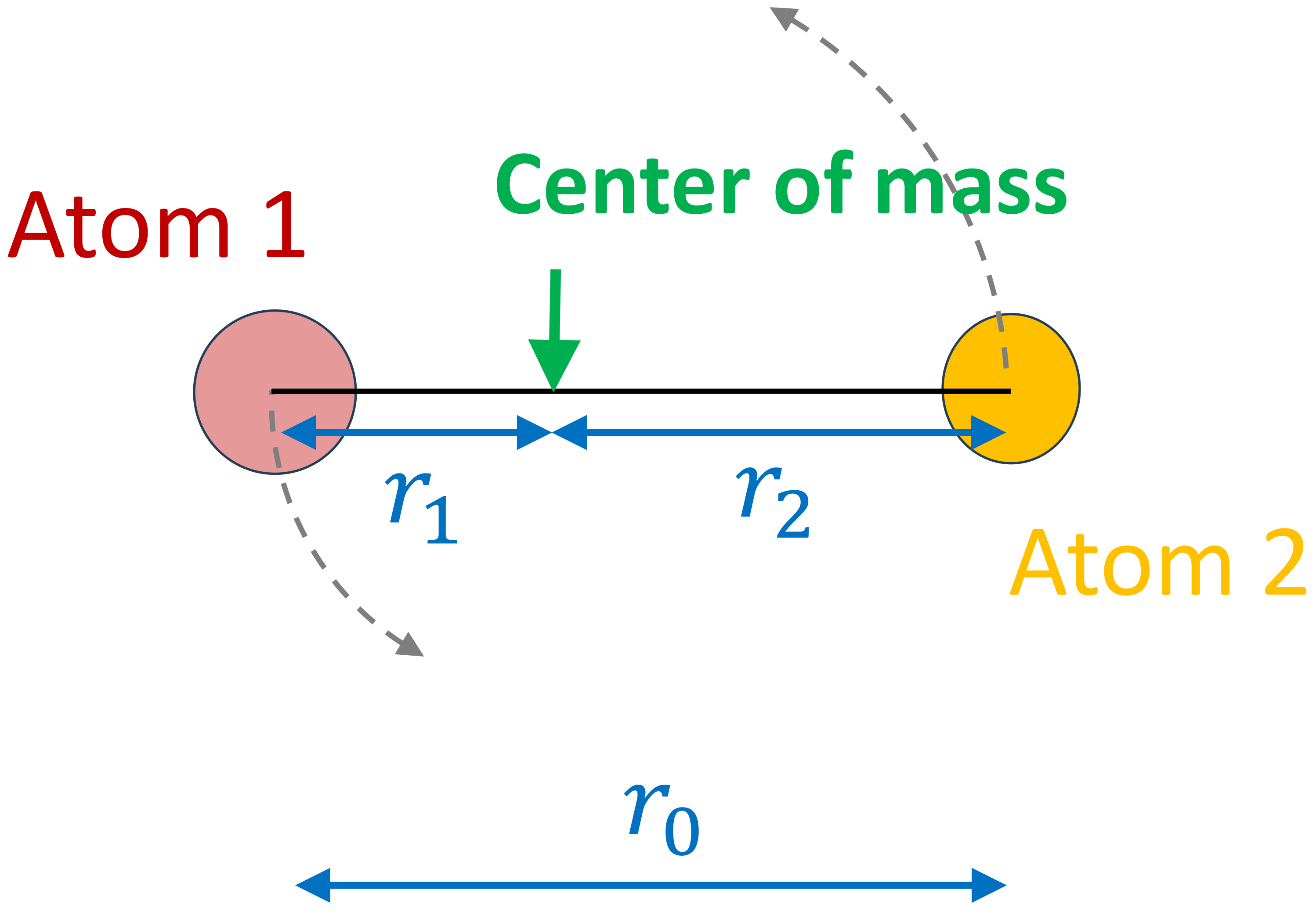
- Rotations and vibrations give **microwave and infrared** spectral lines

MOLECULAR SPECTRA: ROTATIONAL ENERGY-LEVELS

- Assume **diatomic** molecule
- **Angular momentum** rigid body: $L = I\omega$
- **Inertia** of a diatomic molecule: $I = \mu r_0^2$

$$I = m_1 r_1^2 + m_2 r_2^2 = \frac{m_1 m_2}{m_1 + m_2} r_0^2 = \mu r_0^2$$

$$r_1 = \frac{m_2}{m_1 + m_2} \cdot r_0, \qquad r_2 = \frac{m_1}{m_1 + m_2} \cdot r_0$$



- Energy $E_{\text{rot}} = \frac{1}{2} I\omega^2 = \frac{L^2}{2I}$

- Angular momentum similar to hydrogen

MOLECULAR SPECTRA: ROTATIONAL ENERGY-LEVELS

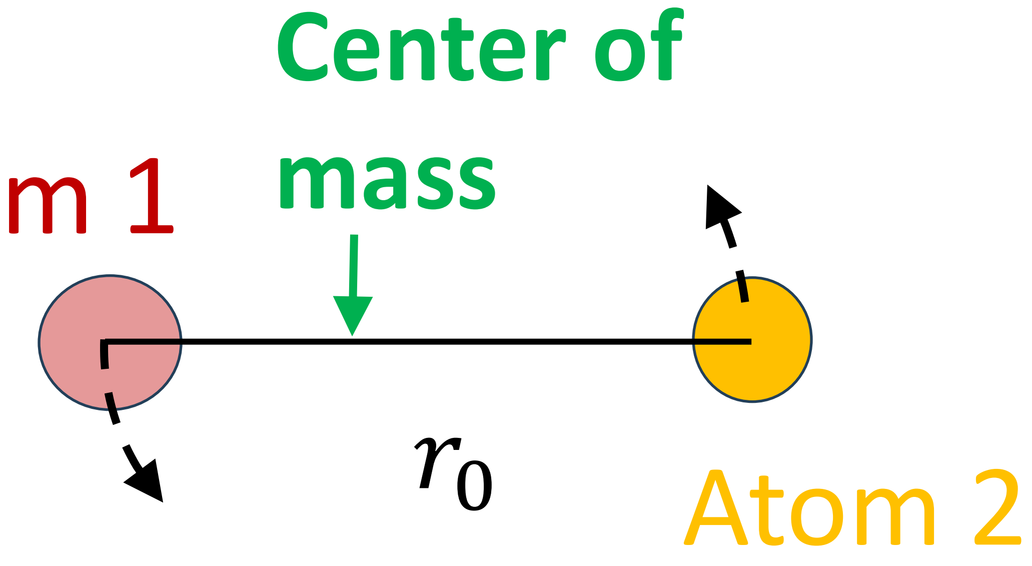
- Rotational energy $E_{\mathrm{rot}} = \frac{L^2}{2I}$
- Schrodinger equation center-symmetric potential:

$$\begin{cases} -\frac{\hbar^2}{2\mu\, r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \left(\frac{\hbar^2 l(l+1)}{2\mu r^2} + U(r)\right)R(r) = E\, R(r) \\ -\frac{1}{\sin\theta}\left(\sin\theta\,\frac{\mathrm{d}\Theta(\theta)}{d\theta}\right) + \left(l(l+1) - \frac{m_l^2}{\sin^2\theta}\right)\Theta(\theta) = 0 \\ \frac{\mathrm{d}^2\Phi(\phi)}{d\phi^2} + m_l^2\Phi(\phi) = 0 \end{cases}$$

- For a diatomic molecule: **radius fixed**, **potential** $U(r) = 0$

MOLECULAR SPECTRA: ROTATIONAL ENERGY-LEVELS

- Energy $E = \frac{L^2}{2I}$ with moment of inertia $I = \mu r_0^2$
- Diatomic molecule: **radius fixed**, **potential** $U(r) = 0$
- Radial part Schrodinger equation center-symmetric potential:



$$-\frac{\hbar^2}{2\mu\, r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \left(\frac{\hbar^2 l(l+1)}{2\mu r^2} + U(r)\right)R(r) = E\, R(r)$$

$$\mu = \frac{\mathrm{m}_1\mathrm{m}_2}{\mathrm{m}_1 + \mathrm{m}_2}$$

$$\Rightarrow \quad \left(\frac{\hbar^2 l(l+1)}{2\mu r^2}\right)R(r) = E\, R(r)$$

$$\Rightarrow \quad \frac{\hbar^2 l(l+1)}{2\mu r^2} = E$$

$$\Rightarrow \quad E_l = \frac{\hbar^2 l(l+1)}{2\mu r_0^2} \quad \Rightarrow \quad L = \sqrt{l(l+1)}\,\hbar$$

MOLECULAR SPECTRA: ROTATIONAL ENERGY-LEVELS

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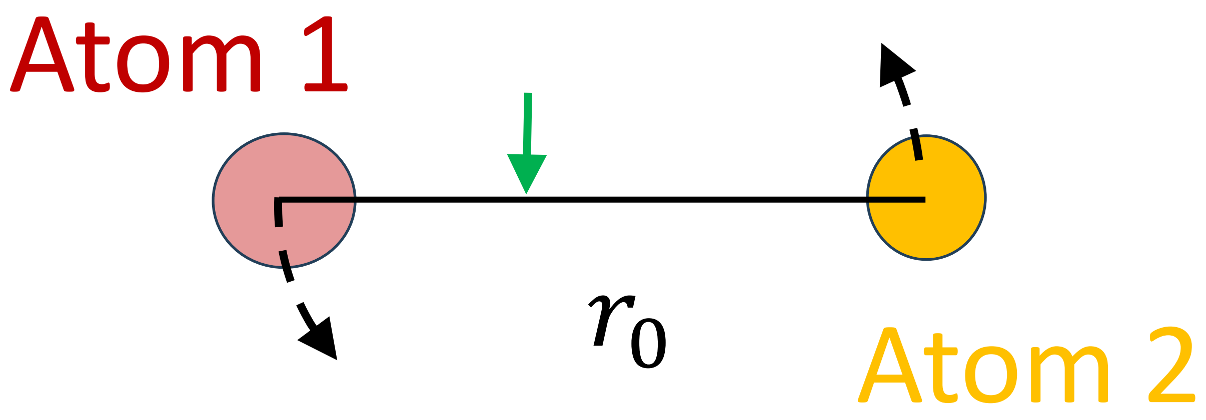
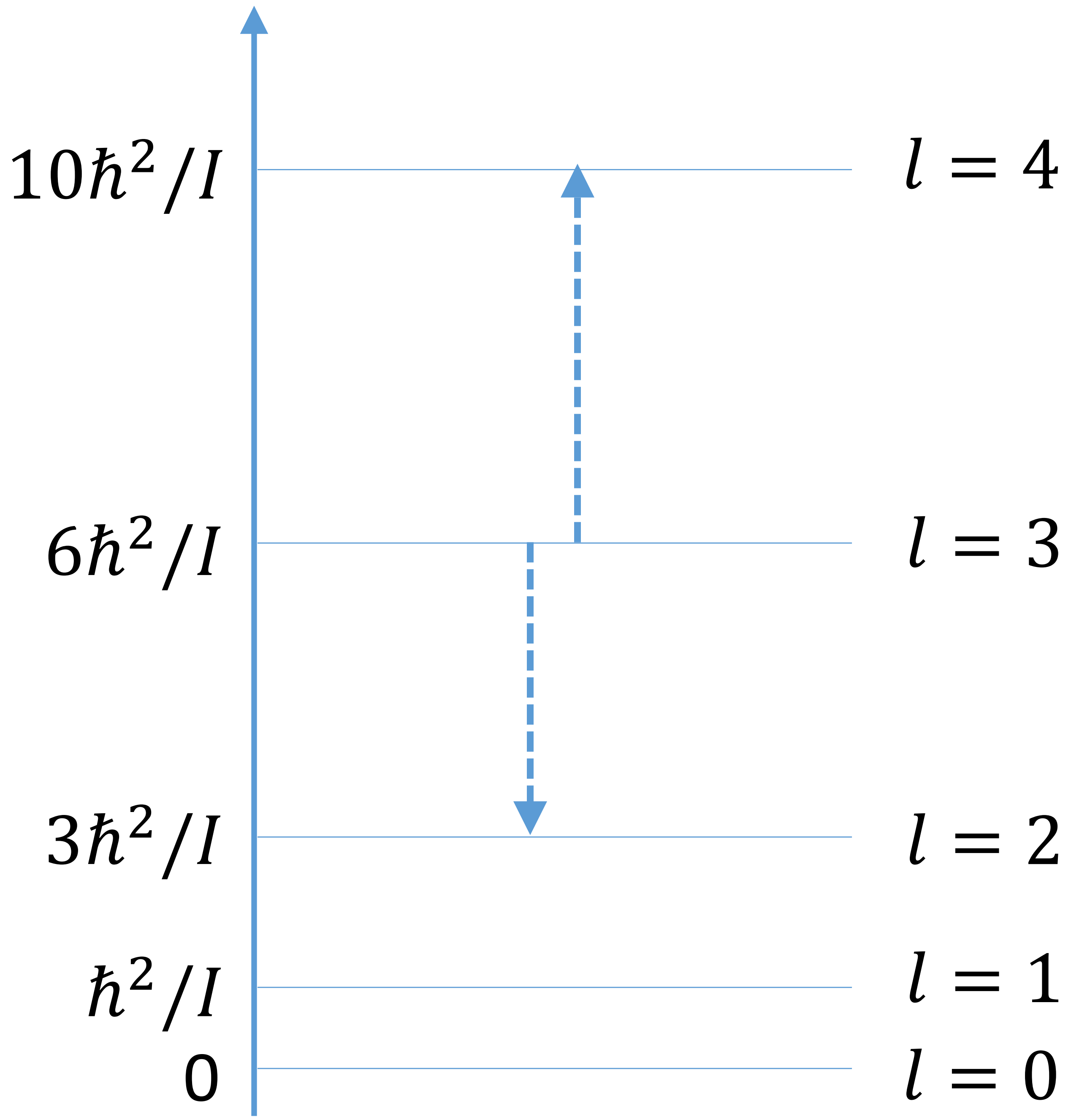
MOLECULAR SPECTRA: ROTATIONAL ENERGY-LEVELS

- Rotational energy $E_{\mathrm{rot}} = \frac{L^2}{2I}$
- Schrodinger equation center-symmetric potential:

$$E_{\mathrm{rot},l} = \frac{L^2}{2I} = l(l+1) \cdot \frac{\hbar^2}{2\mu r_0^2}$$





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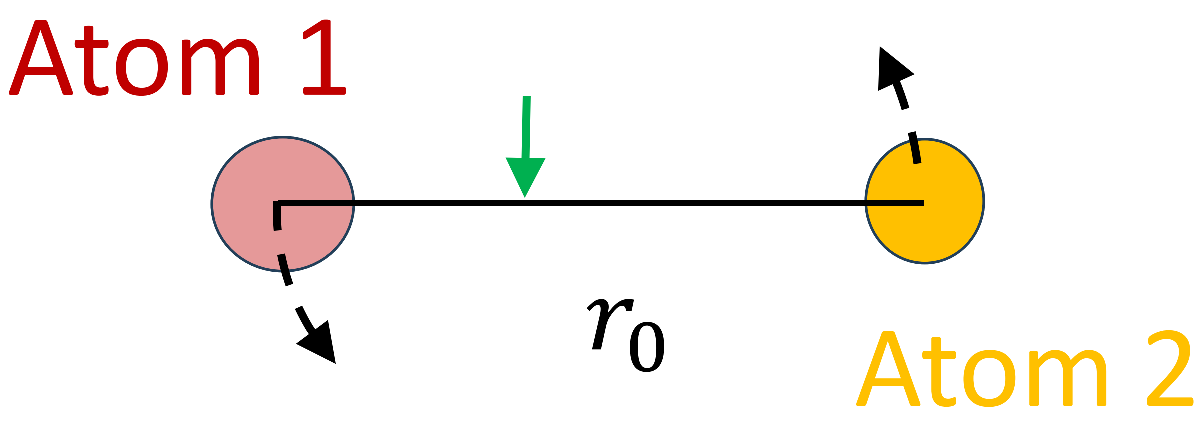
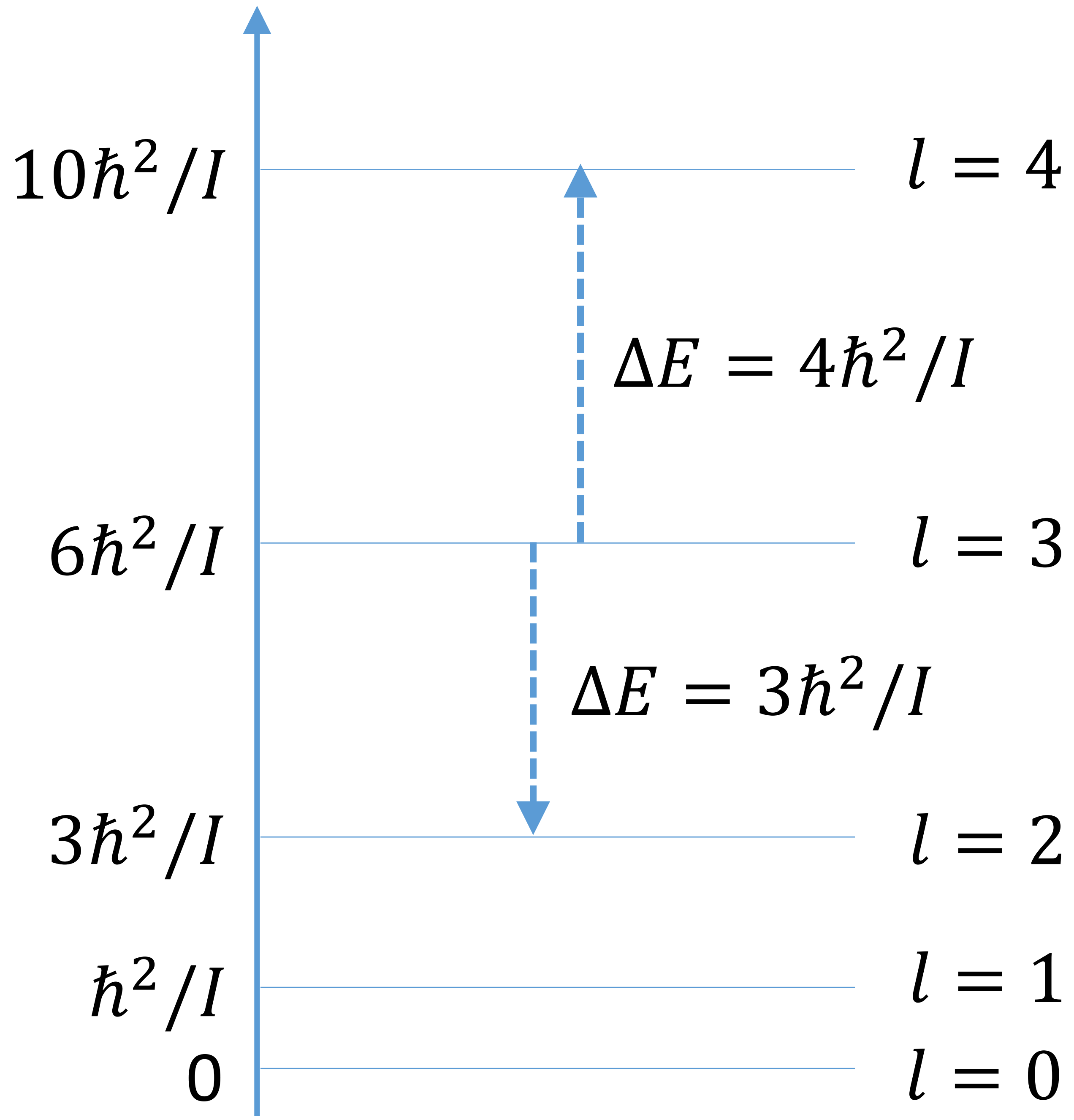


$$E_{\text{rot},l} = \frac{L^2}{2I} = l(l+1) \cdot \frac{\hbar^2}{2\mu r_0^2}$$

- **Spectral lines**: emission/absorption of photons
- **Selection rules**: $\Delta l = \pm 1$

$$\Delta E_{\text{rot}} = \big(l(l+1) - l(l-1)\big) \cdot \frac{\hbar^2}{2I} = \frac{l\hbar^2}{I}$$



MOLECULAR SPECTRA: CLASSICAL ROTATION FREQUENCY

- **Angular momentum** rigid body: $L = I\omega$
- **Inertia** of a diatomic molecule: $I = \mu r_0^2$
- Rotational energy

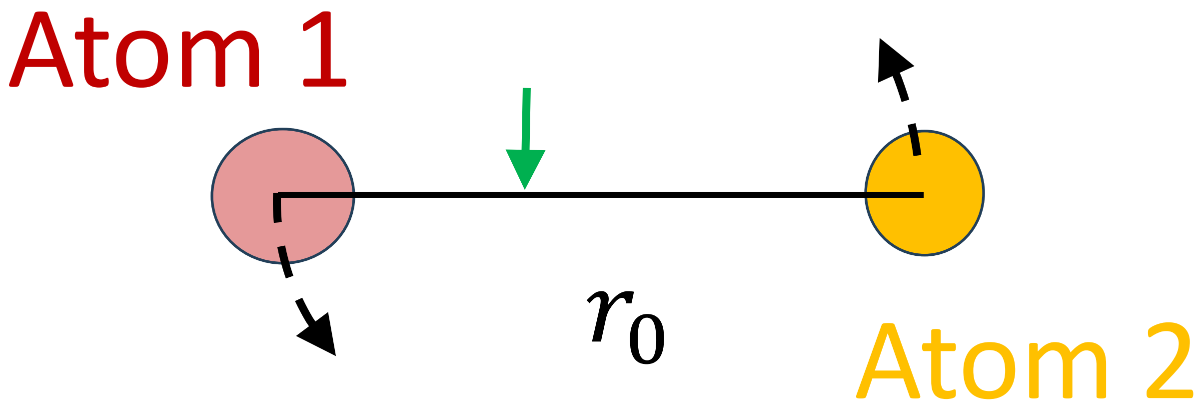
$$E_{\mathrm{rot},l} = \frac{L^2}{2I} = l(l+1)\cdot\frac{\hbar^2}{2\mu r_0^2}$$

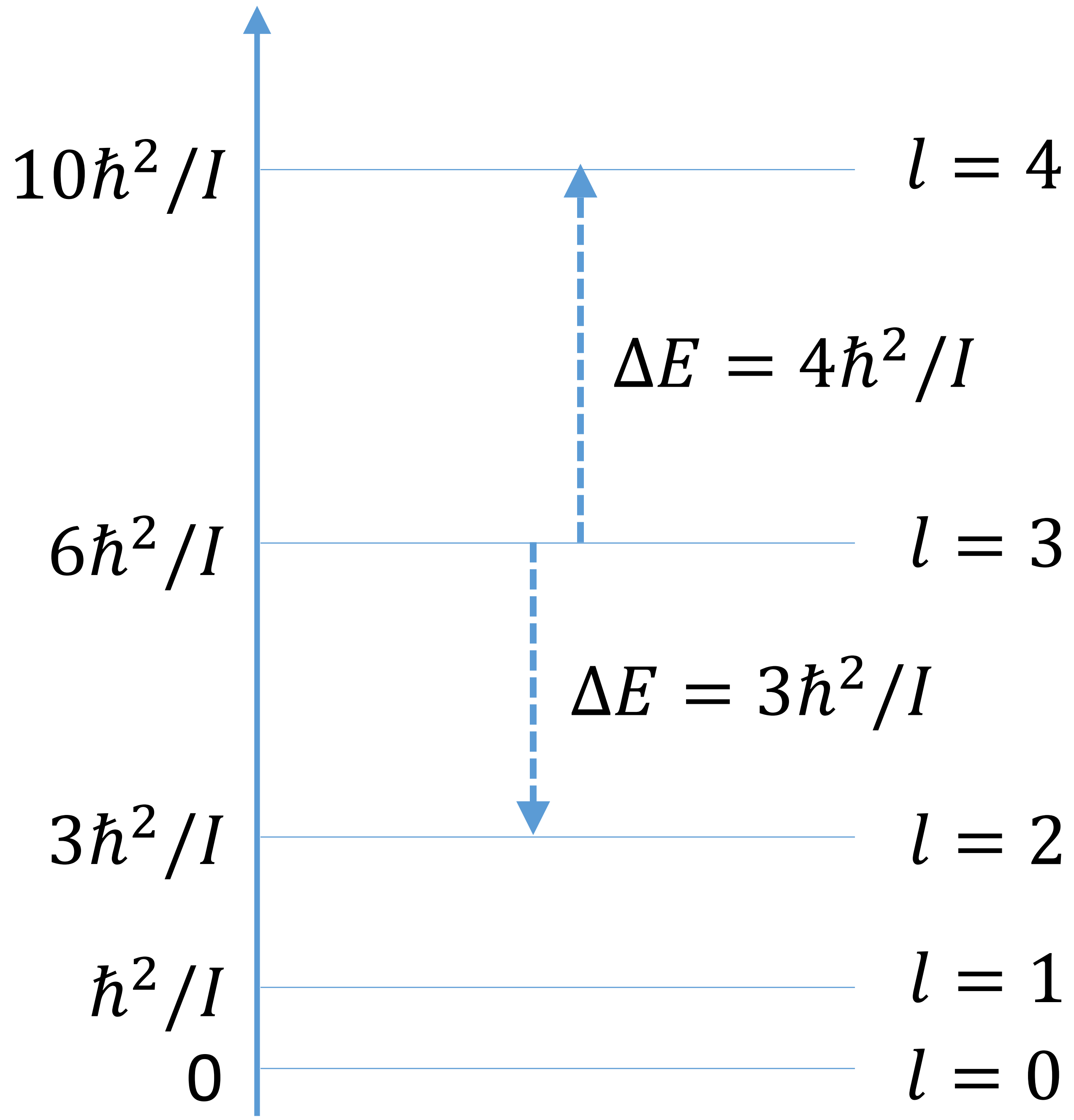
- **Spectral lines**: emission/absorption of photons

$$\Delta E_{\mathrm{rot}} = \frac{l\hbar^2}{I}$$

- Classical rotation frequency:

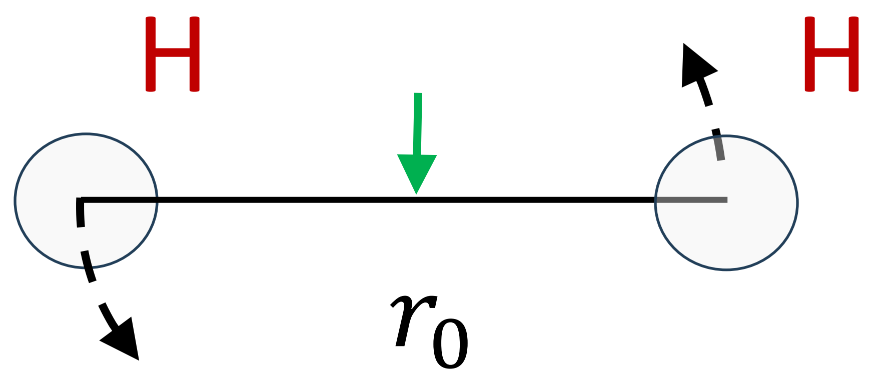
$$\omega = \sqrt{l(l+1)}\frac{\hbar}{\mu r_0^2}$$





EXERCISE ROTATIONAL ENERGY-LEVELS

Exercise: An H_2 molecule exist of two hydrogen atoms separated 0.74 Å apart ($1\ \text{Å} = 10^{-10}\ \text{m}$). Calculate the first 4 rotational energy-levels for an H_2 molecule. Then assume that the molecule is in a (rotational) state with $l\ = 3$ and emits a photon, what is the wavelength of the photon?



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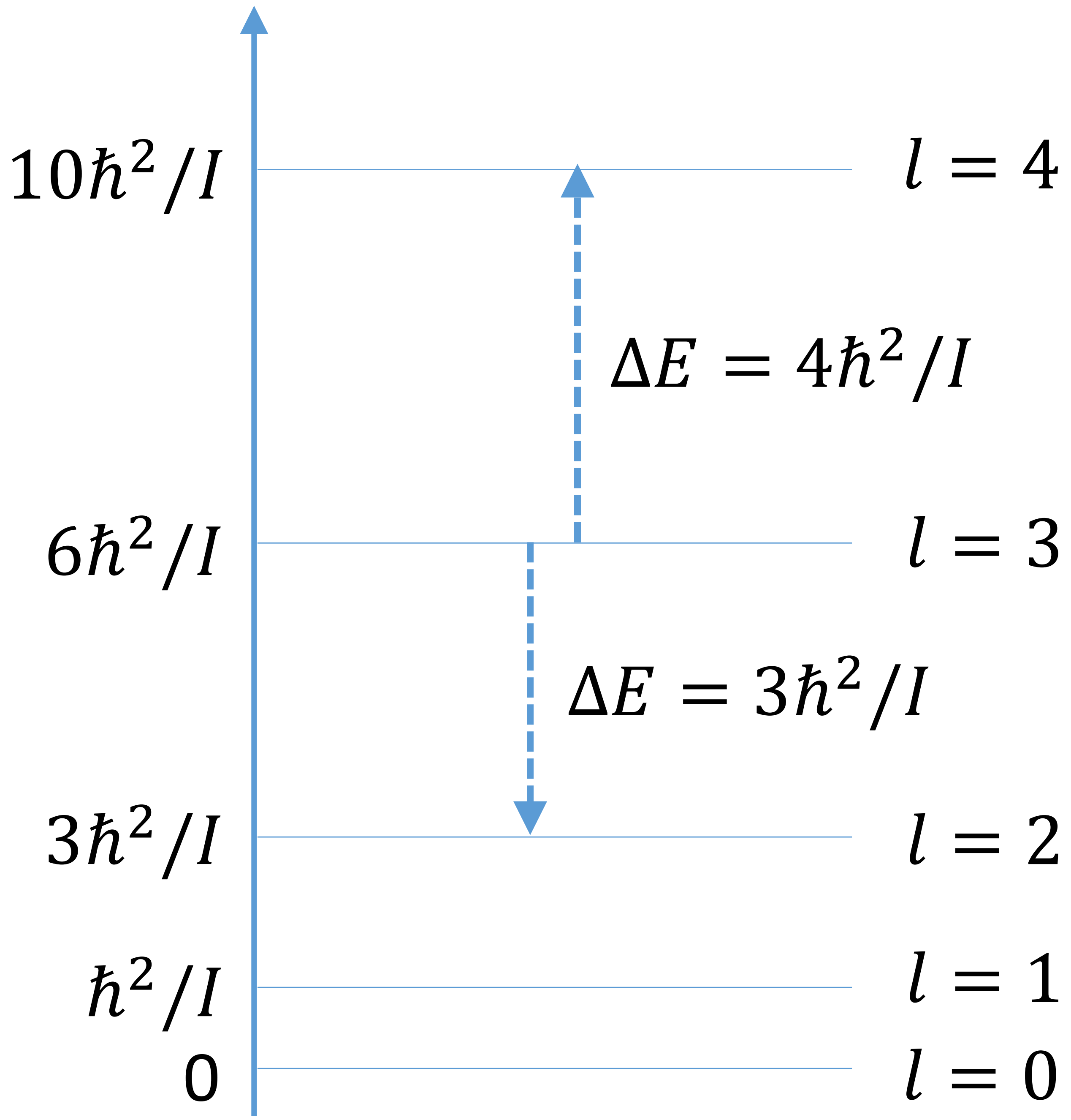

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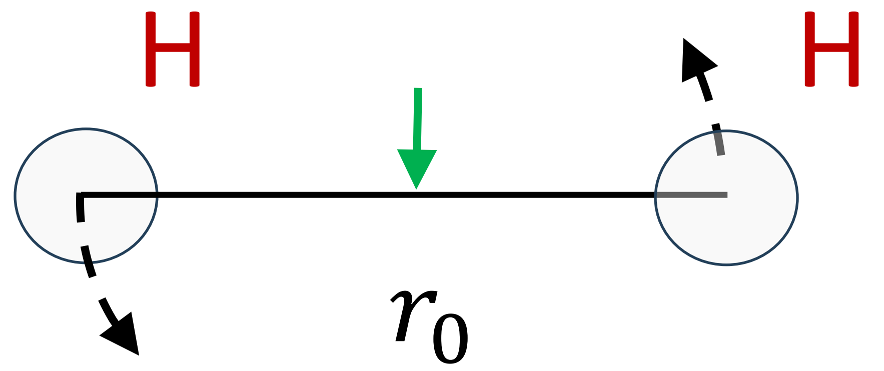


$$E_{\text{rot},l} = l(l+1)\cdot\frac{\hbar^2}{2I} \quad \text{with} \quad I = \mu r_0^2$$

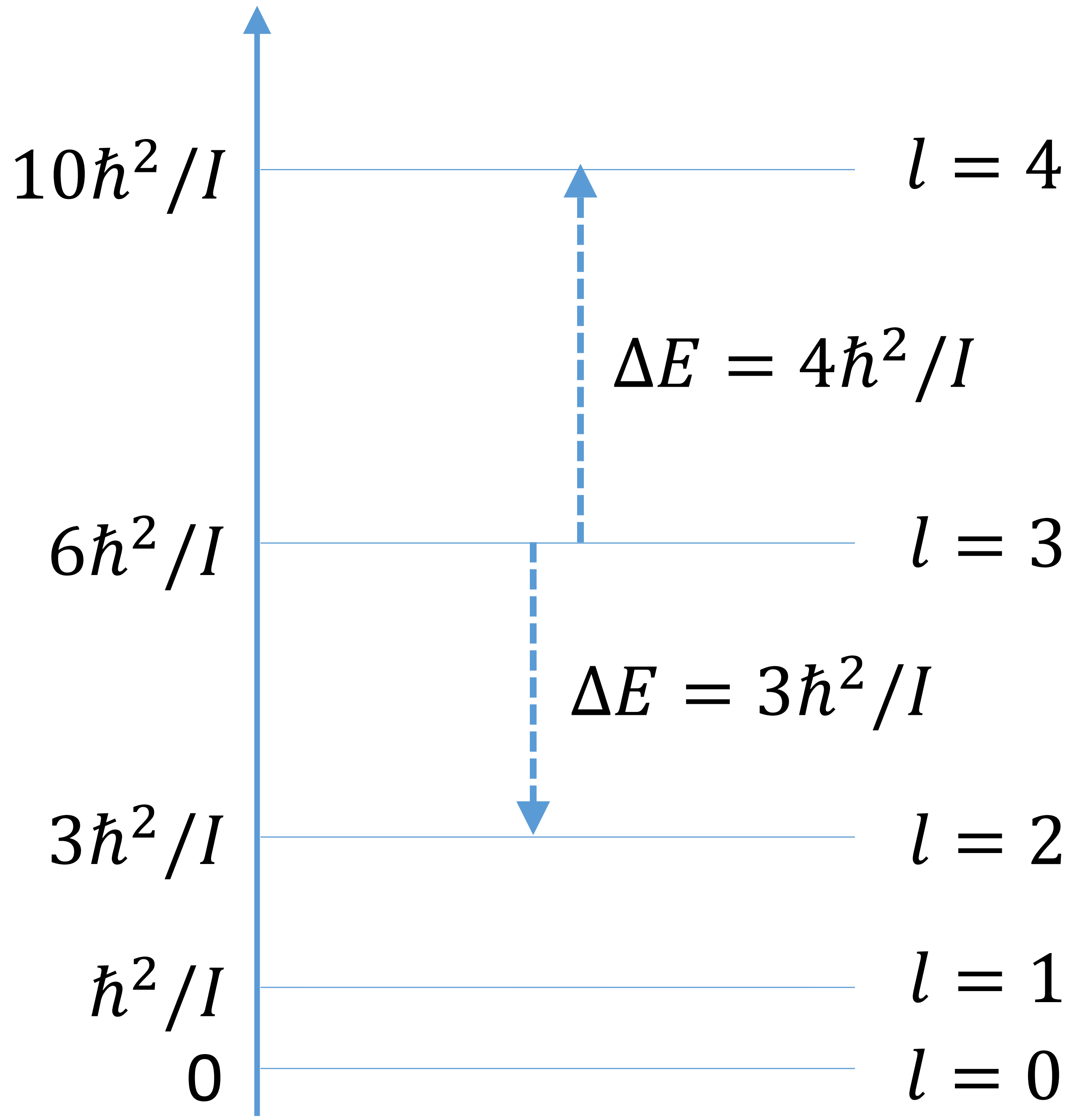
$$\Delta E_{\text{rot}} = \frac{l\hbar^2}{I}$$

Answer: Moment of inertia $I = \mu r_0^2 = \left(\frac{m_p}{2}\right)\ (7.4\times10^{-2}\ \text{nm})^2$

$$\Delta E_{\text{rot}} = \frac{l\hbar^2}{I} = \frac{3\cdot2\cdot h^2c^2}{4\pi^2 m_p c^2 r_0^2} \approx \frac{3\ (1240\ \text{eV nm})^2}{2\pi^2\ 1836\cdot0.511\ \text{MeV}\cdot7.4^2\times10^{-4}\ \text{nm}^2} \approx 0.8\ \text{eV}$$

The wavelength:

$$\lambda = \frac{hc}{\Delta E_{\text{rot}}} = \frac{4\pi^2 m_p c^2 r_0^2}{6\ hc} \approx 2.5\times10^4\ \text{nm}$$



EXERCISE ROTATIONAL ENERGY-LEVELS

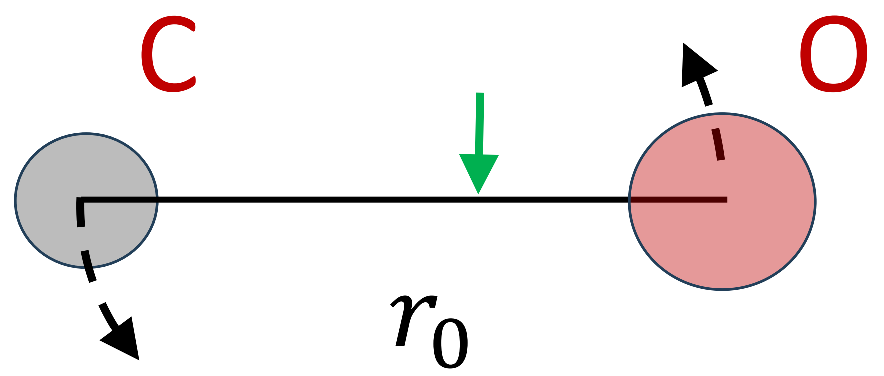
Exercise: An CO molecule exist of a carbon and an oxygen atom separated by distance r_0. If you know that the rotational state transitions from $l = 0$ to $l = 1$ by a photon with frequency $f = 115\ \mathrm{GHz}$

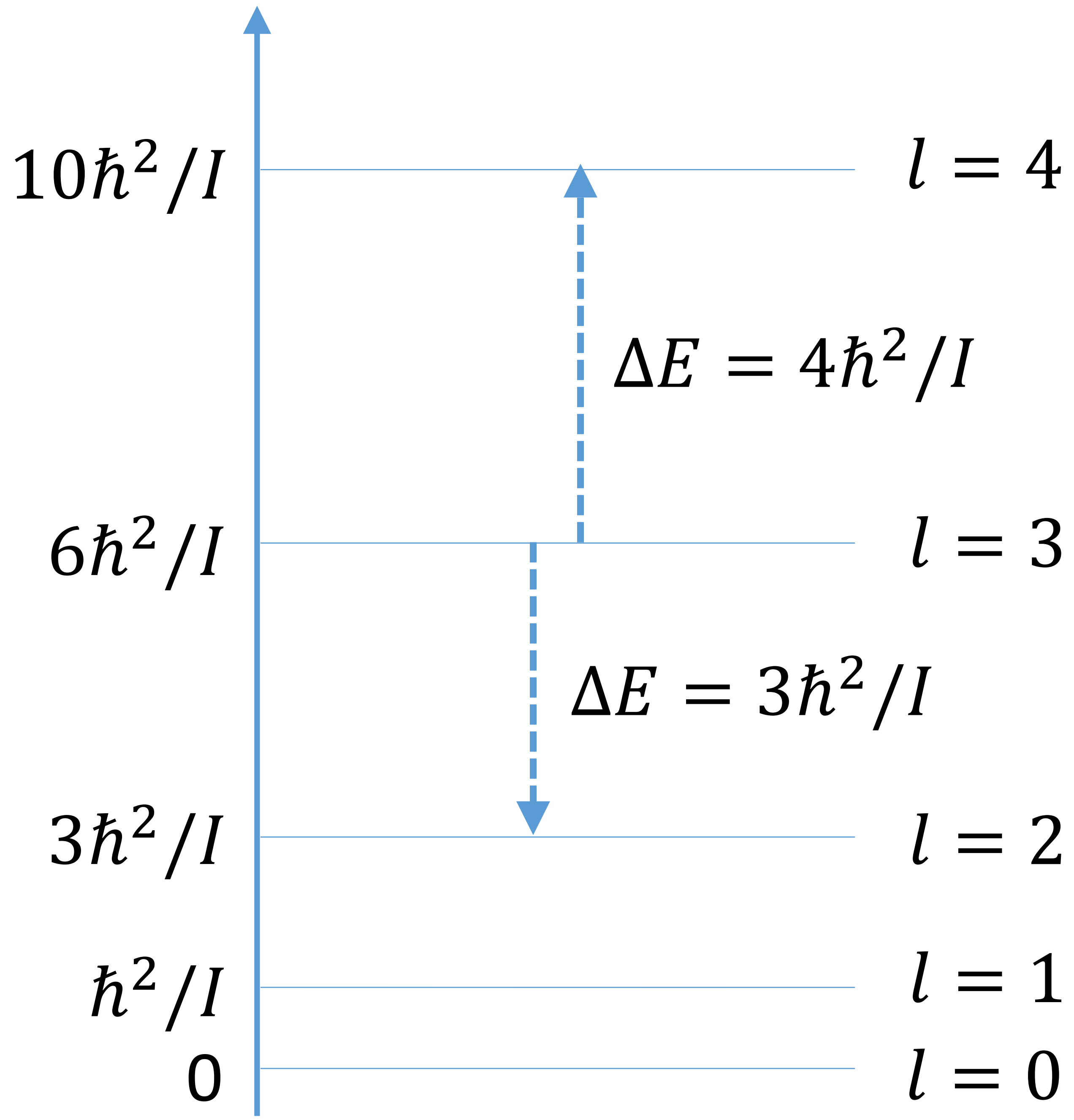
(a) what is the moment of inertia of CO?

(b) What is the separation distance r_0

$$E_{\mathrm{rot},l} = l(l+1) \cdot \frac{\hbar^2}{2I} \quad \text{with} \quad I = \mu r_0^2 \quad \text{and} \quad \mu = \frac{m_1 m_2}{m_1+m_2}$$

$$\Delta E_{\mathrm{rot}} = \frac{l\hbar^2}{I}. \quad \text{One atomic unit (au)} \approx 1.66 \times 10^{-27}\ \mathrm{kg}$$





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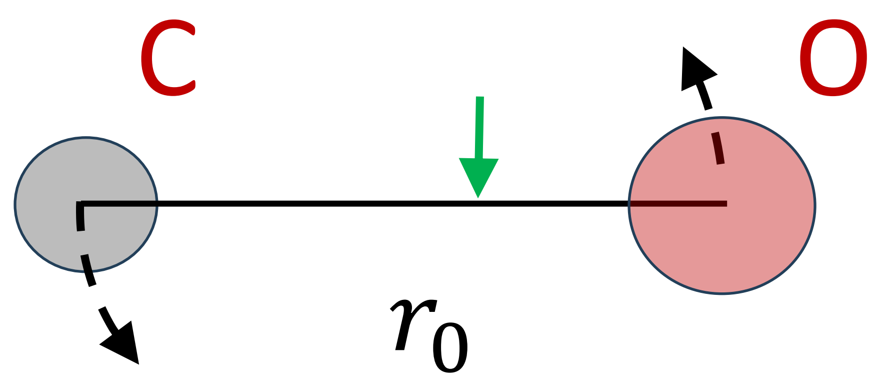


$$E_{\mathrm{rot},l} = l(l+1)\cdot\frac{\hbar^2}{2I} \quad \text{with} \quad I = \mu r_0^2 \quad \text{and} \quad \mu = \frac{m_1 m_2}{m_1+m_2}$$

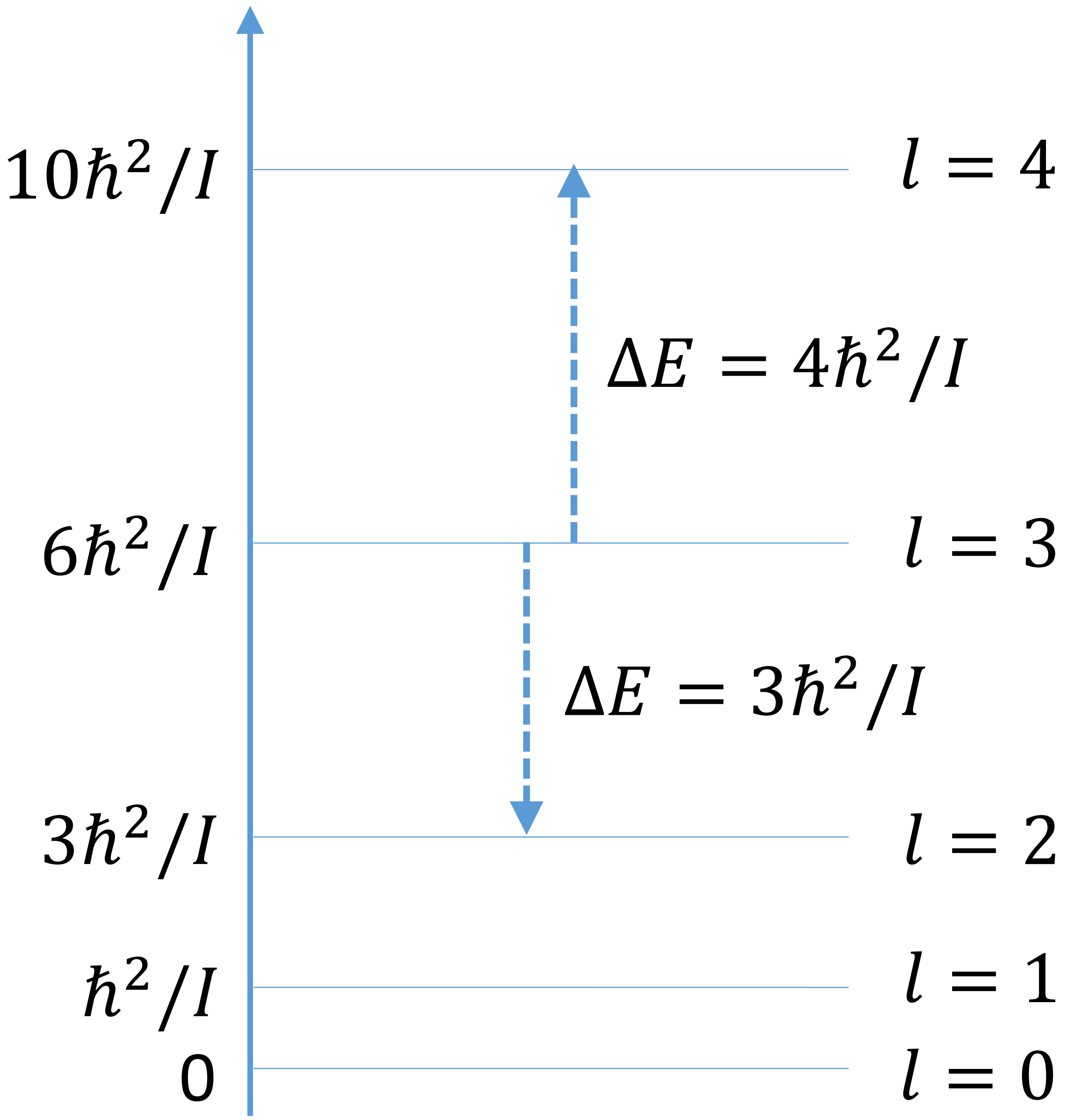
$$\Delta E_{\mathrm{rot}} = \frac{l\hbar^2}{I}. \quad \text{One atomic unit (au)} \approx 1.66\times10^{-27}\ \mathrm{kg}$$

Answer: Energy photon $hf = \Delta E_{\mathrm{rot},1} \Rightarrow hf = \frac{1\hbar^2}{I}$

$$\Rightarrow I = \frac{h}{4\pi^2 f} \approx \frac{(6.63\times10^{-34}\ \mathrm{J\cdot s})}{4\pi^2\ 1.15\times10^{11}\ \ \mathrm{s}^{-1}} \approx 1.5\times10^{-46}\ \mathrm{kg\cdot m^2}$$

The distance:

$$I = \mu r_0^2 \Rightarrow r_0 = \sqrt{\frac{I}{\mu}} = \sqrt{\frac{1.5\times10^{-46}\ \mathrm{kg{\cdot}m^2}}{\frac{12\cdot16}{12+16}\mathrm{au}}} \approx \sqrt{\frac{\frac{3}{2}\times10^{-46}\ \mathrm{kg{\cdot}m^2}}{\frac{12\cdot16}{12+16}\left(\frac{5}{3}\times10^{-27}\ \mathrm{kg}\right)}} \approx 0.113\ \mathrm{nm}$$

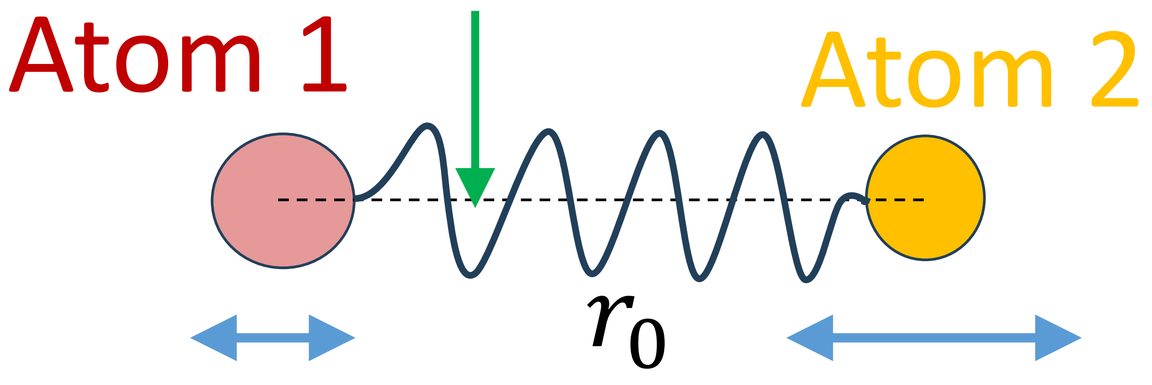


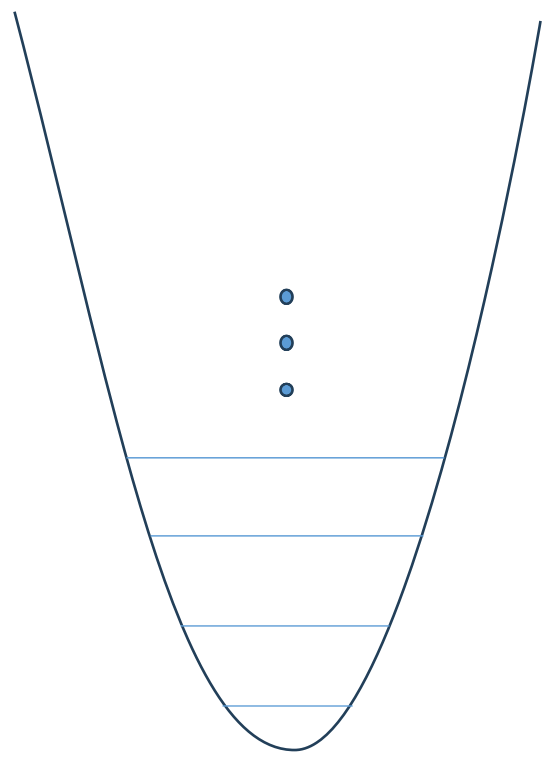
MOLECULAR SPECTRA: VIBRATIONAL ENERGY-LEVELS

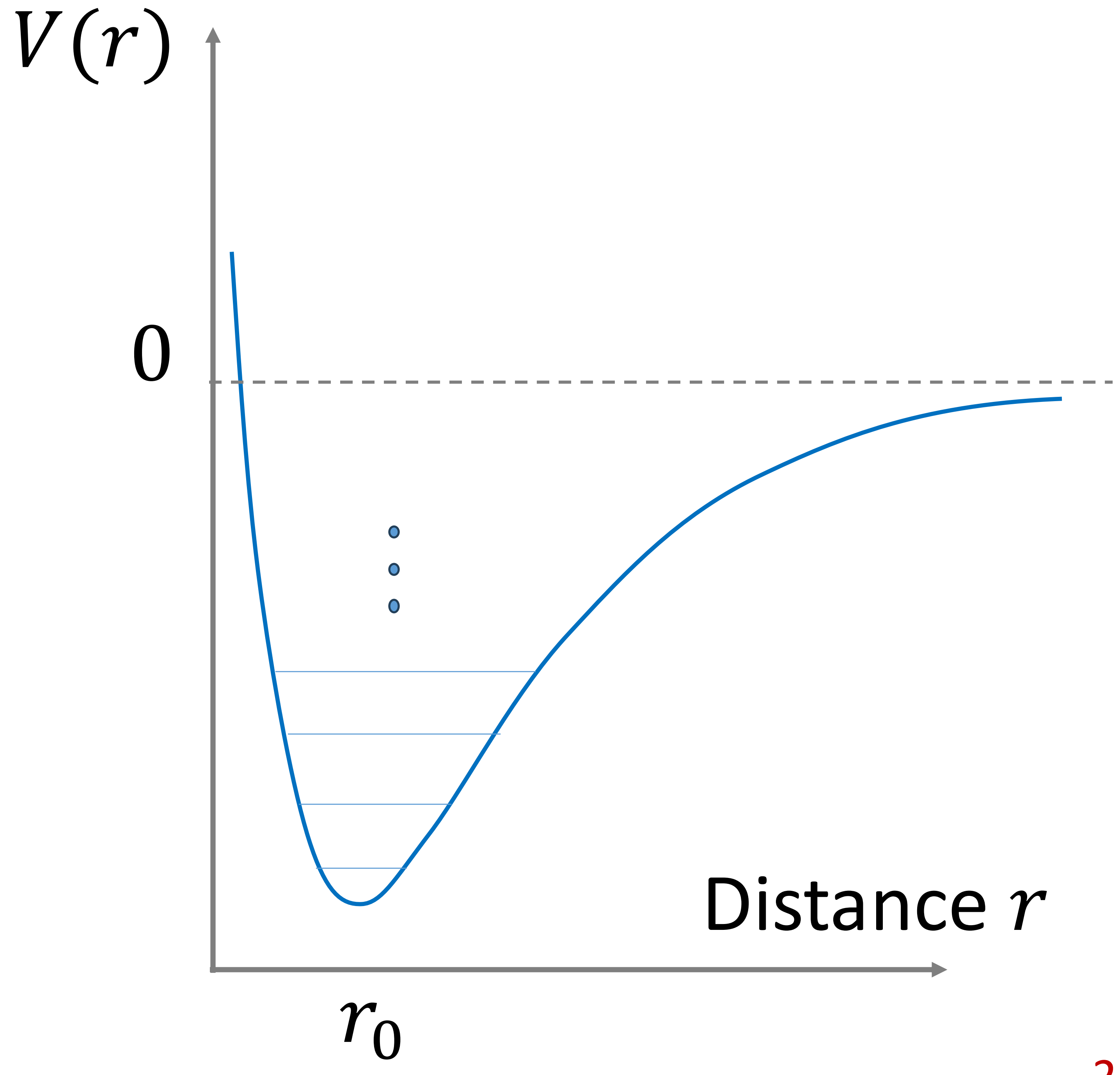
- Approximate potential by parabola
- Similar to spring-ball model
- Quantum Harmonic Oscillator potential:

$$V(r) = \frac{1}{2}\mu\omega^2 r^2 = \frac{1}{2}k' r^2$$

- Connection vibration: $\omega = \sqrt{\frac{k'}{\mu}}$







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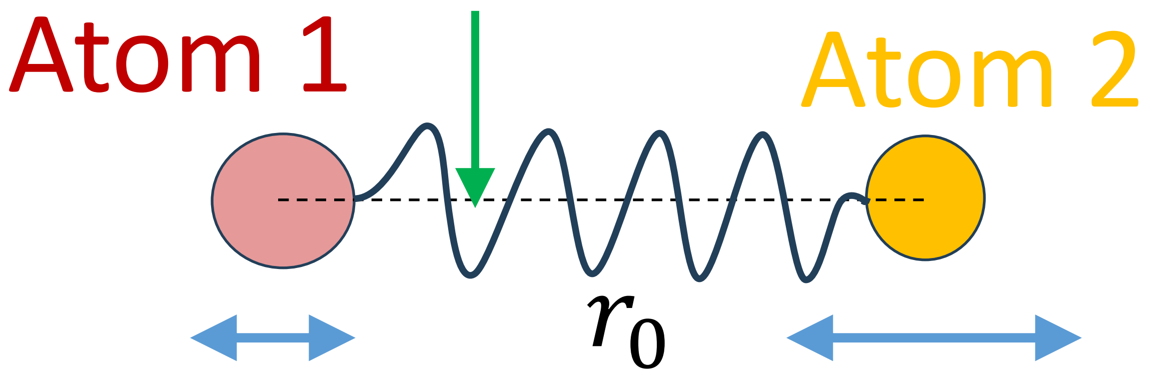
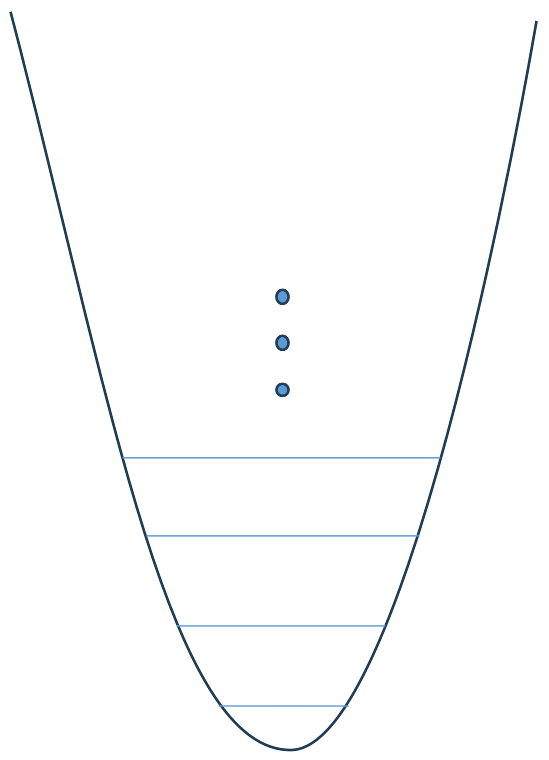
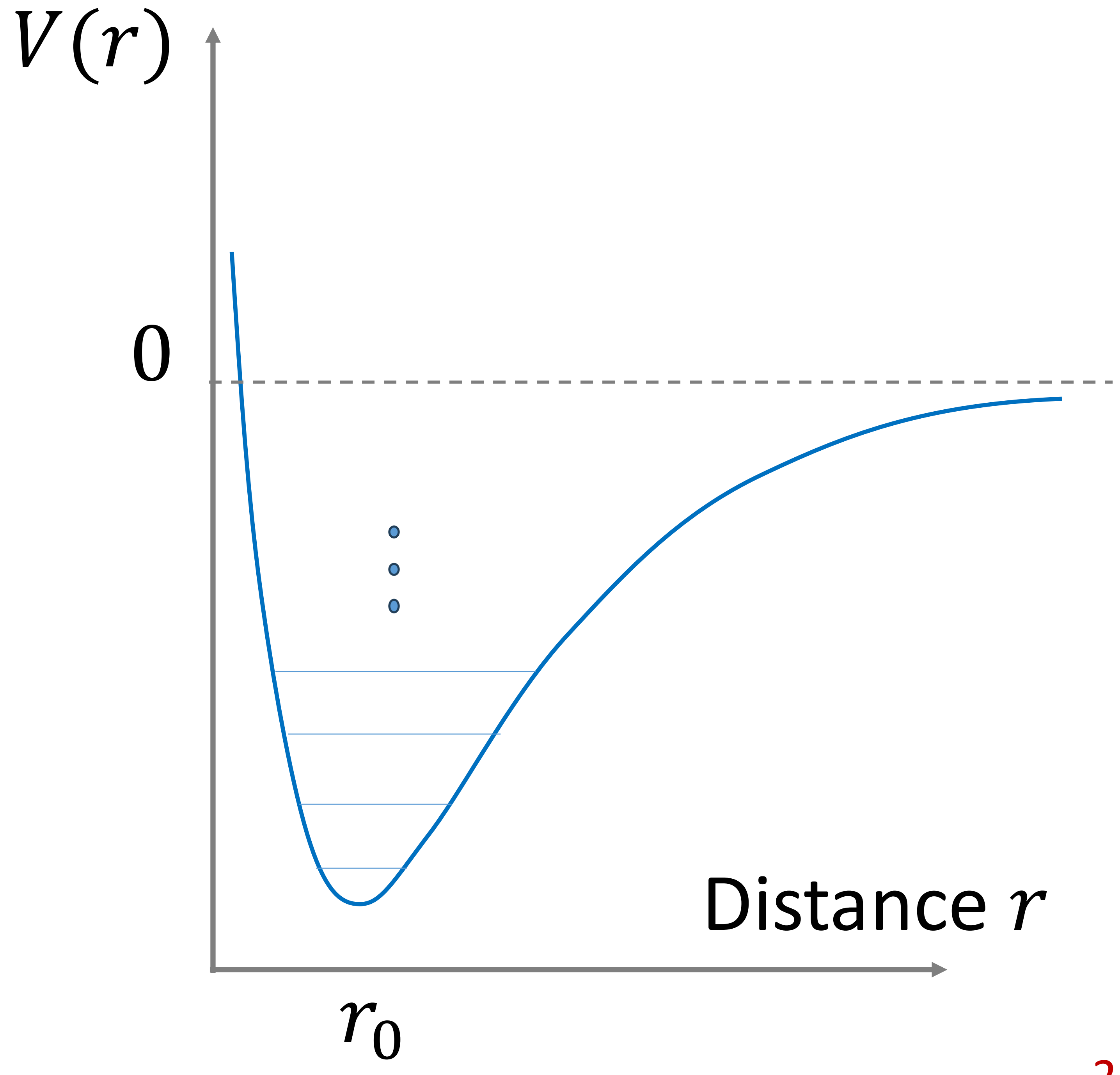
$$V(r) = \frac{1}{2}\mu\omega^2 r^2 = \frac{1}{2}k' r^2$$

- Connection vibration: $\omega = \sqrt{\frac{k'}{\mu}}$
- Energy levels $E_{\mathrm{vib},n}$:

$$E_{\mathrm{vib},n} = \left(n + \frac{1}{2}\right)\hbar\omega = \left(n + \frac{1}{2}\right)\hbar\sqrt{\frac{k'}{\mu}}$$





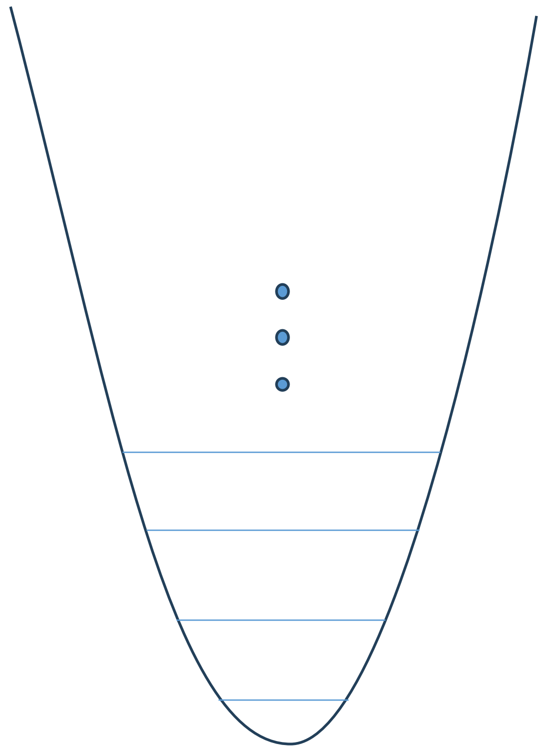


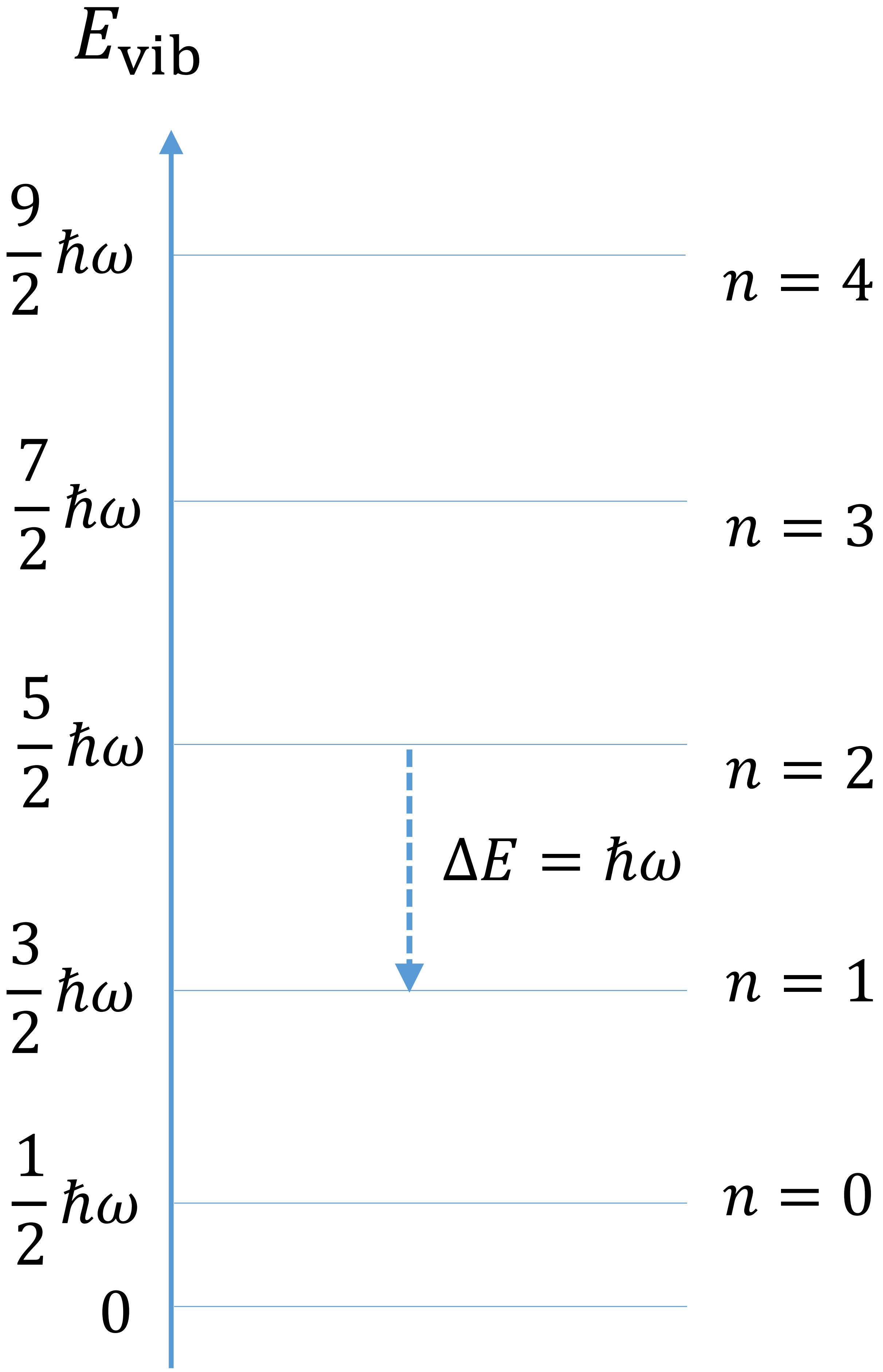
MOLECULAR SPECTRA: VIBRATIONAL ENERGY-LEVELS

- **Energy levels** $E_{\text{vib},n}$:

$$E_{\text{vib},n} = \left(n + \tfrac{1}{2}\right)\hbar\omega = \left(n + \tfrac{1}{2}\right)\hbar\sqrt{\frac{k'}{\mu}}$$

- **Selection rules** (vibration transitions):
  - Emitting a photon: $\Delta n = -1$
  - Absorbing a photon: $\Delta n = 1$
  - Higher transitions $\Delta n = \pm 2, \ \pm 3, \ldots$ possible but much smaller probability
- Transitions: $\Delta E_{\text{vib}} = \pm\hbar\omega$





MOLECULAR SPECTRA: CLASSICAL AMPLITUDE/TURNING

- **Energy levels** $E_{\text{vib},n}$:

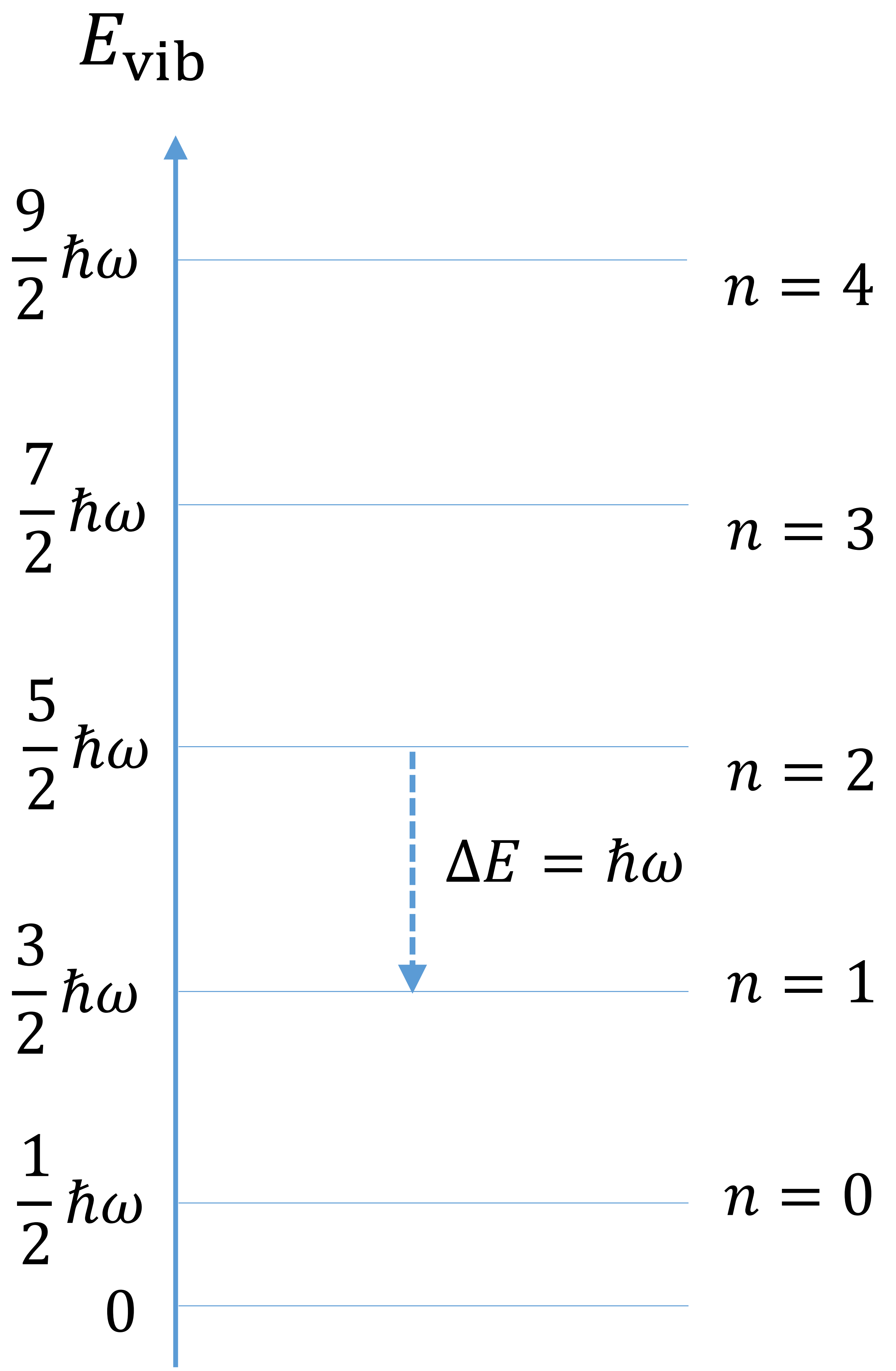
$$E_{\text{vib},n} = \left(n + \tfrac{1}{2}\right)\hbar\omega = \left(n + \tfrac{1}{2}\right)\hbar\sqrt{\frac{k'}{\mu}}$$

- **Transitions**: $\Delta E_{\text{vib}} = \pm\hbar\omega$

- Classical potential energy: $U = \frac{1}{2}k'A^2$

- **Amplitude A** or "turning point":

$$U = E_{\text{vib},n} \quad \Rightarrow \quad A = \sqrt{\frac{2E_{\text{vib},n}}{k'}}$$



EXERCISE: VIBRATIONAL ENERGY-LEVELS

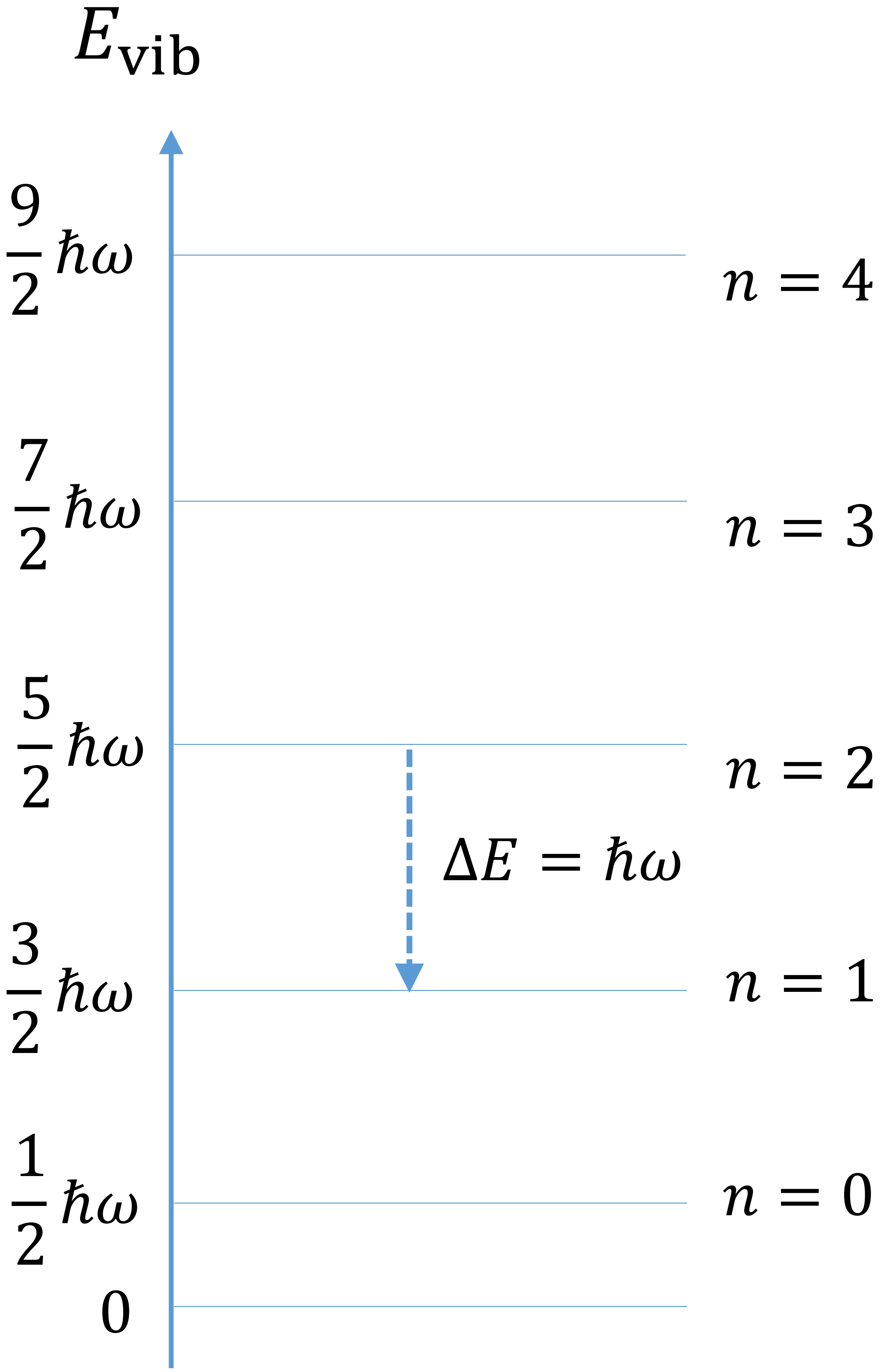
Exercise: A carbon monoxide CO molecule exist of a carbon and an oxygen atom. If you know that the vibrational state transitions from $n = 0$ to $n = 1$ by a photon with frequency $f = 64.2\ \mathrm{THz}$.

(a) Calculate the force constant k'

(b) What is the classical amplitude (turning point)?

$$E_{\mathrm{vib},n} = \left(n + \frac{1}{2}\right)\hbar\omega = \left(n + \frac{1}{2}\right)\hbar\sqrt{\frac{k'}{\mu}}$$

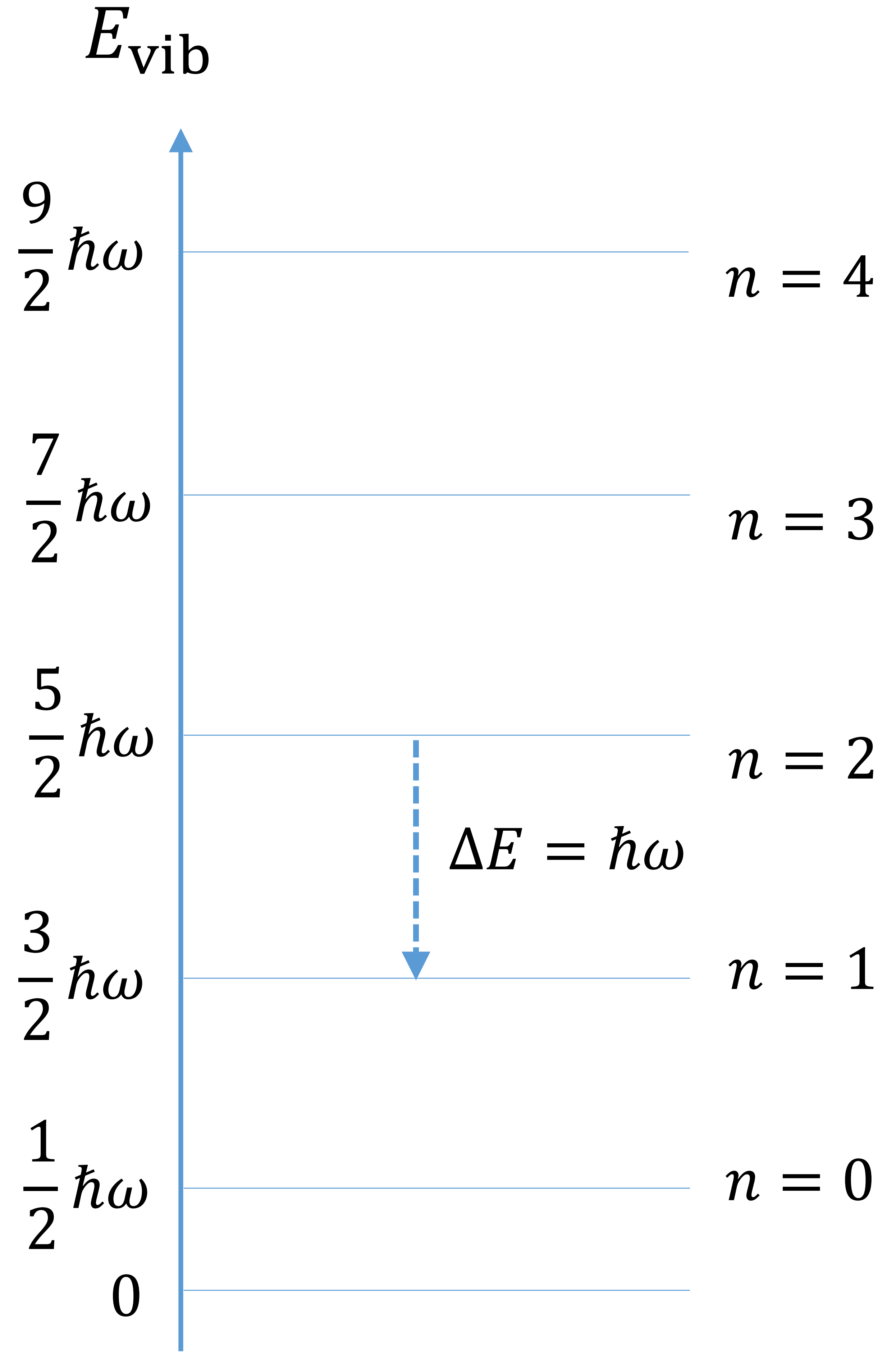
At turning point: $U = E_{\mathrm{vib},n} \quad \Rightarrow \quad A = \sqrt{\frac{2E_{\mathrm{vib},n}}{k'}}$



EXERCISE: VIBRATIONAL ENERGY-LEVELS

Exercise: A carbon monoxide CO molecule exist of a carbon and an oxygen atom separated 1.13 Å apart ($1\ \text{Å} = 10^{-10}\ \text{m}$). The energy difference for CO is $\hbar\omega = 0.269\ \text{eV}$. What is the frequency of the **molecule vibration** when in state $n\ = 5$. Assume then the molecule absorbs a photon thereby reaching a state with $n\ = 6$, what is the frequency of the **photon**?

$$E_{\text{vib},n} = \left(n + \frac{1}{2}\right)\hbar\omega = \left(n + \frac{1}{2}\right)\hbar\sqrt{\frac{k'}{\mu}}$$



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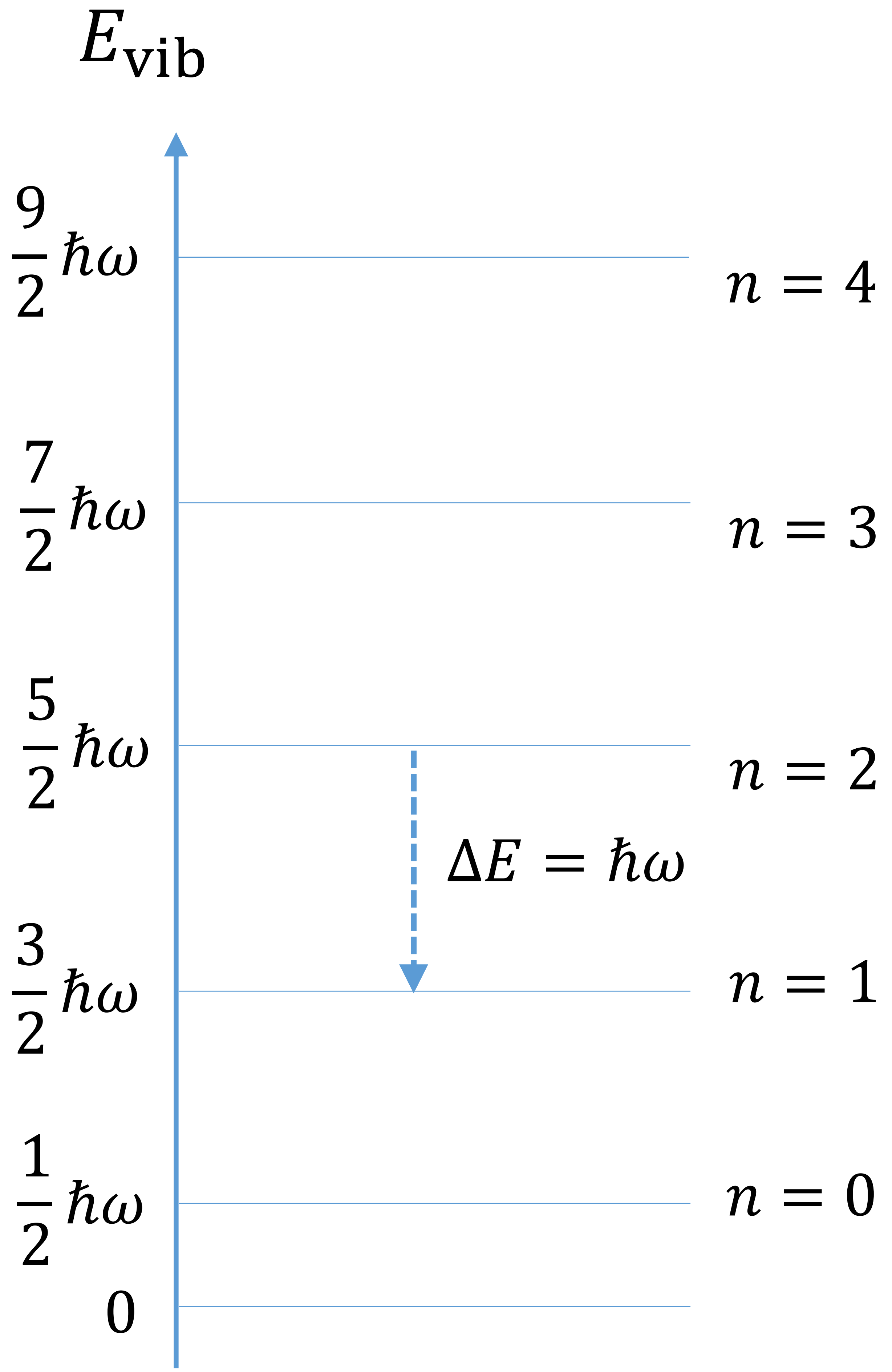
Answer:

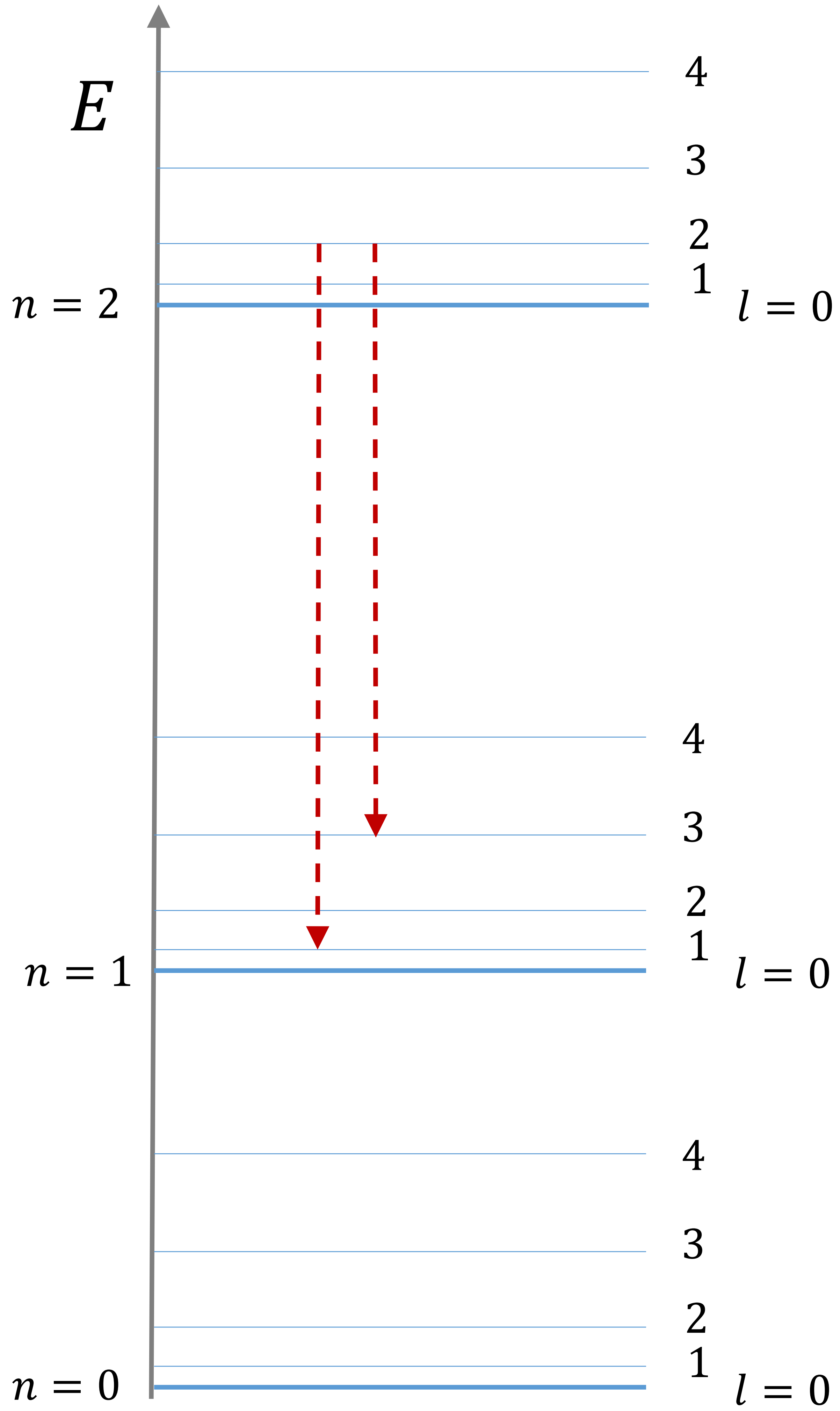


ROTATIONS AND VIBRATIONS

- **Combined** rotations and vibrations
- **Energy levels** $E_{l,n}$:

$$E_{l,n} = l(l+1)\frac{\hbar^2}{2I} + \left(n + \frac{1}{2}\right)\hbar\sqrt{\frac{k'}{\mu}}$$

- **Vibration selection rules**:
  - Emitting a photon: $\Delta n = -1$
  - Absorbing a photon: $\Delta n = 1$
- **Rotational selection rules**: $\Delta l = \pm 1$



ROTATIONS AND VIBRATIONS

- **Combined energy** rotations and vibrations

$$E_{l,n} = l(l+1)\frac{\hbar^2}{2I} + \left(n + \frac{1}{2}\right)\hbar\omega$$

- Absorption: $\Delta n = 1$ and $\Delta l = \pm 1$

$$\Delta E_+ = \hbar\omega + (l+1)\frac{\hbar^2}{I} \qquad l = 0, 1, 2, \ldots$$

$$\Delta E_- = \hbar\omega - l\frac{\hbar^2}{I} \qquad l = 1, 2, \ldots$$