Quantum - Molecular Structures & Interactions

Basis of everything!
Bonding
Spectroscopy

Subfields relevant to biochemistry:

Molecular Dynamics - change over time
Molecular Mechanics - change to lowest $E$

Wave-Particle Duality - electrons (and everything, but...)
electrons exhibit both particle and wave properties

Electron diffraction - clear demonstration of wave.
(Just like x-ray diffraction, light diffraction).

\[ \lambda = \frac{h}{mv} = \frac{\text{Planck's Const}}{\text{momentum of particle}} \]

\textit{WAVE NATURE}

Wave function: $\Psi = \Psi(x,y,z,\tau) \Rightarrow \text{FULL DESCR}$

$\Psi$ is not useful for us

$\Psi^2$ is useful $\Rightarrow$ probability predicts & distribution
Probability of finding the $e^-$ in a small volume around $x_0, y_0, z_0$

\[ \text{Prob} = \left[ \psi_n(x_0, y_0, z_0) \right]^2 \Delta V \]

Prob for a finite volume: \( \int \left[ \psi_n(x, y, z) \right]^2 \, dV \)

integral over $x$, $y$, and $z$

Note that

\[ \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \left[ \psi_n(x, y, z) \right]^2 \, dx \, dy \, dz = 1 = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \psi^2 \, dV \]

"Probability" reflects the uncertainty principle.
We can only predict probabilities.

Note: $\psi$ describes probability for one electron

Fortunately, we're often focusing on a single valence electron, in spectroscopy, for example.
Now, but related, Concept

\[ \bar{\psi} = \sum \psi_n \bar{\psi}_n \, d\mathbf{r} \]

Predicts:
- momentum
- energy
- position
- dipole moment

pp. 452-454 Give good, practical guidance.
Come back to, if you need it.

Expectation value for E (energy)

Particle in a box.

Consider an $e^0$ constrained as above. For $x > 0$ and $x < a$, then the $e^0$'s potential energy is zero.

In this simple system, we define that if the $e^0$ strays \( \leq 0 \) or \( \geq a \), then it's energy becomes infinite.
Result (at least classically): the $\varphi$ stays in the box

Q: Why "the box"?

What is it a model of? $\Rightarrow$ orbital

Not a perfect model, but...

Define: potential energy $= U(x) \quad \text{keep this 1D for simplicity}$

$\overline{E} = \sum n = \varphi_n d\nu$

Energy $\quad \uparrow$

"Hamiltonian" operator $\downarrow$

describes $E$

p. 450 shows you that $\mathcal{H} \varphi = E \varphi$

$$\left[ -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + U(x) \right] \varphi = E \varphi \quad (\text{1D})$$

$$\left[ -\frac{\hbar^2}{2m} \nabla^2 + U \right] \varphi = E \varphi \quad (\text{3D})$$

Don't get excited...
So for particle in a box,

\[ \frac{-h^2}{2m} \frac{d^2}{dx^2} \psi_n + U(x) \psi_n = E_n \psi_n \]

\[ U(x) = 0 \quad 0 < x < a \]
\[ U(x) = \infty \quad x \leq 0 \quad x \geq a \]

So outside the box, the particle will not exist (infinitely high energy). \( \psi \) outside = 0

We're left with \[ \frac{-h^2}{2m} \frac{d^2}{dx^2} \psi_n + \psi_n = E_n \psi_n \]

Solution is:

\[ \psi = A \sin b x + B \cos b x \]

Boundary Conditions: when \( x = 0 \) \( \psi \to 0 \)

So

\[ A \sin(0) + B \cos(0) = 0 \]

\[ \therefore B = 0 \]

\[ \psi = A \sin b x \] but \( \psi(a) = 0 = A \sin b a \)

\[ \Rightarrow b x = n \pi \quad \therefore b = \frac{n \pi}{a} \]

\( \uparrow \)
\( (a) \)

\[ \therefore \psi = A \sin(\frac{n \pi}{a} x) \]
Finally: \( \int_0^a \gamma^2(x) \, dx = 1 \) why?

\[
A^2 \int_0^a \sin^2 \left( \frac{\pi n}{a} x \right) \, dx
\]

\[
A = \sqrt{\frac{2}{a}}
\]

\[
\gamma = \sqrt{\frac{2}{a}} \sin \left( \frac{\pi n}{a} x \right)
\]