

Worksheet 5. **KEY**

1. Write a Slater determinant of orbitals that is appropriate for the *ground* state of the Boron atom. Use the long form of the Slater determinant, writing out all the rows and columns.

$$\Psi = \frac{1}{\sqrt{5!}} \begin{vmatrix} \phi_{1s}(\mathbf{r}_1)\alpha(1) & \phi_{1s}(\mathbf{r}_1)\beta(1) & \phi_{2s}(\mathbf{r}_1)\alpha(1) & \phi_{2s}(\mathbf{r}_1)\beta(1) & \phi_{2p_x}(\mathbf{r}_1)\alpha(1) \\ \phi_{1s}(\mathbf{r}_2)\alpha(2) & \phi_{1s}(\mathbf{r}_2)\beta(2) & \phi_{2s}(\mathbf{r}_2)\alpha(2) & \phi_{2s}(\mathbf{r}_2)\beta(2) & \phi_{2p_x}(\mathbf{r}_2)\alpha(2) \\ \phi_{1s}(\mathbf{r}_3)\alpha(3) & \phi_{1s}(\mathbf{r}_3)\beta(3) & \phi_{2s}(\mathbf{r}_3)\alpha(3) & \phi_{2s}(\mathbf{r}_3)\beta(3) & \phi_{2p_x}(\mathbf{r}_3)\alpha(3) \\ \phi_{1s}(\mathbf{r}_4)\alpha(4) & \phi_{1s}(\mathbf{r}_4)\beta(4) & \phi_{2s}(\mathbf{r}_4)\alpha(4) & \phi_{2s}(\mathbf{r}_4)\beta(4) & \phi_{2p_x}(\mathbf{r}_4)\alpha(4) \\ \phi_{1s}(\mathbf{r}_5)\alpha(5) & \phi_{1s}(\mathbf{r}_5)\beta(5) & \phi_{2s}(\mathbf{r}_5)\alpha(5) & \phi_{2s}(\mathbf{r}_5)\beta(5) & \phi_{2p_x}(\mathbf{r}_5)\alpha(5) \end{vmatrix}$$

2. **Properties of the Second Derivative Operator.**

In this problem, you will derive some properties of the second derivative operator,

$$\left\langle \Psi(x) \left| \frac{d^2}{dx^2} \right| \Psi(x) \right\rangle$$

- 2a. **Explicitly show that the second derivative operator is Hermitian.**

You can do this by (double) integration by parts, but it is easier to remember to remember the link between the second derivative and the momentum operator, $\hat{p}^2 = -\hbar^2 \frac{d^2}{dx^2}$. Then, using the fact the momentum is Hermitian, we have:

$$\begin{aligned} \int \Psi_1^*(x) \left(\frac{d^2}{dx^2} \right) \Psi_2(x) dx &= \int \Psi_1^*(x) \left(\frac{-1}{\hbar^2} \right) \hat{p}_x \cdot \hat{p}_x \Psi_2(x) dx \\ &= \left(\frac{-1}{\hbar^2} \right) \int \Psi_1^*(x) \hat{p}_x \cdot \hat{p}_x \Psi_2(x) dx \\ &= \left(\frac{-1}{\hbar^2} \right) \int \left(\hat{p}_x \Psi_1(x) \right)^* \hat{p}_x \Psi_2(x) dx \\ &= \left(\frac{-1}{\hbar^2} \right) \int \left(\hat{p}_x \cdot \hat{p}_x \Psi_1(x) \right)^* \Psi_2(x) dx \\ &= \int \left(\frac{-1}{\hbar^2} \hat{p}_x \cdot \hat{p}_x \Psi_1(x) \right)^* \Psi_2(x) dx \\ &= \int \left(\frac{d^2}{dx^2} \Psi_1(x) \right)^* \Psi_2(x) dx \end{aligned}$$

- 2b. **Explicitly show that the second derivative operator is negative semidefinite.**

That is, show that for any wavefunction, $\Psi(x)$,

$$\left\langle \Psi(x) \left| \frac{d^2}{dx^2} \right| \Psi(x) \right\rangle \leq 0.$$

The key to this is to note that the wavefunction must be zero at the boundaries of the interval. So if I look at

$$\begin{aligned}
\int_a^b \frac{d^2\Psi^*(x)\Psi(x)}{dx^2} dx &= \left. \frac{d\Psi^*(x)\Psi(x)}{dx} \right|_a^b \\
&= \left(\left. \frac{d\Psi^*(x)}{dx} \right|_{x=b} \Psi(b) + \Psi^*(b) \left. \frac{d\Psi(x)}{dx} \right|_{x=b} \right) \\
&\quad - \left(\left. \frac{d\Psi^*(x)}{dx} \right|_{x=a} \Psi(a) + \Psi^*(a) \left. \frac{d\Psi(x)}{dx} \right|_{x=a} \right) \\
&= 0
\end{aligned}$$

The first line is the fundamental theorem of calculus and the last line follows because the wavefunction vanishes at the boundary of the system, $\Psi(a) = \Psi^*(a) = \Psi(b) = \Psi^*(b) = 0$.

Now simplify the right-hand-side of this equation. I have:

$$\begin{aligned}
\int_a^b \frac{d^2\Psi^*(x)\Psi(x)}{dx^2} dx &= 0 \\
\int_a^b \frac{d}{dx} \left(\frac{d\Psi^*(x)}{dx} \Psi(x) + \frac{d\Psi(x)}{dx} \Psi^*(x) \right) dx &= 0 \\
\int_a^b \frac{d^2\Psi^*(x)}{dx} \Psi(x) + \frac{d^2\Psi(x)}{dx} \Psi^*(x) + 2 \underbrace{\frac{d\Psi^*(x)}{dx} \frac{d\Psi(x)}{dx}}_{\text{this is a function times its complex conjugate}} dx &= 0 \\
\underbrace{\int_a^b \frac{d^2\Psi^*(x)}{dx} \Psi(x) + \Psi^*(x) \frac{d^2\Psi(x)}{dx} dx}_{\text{the two terms are equal because } \frac{d^2}{dx^2} \text{ is Hermitian}} &= -2 \int \underbrace{\left| \frac{d\Psi(x)}{dx} \right|^2}_{\text{the integrand is nonnegative everywhere so the integral is positive}} dx \\
2 \int_a^b \Psi^*(x) \frac{d^2\Psi(x)}{dx} dx &= -2(\text{positive number}) \\
\int_a^b \Psi^*(x) \frac{d^2\Psi(x)}{dx} dx &= (\text{negative number})
\end{aligned}$$

3. Atomic Diffraction and Neutron Diffraction.

Suppose we use a beam of Helium-4 atoms to image a crystal, in a manner similar to X-ray crystallography. Assume that the ${}^4_2\text{He}$ atoms are in thermal equilibrium at temperature T . From fundamental thermodynamics, we know that the kinetic energy of the Helium atoms is

$$\text{kinetic energy} = \frac{3}{2} k_B T \quad (2)$$

where k_B is Boltzmann's constant. Suppose that the substance we want to diffract the Helium atoms from crystallizes in a simple cubic lattice with lattice constant (i.e., nearest-neighbor distance) $a = 3.0 \cdot 10^{-10} \text{ m}$.

3a. At what temperature would diffraction of the ${}^4_2\text{He}$ atoms become appreciable?

The atoms will diffract only if the wavelength of the atoms is similar to the spacing between the atoms in the lattice. So we need to have

$$2.0 \cdot 10^{-10} \text{ m} \approx \lambda_{\text{He}}$$

The wavelength of the Helium atoms is determined by the De Broglie relation,

$$\lambda_{\text{He}} = \frac{h}{p}$$

and the momentum of the Helium atoms is determined from their kinetic energy as:

$$\begin{aligned} \frac{p^2}{2m} &= (\text{k.e.}) \\ p &= \sqrt{2m_{\text{He}} (\text{k.e.})} = \sqrt{2m_{\text{He}} \left(\frac{3}{2}\right) k_B T} = \sqrt{3m_{\text{He}} k_B T} \end{aligned}$$

Putting it all together

$$\begin{aligned} 2.0 \cdot 10^{-10} \text{ m} \approx \lambda_{\text{He}} &= \frac{h}{\sqrt{3m_{\text{He}} k_B T}} \\ \sqrt{3m_{\text{He}} k_B T} &\approx \frac{h}{(2.0 \cdot 10^{-10} \text{ m})} \\ T &\approx \frac{1}{3k_B m_{\text{He}}} \left(\frac{h}{2.0 \cdot 10^{-10} \text{ m}} \right)^2 \end{aligned}$$

From this we can already answer parts (b) and (c). Colder and more massive particles have bigger De Broglie wavelengths. So if we increase the lattice spacing, we need to decrease the temperature. (Alternative viewpoint: look at the last equation. Replacing $2.0 \cdot 10^{-10} \text{ m}$ with a bigger number decreases the temperature.) So the answer to (c) is (ii). If we decrease the mass of the particle we are using for diffraction, the temperature increases. (That is, all else being equal, lighter particles have less momentum and larger De Broglie wavelengths.) So the answer to (b) is (i).

Finally, substituting in for the Helium case gives

$$\begin{aligned} T &\approx \frac{1}{3k_B m_{\text{He}}} \left(\frac{h^2}{2.0 \cdot 10^{-10} \text{ m}} \right) \\ &= \frac{1}{3 \left(1.381 \cdot 10^{-23} \frac{\text{J}}{\text{K}} \right) (4.0 \text{ u})} \left(\frac{6.626 \cdot 10^{-34} \text{ J} \cdot \text{s}}{2.0 \cdot 10^{-10} \text{ m}} \right)^2 \\ &= \left(\frac{1}{4.143 \cdot 10^{-23} \text{ J} \cdot (4.0 \text{ u}) (1.661 \cdot 10^{-27} \frac{\text{kg}}{\text{u}})} \right) (1.098 \cdot 10^{-47}) \frac{\text{J}^2 \text{s}^2 \text{K}}{\text{m}^2} \\ &= (39.9) \left(\frac{\text{J}^2 \text{s}^2 \cdot \text{K}}{\text{J} \cdot \text{kg} \cdot \text{m}^2} \right) \\ &= 39.9 \left(\frac{\text{J} \cdot \text{s}^2 \cdot \text{K}}{\text{kg} \cdot \text{m}^2} \right) \\ &= 39.9 \left(\frac{(\text{kg} \cdot \frac{\text{m}^2}{\text{s}^2}) \cdot \text{s}^2 \cdot \text{K}}{\text{kg} \cdot \text{m}^2} \right) \\ &= 39.9 \text{ K} \end{aligned}$$

Given the accuracy of this sort of heuristic argument, what we learn is that the temperature of the Helium atoms in the beam needs to be **roughly 40 K.**

- 3b. Suppose we use thermal neutrons, instead of ${}^4_2\text{He}$ to diffract off the crystal. **Would the optimal temperature of the neutrons be smaller or larger than that of the Helium atoms in part (a)?**

(i) $T_{\text{neutrons}} > T_{\text{Helium}}$

(ii) $T_{\text{neutrons}} < T_{\text{Helium}}$

- 3c. Suppose we now decide to diffract ${}^4_2\text{He}$ from a cubic lattice with a slightly smaller lattice constant, $a = 2.8 \cdot 10^{-10} \text{ m}$. **Should the temperature of the Helium atom beam be increased or decreased in order to optimize diffraction.**

(i) $T_{\text{He for .28 nm}} > T_{\text{He for .20 nm}}$ (increase T)

(ii) $T_{\text{He for .28 nm}} < T_{\text{He for .20 nm}}$ (decrease T)

4. Mathematical results related to infinitesimal unitary transformations.

Let $\hat{C}(\tau)$ be a time-independent Hermitian operator. Let $\Psi_k(\tau)$ denote the eigenfunctions of the Hamiltonian, $\hat{H}(\tau)$. Denote the ground-state wavefunction as $\Psi_0(\tau)$.

- 4a. **Show that for any eigenfunction of the Hamiltonian, the following expectation value is zero:**

$$\left\langle \Psi_k \left| \left[\hat{H}, \hat{C} \right] \right| \Psi_k \right\rangle = 0$$

First expand out the commutator. Then use the eigenvalue condition, $\hat{H}\Psi_k = E_k\Psi_k$ and the Hermitian property to simplify the expression.

$$\begin{aligned} \left\langle \Psi_k \left| \left[\hat{H}, \hat{C} \right] \right| \Psi_k \right\rangle &= \left\langle \Psi_k \left| \hat{H}\hat{C} - \hat{C}\hat{H} \right| \Psi_k \right\rangle \\ &= \left\langle \Psi_k \left| \hat{H}\hat{C}\Psi_k \right\rangle - \left\langle \Psi_k \left| \hat{C}\hat{H}\Psi_k \right\rangle \right. \\ &= \left\langle \hat{H}\Psi_k \left| \hat{C}\Psi_k \right\rangle - \left\langle \Psi_k \left| \hat{C}E_k\Psi_k \right\rangle \right. && \left(\begin{array}{l} \text{use Hermitian property in the} \\ \text{first term; use eigenvalue cond.} \\ \text{in the second term} \end{array} \right) \\ &= \left\langle E_k\Psi_k \left| \hat{C}\Psi_k \right\rangle - E_k \left\langle \Psi_k \left| \hat{C}\Psi_k \right\rangle \right. \\ &= E_k \left\langle \Psi_k \left| \hat{C}\Psi_k \right\rangle - E_k \left\langle \Psi_k \left| \hat{C}\Psi_k \right\rangle \right. \\ &= 0 \end{aligned}$$

- 4b. **Show that the expectation value of the following double-commutator is always greater than or equal to zero for the ground-state wavefunction,**

$$\left\langle \Psi_0 \left| \left[\hat{C}, \left[\hat{H}, \hat{C} \right] \right] \right| \Psi_0 \right\rangle \geq 0$$

First expand out the double commutator,

$$\begin{aligned}
\left\langle \Psi_0 \left| \left[\hat{C}^\dagger, [\hat{H}, \hat{C}] \right] \right| \Psi_0 \right\rangle &= \left\langle \Psi_0 \left| \hat{C}^\dagger [\hat{H}, \hat{C}] - [\hat{H}, \hat{C}] \hat{C}^\dagger \right| \Psi_0 \right\rangle \\
&= \left\langle \Psi_0 \left| \hat{C}^\dagger (\hat{H}\hat{C} - \hat{C}\hat{H}) - (\hat{H}\hat{C} - \hat{C}\hat{H}) \hat{C}^\dagger \right| \Psi_0 \right\rangle \\
&= \left\langle \Psi_0 \left| \hat{C}^\dagger \hat{H}\hat{C} - \hat{C}^\dagger \hat{C}\hat{H} - \hat{H}\hat{C}\hat{C}^\dagger + \hat{C}\hat{H}\hat{C}^\dagger \right| \Psi_0 \right\rangle \\
&= \left\langle \Psi_0 \left| \hat{C}^\dagger \hat{H}\hat{C} - \hat{C}^\dagger \hat{C}\hat{H} + \hat{C}\hat{H}\hat{C}^\dagger - \hat{H}\hat{C}\hat{C}^\dagger \right| \Psi_0 \right\rangle \\
&= \left\langle \Psi_0 \left| \hat{C}^\dagger \hat{H}\hat{C} \right| \Psi_0 \right\rangle - \left\langle \Psi_0 \left| \hat{C}^\dagger \hat{C}\hat{H} \right| \Psi_0 \right\rangle \\
&\quad + \left\langle \Psi_0 \left| \hat{C}\hat{H}\hat{C}^\dagger \right| \Psi_0 \right\rangle - \left\langle \Psi_0 \left| \hat{H}\hat{C}\hat{C}^\dagger \right| \Psi_0 \right\rangle
\end{aligned}$$

Use the Hermitian property, $\left\langle \Psi_0 \left| \hat{C}^\dagger \hat{C} \Psi_0 \right\rangle = \left\langle \hat{C} \Psi_0 \left| \hat{C} \Psi_0 \right\rangle$, and the eigenvalue property, $\hat{H}\Psi_0 = E_0\Psi_0$, to simplify these terms, obtaining

$$\begin{aligned}
\left\langle \Psi_0 \left| \left[\hat{C}^\dagger, [\hat{H}, \hat{C}] \right] \right| \Psi_0 \right\rangle &= \left\langle \Psi_0 \left| \hat{C}^\dagger \hat{H}\hat{C} \right| \Psi_0 \right\rangle - \left\langle \Psi_0 \left| \hat{C}^\dagger \hat{C}\hat{H} \right| \Psi_0 \right\rangle \\
&\quad + \left\langle \Psi_0 \left| \hat{C}\hat{H}\hat{C}^\dagger \right| \Psi_0 \right\rangle - \left\langle \Psi_0 \left| \hat{H}\hat{C}\hat{C}^\dagger \right| \Psi_0 \right\rangle \\
&= \left\langle \hat{C}\Psi_0 \left| \hat{H} \right| \hat{C}\Psi_0 \right\rangle - \left\langle \Psi_0 \left| \hat{C}^\dagger \hat{C} E_0 \right| \Psi_0 \right\rangle \\
&\quad + \left\langle \hat{C}^\dagger \Psi_0 \left| \hat{H} \right| \hat{C}^\dagger \Psi_0 \right\rangle - \left\langle \hat{H}\Psi_0 \left| \hat{C}\hat{C}^\dagger \right| \Psi_0 \right\rangle \\
&= \left\langle \hat{C}\Psi_0 \left| \hat{H} \right| \hat{C}\Psi_0 \right\rangle - E_0 \left\langle \hat{C}\Psi_0 \left| \hat{C}\Psi_0 \right\rangle \right. \\
&\quad + \left\langle \hat{C}^\dagger \Psi_0 \left| \hat{H} \right| \hat{C}^\dagger \Psi_0 \right\rangle - \left\langle E_0 \Psi_0 \left| \hat{C}\hat{C}^\dagger \right| \Psi_0 \right\rangle \\
&= \left\langle \hat{C}\Psi_0 \left| \hat{H} \right| \hat{C}\Psi_0 \right\rangle - E_0 \left\langle \hat{C}\Psi_0 \left| \hat{C}\Psi_0 \right\rangle \right. \\
&\quad + \left\langle \hat{C}^\dagger \Psi_0 \left| \hat{H} \right| \hat{C}^\dagger \Psi_0 \right\rangle - E_0 \left\langle \hat{C}^\dagger \Psi_0 \left| \hat{C}^\dagger \Psi_0 \right\rangle \right.
\end{aligned}$$

Because $\hat{C}\Psi_0$ is itself a wavefunction, we can expand it in terms of the full set of eigenfunctions of the Hamiltonian. So

$$\begin{aligned}
\hat{C}\Psi_0 &= \sum_{k=0}^{\infty} c_k \Psi_k & \hat{H}\Psi_k &= E_k \Psi_k \\
\hat{C}^\dagger \Psi_0 &= \sum_{k=0}^{\infty} d_k \Psi_k & \hat{H}\Psi_k &= E_k \Psi_k
\end{aligned}$$

Substituting in these expressions, and using the fact that the eigenfunctions are orthogonal, we have:

$$\begin{aligned}
\left\langle \Psi_0 \left[\hat{C}^\dagger, [\hat{H}, \hat{C}] \right] \Psi_0 \right\rangle &= \left\langle \hat{C} \Psi_0 \left| \hat{H} \right| \hat{C} \Psi_0 \right\rangle - E_0 \left\langle \hat{C} \Psi_0 \left| \hat{C} \Psi_0 \right\rangle \right. \\
&\quad + \left\langle \hat{C}^\dagger \Psi_0 \left| \hat{H} \right| \hat{C}^\dagger \Psi_0 \right\rangle - E_0 \left\langle \hat{C}^\dagger \Psi_0 \left| \hat{C}^\dagger \Psi_0 \right\rangle \right. \\
&= \left\langle \sum_{l=0}^{\infty} c_l \Psi_l \left| \hat{H} \right| \sum_{k=0}^{\infty} c_k \Psi_k \right\rangle - E_0 \left\langle \sum_{l=0}^{\infty} c_l \Psi_l \left| \sum_{k=0}^{\infty} c_k \Psi_k \right\rangle \right. \\
&\quad + \left\langle \sum_{l=0}^{\infty} d_l \Psi_l \left| \hat{H} \right| \sum_{k=0}^{\infty} d_k \Psi_k \right\rangle - E_0 \left\langle \sum_{l=0}^{\infty} d_l \Psi_l \left| \sum_{k=0}^{\infty} d_k \Psi_k \right\rangle \right. \\
&= \sum_{k=0}^{\infty} \sum_{l=0}^{\infty} c_l^* c_k \langle \Psi_l | \hat{H} | \Psi_k \rangle - E_0 \sum_{k=0}^{\infty} \sum_{l=0}^{\infty} c_l^* c_k \langle \Psi_l | \Psi_k \rangle \\
&\quad + \sum_{k=0}^{\infty} \sum_{l=0}^{\infty} d_l^* d_k \langle \Psi_l | \hat{H} | \Psi_k \rangle - E_0 \sum_{k=0}^{\infty} \sum_{l=0}^{\infty} d_l^* d_k \langle \Psi_l | \Psi_k \rangle \\
&= \sum_{k=0}^{\infty} \sum_{l=0}^{\infty} c_l^* c_k E_k \langle \Psi_l | \Psi_k \rangle - E_0 \sum_{k=0}^{\infty} \sum_{l=0}^{\infty} c_l^* c_k \delta_{kl} \\
&\quad + \sum_{k=0}^{\infty} \sum_{l=0}^{\infty} d_l^* d_k E_k \langle \Psi_l | \Psi_k \rangle - E_0 \sum_{k=0}^{\infty} \sum_{l=0}^{\infty} d_l^* d_k \delta_{kl} \\
\left\langle \Psi_0 \left[\hat{C}^\dagger, [\hat{H}, \hat{C}] \right] \Psi_0 \right\rangle &= \sum_{k=0}^{\infty} \sum_{l=0}^{\infty} c_l^* c_k E_k \delta_{kl} - \sum_{k=0}^{\infty} |c_k|^2 E_0 \\
&\quad + \sum_{k=0}^{\infty} \sum_{l=0}^{\infty} d_l^* d_k E_k \delta_{kl} - \sum_{k=0}^{\infty} |d_k|^2 E_0 \\
&= \sum_{k=0}^{\infty} |c_k|^2 (E_k - E_0) + \sum_{k=0}^{\infty} |d_k|^2 (E_k - E_0)
\end{aligned}$$

However, because we are considering the ground state wavefunction, $E_0 \leq E_1 \leq E_2 \leq \dots$ and $E_k - E_0 \geq 0$ for all k . Since all of the terms in the sum are positive, the sum is also positive. So,

$$\begin{aligned}
\left\langle \Psi_0 \left[\hat{C}^\dagger, [\hat{H}, \hat{C}] \right] \Psi_0 \right\rangle &= \sum_{k=0}^{\infty} |c_k|^2 (E_k - E_0) + \sum_{k=0}^{\infty} |d_k|^2 (E_k - E_0) \\
&\geq 0
\end{aligned}$$

- 4c.** The results in problem #6 are key results associated with the theory of infinitesimal unitary transformations. The theory of infinitesimal unitary transformations describes, among other things, how wavefunctions change in time, and was the key mathematical concept behind Julian Schwinger's development of quantum field theory, for which he shared the 1965 Nobel Prize and became justly famous. The key idea here is that the following operator,

$$\hat{U}_\varepsilon = \hat{I} + i\varepsilon \hat{C}$$

is an infinitesimal unitary transformation, where \hat{I} is the identity operator (i.e., “multiply by one”). Here ε is a very small (“infinitesimal”) real number.

Using equations, explain why \hat{U}_ε can be interpreted as an “infinitesimal unitary transformation” if \hat{C} is a Hermitian operator, but cannot be interpreted as an “infinitesimal unitary transformation” if \hat{C} is not Hermitian. (5 points) (This

requires you to remember that a unitary transformation/matrix/operator is defined by the fact that it's Hermitian conjugate is equal to its inverse.)
 A unitary transformation/matrix/operator has the property that its conjugate transpose (it's "Hermitian conjugate") is equal to its inverse. So we need to show that

$$\hat{U}_\varepsilon^\dagger \hat{U}_\varepsilon = \hat{I}$$

Substituting in the form for the operator, we have that:

$$\begin{aligned}\hat{U}_\varepsilon^\dagger \hat{U}_\varepsilon &= (\hat{I} + i\varepsilon \hat{C})^\dagger (\hat{I} + i\varepsilon \hat{C}) \\ &= (\hat{I}^\dagger - i\varepsilon \hat{C}^\dagger)(\hat{I} + i\varepsilon \hat{C})\end{aligned}$$

The identity matrix is equal to its Hermitian conjugate, $\hat{I}^\dagger = \hat{I}$ and obviously $\hat{I} \cdot \hat{I} = \hat{I}$ for the identity. So

$$\begin{aligned}\hat{U}_\varepsilon^\dagger \hat{U}_\varepsilon &= (\hat{I}^\dagger - i\varepsilon \hat{C}^\dagger)(\hat{I} + i\varepsilon \hat{C}) \\ &= (\hat{I} - i\varepsilon \hat{C}^\dagger)(\hat{I} + i\varepsilon \hat{C}) \\ &= \hat{I} + i\varepsilon (\hat{C} - \hat{C}^\dagger) + \varepsilon^2 \hat{C}^\dagger \hat{C}\end{aligned}$$

Now, for very, very, very tiny ("infinitesimal") ε , the last term is entirely negligible. So we can omit it. So

$$\hat{U}_\varepsilon^\dagger \hat{U}_\varepsilon = \hat{I} + i\varepsilon (\hat{C} - \hat{C}^\dagger).$$

If $\hat{C}^\dagger = \hat{C}$ (i.e., the operator is Hermitian) then this is an infinitesimal unitary transformation because $\hat{U}_\varepsilon^\dagger \hat{U}_\varepsilon = \hat{I}$. If $\hat{C}^\dagger \neq \hat{C}$, then this is not true because the error term is of the same order as the change in the operator.

Speaking technically, the important point was that for unitary infinitesimal transformations, the normalization of the wavefunctions does not change to first order. The important property is related to the fact that $\left[\partial \hat{U}_\varepsilon^\dagger \hat{U}_\varepsilon / \partial \varepsilon \right]_{\varepsilon=0} = 0$ for an infinitesimal unitary transformation.

5. Some physicists speculate that Planck's constant might not really be constant but, instead, vary slightly in space. A physicist speculates that Planck's constant on the moon is slightly smaller than Planck's constant on earth. We decide to test this hypothesis using the one-dimensional particle in a box. Which of the following observations would support this hypothesis.

(a) the zero-point energy of the "moon box" is less than that of the "earth box."

(b) the zero-point energy of the "moon box" is equal to that of the "earth box."

(c) the zero-point energy of the "moon box" is greater than that of the "earth box."

(d) the average position of the particle is further from the edges of the "moon box" than the "earth box."

(e) the average position of the particle is closer to the edges of the "moon box" than the "earth box."

(f) the average position of the particle in the "moon box" than the "earth box" is the same.

(a) because if you reduce Planck's constant, the zero-point energy, $E = h^2 / (8ma^2)$ reduces.

The next part is a bit ambiguous. The average position of the particle in the box is right in the middle. However, it does “spread about the middle” by different amounts. This is computed by evaluating

$$\begin{aligned}
 \langle x^2 \rangle - \langle x \rangle^2 &= \frac{2}{a} \int_0^a x^2 \sin^2\left(\frac{\pi x}{a}\right) dx - \left(\frac{a}{2}\right)^2 \\
 &= \frac{2}{a} \left[\frac{1}{24\left(\frac{\pi}{a}\right)^3} \left(4\left(\frac{\pi}{a}\right)^3 x^3 + \left(3 - 6\left(\frac{\pi}{a}\right)^2 x^2\right) \sin\left(\frac{2\pi x}{a}\right) - 6\left(\frac{\pi}{a}\right) x \cos\left(\frac{2\pi x}{a}\right) \right) \right]_0^a - \frac{a^2}{4} \\
 &= \frac{a^2}{12\pi^3} (4\pi^3 - 6\pi) - \frac{a^2}{4} \\
 &= a^2 \left(\frac{1}{3} - \frac{1}{2\pi^2} - \frac{1}{4} \right)
 \end{aligned}$$

The average position does not depend on h . Of course we did not need to do the integral to figure this out: this is clear from the fact that the integral is totally independent of h , so the answer cannot depend on h .

6. Write down the time-dependent Schrodinger equation.

$$\hat{H}(x,t)\Psi(x,t) = i\hbar \frac{\partial \Psi(x,t)}{\partial t}$$

7. Assume the Hamiltonian is time-independent, and that it has eigenfunctions $\hat{H}\psi_k(\mathbf{r}) = E_k\psi_k(\mathbf{r})$. Use separation of variables on the time-dependent Schrödinger equation to solve for the space+time-dependent wavefunction, $\Psi(\mathbf{r},t)$.

If the Hamiltonian is time-independent, then replacing $\hat{H}(x,t)$ with $\hat{H}(x)$ in the time-dependent Schrödinger equation gives

$$\hat{H}(x)\psi(x,t) = i\hbar \left(\frac{\partial \psi(x,t)}{\partial t} \right)$$

Whenever you can “divide” a multidimensional differential equation into a sum of two terms, each of which has an explicit dependence on only a subset of the variables, you can simplify the differential equation by a technique called “separation of variables,” where you assume the solution can be written as a product of the a function of the “variables in the first part” and a function of the “variables in the second part.” In this case we have

$$\left[\underbrace{\hat{H}(x)}_{\text{depends only on } x} - \underbrace{i\hbar \left(\frac{\partial}{\partial t} \right)}_{\text{depends only on } t} \right] \psi(x,t) = 0$$

and so we hypothesize a form of the wavefunction like

$$\psi(x,t) = \Psi(x)\phi(t).$$

Substituting this wavefunction into the time-dependent Schrödinger equation gives

$$\phi(t)\hat{H}(x)\Psi(x) = \left(i\hbar \left(\frac{d\phi}{dt} \right) \right) \Psi(\mathbf{x})$$

Divide both sides by $\phi(t)\Psi(x)$. We obtain:

$$\frac{\hat{H}(x)\Psi(x)}{\Psi(x)} = \left(\frac{i\hbar}{\phi(t)} \left(\frac{d\phi}{dt} \right) \right)$$

The left-hand-side depends only on x ; the right-hand-side depends only on t . However, the equation must hold for *all* x and t , which can happen only if this equation is equal to a constant. So we have:

$$\frac{\hat{H}(x)\Psi(x)}{\Psi(x)} = (\text{constant}) = \left(\frac{i\hbar}{\phi(t)} \left(\frac{d\phi}{dt} \right) \right)$$

or

$$\begin{aligned} \left(\frac{d\phi}{dt} \right) &= \frac{1}{i\hbar} (\text{constant}) \phi(t) \\ \hat{H}(x)\Psi(x) &= (\text{constant})\Psi(x) \end{aligned}$$

Identifying the second equation as the time-independent Schrödinger equation, we see that the constant must be the energy. So

$$\hat{H}(x)\Psi(x) = E\Psi(x)$$

We can solve the ordinary differential equation for the time-dependent portion of the wavefunction by explicit integration,

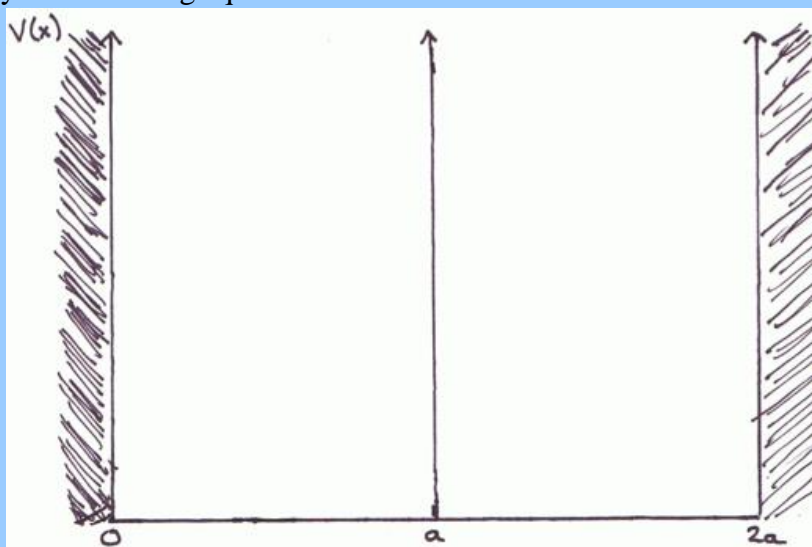
$$\begin{aligned} d\phi &= \frac{E}{i\hbar} \phi(t) dt \\ \int \frac{1}{\phi(t)} d\phi &= \left(\frac{-iE}{\hbar} \right) \int dt \\ \ln(\phi(t)) &= \frac{-iEt}{\hbar} + (\text{const. of integration}) \\ \phi(t) &= e^{(\text{const. of integration})} e^{-\frac{iEt}{\hbar}} \\ &\propto e^{-\frac{iEt}{\hbar}} \end{aligned}$$

It is obvious that if $\psi(x, t)$ is a solution to the Schrödinger equation, then any multiple of the wavefunction, $c\psi(x, t)$, is also. So we can ignore the constant of integration.

The following text refers to problems 8-10.

Consider an electron confined to two one-dimensional boxes with infinitely repulsive sides. The two boxes are adjacent to each other but separated by an infinite barrier, as shown in the following figure and encapsulated by the following equation:

$$V(x) = \begin{cases} +\infty & x \leq 0 \\ 0 & 0 < x < a \\ +\infty & x = a \\ 0 & a < x < 2a \\ +\infty & x \geq 2a \end{cases}$$



8. The system is prepared in its ground state and then its absorption spectrum is taken. The largest-wavelength absorption that is observed has wavelength 1000 nm. **How wide are the boxes? (I.e., what is the value of a ?)**

Since the boxes are separated by an infinite barrier, they are excited separately. So it is equivalent to just exciting one box. Then we have:

$$\frac{h^2(2^2)}{8ma^2} - \frac{h^2(1^2)}{8ma^2} = \frac{3h^2}{8ma^2} = h\nu = \frac{hc}{\lambda}$$

$$a^2 = \frac{3h\lambda}{8mc}$$

$$a = \sqrt{\frac{3h\lambda}{8mc}} = \sqrt{\frac{3 \cdot 6.626 \cdot 10^{-34} \frac{\text{kg} \cdot \text{m}^2}{\text{s}} \cdot 1000 \cdot 10^{-9} \text{ m}}{8(9.11 \cdot 10^{-31} \text{ kg})(3.00 \cdot 10^8 \frac{\text{m}}{\text{s}})}}$$

$$a = 9.53 \cdot 10^{-10} \text{ m} = 0.953 \text{ nm}$$

9. **What is the ground state energy of this system?**

It is the energy of the particles-in-a-box of width a . This is the same as the ground-state energy of a particle-in-a-box with double the width, as it must be since the first-excited-eigenfunction of the “ $2a$ box” has a node in the location of the barrier in this system.

$$E_{g.s.} = \frac{h^2}{8ma^2} = \frac{h^2(2^2)}{8m(2a)^2} = \frac{4h^2}{8m(2a)^2}$$

10. An experiment reveals that the system has a 90% chance of being observed in the first box and a 10% chance of being observed in the second box. **Write TWO wavefunctions, which differ from each other by more than a constant factor, that are consistent with this observation.**

$$\Psi(x) = \sqrt{\frac{9}{10}}\psi_1(x) \pm \sqrt{\frac{1}{10}}\psi_2(x)$$

$$\psi_1(x) = \begin{cases} \sqrt{\frac{2}{a}} \sin\left(\frac{\pi x}{a}\right) & 0 < x < a \\ 0 & \text{otherwise} \end{cases}$$

$$\psi_2(x) = \begin{cases} \sqrt{\frac{2}{a}} \sin\left(\frac{\pi x}{a}\right) & a < x < 2a \\ 0 & \text{otherwise} \end{cases}$$