Outline:
- background
- "postulates" of QM
- applications #1: particle in a box
- applications #2: atomic orbitals

Is it relevant to biology?
- sets lower bounds on size of organisms?
- specific heats of solids, energy \( \leftrightarrow \) wavelength of light

1) Background

Problems that led to QM (some of them):
- discrete spectral lines, why don't e\(^{-}\) "orbiting" nuclei crash into the nucleus?
- specific heats of solids - Law of Dulong and Petit - 1830's:
  all crystalline solids have specific heat = \( 3R \) @ high temp; goes to 0 @ 0 K
- photoelectric effect; is light a wave or a particle?
- Davisson and Germer experiment - electron diffraction

\( \Rightarrow \) read 1st 3 Chs of Feynman lectures on QM - posted on website

2) Postulates of QM (hard-core version)

Theoretical responses to the above paradoxes:
- discrete spectral lines: Niels Bohr - energies/orbitals must be quantized \( \Rightarrow E_n = -\frac{13.6}{n^2} \text{ eV} \) (for hydrogen atom)

\( \begin{align*}
&= -2 \pi^2 \text{me}^4 / \hbar^2 \quad \text{or} \\
&= -\frac{\hbar^2}{4\pi^2 m e^4} \\
&= \frac{\hbar}{m c} \\
&= \frac{1}{P} \text{-momentum}
\end{align*} \)

- de Broglie "pilot waves"
  attribute a wavelength to matter:
  \( n = \frac{P}{\hbar} \text{-momentum} \)

\( \Rightarrow \) use this to insist orbitals must have integral #s of \( n \)'s - recover
2) "Postulates" of QM (hard-way version)

<table>
<thead>
<tr>
<th>Classical Mechanics</th>
<th>Quantum Mechanics</th>
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<tbody>
<tr>
<td><strong>The &quot;state of the system&quot;</strong></td>
<td><strong>Wave function</strong></td>
</tr>
<tr>
<td>( { \hat{q}_i, \hat{p}_i } )</td>
<td>( \Psi(x) ) or ( \Psi(x, ..., \hat{p}_n) ) for ( n ) particles</td>
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<tr>
<td>position/ momentum coordinates</td>
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<tr>
<td>- describe the whole system by writing down position, momentum for each particle ( \Rightarrow ) know all history + future of system (( \sim ) Newton's laws)</td>
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<tr>
<td>- deterministic</td>
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<thead>
<tr>
<th>Evolution equations</th>
<th>Time-dependent Schrodinger eqn:</th>
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<tbody>
<tr>
<td>(time dependence/ order of the system)</td>
<td>( \hat{H} \Psi = \hat{H} \Psi )</td>
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<tr>
<td>- Hamiltonian ( (\text{basically } F=ma) )</td>
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<tr>
<td>- Lagrangian/Hamiltonian version of mechanics</td>
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<td>Feynman noted lecture power of stating the same problem multiple ways</td>
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<th>Observables + measurements</th>
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<td>Any mechanical variable we might be interested in is a function of ( \hat{q}_i, \hat{p}_i )</td>
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<tr>
<td>eg. energy for harmonic oscillator ( E = \frac{\hat{p}^2}{2m} + \frac{1}{2}k\hat{q}^2 )</td>
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<tr>
<td>angular momentum ( \hat{L} = \hat{\vec{r}} \times \hat{\vec{p}} )</td>
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<tr>
<td>(</td>
<td>\Psi(x)</td>
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<tr>
<td>( \Rightarrow ) not deterministic, probability density</td>
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<tr>
<td>- the &quot;expected value&quot; of an observable ( \hat{O} ) is given by ( \langle \hat{O} \rangle = \int \Psi^*(x) \hat{O} \Psi(x) , dx )</td>
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<tr>
<td>- basically a weighted avg, weighted by the probability</td>
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<td>An observable could be energy, ...</td>
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</table>
more on observables in QM:

in QM observables are represented by operators, e.g.

momentum: \( \hat{p} = -i\hbar \frac{d}{dx} \)

energy might be: \( \hat{H} = \frac{i\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2}kx^2 \)

angular momentum: \( \hat{L} = \hat{r} \hat{x} \hat{p} \) but replace \( \hat{p} \) by \( i\hbar \frac{d}{dx} \) or something

Free electron gas model:
look up the bulk moduli for Na, Li, K, etc - it's not such a bad model to say they're boxes containing free electrons; so we'll model pigments like lycopene as one long box of free electrons

the other extreme of models: atomic orbital theories: s, p, d, etc orbitals for an atom - these are the angular parts of the wave equation; radically they decay exponentially; so another model is the total \( \psi \) for a molecule is a sum of the wave functions for the individual atoms - there's only a small perturbation in bonding

3. Particle in a box in 1D:

\[
v(x) = \begin{cases} 0 & 0 < x < a \\ \infty & \text{otherwise} \end{cases}
\]

\[
\frac{-\hbar^2}{2m} \frac{d^2 \psi}{dx^2} + V(x) \psi = E \psi
\]

\[
0 < x < a:
\frac{-\hbar^2}{2m} \frac{d^2 \psi}{dx^2} = E \psi 
\Rightarrow \frac{d^2 \psi}{dx^2} + \frac{2mE}{\hbar^2} \psi = 0
\]

\[
\Rightarrow \psi(x) = A \cos \sqrt{\frac{2mE}{\hbar^2}}x + B \sin \sqrt{\frac{2mE}{\hbar^2}}x
\]
Imposing boundary conditions:
\[ \psi(0) = \psi(a) = 0 \quad \Rightarrow \quad \psi(x) = B \sin \sqrt{\frac{2mE}{\hbar^2}} x \]

and \[ \sqrt{\frac{2mE}{\hbar^2}} a = n \pi \Rightarrow E_n = \frac{n^2 \pi^2 \hbar^2}{2ma^2} \]

Now, toy model for a molecular bond:
Bond energy = diff. between energies of two atoms separated
and the energies of them together

atom 1: \[ \text{atom 2: } \]

\[ E \] \quad \text{1st eigenfunction}

\[ \frac{E}{\hbar^2 \pi^2 / 2ma^2} \]

\[ \chi \]

\[ \text{2nd eigenfunction} \]

Now, in the 2 separate atoms, \( n = 1 \) for both, so total energy:
\[ E = 2 \frac{\hbar^2 \pi^2}{2ma^2} \]

What about in the "molecule"? \( n = 1 \) still!
\[ E = 2 \frac{\hbar^2 \pi^2}{2m(ax)^2} \]

the size has changed!
There's 2 electrons

\[ E_{\text{bond}} = 2 \left( \frac{\hbar^2 \pi^2}{2ma^2} - \frac{\hbar^2 \pi^2}{2ma^2} \right) = \frac{\hbar^2 \pi^2}{ma^2} \]

\[ \alpha > 1 \text{ so term is negative} \]

What is \( \alpha \) usually? Size of a C-C bond = 1.3 Å
energy of a typical molecular bond: a glucose is worth $\approx 2800 \frac{kJ}{mol}$

$\approx 5 \text{ eV/bond}$

$$E_{\text{bond}} = \frac{n^2 \pi^2}{ma^2} \left(1 - \frac{\alpha}{\alpha^2}\right) \approx \frac{1}{4\pi^2} \frac{(6 \times 10^{34} \text{ J/s})^2}{(9 \times 10^{-31} \text{ kg})(10^{-10} \text{ m})^2} \left(1 - \frac{\alpha}{\alpha^2}\right)$$

$\approx -\frac{36}{4} \times 10^{-68} \frac{10^{-30}}{10^{-20}}$

$\approx -9 \times 10^{-18} \approx -10^{-17} \text{ J} \left(1 - \frac{\alpha}{\alpha^2}\right)$

(about a factor of 5 too large, but not physically still close!)

(and negative because it's a bonding orbital)

for ex, let $\alpha = 2$: then $\frac{1 - \alpha^2}{\alpha^2} = \frac{3}{4}$ so $E_{\text{bond}} = -\frac{3}{4} \times 10^{-17} \text{ J}$
Plan of action:
- Background;
- “Postulates” of QM;
- Application #1: Particle in a Box
  Application #2: Atomic orbitals;

Hints leading to QM:
- Discrete spectral lines;
- Specific heats of solids (Law of Dulong and Petit, 3R);
- Photoelectric effect;
- Davisson-Gerner experiment (electron diffraction);

Theoretical Responses:
- Discrete spectral lines: Niels Bohr →
  \[ E_n = -\frac{13.6}{n^2} - eV = -\frac{2\pi^2 me^4}{\hbar^2} \frac{1}{n^2}; \]
- De Broglie: “pilot waves”
  Attribute a wavelength to matter: \( \lambda = \frac{h}{p} \);

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<td>“wave function” ( \psi(\vec{x}) )</td>
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| 2) Evolution Equations      |                     |                     |
| \( \dot{p}_i = -\frac{\partial H}{\partial q_i}; \dot{q}_i = \frac{\partial H}{\partial p_i} \) | \( i\hbar \frac{\partial \psi}{\partial t} = \hat{H}\psi \) |

| 3) Observables and measurements | Any mechanical variable we might be interested in is a function of \( p \)'s and \( q \)'s, e.g. \( E = \frac{p^2}{2m} + \frac{1}{2} kq^2 \) | i) \( |\psi(x)|^2 \, dx \equiv \text{probability that particle will be found between } x \text{ and } x+dx \)
| ii) “Expected” value of an observable, \( \hat{C} \), is given by \( \langle \psi | \hat{C} | \psi \rangle = \int \psi^*(x) \hat{C} \psi \) |

Question: What observables?

In QM, observables are represented by “operators”

3D: \( \vec{p} = -i\hbar \vec{V} \); 1D: \( p_x = -i\hbar \frac{d}{dx} \)

**Particle in a box:**

Schrödinger equation:
\[-\frac{\hbar^2}{2m} \frac{d^2 \psi}{dx^2} + V(x) \psi = E \psi\]
\[V(x) = 0\]

by rearranging:
\[\frac{d^2 \psi}{dx^2} + \frac{2mE}{\hbar^2} \psi = 0 \rightarrow \psi = A \cos \sqrt{\frac{2mE}{\hbar^2}} x + B \sin \sqrt{\frac{2mE}{\hbar^2}} x\]

Boundary conditions: \(\psi(0) = \psi(na) = 0 \rightarrow \text{ditch cosine}\)

\[\sqrt{\frac{2mE}{\hbar^2}} a = n \pi \rightarrow E_n = \frac{\hbar^2 \pi^2 n^2}{2ma^2}\]

**Toy model of molecular binding:**

\[E_{\text{atom}} = 2 \times \frac{\hbar^2 \pi^2}{2ma^2}\]
\[E_{\text{molecule}} = 2 \times \frac{\hbar^2 \pi^2}{2m(aa)^2}\]

\[E_{\text{bond}} = 2 \cdot \left(\frac{\hbar^2 \pi^2}{2ma^2} - \frac{\hbar^2 \pi^2}{2ma^2}\right) = \frac{\hbar^2 \pi^2}{ma^2} \left(1 - \frac{\alpha^2}{\alpha^2}\right)\]

\[E_{\text{bond}} \approx \frac{(6 \times 10^{-34} \text{ J} \cdot \text{s})^2 \pi^2}{4 \pi^2 (9 \times 10^{-31} \text{ kg})(10^{-10} \text{ m})^2} = \frac{36 \times 10^{-68}}{4 \times 10^{-30} \times 10^{-20}} = 9 \times 10^{-18} \text{ J} \approx 10^{-17} \text{ J}\]