Introduction to Quantum Mechanics for Engineers

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Problem Sets

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Problem Set #1:

1. Consider the **Gaussian** distribution, $\rho(x) = Ae^{-\lambda(x-a)^2}$, where A, a, and λ are positive real constants.

    (i)   If ρ is a normalized probability density, determine A.

    (ii) Find $\langle x \rangle$, $\langle x^2 \rangle$, and σ_x.

    (iii) Sketch the graph of $\rho(x)$.

2. Consider the wave function, $\Psi(x,t) = Ae^{-\lambda|x|}e^{-i\omega t}$, where A, λ, and ω are positive real constants.

    (i)   Normalize $\Psi(x,t)$.

    (ii) Determine the expectation values of x and x^2.

    (iii) Find σ_x, sketch the graph of $|\Psi|^2$ as a function of x, and mark the points $(x = +\sigma_x)$ and $(x = -\sigma_x)$. What is the probability that the particle would be found outside this range?

3. Show that $\dfrac{d\langle p \rangle}{dt} = \left\langle -\dfrac{\partial V}{\partial x} \right\rangle$, where p is the linear momentum and V is the potential energy function. Note this is an example of **Ehrenfest's theorem**, which states that expectation values obey classical laws.

4. In general, quantum mechanics is relevant when the de Broglie wavelength of the particle in question (h/p) is greater than the characteristic size of the system, d. In thermal equilibrium at temperature T (in Kelvin), the average kinetic energy of a particle is:

    $$\frac{p^2}{2m} = \frac{3}{2}k_B T,$$

    where k_B is Boltzmann's constant. Thus, the typical de Broglie wavelength is

    $$\lambda = \frac{h}{\sqrt{3mk_B T}}.$$

    Below we determine when a quantum mechanical description of a system is necessary.

    (i)   In a typical **solid**, the atomic spacing is around $d = 0.3$ nm. Find the temperature below which the valence electrons in a solid are quantum mechanical. Below what temperature are the nuclei in a solid quantum mechanical? (Use sodium as a typical case.) Note: your answer would be the same for most liquids.

(ii) Show that one would expect that an **ideal gas** at pressure P would show quantum mechanical behavior for $T < (1/k_B)(h^2/3m)^{3/5} P^{2/5}$. Thus, a gas molecule with small m at high P will require a quantum mechanical description. Calculate the temperature needed for helium at atmospheric pressure. Is hydrogen in outer space (where $d = 1$ cm and $T = 3$ K) quantum mechanical?

Problem Set #2:

1. Find σ_x and σ_p for the nth stationary state of the infinite square well. Check that the uncertainty principle is satisfied. Which state comes closest to the uncertainty limit?

2. Consider a particle in the infinite square well with an initial wave function:
$$\Psi(x,0) = A[\psi_1(x) + \psi_2(x)]$$
(i) Normalize $\Psi(x,0)$.
(ii) Determine $\Psi(x,t)$ and $|\Psi(x,t)|^2$.
(iii) Compute $\langle x \rangle$. Notice that it oscillates in time.
(iv) Compute $\langle p \rangle$.
(v) If you measure the energy of this particle, what are the possible values?
(vi) What is the probability of obtaining each of the possible energies?
(vii) Compute $\langle H \rangle$ and compare to E_1 and E_2.

3. Show that E must exceed the minimum value of $V(x)$ for every normalizable solution to the time-independent Schrödinger equation. Hint: rewrite the time-independent Schrödinger equation as:
$$\frac{d^2\psi}{dx^2} = \frac{2m}{\hbar^2}[V(x) - E]\psi,$$
and consider what happens to the shape of ψ if $E < V_{min}$. In this case can ψ be normalized?

4. Consider a free particle with an initial normalized wave function:

$$\Psi(x,0) = \left(\frac{2a}{\pi}\right)^{1/4} \exp\left(-ax^2\right) \qquad \text{“Gaussian Wave Packet”}$$

where a is a real positive constant.

(i)   Determine $\Psi(x,t)$.

(ii) Determine $\left|\Psi(x,t)\right|^2$.

(iii) Sketch $\left|\Psi(x,t)\right|^2$ versus x at $t = 0$ and at a later t. Describe qualitatively what happens to $\left|\Psi\right|^2$ as a function of time.

(iv) Find σ_x and σ_p

(v)   Is the uncertainty principle satisfied?

(vi) At what time does the system come closest to the uncertainty limit?

5. Prove the following two theorems:

(i)   For normalized wave functions $\Psi(x,t) = \psi(x)e^{-iEt/\hbar}$, the separation constant E must be real. Hint: write E as $E_o + i\Gamma$ where E_o and Γ are real and then use the normalization condition.

(ii) $\psi(x)$ can always be taken to be real [unlike $\Psi(x,t)$ which is necessarily complex]. This does not mean that every solution $\psi(x)$ to the time-independent Schrödinger equation is real. But if it is not, we can always express it as a linear combination of solutions (with the same E) that are real. Hint: if $\psi(x)$ satisfies the time-independent Schrödinger equation for a given E, show that $\psi^*(x)$ does also. Thus, real linear combinations $(\psi + \psi^*)$ and $i(\psi - \psi^*)$ are also solutions.

Problem Set #3:

1. Evaluate the following commutators:

(i) $\left[\hat{a}_+, C\right]$, where $\hat{a}_+$ is the raising operator and C is any constant,

(ii) $\left[\hat{x}, \hat{p}\right]$, where $\hat{x}$ is the position operator and $\hat{p}$ is the momentum operator,

(iii) $\left[\hat{a}_-, \hat{a}_+\right]$, where $\hat{a}_-$ is the lowering operator, and

(iv) $\left[\hat{O}_1, \hat{x}\right]$, where $\hat{O}_1 = \dfrac{d^2}{dx^2}$.

2.   For the quantum harmonic oscillator:

   (i)   Prove that if ψ is a solution to the Schrödinger equation with energy E, that $\hat{a}_+\psi$ is also a solution with energy $E + \hbar\omega$.

   (ii)   Determine the functional form of $\psi_0(x)$ by solving $\hat{a}_-\psi_0 = 0$.

3.   Determine the first excited state, $\psi_1(x)$, for the harmonic oscillator. Make sure your answer is normalized.

4.   For both the ground state and the first excited state of the harmonic oscillator:

   (i)   Compute $\langle x \rangle$, $\langle x^2 \rangle$, $\langle p \rangle$, and $\langle p^2 \rangle$.   Hint: introduce $\xi = \sqrt{\dfrac{m\omega}{\hbar}}\, x$ and

   $\alpha = \left(\dfrac{m\omega}{\pi\hbar}\right)^{\frac{1}{4}}$ and then do only the integrations you must (*i.e.* think first)!

   (ii)   Check the uncertainty principle.

   (iii) Evaluate $\langle T \rangle$, the average kinetic energy, and $\langle V \rangle$, the average potential energy. Is the sum of $\langle T \rangle$ and $\langle V \rangle$ what you would expect?

Problem Set #4:

1.   (i)   For the quantum harmonic oscillator, explicitly show the symmetry (*i.e.*, even or odd) of $\psi_1(x)$ and $\psi_3(x)$. Use the Hermite polynomial form for $\psi_n(x)$:

$$\psi_n(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{4}} \frac{1}{\sqrt{2^n n!}}\, H_n(\xi)\exp\left[\frac{-\xi^2}{2}\right], \text{ where}$$

$$H_1(\xi) = 2\xi, \; H_3(\xi) = 8\xi^3 - 12\xi, \text{ and } \xi = \sqrt{\frac{m\omega}{\hbar}}\, x$$

   (ii)   For the infinite square well, explicitly show that $\psi_1(x)$ and $\psi_3(x)$ are orthogonal.

2.   (i)   Show that the position operator $\hat{x}$ is Hermitian.

      (ii)   Show that the momentum operator $\hat{p}$ is Hermitian.

      (iii) Show that the sum of two Hermitian operators is Hermitian.

      (iv)   When is the product of two Hermitian operators also Hermitian?

3. Show that if $\langle h|\hat{Q}h\rangle = \langle \hat{Q}h|h\rangle$ for all functions h in Hilbert space, then $\langle f|\hat{Q}g\rangle = \langle \hat{Q}f|g\rangle$ for all functions f and g. Each of these expressions are used as the definition of a Hermitian operator. This problem shows that they are equivalent. Hint: First let $h = f + g$ and then let $h = f + ig$.

4. Show that the Dirac delta function, $\delta(x)$, can be written as:

$$\delta(x) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} \exp(ikx)dk$$

Hint: Use Plancherel's theorem and take the Fourier transform of $\delta(x)$ and then take the inverse Fourier transform.

5. Is the ground state of the infinite square well an eigenfunction of momentum? If so, what is its momentum? If not, why not?

Problem Set #5:

1. Prove the generalized uncertainty principle:

$$\sigma_{\hat{A}}^2 \, \sigma_{\hat{B}}^2 \geq \left(\frac{1}{2i}\langle[\hat{A},\hat{B}]\rangle\right)^2$$

where $\hat{A}$ and $\hat{B}$ are linear Hermitian operators. Hint: the proof is on p. 110 of Griffiths. I just want you to go over it and understand it.

2. (i) Show that $[\hat{A}\hat{B}, \hat{C}] = \hat{A}[\hat{B}, \hat{C}] + [\hat{A}, \hat{C}]\hat{B}$
   (ii) Show that $[\hat{x}^n, \hat{p}] = i\hbar n x^{n-1}$
   (iii) Show that $[f(\hat{x}), \hat{p}] = i\hbar \dfrac{df}{dx}$

3. Prove the specific uncertainty relation that is written below, which is between position ($\hat{A} = x$) and energy ($\hat{B} = \hat{H}$):

$$\sigma_{\hat{x}} \, \sigma_{\hat{H}} \geq \frac{\hbar}{2m}|\langle p\rangle|.$$

For a stationary state, does this relation tell you anything?

4.   Given a system that is in a linear combination of infinite-square-well stationary states,

$$\Psi(x,t) = \frac{1}{\sqrt{2}}\left\{\psi_1(x)\exp(-iE_1 t/\hbar) + \psi_2(x)\exp(-iE_2 t/\hbar)\right\},$$

calculate:
(i) $\sigma_{\hat{H}}$
(ii) $\sigma_{\hat{x}}$,
(iii) $d\langle\hat{x}\rangle/dt$, and
(iv)   then test the time-energy uncertainty relationship, *i.e.*

$$\sigma_{\hat{x}}^2 \sigma_{\hat{H}}^2 \geq \left(\frac{\hbar}{2}\right)^2 \left(\frac{d\langle x\rangle}{dt}\right)^2$$

Note: some answers from problems 1 and 2 from problem set #2 will be helpful here.

Problem Set #6:

1.   (a)   Determine the **canonical commutation relations** for the Cartesian components of the operators $\hat{\vec{r}}$ and $\hat{\vec{p}}$: $[\hat{x},\hat{y}]$, $[\hat{x},\hat{z}]$, $[\hat{y},\hat{z}]$, $[\hat{x},\hat{p}_x]$, $[\hat{x},\hat{p}_y]$, $[\hat{x},\hat{p}_z]$, $[\hat{y},\hat{p}_x]$, $[\hat{y},\hat{p}_y]$, $[\hat{y},\hat{p}_z]$, $[\hat{z},\hat{p}_x]$, $[\hat{z},\hat{p}_y]$, $[\hat{z},\hat{p}_z]$, $[\hat{p}_x,\hat{p}_y]$, $[\hat{p}_x,\hat{p}_z]$, and $[\hat{p}_y,\hat{p}_z]$.

        (b)   Determine the fundamental commutation relations for angular momentum: $[\hat{L}_x,\hat{L}_y]$, $[\hat{L}_y,\hat{L}_z]$, and $[\hat{L}_z,\hat{L}_x]$.   Use the classical definition of angular momentum, $\vec{L} = \vec{r}\times\vec{p}$, which means $L_x = yp_z - zp_y$, $L_y = zp_x - xp_z$, and $L_z = xp_y - yp_x$.

2.   Use separation of variables in Cartesian coordinates to solve the infinite cubical well (or "particle in a box"):

$$V(x,y,z) = \begin{cases} 0, & \text{if } x,\ y,\ z,\ \text{are all between 0 and } a; \\ \infty, & \text{otherwise.} \end{cases}$$

        (a)   Find the stationary states and their corresponding energies.
        (b)   Call the distinct energies E_1, E_2, E_3, *etc.*, in order of increasing energy. Find the first six energies and determine their degeneracies (*i.e.*, the number of different states that share the same energy). Note: In one dimension, one can prove that bound states are never degenerate, but in three dimensions they are very common.
        (c)   What is the degeneracy of E_{14}, and why is this case interesting?

3. (a) Use equations 4.27, 4.28, and 4.32 from Griffiths below to construct Y_0^0 and Y_2^1.

    (b) Confirm that Y_0^0 and Y_2^1 are normalized and orthogonal.

The solution is

$$\Theta(\theta) = A P_l^m (\cos\theta), \qquad\qquad [4.26]$$

where P_l^m is the **associated Legendre function**, defined by

$$P_l^m(x) \equiv (1 - x^2)^{|m|/2} \left(\frac{d}{dx}\right)^{|m|} P_l(x), \qquad\qquad [4.27]$$

and $P_l(x)$ is the lth **Legendre polynomial**, defined by the **Rodrigues formula**:

$$P_l(x) \equiv \frac{1}{2^l l!} \left(\frac{d}{dx}\right)^l (x^2 - 1)^l. \qquad\qquad [4.28]$$

$$Y_l^m(\theta,\phi) = \epsilon \sqrt{\frac{(2l+1)}{4\pi} \frac{(l - |m|)!}{(l + |m|)!}} \, e^{im\phi} \, P_l^m(\cos\theta), \qquad\qquad [4.32]$$

where $\epsilon = (-1)^m$ for $m \geq 0$ and $\epsilon = 1$ for $m \leq 0$.

4. (a) Using the tables below, construct the wavefunction ψ_{200} for the hydrogen atom.

    (b) Using the tables below, construct the wavefunctions ψ_{211}, ψ_{210}, and $\psi_{21\text{-}1}$ for the hydrogen atom.

TABLE 4.3: The first few spherical harmonics, $Y_l^m(\theta,\phi)$.

$$Y_0^0 = \left(\frac{1}{4\pi}\right)^{1/2}$$

$$Y_2^{\pm 2} = \left(\frac{15}{32\pi}\right)^{1/2} \sin^2\theta \, e^{\pm 2i\phi}$$

$$Y_1^0 = \left(\frac{3}{4\pi}\right)^{1/2} \cos\theta$$

$$Y_3^0 = \left(\frac{7}{16\pi}\right)^{1/2} (5\cos^3\theta - 3\cos\theta)$$

$$Y_1^{\pm 1} = \mp \left(\frac{3}{8\pi}\right)^{1/2} \sin\theta \, e^{\pm i\phi}$$

$$Y_3^{\pm 1} = \mp \left(\frac{21}{64\pi}\right)^{1/2} \sin\theta \, (5\cos^2\theta - 1) e^{\pm i\phi}$$

$$Y_2^0 = \left(\frac{5}{16\pi}\right)^{1/2} (3\cos^2\theta - 1)$$

$$Y_3^{\pm 2} = \left(\frac{105}{32\pi}\right)^{1/2} \sin^2\theta \cos\theta \, e^{\pm 2i\phi}$$

$$Y_2^{\pm 1} = \mp \left(\frac{15}{8\pi}\right)^{1/2} \sin\theta \cos\theta \, e^{\pm i\phi}$$

$$Y_3^{\pm 3} = \mp \left(\frac{35}{64\pi}\right)^{1/2} \sin^3\theta \, e^{\pm 3i\phi}$$

TABLE 4.5: The first few Laguerre polynomials, $L_q(x)$.

$$L_0 = 1$$
$$L_1 = -x + 1$$
$$L_2 = x^2 - 4x + 2$$
$$L_3 = -x^3 + 9x^2 - 18x + 6$$
$$L_4 = x^4 - 16x^3 + 72x^2 - 96x + 24$$
$$L_5 = -x^5 + 25x^4 - 200x^3 + 600x^2 - 600x + 120$$
$$L_6 = x^6 - 36x^5 + 450x^4 - 2400x^3 + 5400x^2 - 4320x + 720$$

TABLE 4.6: Some associated Laguerre polynomials, $L_{q-p}^p(x)$.

$L_0^0 = 1$	$L_0^2 = 2$
$L_1^0 = -x + 1$	$L_1^2 = -6x + 18$
$L_2^0 = x^2 - 4x + 2$	$L_2^2 = 12x^2 - 96x + 144$
$L_0^1 = 1$	$L_0^3 = 6$
$L_1^1 = -2x + 4$	$L_1^3 = -24x + 96$
$L_2^1 = 3x^2 - 18x + 18$	$L_2^3 = 60x^2 - 600x + 1200$

TABLE 4.7: The first few radial wave functions for hydrogen, $R_{nl}(r)$.

$$R_{10} = 2a^{-3/2} \exp(-r/a)$$

$$R_{20} = \frac{1}{\sqrt{2}} a^{-3/2} \left(1 - \frac{1}{2}\frac{r}{a}\right) \exp(-r/2a)$$

$$R_{21} = \frac{1}{\sqrt{24}} a^{-3/2} \frac{r}{a} \exp(-r/2a)$$

$$R_{30} = \frac{2}{\sqrt{27}} a^{-3/2} \left(1 - \frac{2}{3}\frac{r}{a} + \frac{2}{27}\left(\frac{r}{a}\right)^2\right) \exp(-r/3a)$$

$$R_{31} = \frac{8}{27\sqrt{6}} a^{-3/2} \left(1 - \frac{1}{6}\frac{r}{a}\right)\left(\frac{r}{a}\right) \exp(-r/3a)$$

$$R_{32} = \frac{4}{81\sqrt{30}} a^{-3/2} \left(\frac{r}{a}\right)^2 \exp(-r/3a)$$

$$R_{40} = \frac{1}{4} a^{-3/2} \left(1 - \frac{3}{4}\frac{r}{a} + \frac{1}{8}\left(\frac{r}{a}\right)^2 - \frac{1}{192}\left(\frac{r}{a}\right)^3\right) \exp(-r/4a)$$

$$R_{41} = \frac{\sqrt{5}}{16\sqrt{3}} a^{-3/2} \left(1 - \frac{1}{4}\frac{r}{a} + \frac{1}{80}\left(\frac{r}{a}\right)^2\right) \frac{r}{a} \exp(-r/4a)$$

$$R_{42} = \frac{1}{64\sqrt{5}} a^{-3/2} \left(1 - \frac{1}{12}\frac{r}{a}\right)\left(\frac{r}{a}\right)^2 \exp(-r/4a)$$

$$R_{43} = \frac{1}{768\sqrt{35}} a^{-3/2} \left(\frac{r}{a}\right)^3 \exp(-r/4a)$$

5. (a) Find $\langle r \rangle$ and $\langle r^2 \rangle$ for an electron in the ground state of hydrogen. Express your answers in terms of the Bohr radius, a.

(b) Find $\langle x \rangle$ and $\langle x^2 \rangle$ for an electron in the ground state of hydrogen. Hint: this requires no new integration. Use $r^2 = x^2 + y^2 + z^2$ and the symmetry of the ground state.

(c) Find $\langle x^2 \rangle$ for an electron in the state $n = 2$, $l = 1$, and $m = 1$ of hydrogen. Hint: this state is not symmetric in x, y, z. Use $x = r\sin\theta\cos\phi$.

Problem Set #7:

1. A **hydrogenic atom** consists of a single electron orbiting a nucleus with Z protons. For example, $Z=1$ for hydrogen itself, $Z=2$ for helium with one electron removed, $Z=3$ for lithium with two electrons removed, *etc.* Determine the Bohr energies $E_n(Z)$, the binding energy $E_1(Z)$, and the Bohr radius $a(Z)$ for a hydrogenic atom. Hint: there is nothing new to calculate here. The potential is still spherically symmetric, but the strength of the potential is increased by a factor of Z.

2. (a) Starting with the **canonical commutation relations** for the Cartesian components of the operators $\hat{\vec{r}}$ and $\hat{\vec{p}}$, determine the following:

$$\left[\hat{L}_z, \hat{x}\right], \left[\hat{L}_z, \hat{y}\right], \left[\hat{L}_z, \hat{z}\right], \left[\hat{L}_z, \hat{p}_x\right], \left[\hat{L}_z, \hat{p}_y\right], \text{ and } \left[\hat{L}_z, \hat{p}_z\right].$$

(b)   Evaluate the commutators: $\left[\hat{L}_z, \hat{r}^2 \right]$ and $\left[\hat{L}_z, \hat{p}^2 \right]$.

(c)   Show that the Hamiltonian $\hat{H}$ commutes with all three components of $\hat{\mathbf{L}}$ if the potential is spherically symmetric. Thus, $\hat{H}$, $\hat{L}^2$, and $\hat{L}_z$ all commute. What is the significance of this?

3.   Two particles of mass m are attached to the ends of a massless rigid rod of length a. The system is free to rotate in three dimensions about the center, but this center point cannot move.

(a)   Show that the allowed energies of this **rigid rotor** are:
$$E_n = \frac{\hbar^2 n(n+1)}{ma^2}, \text{ for } n = 0, 1, 2 \ldots$$
Hint: First express the classical energy in terms of the total angular momentum.

(b)   What are the normalized eigenfunctions for this system? What is the degeneracy of the nth energy level?

4.   An electron is in the spin state:
$$|\chi\rangle = A \begin{pmatrix} 3i \\ 4 \end{pmatrix}$$

(a)   Determine the normalization constant, A.

(b)   Find the expectation values of $\hat{S}_x$, $\hat{S}_y$, and $\hat{S}_z$.

(c)   Find the standard deviations in $\hat{S}_x$, $\hat{S}_y$, and $\hat{S}_z$.

(d)   Confirm that your results are consistent with the generalized uncertainty principle for $\hat{S}_x$, $\hat{S}_y$, and $\hat{S}_z$.
$$\sigma_{\hat{A}}^2 \, \sigma_{\hat{B}}^2 \geq \left(\frac{1}{2i} \langle [\hat{A}, \hat{B}] \rangle \right)^2.$$

5.   We introduced a specific spin 1/2 basis in lecture, $i.e.$,
$$\left| \frac{1}{2}, +\frac{1}{2} \right\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \text{ and } \left| \frac{1}{2}, -\frac{1}{2} \right\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix},$$
where the ket notation represents $|s, m_s\rangle$.

(a)   In this basis, determine the eigenvalues and eigenvectors for $\hat{S}_y$.

(b)   If you measure S_y on the general spin state,
$$|\chi\rangle = a \begin{pmatrix} 1 \\ 0 \end{pmatrix} + b \begin{pmatrix} 0 \\ 1 \end{pmatrix},$$

what values would you get and with what probabilities?   Check that the probabilities add to one.   Note: a and b do not have to be real.

(c) If you measure S_y^2 on the same general state, what values would you get and with what probabilities?

Problem Set #8:

1. For typical two-particle quantum mechanical systems, the interaction potential $V(\vec{r}_1,\vec{r}_2)$ only depends on the vector $\vec{r} \equiv \vec{r}_1 - \vec{r}_2$. In that case, the Schrödinger equation separates if we change variables from $\vec{r}_1$, $\vec{r}_2$ to $\vec{r}$ and $\vec{R} \equiv (m_1\vec{r}_1 + m_2\vec{r}_2)/(m_1 + m_2)$, where $\vec{R}$ is the **center of mass**.

    (a) Show that $\vec{r}_1 = \vec{R} + (m_r/m_1)\vec{r}$, $\vec{r}_2 = \vec{R} - (m_r/m_2)\vec{r}$, $\vec{\nabla}_1 = \vec{\nabla}_r + (m_r/m_2)\vec{\nabla}_R$, and $\vec{\nabla}_2 = -\vec{\nabla}_r + (m_r/m_1)\vec{\nabla}_R$, where m_1 and m_2 are the masses of particles 1 and 2 and
    $$m_r \equiv \frac{m_1 m_2}{m_1 + m_2}$$
    is the **reduced mass** of the system.

    (b) Show that the T.I.S.E. becomes
    $$\left[\frac{-\hbar^2}{2(m_1 + m_2)}\nabla_R^2 - \frac{\hbar^2}{2m_r}\nabla_r^2 + V(\vec{r})\right]\psi = E\psi$$

    (c) Separate the variables, letting $\psi(\vec{R},\vec{r}) = \psi_R(\vec{R})\,\psi_r(\vec{r})$. Note that ψ_R satisfies the one-particle Schrödinger equation, with total mass $(m_1 + m_2)$ in place of m, zero potential, and energy E_R, while ψ_r satisfies the one-particle Schrödinger equation, with reduced mass m_r in place of m, potential $V(\vec{r})$, and energy E_r. The total energy is $E = E_R + E_r$. This shows that the center of mass moves like a free particle, and the relative motion (*i.e.* the motion of particle 2 with respect to particle 1) is the same as if we had a single particle with the reduced mass subject to the potential V. Exactly the same decomposition occurs in classical mechanics, where a two-body problem is reduced to an equivalent one-body problem.

    (d) Using the above, determine the percentage error (to two significant digits) in our calculated binding energy of the hydrogen atom where previously we used just the electron mass instead of the reduced mass of the electron and the proton.

2. In lecture, we discussed a two-particle system where each particle was sitting in a one-particle state (neglecting spin), $\psi_a(\vec{r})$ or $\psi_b(\vec{r})$. If the two particles are indistinguishable, we must construct the two wavefunctions (neglecting spin):
    $$\psi_\pm = C\left[\psi_a(\vec{r}_1)\,\psi_b(\vec{r}_2) \pm \psi_b(\vec{r}_1)\,\psi_a(\vec{r}_2)\right]$$

(a) If ψ_a and ψ_b are orthogonal, and both normalized, what is the constant C?

(b) If $\psi_a = \psi_b$ and it is normalized, what is the constant C? Is this case possible for bosons, fermions, or both?

3. Neglecting spin, imagine that you are given two noninteracting particles, each of mass m, in an infinite square well. If one particle is in the state $\psi_{n'}$ and the other is in $\psi_{n''}$ where $n' \neq n''$, calculate $\langle (x_1 - x_2)^2 \rangle$ for the following cases:

(a) The two particles are distinguishable.

(b) The two particles are indistinguishable and the wavefunction is symmetric with respect to exchange of the two particles.

(c) The two particles are indistinguishable and the wavefunction is antisymmetric with respect to exchange of the two particles.

Note: the solution to problem #1 from problem set #2 will be helpful to do this problem.

Problem Set #9:

1. (a) Which of the following combinations of quantum numbers are allowed for a single-particle hydrogenic state?

$$n = 3,\ \ell = 2,\ m_\ell = 1,\ \text{and}\ m_s = 0$$

$$n = 2,\ \ell = 0,\ m_\ell = 0,\ \text{and}\ m_s = -\frac{1}{2}$$

$$n = 7,\ \ell = 2,\ m_\ell = -2,\ \text{and}\ m_s = \frac{1}{2}$$

$$n = 3,\ \ell = -3,\ m_\ell = -2,\ \text{and}\ m_s = -\frac{1}{2}$$

(b) Determine the electronic configurations for the following elements:

B, F, Na, P, C, Cr, Mn, Fe, Cu, and Kr

(c) Using the rules for the addition of angular momenta (i.e. do not worry about exchange symmetry), determine all the possible electronic states for the elements B, C, and N in terms of their possible "term symbols", i.e. $^{2S+1}L_J$, where S is the total electronic spin, L is the total orbital angular momentum, and J is the total angular momentum.

2. (a) What are *L*, *S*, and *J* for a filled *d* subshell (*i.e.* nd^{10})? What is the corresponding term symbol?

    (b) Using the table from lecture below for the 15 possible configurations for the two p-electrons in carbon ($2p^2$), show how one obtains 5 term symbols.

	$m_{\ell 1}$	m_{s1}	$m_{\ell 2}$	m_{s2}	M_L	M_S	M_J
1.	$+1$	$+\frac{1}{2}$	$+1$	$-\frac{1}{2}$	$+2$	0	$+2$
2.	$+1$	$+\frac{1}{2}$	0	$+\frac{1}{2}$	$+1$	$+1$	$+2$
3.	$+1$	$+\frac{1}{2}$	0	$-\frac{1}{2}$	$+1$	0	$+1$
4.	$+1$	$+\frac{1}{2}$	-1	$+\frac{1}{2}$	0	$+1$	$+1$
5.	$+1$	$+\frac{1}{2}$	-1	$-\frac{1}{2}$	0	0	0
6.	$+1$	$-\frac{1}{2}$	0	$+\frac{1}{2}$	$+1$	0	$+1$
7.	$+1$	$-\frac{1}{2}$	0	$-\frac{1}{2}$	$+1$	-1	0
8.	$+1$	$-\frac{1}{2}$	-1	$+\frac{1}{2}$	0	0	0
9.	$+1$	$-\frac{1}{2}$	-1	$-\frac{1}{2}$	0	-1	-1
10.	0	$+\frac{1}{2}$	0	$-\frac{1}{2}$	0	0	0
11.	0	$+\frac{1}{2}$	-1	$+\frac{1}{2}$	-1	$+1$	0
12.	0	$+\frac{1}{2}$	-1	$-\frac{1}{2}$	-1	0	-1
13.	0	$-\frac{1}{2}$	-1	$+\frac{1}{2}$	-1	0	-1
14.	0	$-\frac{1}{2}$	-1	$-\frac{1}{2}$	-1	-1	-2
15.	-1	$+\frac{1}{2}$	-1	$-\frac{1}{2}$	-2	0	-2

    (c) Use Hund's rules to determine the ground state for carbon.

3. Suppose that you have three particles with three distinct one-particle spatial wavefunctions [$\psi_a(x)$, $\psi_b(x)$, and $\psi_c(x)$] available. How many different three-particle states can be constructed in the following cases?

    (a) The three particles are distinguishable.
    (b) The three particles are identical and the spatial wavefunction is symmetric with respect to exchange of any two particles.
    (c) The three particles are identical and the spatial wavefunction is antisymmetric with respect to exchange of any two particles.

Problem Set 10:

1. The density of copper is 8.96 g/cm^3, and its atomic weight is 63.5 g/mole.

    (a) Calculate the Fermi energy for copper. Assume $q = 1$, and give your answers in electron volts.
    (b) What is the corresponding electron velocity? Is it safe to assume that electrons in copper are nonrelativistic?

(c)   At what temperature would the characteristic thermal energy k_BT (where k_B is the Boltzmann constant and T is the temperature in Kelvin) be equal to the Fermi energy for copper? This is called the **Fermi temperature**. As long as the actual temperature of the solid is well below the Fermi temperature, the material can be regarded as "cold" with most of its electrons in the lowest accessible state. Considering that the melting point of copper is 1356 K, is copper always "cold?"

2.   Calculate the Fermi energy for non-interacting electrons in a two-dimensional infinite square well. Let σ be the number of free electrons per unit area of the well.

3.   In lecture, we considered a Dirac comb as a model for a one-dimensional solid of N atoms. The allowed energies for the electron were found from the equation
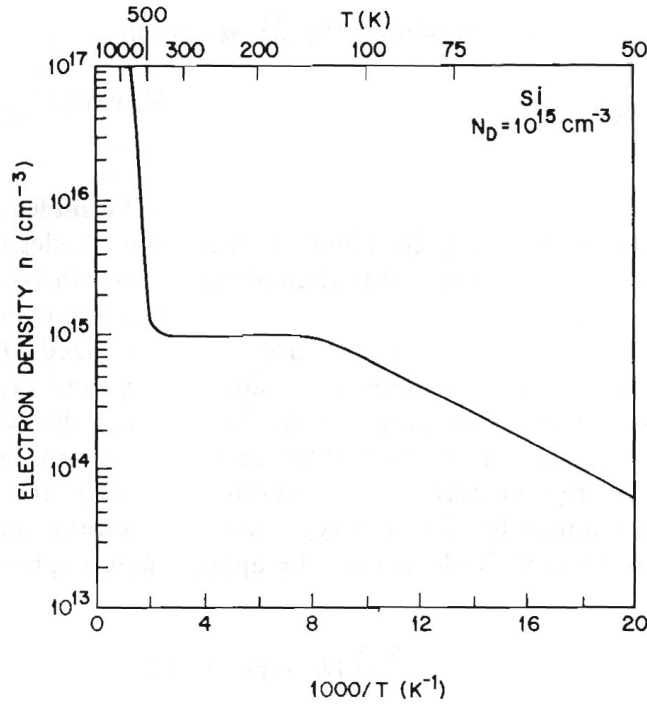
$$\cos(Ka) = \cos(ka) + \beta \frac{\sin(ka)}{ka}$$

where K is a real constant, a is the periodicity of the potential, $\beta \equiv \dfrac{m\alpha a}{\hbar^2}$, m is the particle mass, and α is the strength of the Dirac comb. In other words, the potential is of the form

$$V(x) = \alpha \sum_{j=0}^{N-1} \delta(x - ja).$$

Find the energy at the bottom of the first allowed electronic band for the case $\beta = 10$ to three significant digits. You can assume that α/a is equal to 1 eV. Hint: use a numerical solver.

4.   In lecture, we proved Bloch's theorem as $\psi(x+a) = e^{iKa}\psi(x)$ with K a real constant and a the spacing between the atoms (*i.e.* the periodicity of the atomic lattice). Prove that this is equivalent to $\psi(x) = e^{iKx}u(x)$ where $u(x)$ is a function that is periodic with the lattice spacing. This alternative form of Bloch's theorem states that the electronic wavefunction can be written as the product of a plane wave with a function that is the same for every atom in the lattice.

5.   (a) For intrinsic (*i.e.*, undoped) silicon, calculate the approximate temperature required to thermally excite free electrons at a concentration of 2×10^{17} per cm^3. Silicon is a semiconductor with a band gap of 1.12 eV and an effective intrinsic carrier concentration, N_i, of 1.71×10^{19} per cm^3.
   (b) Repeat the above calculation for silicon that is doped with phosphorous at a concentration of 10^{18} per cm^3. The binding energy of the donor electron on P is 0.045 eV.
   (c) Explain (in words) the temperature dependence of the electron density shown in the plot below for silicon that is doped with donors at a concentration of 10^{15} per cm^3.

500
T (K)
1000| 300   200   100   75   50
10^{17}

Si
$N_D = 10^{15}$ cm^{-3}

10^{16}

10^{15}

10^{14}

10^{13}

0   4   8   12   16   20

ELECTRON DENSITY n (cm^{-3})

1000/T (K^{-1})

Problem Set 11:

1.   Suppose we put a delta-function bump in the center of the infinite square well:

$$\hat{H}' = \alpha \, \delta(x - a/2)$$

where α is a constant.

(a) Find the first-order correction to the allowed energies. Explain why the energies are not perturbed for even n.

(b) Find the first three nonzero terms in the expansion of the correction to the ground state wavefunction, i.e. $\psi_1^{(1)}$.

(c) Find the second-order correction to the energies, $E_n^{(2)}$. Hint: you can sum the series explicitly, obtaining $-2m(\alpha/\pi\hbar n)^2$ for odd n.

2.   Use a Gaussian trial function, $(\alpha/\pi)^{1/4} \exp[-\alpha x^2/2]$, to obtain the lowest upper bound on the ground state energy of the linear potential: $V(x) = C |x|$, where C is a constant.

3. Consider a quantum system with just three linearly independent states. Suppose the Hamiltonian, in matrix form, is

$$\hat{H} = V_0 \begin{pmatrix} (1-\varepsilon) & 0 & 0 \\ 0 & 1 & \varepsilon \\ 0 & \varepsilon & 2 \end{pmatrix}$$

where V_0 is a constant, and ε is some small number ($\varepsilon \ll 1$).

(a) Write down the eigenvectors and eigenvalues of the unperturbed Hamiltonian ($\varepsilon = 0$).

(b) Solve for the exact eigenvalues of $\hat{H}$. Expand each of them as a power series in ε, up to second order.

(c) Use first- and second-order nondegenerate perturbation theory to find the approximate eigenvalue for the state that grows out of the nondegenerate eigenvector of $\hat{H}^{(0)}$. Compare the exact result, from (a).

(d) Use degenerate perturbation theory to find the first-order correction to the two initially degenerate eigenvalues. Compare the exact results.

4. Prove the following corollary to the variational principle: If $\langle \psi | \psi_{gs} \rangle = 0$, then $\langle \hat{H} \rangle \geq E_{fe}$, where ψ_{gs} is the grounds state and E_{fe} is the energy of the first excited state.

Thus, if we can find a trial function that is orthogonal to the exact ground state, we can get an upper bound on the first excited state. In general, it is difficult to be sure that ψ is orthogonal to ψ_{gs}, since we do not typically know ψ_{gs}. However, if the potential $V(x)$ is an even function of x, then the ground state is likewise even, and hence any odd trial function will automatically meet the condition for the corollary.

Problem Set #12

1. Nodes in the eigen-wavefunctions

In the lecture you have seen the example of the infinite square well, that the number of nodes increases by one with every energetically higher lying state. In this problem you will show that it is generally true that the number of nodes of the stationary states of a 1D potential increases with energy. Consider two (real, normalized) solutions ψ_n and ψ_m to the time-independent Schroedinger equation for a given potential $V(x)$. We denote the eigenenergies E_n and E_m and $E_n > E_m$.

a) Show that

$$\frac{d}{dx}\left(\frac{d\psi_m}{dx}\psi_n - \psi_m\frac{d\psi_n}{dx}\right) = \frac{2m}{\hbar^2}(E_n - E_m)\psi_m\psi_n \tag{1}$$

b) Let x_1 and x_2 be two adjacent nodes of the function $\psi_m(x)$. Show that

$$\psi'_m(x_2)\psi_n(x_2) - \psi'_m(x_1)\psi_n(x_1) = \frac{2m}{\hbar^2}(E_n - E_m)\int_{x_1}^{x_2}\psi_m\psi_n dx \tag{2}$$

c) If $\psi_n(x)$ has no nodes between x_1 and x_2, then it must have the same sign everywhere in the interval. Show that (b) then leads to a contradiction. Therefore between every pair of nodes of $\psi_m(x)$, $\psi_n(x)$ must have *at least* one node and in particular the number of nodes increases with energy.

2. Matrix representation of operators

Consider the operator $\hat{A}$ and a state $|\Psi\rangle$. We can expand the state $|\Psi\rangle$ in some basis $\{|n\rangle\}$ as

$$|\Psi\rangle = \sum_n c_n |n\rangle.$$

We can also represent $|\Psi\rangle$ as a vector in the basis of $\{|n\rangle\}$:

$$|\Psi\rangle \doteq c_1\begin{pmatrix}1\\0\\\vdots\\0\end{pmatrix} + c_2\begin{pmatrix}0\\1\\\vdots\\0\end{pmatrix} + \cdots = \begin{pmatrix}c_1\\c_2\\\vdots\\c_N\end{pmatrix},$$

where N is the dimensionality of the Hilbert space (the number of basis states $|n\rangle$). Similarly, the operator $\hat{A}$ can be represented as a matrix in the basis $\{|n\rangle\}$:

$$\hat{A} \doteq \begin{pmatrix}A_{11} & A_{12} & A_{13} & \cdots & A_{1N}\\A_{21} & A_{22} & A_{23} & \cdots & A_{2N}\\\vdots & & \ddots & & \vdots\\A_{N1} & A_{N2} & A_{N3} & \cdots & A_{NN}\end{pmatrix}$$

a) Show that the matrix element $A_{nn'}$ is found by

$$A_{nn'} = \langle n|\hat{A}|n'\rangle.$$

(Hint: Either insert the completeness relation on either side of $\hat{A}$, or try different values of n and n' and use the vector/matrix representation and see what the matrix multiplication gives for $A_{nn'}$. Note that the bra $\langle n|$ is a *row* vector!)

b) Write down the matrix representation of the Hamiltonian in the basis of energy eigenstates! (Hint: Replace $\hat{A}$ by $\hat{H}$ and take $\{|n\rangle\}$ to be energy eigenstates. Use the orthonormality of the basis! No calculation is necessary in this exercise!)

c) Write down the matrix representation of the $\hat{L}_z$ operator in the basis of eigenstates to L_z with $l = 1$:

$$\{|l = 1; m_l = -1\rangle, \quad |l = 1; m_l = 0\rangle, \quad |l = 1; m_l = 1\rangle\}$$

and use

$$L_\pm|l, m_l\rangle = \hbar\sqrt{l(l+1) - m_l(m_l \pm 1)} \, |l, m_l \pm 1\rangle$$

and

$$L_x = \frac{1}{2}(L_+ + L_-),$$

$$L_y = \frac{1}{2i}(L_+ - L_-),$$

to find the matrix elements of L_+, L_-, L_x and L_y in the basis $\{|l = 1; m_l = -1\rangle, \quad |l = 1; m_l = 0\rangle, \quad |l = 1; m_l = 1\rangle\}$.

(Hint: It may be convenient to define $|l = 1, m_l = p\rangle \equiv |p\rangle$.)

d) Show by matrix multiplication that $L_+|l = 1, m_l = -1\rangle = \hbar\sqrt{2}|l = 1, m_l = 0\rangle$.

3. Feynman − Hellman theorem

The Feynman-Hellmann theorem relates the eigenvalues of a time-independent Hamiltonian to the parameters that it contains. According to the theorem, once the eigenfunctions of a system have been found by solving the Schrödinger equation, all forces in the systems can be calculated. This you will see in the following exercise.

Suppose the Hamiltonian H for a particular quantum system, is a function of some parameter λ; let $E_n(\lambda)$ and $\psi_n(\lambda)$ be the eigenvalues and eigenfunctions of $H(\lambda)$. the Feynman-Hellmann theorem states that

$$\frac{\partial E_n}{\partial \lambda} = \langle \psi_n | \frac{\partial H}{\partial \lambda} | \psi_n \rangle \tag{1}$$

(assuming either that E_n is nondegenerate, or − if degenerate − that the ψ_ns are the "good" linear combinations of the degenerate eigenfunctions).

a) Prove the Feynman-Hellman theorem. Hint: Use $E_n^{(1)} = \langle \psi_n^{(0)} | H' | \psi_n^{(0)} \rangle$ where $E_n^{(1)}$ denotes the first-order energy correction and H' is the perturbation.

b) Apply it to the one-dimensional harmonic oscillator

    i) using $\lambda = \omega$. This yields a formula for the expectation value of V.

    ii) using $\lambda = \hbar$. This yields $\langle T \rangle$.

    iii) using $\lambda = m$. This yields a relation between $\langle T \rangle$ and $\langle V \rangle$.

4. Two particles with spin in potential well

Two electrons with spin are located in an infinitely deep potential well of width L. As known from the lecture, the corresponding one-particle wave functions are, for a certain quantum number n, given by:

$$\Psi_n(x) = \sqrt{\frac{2}{L}}\sin(\frac{n\pi x}{L}).$$

Hint: In this exercise we ignore the Coulomb interaction of the two electrons.

a) Assume that we prepared both electrons in the same spin state (spin-up), so that the total spin part of the two-particle wavefunction is given by $\chi_{s_1,s_2} = \chi_+\chi_+$. Write down the spatial part of the wavefunction for the two-particle system in the state with the lowest total energy permitted by symmetrization. What is the total wave function of the system (spatial and spin)?

b) Calculate the total energy of the system in this case.
   Hint: In order to calculate the total energy you need to calculate the expectation value of the total Hamiltonian $\langle H \rangle = \langle H^{(1)} + H^{(2)} \rangle$, where $H^{(1)}$ ($H^{(2)}$) only acts on particle one (two). Ignore the Coulomb interaction part! Consider using Dirac notation in order to simplify your calculations.

c) If we consider all the possibilities for the total spin part of the wavefunction, what would be the ground state of the system? Write down the total wavefunction and calculate the energy of the two-particle system for the ground state.